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SINTERED SILICON-CARBIDE MOLDED BODY AND METHOD FOR ITS PRODUCTION

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Translation of "Gesinterter Siliciumcarbid-Formkorper und Verfahren zu dessen Herstellung", German patent No. DE 33 26 176, July 20, 1983, pages 1-37.

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SINTERED SILICON CARBIDE WOLDED BODY AND METHOD FOR ITS PRODUCTION

The invention described sintered silicon carbide shapes produced by use $\frac{1*}{1*}$ as a sintering aid of a composition containing an oxide of at least one element chosen from the group: Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th as a supplement to known sintering aids used for manufacture of sintered silicon carbide shapes, such as oxides of rare earth elements, boron oxide and aluminum oxide, as well as a process for their manufacture.

*Numbers in margin indicate foreign pagination

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Sintered silicon Carbide Molded Body and Method for its Production

Patent Claims

 Sintered silicon carbide shape characterized by the fact that it contains or consists of 0.01 to 65.00 atom-percent of at least one representative of the following group (a), 0.01 to 70 atom-percent of at least one representative of the following group (b), and the remainder essentially SiC:

Group (a): Oxide(s) of at least one element chosen from the group Sc, Y, La,Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm and Lu, and Group (b): Oxide(s) of at least one element chosen from the group Li, Be, Mg, Si, Ca,Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th.

2. Sintered silicon carbide shape characterized by the fact that it contains or consists of 0.01 to 65.00 atom-percent of at least one member of the following group (a), 0.01 to 70.00 atom-percent of at least one member of the following group (b), 0.01 to 50.00 atom-percent of at least one member of the following group (c), with the remainder consisting essentially of SiC. Group (a): Oxide(s) of at least one element chosen from the group Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm and Lu. Group (b): Oxide(s) of at least one element chosen from the group Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th, and

Group (c): oxide(s) of at least one of the elements Al and B.

3. Process for manufacture of sintered silicon carbide shapes by adding at least one sintering aid chosen from the following groups (I) and (II) to silicon carbide powder, characterized by the fact that the amounts A, B, and C, which satisfy the following formula, are to be in the ranges of 0.01 to 70.00 atom-percent, 0.01 to 75.00 atom-percent, and 0.01 to 55.00 atom-percent, respectively,

A + B + C = 100 atom-percent

where:

- A is the amount of an element (as the oxide) of the following group (a),
- B is the amount of an element (as the oxide) of the following group (b), and
- C is the amount of an element (as the oxide) of the following group (c),

to make a mixture, so that the resultant mixture is formed and sintered either in separate steps or simultaneously;

- (I) Sintering aids, containing up to 99.9% by weight of at least one representative of the following group (a), with the rest consisting essentially of at least one representative of the following group (b), and
- (II) Sintering aids, containing up to 99.9% by weight of at least one representative of the following group (a), up to 99% by weight of at least one representative of the following group (c), with the remainder consisting

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of at least one representative of the following group (b):

Group (a): at least one representative, chosen from the group of elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm and Lu, and compounds of them;

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Group (b): at least one representative, chosen from the group of elements: Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th, and compounds of them, and

Group (c): at least one representative chosen from the group consisting of the elements: Al, B, and C, and their compounds.

Description

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This invention concerns a sintered silicon carbide shape and a process for its manufacture.

In particular, this invention concerns a sintered silicon carbide shap, containing an oxide of a rare earth element and at least one representative chosen from the group consisting of oxides of aluminum, boron, lithium, beryllium, magnesium, silicon, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, zinc, strontium, zirconium, niobium, molybdenum, technetium, barium, tantalum, tungsten and thorium, added to the starting materials used in the sintered silicon carbide shape, as well as a process for its manufacture, as described in Japanese Patent Application No. 44109/1981 (Patent number 160970/1982), which originated with the inventor named herein.

Because of its outstanding high temperature resistance, resistance to sudden temperature change, oxidation resistance, abrasion resistance and strength, silicon carbide is used to produce heat-resistant shapes and heating elements used to attain high temperatures. Quite recently the use of silicon carbide has increased significantly for hightemperature construction materials and wear-resistant materials.

It is difficult, though, to obtain a sintered shape with high density and strength from silicon carbide (designated in the following as SiC) itself because SiC is difficult to sinter. Therefore, in production of such sintered shapes, a process is used in which $A1_20_3$, iron oxide, A1N, BeO, Be, B, B_4C , BN, A1 or $A1PO_4$ is worked into the forming material as a sintering aid. The mixture is hotpressed, or a reactive sintering process is used. In such a process the shape is obtained from a powder mixture of SiC with carbon, and reacted with fused or gaseous silicon. But production of complex shapes by this method is difficult, so that this process is not suitable for mass production. Recently, too, a pressure-less sintering process has been suggested and used as the most suitable method for preparation of sintered SiC shapes. This process involves addition of carbon and boron as sintering aids to SiC powder, shaping the mixture, and sintering the resulting shape without using pressure. This is described, for instance, in the U. S. Patent Application No. 409 073.

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In this process, the boron carbide formed by the reaction of boron with carbon accelerates the sintering of the SiC powder in the silicon carbide shapes. It was well known that even if an oxide used as a sintering aid in the hot press method is used in the pressure-less sintering process, the sinter-accelerating effect cannot be obtained completely. In general, it is considered that oxides are actually harmful in the pressure-less sintering of SiC.

The inventors named herein have already found previously that oxides of the rare earth elements, aluminum oxide, and boron oxide are effective as sintering aids for SiC. On the basis of this discovery, as described above (Japanese patent application No. 44109/1981 was filed for this invention.

After further investigation it was found, according to the invention, that sintering of SiC powder is accelerated by use of oxides of rare earth elements, boron oxide, and aluminum oxide

combined with previously unknown sintering aids, and that the properties of the r sulting sintered SiC shape, such as tenacity and strength, can be improved.

It is the objective of this invention to provide a new sintered SiC shape as well as a process for its manufacture, based on these discoveries.

This objective is attained, as shown in the invention, by producing the following sintered SiC shapes (1) and (2) as well as by the manufacturing process (3).

(1) Sintered silicon carbide shape containing or consisting of 0.01 to 65.00 atom-percent of at least one representative of the following group (a), 0.01 to 70.00 atom-percent of at least one representative of the following group (b), the rest being essentially SiC.

Group (a): Oxide(s) of at least one element, chosen from the group Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm, and Lut, and Group (b): Oxide(s) of at least one element chosen from the group Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th.

(2) Sintered silicon carbide shape containing or consisting of 0.01 to 65.00 atom-percent of at least one representative of the following group (s), 0.01 to 70.00 atom-percent of at least one representative of the following group (b), 0.01 to 50.00 atom-percent of at least one representative of the following group (c), with the rest being essentially SiC.

Group (a): oxide(s) of at least one element, chosen from the group: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm and Lu,

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Group (b): oxide(s) of at least one element selected from the group Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th, and Group (c): oxide(s) of at least one of the elements Al and B.

3. Process for manufacturing a sintered silicon carbide shape by addition of at least one sintering aid, selected from the following groups (I) and (II), characterized by the fact that the amounts A, B, and C which satisfy the following formula will be set to 0.01 to 70.00 atom-percent, 0.01 to 75.00 atom-percent, and 0.01 to 55.00 atom-percent, respectively.

A + B + C = SiC = 100 atom-percent

in which

A is the amount of an element (as the oxide) from the following group (a)

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- B is the amount of an element (as the oxide) from the following group (b) and
- C is the amount of an element (as the oxide) from the following group (c),

producing a mixture, so that the resulting mixture is formed and sintered either in separate steps or simultaneously;

(I) Sinter aid, consisting of up to 99.9 % by weight of at least one representative of the following group (a), with the rest consisting essentially of at least one representative of the following group (b), and

(II) Sinter aid, consisting of up to 99.9% by weight of at least one representative of the following group (a), up to 99% by weight of at least one representative of the following group (c), with the remainder essentially of at least one representative of the following group (b):

Group (a): at least one representative, selected from the group consisting of the elements Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Hc, Er, Tm, Xb, Pm and Lu and their compounds,

Group (b): at least one representative selected from the group consisting of the elements Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W, and Th and their compounds, and

Group (c): at least one representative selected from the group of elements Al, B, and C, and their compounds.

The sintered SiC shape according to the first embodiment contains 0.0! to 65.00 atom-percent of at least one oxide of a rare earth element (indicated below as "R-oxide"), 0.01 to 70.00 atom-percent of at least one oxide of a metal (indicated below as "M-oxide") selected from the group listed below, with the remainder consisting of SiC.

The R-oxide(s) is(are) selected from the group consisting of oxides of Sc, Y, La, Ce, Fr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm and Lu.

The M-oxide(s) is(are) selected from the group consisting of oxides of Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W and Th. We start from the fact that these oxides act to reduce the surface energy of the SiC powder so as to accelerate the sintering reaction and to bind the SiC molecules together.

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According to the invention, the high-temperature oxidationresistant well known SiC shapes produced using carbon and boron as sintering aids, and shaped products of the above-mentioned first embodiment of the patent, were tested. The result showed that the shaped products containing the oxides according to the invention showed only a slight weight increase, while the weight of the known products was increased by at least two-fold. The drop in strength

of the sintered shapes according to the first embodiment of the patent at high temperatures is negligible. When the sintered shapes were treated in air for 100 hours at 1350°C the strength was hardly damaged. The strength of the commercial sintered shapes, however, was reduced to half. In particular, as compared with known sintered shapes containing only R-oxides, the shapes sintered according to the invention, obtained using zirconium oxide as a sintering aid, have higher tenacity and lower variation of properties among samples. The latter had an m-value, determined from a Weibull plot, of at least 10 and a bending strength 1.4 times as high as the former.

The R-oxide content of the sintered shape according to the first embodiment should be controlled within the range of 0.01 to 65.00 atom-percent because, if it is less than 0.01 atom-percent the strength of the product is insufficient, and if it is more than 65.00 atom-percent the SiC content of the sintered shape is too low. Further, the M-oxide content of the sintered shape should be controlled within the range of 0.01 to 70.00 atom-percent because if it is less than 0.01 atom-percent no difference is found form a sintered shape containing only R-oxide, and if it exceeds 70.00 atom-percent the SiC content of the sintered shape is too low.

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Compared with the known sintered shapes containing Al_2O_3 or AlN or both R-oxide and Al_2O_3 , the sintered SiC shapes according to the second embodiment of the invention, containing R-oxide, aluminum oxide (indicated below as Al oxide) and M-oxide (especially zirconium oxide) have a higher tenacity and lower variation of the properties among samples, with the latter having a m-value of at least 12 and a mean bending strength 1.4 times as high as that of the former.

Compared with the known sintered shapes containing boron and carbon as sinter aids, or R-oxide and boron oxide (indicated below as "B-oxide") the sintered SiC shapes according to the second embodiment of the invention, containing R-oxide, B-oxide and M-oxide

The sintered shapes according to the second embodiment of the invention, containing Al oxide, B-oxide, M-oxide and-R oxide, have a high-temperature strength which is at least 5 times as high as that of sintered SiC products obtained using boron-containing glass. They also have a temperature working limit that is some 100° higher than that of the latter. As compared with known products contining R-oxide, Al oxide, and B-oxide, the sintered shapes from this invention (and especially those that contain zirconium), and which contain M-oxide, have a much improved tenacity, a M-value of at least 10, less variation of the strength among samples, and an average bending strength that is 1.5 times as great as that of the former.

The R-oxide content of the sintered shapes made according to the second embodiment should be controlled in the range of 0.01 to 65.00 atom-percent because if this amount is less than 0.01 atompercent the strength of the product is insufficient. If it is greater than 65.00 atom-percent the SiC content of the sintered shape becomes too low.

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The amount of at least one oxide of Al and B should be adjusted up to 50.00 atom-percent. If it reaches 50.00 atom-percent the SiC content of the sintered shape becomes too low.

The amount of the M-oxide should be controlled within the range of 0.01 to 70.00 atom-percent. If it is less than 0.01 atompercent the improvement of the properties, and especially of the tenacity, of the sintered SiC shapes is insignificant. But if it amounts to more than 70.00 atom-percent the SiC content of the sintered shape becomes too low.

The process, according to the invention, of producing the sintered SiC shapes is described in the following.

According to the invention, at least one of these can be used: SiC, SiC, and amorphous SiC. It has been found that if a mixture of at least a finely divided β SiC and amorphous SiC with 0.1 to 10% by weight of α SiC is used as the starting material the nonuniform growth of the SiC particles can be regulated and the high-temperature strength and resistance can be improved.

Also, it is possible to use compounds with Si - C bonds, such as organo-silicon compounds and higher-molecular-weight organosilicon compounds, either by themselves or in the form of a mixture with SiC powder as the SiC starting material.

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According to the invention, the following sintering aids (I) and (II) can be used:

(I) Sintering aid, consisting of up to 99.9% by weight of at least one member of the following group (a), with the remainder consisting essentially of at least one member of the following group (b), and

(II) Sintering aid, consisting of up to 99.9% by weight of at least one member of the following group(a), up to 99% by weight of at least one member of the following group (c), with the remainder consisting of at least one member of the following group (b):

Group (a): at least one member selected from the group of elements: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pm, and Lu, and their compounds;

Group (b): at least one member selectred from the group of elements: Li, Be, Mg, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Sr, Zr, Nb, Mo, Ba, Tc, Ta, W, and Th and their compounds; and

Group (c): at least one member selected form the group of elements: Al, B and C, and their compounds.

Suitable compounds of the elements of the above-named groups (a), (b), and (c) are the oxides, compound oxides, hydroxides, acid adducts of hydroxides, phosphate, carbonate, basic carbonate, nitrate, sulfate, organic acid salts, halides, organometallic compounds, coordination compounds, and their alcoholoates.

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These sintering aids include the acid adducts of hydroxides, made by reacting a hydroxide with an acid. If the hydroxide is mixed with the acid in an amount smaller than the amount that would be equivalent to the metal hydroxide, an acid adduct is formed when the acid has reacted partially with the metal in the hydroxide, when the product is water-soluble. The acids used include hydrochloric acid, nitric acid, sulfuric acid, hydofluoric acid, phosphoric acid, perchloric acid, carbonic acid, and organic acids (such as formic, acetic, propionic, tartaric, fumaric, lactic, oxalic, stearic, maleic, benzoic, malic, malonic, citric, and butyric acid).

The following four processes are effective to produce the mixture of silicon carbide powder with the sintering aid, for use as a starting material for sintered shapes:

A first process involves mixing of a solvent-insoluble sinter aid (such as an oxide, hydroxide, or metal) with the silicon carbide powder. If a dry mixing process that requires no liquid is used, the mixing is completed _y mixing it in a mixer for a period that is required to achieve complete mixing. In a wet mixing process the powder is mixed with a solvent such as water or alcohol in a mixer for a period required to produce thorough mixing.

A second process is used if the sinter aid, such as an acid adduct of a hydroxide, nitrate, sulfate, organic acid salt, basic carbonate, carbonate, phosphate, perchlorate, halide, organometallic compound, alcoholate or coordination compound is soluble

in a solvent. In this process the sinter aid is dissolved in a suitable solvent such as water, alcohol, ether, ketone, hydrocarbon, DMSO, or SMF. The resulting solution is mixed with the silicon carbide powder in a mixer for a period required to achieve thorough mixing. By means of this mixing process the surface of the silicon carbide powder can be coated with a thin film of the sinter aid. In that way, large sintering effects can be obtained even with a small amount of the sinter aid. Now we shall describe the relations between the solvents and the sinter aids soluble in them. The acid adducts of hydroxides are water-soluble. Some alcoholates are soluble in ethers and aromatic hydrocarbons. Some complexes are soluble in water, alcohols, ethers and hydrocarbons. The organometallic compounds are soluble in organic solvents such as hydrocarbons and ethers. Some of the nitrates, sulfates, organic acid salts, and halides are water-soluble.

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A third process is used with a sinter aid which is a liquid at room temperature or which can be liquified by warming (such as some of the organometallic compounds, complexes and organic acid salts). In this process the sinter aid is mixed with the silicon carbide powder and the mixture is mixed in a mixer at room temperature or at an elevated temperature with heating until thorough agitation has been attained.

A fourth process is a combination of the first, second and third processes. In this process, for instance, components which are insoluble in a solvent and a solution of the sinter aid(s) can be mixed with the silicon carbide powder. This process can utilize any mixing equipment generally used to mix powders. The mixing can be done in an oxidizing gas atmosphere of air, carbon dioxide and/or oxygen gas; in a non-oxidizing gas atmosphere of nitrogen, argon, helium, hydrogen, neon, carbon monoxide, and/or hydrocarbons; or under vacuum. It is simplest to do the mixing in air. In the case of mixing in air, some of the organometallic compounds, alcoholates and complexes and halides react with oxygen, carbon dioxide or water in the course of the mixing, forming oxides, hydroxides or carbonates.

Extremely fine particles of these compounds adhere to the surfaces of the silicon carbide powder particles in such a way as to improve the sintering-accelerating action.

The mixture of starting materials, obtained as above, is shaped into the desired form. The forming step can use any commercial shaping process such as generally used for powders in industry to obtain unsintered shapes.

If a starting mixture of sinter aid in powder form is used with the silicon carbide powder, about 1% by weight of a lubricant such as stearic acid or one of its salts is applied to the mold to make the pressing better.

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In the shaping step the pressure can be applied by means of an ordinary single-force press, a double-force press, a hydrostatic press, and the like.

Moldings with simple shapes can be taken to the next processing stage immediately after pressing. Moldings with complex shapes should, however, be treated by grinding or milling to adjust the shape after pressing. If high strength is required of the molding the molding can be preformed at a temperature for the shaping, in the range of 300 to 1600°C in an oxidizing or nonoxidizing atmosphere, or in a vacuum. Also, the starting mixture can be slip-cast. If no solvent is used in the mixing step, it is preferred to use water as the dispersion medium during the slip-casting step (with a slide mechanism). An anticoagulant is added, and then silicon carbide powder and the sinter aid are added and mixed for some hours to obtain a starting material for slip-casting. On the other hand, if a solvent is used in the mixing stage, the amount of this solvent is increased in order to obtain the starting material for slip-casting directly. The resulting starting material for slip-casting can be rammed into a form made of sintered gypsum according to a commercial ·lip-casting process, to bet an unsintered shape. The silicon carbide starting material in the form of a paste can be used in injection molding. It is preferable to use a binder in addition

to the solvent when the paste is made. Effective substances can be used as binders. They evaporate in the sintering step without leaving any residue. Such substances include polyvinyl alcohol, polyethylene glycol and wax. If the solution of the sintering aid is itself viscous, i. e., on use of an acid adduct of a hydroxíde, a good paste can be obtained without using any other agent. In this case the sinter aid also acts as a binder, as the acid adduct of the hydroxide makes the paste viscouse, and it also acts as a sinter aid on calcification.

According to the invention the above-mentioned unsintered SiC molding is calcined in the next step. An ordinary calcining oven can be used. It is appropriate to use an oven in which the atmosphere can be varied to give an oxidizing or non-oxidizing atmosphere or a vacuum. The calcining temperature is in the range from 1600 to 2300°C. Below 1600°C the sintering reaction hardly proceeds at all. Above 2300°C the SiC decomposition becomes unfavorably vigorous. The sintering of the silicon carbide molding can be completed in this temperature range. But if a large amount of sinter aid is used, the sintering can be completed at a relatively low temperature. The calcining can be done in two separate steps; i. e., a low-temprature step and a high-temperature calcining step. The steps are designed so that the calcining temperature is at least as high at 1600°C. The two-stage calcining is particularly advantageous if the mold has large dimensions or of the sinter aid releases a gas during calcining. The calcining is preferably done in a non-oxidizing atmosphere or in vacuum when a high temperature is used. The non-oxidizing atmosphere may be nitrogen with a low content of oxygen, argon, helium, neon, hydrogen or carbon monoxide, or an atmosphere surrounded by carbon or SiC can be used. Although the pressure of the atmospheric gas is preferably high, this is economically disadvantageous. Favorable results can even be obtained at a pressure of up to 1 atm. On the other hand, a non-oxidizing temperature or vacuum is not always needed with the low-temperature calcining.

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If the calcining is done at a temperature of up to 1300 °C, at which the oxidation of silicon carbide is not vigorous, an oxidizing atmosphere like air can be used. If a sinter aid other than an oxide is used in this reaction, it reacts to form an oxide during calcining. The conversion of the sinter aid into the oxide during the low-temperature calcining is not unfavorable, as the sinter aid shows its greatest effect if it is present in the oxide form. If the elements or their compounds from the above-named groups (a), (b), and (c) are used as components of the sintering aid it is impossible to prevent their oxidation completely at a high temperature, so that these materials are either partially or completely oxidized. Even in this case, the oxidation presents no problems, as the oxides formed in this manner carry out a function as sinter aids.

The rate of temperature rise up to the intended calcining temperature varies depending on the shape of the molding. It is preferable to reduce the rate if the size of the molding increases. If the calcining is done at a temperature of up to 1600°C, the sintering of the molding proceeds only slightly, so that the temperature can be raised quickly, e. g., in an hour. But if an oxide and a compound that is not a metal and which can be decomposed by heat are used as the sinter aid, heating in low-temperature calcination accelerates a reaction which liberates a gas, even if only a little. Therefore, it is desirable to raise the temperature rathere slowly. It is better to raise the temperature from room temperature up to 1600°C over a period of 3 hours or longer. Advantages are attained if the temperature is slowly raised to the intended calcining temperature at a rate of less than 7°C per minute, because the molding shrinks if it is calcined at 1600°C or a higher temperature.

If a rare earth element or compound, and a metal or compound of the metal are used, the rare earth compound (usually an oxide) and the metal compound (usually an oxide) form a compound, if possible in the sintered molding, such as obtained in the course of calcining. The compound formed in this manner reduces the surface <u>/17</u>

energy of SiC, accelerating the sintering. If such a compound is not formed, part of the rare earth compound and the metal compound (usually an oxide) are dissolved in the silicon carbide forming a solid solution, and part of the silicon carbide is dissolved in the rare earth compound and the metal compound (usually an oxide) with formation of a solid solution, so that the sintering of the silicon carbide powder is accelerated. In case of the use of rare earth elements, metals and carbon or their compounds as sinter aids, carbon or its compound reacts with the rare earth element or its compound and with SiO₂ on the silicon carbide surface during the calcining. A considerable part of it is gasified and removed from the system, and part of the rest of it diffuses into the silicon carbide. As a result, the silicon carbide surface is activated and the mutual diffusion of the compound of a rare earth element, metal compound (usually an oxide) and silicon carbide is facilitated by carbon in the solid solution in silicon carbide and the sintering reaction rate is increased. Only a small part of the added carbon remains in the sintered SiC shape, so as to increase the strength and hardness of the sintered shape.

In case of use of a rare earth element or its compound, at least one of either aluminum, boron, or their compounds, and at least one of the metallic elements or their compounds, as components of the sintering aid, the rare earth element or its compound reacts with aluminum, boron or their compounds in the molding to produce a compound, or they form a solid solution. It is possible to react part of the metal element or its compound with the compound thus formed, or to dissolve the former in the latter, even if only a very little, to make a solid solution. It is obvious that SiO₂ reacts or forms a solid solution with the compound obtained in the reaction mentioned above, or with the solid solution formed. Aluminum or boron in this compound or solid solution diffuses easily into silicon carbide. Accordingly, the diffusion rate of silicon carbide into the rare earth compound (usually an oxide) is increased. As a result, it is possible to obtain a sintering reaction rate /18

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higher than that obtained with use of the rare earth elements and metallic elements. In a sintered shape such as obtained by using the rare earth elements, metal elements, aluminum, boron and carbon or their compounds as components of the sinter aid, carbon, aluminum and boron have effects equal to those obtrined if carbon, aluminum or boron is reacted with the rare earth element and the metal element is added. Additional effects such as improved acceleration of the calcination are obtained. Forms of carbon and its compounds which can be worked into the unsintered molding include acetylene soot, soot, graphite powder, wood charcoal powder, activated charcoal, high-molecular-weight aromatic compounds (like tar and pitch), and organic compounds that form carbon residues after calcination (such as phenolic resin, aniline/formaldehyde resin, cresol/formaldehyde resin and furan resin).

It was well known that the above-mentioned carbon and carbon compounds, worked into the unsintered moldings, react with the SiO_2 on the SiC_2 powder surface, forming SiC during the calcination, and that B_4C is formed by reaction with boron, so that the sintering is accelerated. If the sinter aid contains carbon as well as boron, the sintering-accelerating action of B_4C is observed, sometimes even in the presence of rare earth oxides. It is assumed, therefore, that a solid sintered product can be obtained in such a case.

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It is desirable for the added carbon to have reacted essentially completely before the end of the calcining so as to reduce the content of free carbon in the sintered shape. A sintered shape with a high content of free carbon has low resistance to oxidation at high temperature, and cannot be used satisfactorily at high temperatures.

According to the invention, the calcining can be carried out either under pressure, or without use of any certain pressure. Even in the latter case, a shape with high density and strength can be obtained. With sintered shapes obtained in the current state of the technology, Al_2O_3 , Fe_2O_3 , BeO, B_4C and such compounds, which were worked into the SiC powder as sinter aids, remain in

the particles of the SiC structure, and as a result the strength of the resulting molding is significantly lower than would be expected theoretically. The strength is particularly reduced at high temperatures if the amount of sinter aid is increased. It is desirable, therefore, that the amount of sinter aid to be worked into the SiC powder be set at a low value so as to get sintered shapes with high strength, especially at high temperature.

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According to the invention, most of the sinter aid mixed with the SiC powder precipitates in the particles of thestructure, although part of it is dissolved in the SiC, forming a solid solution. The precipitate in the grains reduces the brittleness of the SiC, which is a weak point of a sintered SiC shape. Part of this mechanism will be described below.

If ZrO is worked into the sinter aid, then part or all of the ZrO, crystals which precipitate in the grains are tetragonal due to the effects of the R-oxide, aluminum oxide and boron oxide. The tetragonal crystals are stable at high temperature and metastable at room temperature. If an external stress or load, higher than a specified value, is applied to the sintered SiC shape, small cracks are formed within the shape. The tetragonal crystals absorb the fracture energy of the cracks, and they transform into monoclinic crystals. As a result, the growth of the small cracks is prevented and the sintered SiC shape becomes resistant to higher load. If Fe₂O₂ is worked into the sinter aid, it is precipitated in the grains in the form of fine fibers, due to the effects of R-oxide, aluminum oxide and boron oxide. If an external load or stress higher than a specified value is applied to the sintered shape, small cracks are formed within the shape. The fibrous oxide scatters the directions of the crack fracture energy and prevents the propagation of the cracks. As a result, the sintered SiC shape is resistant to higher load. In some cases, both of the two mechanisms mentioned above are realized, with a greater preventive effect on crack growth. This considerably reduces the brittleness of SiC. The oxide precipitate in the grains has the effect of reducing the brittleness of the

sintered SiC shape. But if the amount of oxide is increased, the hardness and strength of the product are lower than those of SiC. This reduction is particularly considerable at high temperatures. If, on the other hand, the amount of sinter aid is reduced, then the reduction in brittleness becomes insignificant and the sintering properties of the product are poor. Sintering becomes difficult without application of pressure, although the strength and harness in the product is essentially equal to that of SiC, and the loss of strength and hardness at high temperatures is low.

If sinter aid is used in an amount smaller than mentioned above, it is advantageous to calcine under pressure to supplement the inherent sintering capacity. This calcination can be done by means of an ordinary hot press, isostatic hot press, or an atmospheric pressure calcining process.

In the following we describe the reasons why the components of the molding must be limited. In the sintered silicon carbide shape according to the first embodiment, the R-oxide content should be set in the range from 0.01 to 65.00 atom-percent . With less than 0.01 atom-percent of R-oxide it is difficult to produce a sintered product with high strength. With more than 65.00 atompercent R-oxide the SiC content of the sintered shape is insufficient and production of a shape with high strength becomes difficult. The M-oxide content should be kept within the range of 0.01 to 70.00 atom-percent. With less than 0.01 atom-percent M-oxide the resulting effects are only equivalent to those obtained if the R-oxide alone is used as a sinter aid. The improvement in properties, especially the tenacity, of the sintered shape is insufficient. On the other hand, with more than 70.00 atom-percent of M-oxide the SiC content of the sintered shape becomes insufficient and the resulting product has lower strength.

In a sintered silicon carbide shape made according to the second embodiment, the R-oxide content should be held within the range of 0.01 to 65.00 atom-percent. With less than 0.01 atom-percent /24

of R-oxide the production of a sintered shape with high strength becomes difficult. On the other hand, with more than 65.00 atompercent of R-oxide the SiC content of the sintered shape becomes insufficient and production of a shape with high strength becomes difficult.

The amount of aluminum and/or boron oxide in the shape should be held within the range of 0.01 to 50.00 atom-percent. With less than 0.01 atom-percent a sintered shape with sufficient strength is not obtained. On the other hand, with more than 50.00 atompercent the SiC content of the sintered shape becomes insufficient and a sintered shape with satisfactory strength is not obtained. The M-oxide content should be held within the range of 0.01 to 70.00 atom-percent. With less than 0.01 atom-percent of M-oxide the improvement of the properties, especially the tenacity, of the sintered shape is insufficient. On the other hand, with more than 70.00 atom-percent of M-oxide the SiC content of the sintered shape becomes insufficient and the resulting product has low strength.

The amount of sinter aid to be added to the SiC powder is as follows: When using a sinter aid containing up to 99.9% of the above-named component (I)-(a) and the remainder consisting essentially of component (b), then if the sum of the amounts of the elements (as the oxides) of which the sinter aid is composed, the (n) rare earth element(s) or their compounds (group (a)) i. e., and the (n) metallic element(s) or their compounds (group (b)) and the SiC are assumed to make up 100 atom-percent, the amounts of the components (a) and (b) (as oxides) are set within the ranges of 0.01 to 70.00 atom-percent and 0.01 to 75.00 atom-percent, respectively. If the amount of group (a) is lower than 0.01 atom-percent or more than 70-00 atom-percent the amount of SiC remaining in the sintered shape is small, so that no sintered shape with high strength can be obtained. If the amount of group (b) is less than 0.01 atom-percent the sintered shape has inadequate properties, especially low tenacity. If, on the other hand, the amount is greater than 75.00 atom-percent, then the amount of SiC remaining in the sinterd shape is low and its strength is reduced.

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In use of a sinter aid containing up to 99.9 percent by weight of the above-mentioned components (II)-(a), up to 99 percent by weight of the components (c) and with the rest consisting essentially of component (b), then, if the sum of the amounts of the elements (as the oxides) of which the sinter aid is composed, that is, the components (a) and (b) and Al, B, and/or C or compounds of them and of SiC are taken to be 100 atom-percent, the amounts of components (a), (b) and (c) should be set within the ranges of 0.01 to 70.00 atom-percent, 0.01 to 75.00 atom percent, and 0.01 to 55.00 atompercent, respectively. Outside these ranges it becomes impossible to obtain a sintered shape with satisfactory strength. Although the sintered SiC shape according to the invention includes the abovementioned components, impurities in the starting SiC used th manufacture the sintered silicon carbide shape according to the invention are naturally included in the finished shape according to the invention. Thus, sintered silicon carbide shape containing such impurities likewise are covered by this invention.

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The following examples explain the invention.

<u>Example l</u>

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l g scandium oxide, l g aluminum oxide and l g iron oxide were added to 27.0 g alpha-silicon carbide having a mean particle size of 0.40 μ m. After addition of alcohol, the mixture was stirred for three hours in an agate mortar. The resulting powdery mixture was dried, placed in a form, and shaped with a double-force press to obtain an unsintered molding. The molding thus formed was heated to 1850 °C by raising the temperature at a rate of 200 °C/hour, using a graphite heating element in an argon atmosphere, in a Tammann oven. It was held for one hour at 1850°C to obtain a sintered silicon carbide shape. The product had a linear shrinkage coefficient of 15% and a specific gravity of 3.14. The bending strength of the product was determined with the three-point bending process using a clamp width of 20 mm and a stress rate of 0.5 mm/min. The bending strength was 85 kg/mm² at room temperature, 65 kg/mm² at 1100°C, and 75 kg/mm² at 1400°C.

The product formed had an excellent oxidation resistance at high temperature. After an oxidation test carried out in oxygen at 1350°C for 100 hours, hardly any weight loss could be detected. The m-value, determined from the Weibull plot, was 10.

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Example 2

9 g yttrium oxide was dissolved in 180 ml of 2 N hydrochloric acid solution. Then 40 ml aqueous ammonia was added to the solution to precipitate the yttrium hydroxide, which was filtered off. The yttrium hydroxide thus obtained was added to 260 ml of a formic acid solution solution with a pH of 2, and the mixture was stirred for 3 hours at room temperature to react the hydroxide with formic acid. The reaction solution was concentrated under reduced pressure and then dried in vacuum, so as to obtain 18.5 g of an acid adduct of yttriumhydroxide. Separately, 30 g aluminum isopropoxide was dissolved in 120 ml benzene, 200 ml of a | N hydrochloric acid solution was added to the solution. The aluminum hydroxide thus formed was immediately reacted with hydrochloric acid. All the reactions were complete within a few hours. The aqueous part of the reaction solution was concentrated under reduced pressure and dried in vacuum. 20 g of an acid adduct of aluminum hydroxide was obtained. 1.5 g of the acid adduct of yttrium hydroxide and 1.5 g of the acid adduct of aluminum hydroxide were dissolved in water. 6 g of ZrO, with an average particle diameter of 0.5 μm and 21 g beta-SiC (containing 5% of alpha-SiC) with an average particle diameter of 0.27 µm were added to the solution. The mixture was stirred. Water was evaporated off and the residue was dried. The dry posder was placed in an 8 x 36 mm form and shaped with a double-force press to get an unsintered molding. The molding was calcined by raising the temperature to 500°C at a rate of 100°C/hour in air. Then it was further calcined by raising the temperature at a rate of 200°C/hour to 1400°C in a stream of nitrogen. The shape of the molding was adjusted. The shaped product, calcined in this manner at 1400°C, was placed in a graphite crucible. Alpha-SiC powder with a particle size of 100 µm was placed around the sample in the

crucible. The temparature was raised at a rate of 200°C/hour to 1900°C by means of a high-frequency oscillator. The molding was held for 30 minutes at 1900°C to obtained a sintered silicon carbide shape. The product had a specific gravity of 3.17 and a bending strength at room temperature of 90 kg/mm². It has been shown that the silicon carbide shape has excellent tenacity, oxidation resistance, resistance to sudden temperature changes, and stability. The m-value determined from the Weibull plot was 12.

Example 3

Aluminum yttrium oxide $(A1_2Y_4O_9)$ (a complex or double oxide) was pulverised to a particle size down to 2 µm. 2 g of this powder was mixed with 1 g beryllium oxide and 97 g alpha-SiC having an average particle diameter of 0.4 µm. The mixture was thoroughly stirred in a mixer. The powdery mixture was placed in a graphite form with an inside diameter of 35 mm. The temperature was raised at a rate of 10°C/minute to 1900°C, by means of a high-frequency oscillator, under a pressure of 200 kg/cm². The temperature was held at 1850°C for two hours to complete the hot-pressing. The sintered silicon carbide shape obtained in this manner had a specific gravity of 3.18. The product had a bending strength at room temperature of 99 kg/mm². The high-temperature strength of the product at 1400°C was only 7% lower than the strength at room temperature. The m-value determined from the Weibull plot was 11.

Example 4

3 g aluminum sulfate was dissolved in water. 81 g alpha-SiC having an average particle diameter of 1 μ m, and 10 g calcium oxide were added to the solution. The solution was stirred for an hour in a mixer and dried. 6 g lanthanum tris(acetylacetonate) were dissolved in benzene. The dry powder obtained above was added to the solution, and the mixture was stirred thoroughly. The benzene was evaporated off, and the residue was left to stand for 5 days to get a powdery mixture. The powdery mixture was placed in a

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8 x 36 mm form and shaped with a double-force press to get a molding. The unsintered molding obtained in this way was calcined by raising the temperature at a rate of 100°C/hour to 600°C, after which the temperature was raised at a rate of 200°C/hr to 1400°C to continue the calcining. The shape was placed in a graphite crucible, and the temperaturewas raised from 1400 to 1900°C by means of a highfrequency oscillator. The shape was held at 1900°C for 30 minutes to get a sintered silicon carbide shape. The product had a specific gravity of 3.11 and a bending strength at room temperature of 85 kg/mm². The m-value determined from the Weibull plot was 10.

Example 5

10 g cerium isopropoxide, 25 g aluminum isopropoxide and 10 g titanium isopropoxide were dissolved in benzene. 290 g beta-SiC (containing 5% of alpha-SiC) having an average particle diameter of 0.27 μ m was added to the solution. After thorough stirring with a small kneader, the benzene was evaporated off and the residue was dried.

The resulting dry powder was left to stand for 3 days in air, then placed in a form with a diameter of 20 mm and shaped with a single-force press. The resulting molding was placed in a rubber tube and compressed with a hydrostatic press using water as the pressure medium to get an unsintered molding. This molding was sintered by raising the temperature at a rate of 100°C/hour to 500°C in air. Then the temperature was raised at a rate of 200°C/hour to 1400°C in an argon atmosphere to continue the calcining. Then The shape was heated at a rate of 200°C/hour to 2000°C in an argon atmosphere in a Tammann oven to produce calcination. The product had a linear shrinkage coefficient of 16%, referred to the molding sintered at 500°C. The sintered silicon carbide shape had a specific gravity of 3.15 and a room-temperature bending strength of 90 kg/mm², The m-value determined from the Weibull plot was 12. /30

Example 6

5 g praesodymium sylfate and 4 g vanadium nitrate were dissolved in water. 80 g beta-SiC (containing 5% alpha-SiC) with an average particle diameter of 0.27 µm were added to the solution and the mixture was stirred thoroughly. Then the water was evaporated off and the residue was dried. The resulting dry powder was placed in a form and shaped with a double-force press. The resulting unsintered molding was calcined by raising the temperature at a rate of 100°C/hr to 500°C, after which the temperature was raised at a rate of 200°C/hr to 1400°C in a stream of nitrogen to continue the calcining. Then the shape calcined at 1400°C was placed in a graphite crucible. After the crucible was closed, the shape was heated with a highfrequency oscillator. In this step the temperature was raised at a rate of 200°C/minute from 1400 to 1900°C, in order to complete the calcining. A singered silicon carbide shape was obtained. The product had a specific gravity of 3.08 and a bending strength at room temperature of 85 kg/mm². The m-value determined from the Weibull plot was 11.

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<u>Example 7</u>

3 g of the acid adduct of yttrium hydroxide and 3 g of the acid adduct of aluminum hydroxide, produced in example 2, were dissolved in water. 20 g alpha-SiC having an average particle diameter of ! μ m and 7 g niobium oxide were added to the solution and the mixture was sitrred. The water was evaporated off to get a dry powder. The dry powder was placed in a form and molded to get an unsintered molding with a diameter of 30 mm and a thickness of 5 mm. The unsintered product was calcined by raising the temperature at a rate of 100°C/hour to 500°C. The molding thus calcined at 500°C was heated at a rate of 400°C/minute to 1950°C and held at 1950°C for 30 minutes to get a sintered shape. The sintered shape had a density of 3.06 and a bending strength of 73 kg/mm². The m-value, determined from the Weibull plot, was 10.

Example 8.

3 g metallic lanthanum, 1 g metallic boron and 4 g metallic molybdenum were pulverised and added to 93 g beta-SiC powder (containing 5% alpha-SiC). the mixture was stirred for one hour in an agate mortar. The resulting powdery mixture was placed in a form 8 x 36 mm and pressure-formed with a double-force press to obtain an unsintered molding. The unsintered molding was placed in a Tammann oven. The temperature was raised at a rate of 300°C/hour from room temperature to 1600°C in vacuum (1 x 10⁻³ mm Hg), and than, by means of a graphite heating element, from 1600°C to 2000°C at a rate of 200°C/hr. The shape was held at 2000°C for two hours to get a sintered silicon carbide shape. The product had a bending strength of 70 kg/mm² and a specific gravity of 3.11.

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Example 9.

9 g cerium nitrate was dissolved in water. 1 g of soot, 86 g alpha-SiC with an average particle diameter of 1 μ m and 4 g cobalt oxide were added to the solution. The mixture was stirred for three hours in a mixer. After completion of the stirring the mixture was dried and placed in a graphite mold with a diameter of 50 mm. The temperature was raised in two stages to 2000°C by means of a high-frequency oscillator, under a pressure of 250 kg/cm². The molding was held at 2000°C for 30 minutes to complete the hot pressing. The resulting sintered shape had a density of 3.14 and a bending strength of 80 kg/mm². The m-value, determined from the Weibull plot, was 14.

Example 10.

4 g lutecium acetylacetonate and 6 g barium isopropoxide were dissolved in benzene. 3 g boron oxide, 2 g soot and 85 g alpha-SiC with an average particle diameter of 1 μ m were added to the solution. The mxiture was stirred for 2 hours in a mixer. The benzene was evaporated off and the residue was dried. The resulting

dry powder was placed in a mold and pressure-formed by means of a double-force press to get an unsintered molding. This produce was calcined by raising the temperature at a rate of 200 °C/hour in nitrogen gas in a resistance oven, to 1400°C. The molding thus calcined at 1400°C was heated to 1950°C in a Tammann oven, at a heating rate of 200°C/hour in argon gas atmosphere, so obtain a sintered silicon carbide shape. The product had a specific gravity of 3.13 and a bending strength at room temperature of 73 kg/mm². The m-value, determined from the Weibull plot, was 11.

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Example 11

10 g gadolinium oxide was dissolved in 250 ml of a 2 N hydrochloric acid solution. 40 ml aqueous ammonia was added to the solution to precipitate gadolinium hydroxide. The gadolinium hydroxide precipitate was added to 220 ml of a 1 N acetic acid solution and allowed to react for 5 hours. Then the water was evaporated to obtain an acid adduct of gadolinium hydroxide. 10 g of this adduct and 10 g of the acid adduct of aluminum hydroxide, prepared in Example 2, were dissolved in water. 70 g beta-SiC (containing 5% alpha-SiC) with an average particle diameter of 0.27 µm and 10 g tantalum oxide were added to the solution and mixed for two hours in a mixer. The resulting powdery mixture was dried in a dried, placed in a graphite mold, andheated by means of a high frequency oscillator, in an argon atomosphere, at a temperature rise rate of 9°C/minute to 1900°C under a pressure of 250 kg/cm². The shape was held for 30 minutes at 1900°C to obtain a sintered shape. The product had /34 a density of 4.10 and an average bending strength of 75 kg/mm². The m-value, determined from the Weibull plot, was 15. The product had a tenacity higher than known SiC shapes.

Example 12.

10 g dysprosium chloride was dissolved in water. 80 g alpha-SiC with an average particle diameter of 1 μ m, 3 g aluminum oxide and 7 g tungsten oxide were added to the solution. The combination

was mixed for one hour in a mixer and then left standing in the air to dry. The resulting powder was placed in a graphite mold. It was heated by means of a high frequency oscillator in a nitrogen atmosphere under a pressure of 250 kg/cm² to 1950°C at a rate of 10°C/minute. The shape was held for 30 minutes at 1950°C to obtain a sintered SiC shape. The product had a density of 3.16 and an average bending strength of 85 kg/mm². The m-value, determined from the Weibull plot, was 13.

Example 13

12 g holmium nitrate and 2 g boric acid were dissolved in water. 84 g beta-SiC (containing 5% alpha-SiC) with an average particle diameter of 0.27 µm smf 2 g lithium carbonate were added to the solution, which was then mixed for one hour in a mixer. The resulting mixture was dried by standing in air, and then pulverized. The resulting powder was placed in a mold and pressure-formed by means of a double-force press to get an unsintered molding. This molding was calcined in air by raising the temperature at a rate of 100°C/hour to 500°C, and then heated at a rate of 200°C/hour in nitrogen gas to 1400°C. The molding calcined in this manner at 1400°C was placed in a graphite crucible, which was heated at 400°C/hour by means of a high-frequency oscillator from 1400 to 1950°C. The shape was held for an hour at 1950°C to get a sintered silicon carbide shape. The product had a specific gravity of 3.08 and a bending strength of 70 kg/mm². The m-value, determined from the Weibull plot, was 11.

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Example 14

10 g cerium acetylacetonate, 2 g erbium acetylacetonate and 2 g nickel isopropoxide were dissolved in benzene. 1.5 g soot and 84.5 g beta-SiC (containing 5% alpha-SiC) with an average particle diameter of 0.27 μ m were added to the solution, which was mixed in a mixer for 30 minutes. Benzene was evaporated from the mixture and thr residue was pulverized. The powder obtained in this manner

was allowed to stand in air for 2 days. Then it was pressure-formed with a double-force press to get an unsintered molding. This molding was calcined by heating at a rate of 200°C/hour to 1400°C in nitrogen gas. The shape calcined at 1400°C was placed in a graphite crucible. The temperature was raised at 400°C/hour from 1400 to 1900°C, and the shape was held for an hour at 1900°C to get a sintered silicon carbide shape. The product had a specific gravity of 3.12 and a bending strength of 75 kg/mm². The m-value, determined from the Weibull plot, was 10.

Example 15

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22 g lanthanum oxide was dissolved in 160 ml 2 N hydrochloric acid. 30 ml aqueous ammonia was added to the solution to precipitate lanthanum hydroxide. The precipitate was filtered off, dried, and dissolved in 280 ml | N hydrochloric acid solution. The solution was concentrated to obtain an acid adduct of lanthanum hydroxide. 6 g of this acid adduct was dissolved in water. 1.5 g soot, 87 g of alpha-SiC with an average particle diameter of 1 μ m and 5.5 g MgO were added to the solution and mixed in a mixer for 3 hours. Then the water was evaporated and the mixture was pulverized. The powder obtained was placed in a mold and pressure-formed by means of a double-force press to get an unsintered molding. This molding was calcined by heating to 1400°C at a rate of 100°C/Hour. The shape calcined at 1400°C was placed in a graphite crucible. The temperature was raised at 300°C/hr from 1400 to 1900°C by means of a high-frequency oscillator. The shape was held for one hour at 1900°C for an hour to obtain a sintered silicon carbide shape. The product had a specific gravity of 3.08 and a bending strength of 70 kg/mm².

As described above, the silicon carbide shape according to the invention has high density and strength and excellent oxidation resistance, abrasion resistance, stability and resistance to sudden temperature change. The electrical resistance of the shapes varied <u>/36</u>

from 10^{-1} Ω cm to 10^{12} Ω cm, depending on the amount and variety of the sinter aids. Thus, the sintered silicon carbide shapes produced according to the invention are of higher quality than the commercial products. According to the invention, moldings with complicated shapes, hollow moldings, and thin ribbons can be produced directly by means of a commercial process. This fact is very advantageous economically. The sintered silicon carbide shapes produced according to the invention can be used as gas turbine blades, round shapes, gas turbine parts, parts for equipment for corrosive liquids (melts), crucibles, coagings for ball mills , heat exchangers, and fireresistant materials, for high-temperature ovens, electrical heating elements, combustion tubes, injection pumps, thin tubes, materials for nuclear fusion reactors, materials for nuclear reactors, materials for solar heating plants, industrial machinery and parts for them, grinding materials, thermal insulators, bases for single crystals, IC substrates, varistors, or the like.