

METHOD OF PREPARING SILICON CARBIDE
SINTERED BODY

BACKGROUND OF THE INVENTION

(1) Field of the Invention

Silicon carbide sintered bodies have excellent chemical and physical properties, i.e., high thermal conductivity, low thermal expansibility, high oxidation resistance, good anticorrosion, high thermal shock resistance, and a high strength at a temperature of from an ordinary temperature to a high temperature. Sintered bodies have been used, for example, for parts for gas turbines, high-temperature structural parts such as heat exchangers used at high temperatures, and parts having a high wear-resistance. The present invention relates to a method of preparing silicon carbide sintered bodies in which the above-mentioned properties are further improved, and in particular, the present invention relates to a method of preparing silicon carbide sintered bodies which can be applied to not only the above exemplified parts but also to wear-resistant sliding parts such as mechanical seals, bearings, and plungers.

(2) Description of the Related Art

Although silicon carbide sintered bodies have the excellent characteristics mentioned above, it is difficult to sinter a silicon carbide fine powder, which is the starting material of the silicon carbide sintered bodies, and thus, when a high-density sintered body is required, a pressure sintering process is applied using several kinds of pressing machines. It is difficult, however, to manufacture sintered bodies having complex shapes by this pressure sintering process.

To solve the problems of the above-mentioned pressure sintering process, another method has been suggested by, e.g., U.S. Patent Nos. 4312954, 4346049,

and 4318876, in which boron and carbon are added to the silicon carbide fine powder as sintering aids, followed by sintering under atmospheric pressure (pressureless sintering), to obtain the required high-density silicon carbide sintered bodies. Furthermore, other method has been suggested by, e.g., Japanese Unexamined Patent Publication (Kokai) No. 62-113764 in which silicon carbide fine powder added with boron and carbon is sintered under a vacuum pressure. Such the sintering under a vacuum pressure are disclosed in U.S. Patent Nos. 4336216, 4525461, 4579704, 4668452, and 4692418 and EP-A-0257134. The addition of boron suppresses the surface diffusion which causes grain growth at an early stage of the sintering process, and accelerates the volume diffusion, to thus improve the densification in the second half stage of the sintering process. The addition of carbon reduces and removes SiO_2 included in the silicon carbide fine powder, which has not been completely removed by a pretreatment such as a hydrofluoric acid treatment, to thereby improve the contact between the boron and the silicon carbide fine powder. For example, in Japanese Patent Unexamined Publication (Kokai) No. 51-148712 entitled, "Silicon Carbide Sintered Ceramics and a Method of Preparing Same" (corresponding to U.S. Patent No. 4312954), a method is disclosed which comprises the steps of mixing silicon carbide, a boron-containing additive, a carbonizable organic solvent material, and a primary binder, to form a material composition, molding the mixture, and sintering the molded products under atmospheric pressure to obtain silicon carbide sintered bodies having a density of 75% or more of the theoretical density.

In the conventional methods of preparing silicon carbide sintered bodies, the silicon carbide fine powder must be subjected to, for example, a hydrofluoric acid treatment, to lower the SiO_2 content,

as disclosed in U.S. Patent No. 4123286, because if a large amount of SiO_2 is present in the silicon carbide fine powder, a sufficient density of the sintered body cannot be obtained. But such a process increases the cost of manufacturing sintered products and limits the wider application thereof in comparison to other existing materials.

SUMMARY OF THE INVENTION

The present invention has been created to solve the above-mentioned problems, and according to the present invention, there are provided a method of preparing a high-strength and high-density sintered body from a less expensive silicon carbide fine powder containing a large content of SiO_2 without using a hydrofluoric acid treatment, the properties of the sintered body being equal to those of a sintered body, from a conventional silicon carbide fine powder containing a low SiO_2 content, and a method of preparing parts subject to wear and made of a silicon carbide in which the smallest possible amount of a boron-containing additive (i.e., a boron sintering aid) is used, to also obtain an excellent anticorrosion property. Namely, the present invention is directed to a method of sintering silicon carbide bodies, which comprises the steps of, uniformly mixing 100 parts by weight of a silicon carbide fine powder containing more than 2.0 to 6.0% by weight of SiO_2 with 0.05 to 4.0 parts by weight of boron or a boron compound in terms of boron, 1.0 to 4.0 parts by weight of carbon or a carbon compound in terms of carbon, and a binding agent, forming the mixture into compact bodies having a bulk density of 1.7 to 2.2 g/cm^3 ; removing the binding agent from the formed bodies; and sintering the formed bodies at a temperature of 1100 to 1550°C under a reduced pressure of 5×10^{-1} Torr or less and then in an inert gas atmosphere at 1550 to 2100°C under atmospheric pressure or an increased gas pressure. Further, the present invention

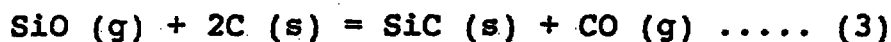
is directed to a method of preparing silicon carbide sintered bodies having a boron content of preferably from 0.05 to 0.15 part by weight in terms of boron.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 In the present invention, the SiO_2 content in the silicon carbide fine powder which has not been subjected to a hydrofluoric acid treatment is from more than 2 to 6% by weight. This is based on the fact that the present invention can form dense and strong silicon
10 carbide sintered bodies even with the use of a silicon carbide fine powder containing more than 2 to 6% by weight of SiO_2 . The reason why the high-density and high-strength silicon carbide sintered bodies can be obtained in spite of the use of silicon carbide fine
15 powders containing more than 2 to 6% by weight of SiO_2 is not theoretically proven, but the following mechanism can be presumed: Namely, SiO_2 in the silicon carbide fine powder covers the surface of silicon carbide grains. The SiO_2 layer covering the grains is
20 eliminated through a reaction with an active carbonaceous material, such as carbon black, charcoal, coke, carbonized chaff, activated carbon or carbonized phenolic resin, and such active grain surfaces of the silicon carbide fine powder are very effective for
25 accelerating sintering. Furthermore, the reason why the optimum amount of SiO_2 in the silicon carbide fine powder is from more than 2 to 6% by weight is that more than 2% by weight of SiO_2 is usually enough to cover the whole surface of the silicon carbide fine powder, and
30 that a too high SiO_2 content such as 6% by weight or more leads to the formation of SiO_2 films having an undesirably large thickness to be reduced and eliminated by the reaction with carbon. Note, even if the hydrofluoric acid treatment is carried out to lower the
35 SiO_2 content to a level of under 2% by weight, the silica content will quickly increase up to or higher than 2% by weight during storage and handling. Also, in

steps such as mixing and molding before sintering, the SiO_2 content is increased. From the viewpoint of the relationship between the amount of carbon as the undermentioned sintering aid and that of SiO_2 , a preferable, relatively small range of carbon content exists, which enables a stable manufacturing operation.

The whole reaction between the SiO_2 film and carbon is represented by the formula (1), but it can be considered that the reaction actually proceeds through a chain reaction in two steps, as expressed by the following formulae (2) and (3).



Namely, as is clearly shown by formulae (2) and (3), SiC is formed by a gas-solid reaction between the SiO gas and C, as shown in formula (3), and thus the SiC compound has a fine structure. This contributes to the formation of dense and strong sintered bodies. As a whole a free energy change ΔG of the reaction in the formula (1) is 20 kcal/mole at 1200°C and -20 kcal/mole at a CO gas partial pressure of 0.001 atm (0.76 Torr). Accordingly, the reaction (1) is thermodynamically possible.

Carbon as the sintering aid should be active, since it reacts with the SiO_2 films on the grain surface of the silicon carbide fine powder during the sintering process. From investigations into carbon sources, it was found that the preferable carbon sources are carbon black, charcoal, coke, carbonized chaff, and activated carbon. In addition, where the sintered body is to be applied for other than sliding parts and parts subjected to wear, carbonized phenolic resin also can be used as the carbon source. These carbon sources are preferred because the specific surface area of each carbon source is large and the crystallization grade is low. The amount of carbon to be blended is preferably in the

range of 1.0 to 4.0 parts by weight in terms of carbon based on 100 parts by weight of silicon carbide fine powder, depending upon the content of SiO_2 in the silicon carbide fine powder. The carbon meant by "in terms of carbon" denotes substantial carbon, taking the carbonization rate during the sintering process into consideration. For example, where the silicon carbide fine powder contains 1% by weight of SiO_2 , the optimum amount of carbon is from 1 to 2 parts by weight in terms of carbon, and where the SiO_2 content in the raw material is 2 to 3% by weight, the optimum amount of carbon is from 1 to 3 parts by weight in terms of carbon. Furthermore, when the content of SiO_2 is 3 to 6% by weight, a carbon amount of 3 to 4 parts by weight is optimum.

The amount of boron or a boron compound is preferably 0.05 to 4.0 parts by weight in terms of boron based on 100 parts by weight of the silicon carbide fine powder. The function of boron in the sintering process is considered to be as follows: Boron diffuses over surfaces of the silicon carbide fine powder grains, whereby surface diffusion, which causes the growth of coarse crystalline grains, is suppressed at an early stage of the sintering. In a later stage of the sintering, boron is dissolved in the silicon carbide fine powder, whereby the volume diffusion is accelerated to increase the density of the sintered body. According to research by the inventors of the present application, the minimum boron amount is 0.05 parts by weight. If the amount of boron is more than 4.0 parts by weight, the excess boron cannot be dissolved in the silicon carbide fine powder, so that a second phase is formed in grain boundaries of the silicon carbide and impedes the diffusion, and thus prevents an increase of the density of the sintered body and deteriorates such properties as the mechanical strength and corrosion resistance.

Where parts subject to wear such as a mechanical

seal, for which good frictional characteristics and a good chemical resistance are required, are manufactured by sintering, the amount of boron or the boron compound is preferably 0.05 to 0.15 part by weight in terms of boron. If the boron content is more than 0.15 parts by weight, the anticorrosion properties of silicon carbide sintered bodies are impaired.

Examples of the boron and boron compound that can be used as the sintering agent (aid) include boron, boron carbide (typical composition, B_4C), and silicon borides (SiB_4 and SiB_6).

To ensure a good molding and processing, the silicon carbide fine powder is granulated into granules, and therefore, a molding binder (i.e., temporary binder) such as polyvinyl alcohol is used. The amount of the binder is preferably in 1 to 4 parts by weight based on 100 parts of the silicon carbide fine powder. When the binder content is less than 1 part by weight, the density of a green compact body is not sufficiently increased, and accordingly, the density of the sintered body cannot be sufficiently increased. But, if the amount of binder is more than 4 parts by weight, a too high a rate of removal vaporization of the binder phase which occurs during heating causes cracks in the compact body.

The raw material mixture in which such various sintering aids as mentioned above are uniformly mixed with the silicon carbide fine powder is usually granulated and fed into a mold and pressed to form a compact body, preferably having a density of 1.7 to 2.2 g/cm³. When the density of the compact body is within this range, the number of adjacent silicon carbide powder grains is increased and the contact surface area is also increased to improve the material transfer during the sintering process.

The thus obtained compact body is heated to remove the binder therefrom and sintering is carried out at a

temperature of 1100 to 1550°C under a reduced pressure of 5×10^{-1} Torr or less, and then at a temperature of 1550 to 2100°C in an inert gas atmosphere under atmospheric pressure or a relatively increased pressure.

5 The reason why the above-mentioned reduced pressures are set at a temperature of 1100 to 1550°C is that the SiO_2 layer on the surface of the silicon carbide fine powder is reduced by carbon, as shown by the chemical formula (1) above, in this temperature
10 range, and that the pressure in the furnace must be lowered to efficiently remove CO gas from the reaction system. Namely, in this temperature range, the total pressure in the furnace must be lowered, and resulting gases must be efficiently removed from the reaction
15 system.

 The reason why the inert gas atmosphere is set to atmospheric pressure or a relatively increased pressure at a temperature of 1550 to 2100°C is that decomposition of the silicon carbide must be suppressed. The extent
20 of the increased pressure in this temperature range is such that air is prevented from flowing into the sintering furnace from outside, and is preferably from 0.8 to 1.2 atm over atmospheric pressure.

 The final sintering temperature is preferably from
25 1900 to 2100°C. When the final sintering temperature is higher than 2100°C, the silicon carbide is dissociated and coarse grains are formed, which lower the mechanical strength properties. Conversely, when this temperature is less than 1900°C, a sufficient sintering rate cannot
30 be obtained, and as a result, the density of sintered body is insufficient.

 The present invention will be described in detail with reference to examples.

Examples 1 to 5

35 In these examples were used α -SiC fine powders produced by the Acheson method and having an average grain diameter of 0.5 μm , each containing 2.2% by weight

or 6% by weight of SiO_2 . As shown in Table 1, B_4C and carbon black were blended with the SiC fine powders, and 0.8 part by weight of polyvinyl alcohol as forming binder, 1.5 parts by weight of polyethylene glycol, and 80 parts by weight of water were added to each mixture. Each mixture was then stirred for 20 hours by a ball mill, and spray dried to form granules. The granules were then pressed to form green compact bodies each having a diameter of 50 mm, a thickness of 6 mm, and a density of 1.9 to 2.1 g/cm^3 , and the compact bodies were then heated to remove the binder. Sintering was then carried out by heating at a temperature of 1100 to 1550°C under a reduced pressure of 5×10^{-1} Torr or less, at a temperature of 1550 to 2070°C under atmospheric pressure in an argon gas atmosphere, and then at 2070°C for 5 hours. Table 1 shows the densities of the sintered bodies obtained in accordance with the above-mentioned procedure.

Comparative Examples 1 to 9

Silicon carbide (α - SiC) fine powders containing 2.0% by weight or less of SiO_2 or more than 6.0% of SiO_2 were used. The former silicon carbide fine powder had been subjected to a hydrofluoric acid treatment to decrease the SiO_2 content. The mixing, granulating, pressing, and sintering were successively carried out in the same manner as in Examples 1 to 5. The properties of the resultant sintered bodies are shown in Table 1.

Comparative Example 10

A silicon carbide sintered body was prepared in the same manner as in Example 1 except that, during the heating step at 1100 - 1550°C, an argon gas was fed at a flow rate of 7.5 m^3/hr at atmospheric pressure (i.e., a reduced pressure condition was not used). The properties of the resultant sintered body are shown in Table 1.

TABLE 1

Exam- ple No.	SiO ₂ Content in Silicon Carbide Fine Powder (wt%)	Amount of B ₄ C in Terms of Boron (parts by weight)	Amount of Carbon-black (parts by weight)	Density of Green Com- pact Body (g/cm ³)	Density of Sintered Body (g/cm ³)
1	2.2	0.120	3.0	1.98	3.08
2	2.2	0.150	3.0	2.00	3.14
3	2.2	0.37	3.0	2.00	3.14
4	6.0	0.37	4.0	1.95	3.08
5	6.0	3.50	4.0	1.94	3.00

*1	0.05	0.135	1.0	2.02	3.15
*2	0.1	0.135	1.0	2.01	3.15
*3	0.7	0.05	2.0	2.01	3.00
*4	0.7	0.105	2.0	2.00	3.14
*5	0.7	0.120	2.0	2.00	3.15
*6	0.7	0.37	2.0	2.00	3.16
*7	0.7	3.00	2.0	2.02	3.05
*8	7.0	0.150	2.8	2.03	2.86
*9	8.0	0.150	4.5	1.97	2.80
*10	2.2	0.120	3.0	1.98	2.90

Note: * Comparative Example

As apparent from Table 1, the silicon carbide sintered bodies of Examples 1 to 5 of the present invention have a sintered body density equal to that of the sintered bodies of Comparative Examples 1 to 7 made of the SiC fine powder containing a low SiO₂, although the SiC fine powder of Examples 1 to 5 was not subjected to the hydrofluoric acid treatment to decrease the SiO₂ content.

Examples 6 to 11

Carbon sources (listed below) other than carbon black were used, and the mixing, granulating, pressing and sintering were successively carried out in the same manner as in the above-mentioned Examples. The properties of the resultant sintered bodies are shown in Table 2.

Example 6	Phenolic resin
Examples 7 and 8	Charcoal
Example 9	Coke
Example 10	Carbonized chaff
Example 11	Activated carbon

TABLE 2

Exam- ple No.	SiO ₂ Content in Silicon Carbide		Amount of B ₄ C in Terms of		Amount of Carbon Compound in Terms of Carbon (parts by weight)		Density of Green Com- pact Body		Density of Sintered Body	
	Fine Powder	(wt%)	Boron (parts by weight)				(g/cm ³)		(g/cm ³)	
6	2.2		0.150		3.0 (phenolic resin)		2.02		3.14	
7	2.2		0.135		3.0 (charcoal)		1.97		3.10	
8	2.2		0.37		3.0 (ditto)		1.97		3.11	
9	2.2		0.135		3.0 (coke)		1.98		3.07	
10	2.2		0.135		3.0 (carbonized chaff)		1.99		3.08	
11	2.2		0.135		3.0 (activated carbon)		1.97		3.10	

The corrosion resistance and wear properties of the sintered bodies of Examples 1 to 5 and Comparative Examples 1 to 9 when brought into contact with a carbon material are shown in Table 3.

5 The corrosion resistance was evaluated as follows:
First, 10 mm x 10 mm x 10 mm specimens of the sintered
bodies were prepared in the same manner as described
above, and 10 such specimens were dipped in a 1:1
mixture of 20% nitric acid and 5% hydrofluoric acid at
10 70°C for 800 hours and then the weight loss of each
specimen was measured. The wear was evaluated as
follows: Specimens of ring-like sintered bodies each
having an outer diameter of 114 mm, an inner diameter of
94 mm, and a thickness of 20 mm were prepared in the
15 same manner as described above, and each specimen was
brought into contact with a carbon disc in water at 50°C
and rotated at peripheral speed of 15 m/second. The
amount of weight loss (sliding abrasive wear) of the
carbon disc was then measured, and the results are shown
20 in Table 3.

As apparent from Table 3, although the SiO₂ content
of the SiC fine powder of Examples 1 to 5 was not
decreased by the hydrofluoric acid treatment, the
corrosion resistance and the wear of the specimens of
25 Examples 1 to 5 are equal to those of specimens of the
Comparative Examples 1 to 9 using the SiC fine powder
having a decreased SiO₂ content.

From Table 3, it is apparent that the specimens in
Examples 1 and 2, in which the amount of added boron was
30 from 0.05 to 0.15 part by weight in terms of boron, had
an excellent corrosion resistance and wear, and thus it
is clear that these specimens are excellent for parts
subjected to wear.

TABLE 3

Example No.	Corrosion Resistance (weight loss) (g/cm ²)	Wear when in contact with Carbon Material (weight loss) (mm/100 hr)
1	3.1×10^{-5}	0.015
2	3.3×10^{-5}	0.013
3	5.1×10^{-5}	0.014
4	4.9×10^{-5}	0.018
5	7.2×10^{-5}	0.019
Comparative Example 1	3.4×10^{-5}	0.017
" 2	3.1×10^{-5}	0.016
" 3	2.5×10^{-5}	0.014
" 4	2.7×10^{-5}	0.014
" 5	2.7×10^{-5}	0.015
" 6	4.8×10^{-5}	0.018
" 7	6.5×10^{-5}	0.019
" 8	3.6×10^{-5}	0.048
" 9	5.8×10^{-5}	0.035

30 As apparent from the results obtained from the respective examples, the silicon carbide sintered bodies prepared under from a SiC fine powder containing more than 6% by weight of SiO₂ have a low density and a low wear.

35 According to the present invention, high-quality sintered bodies can be obtained by using silicon carbide fine powders without lowering the SiO₂ layer content,

and sintered bodies of silicon carbide having an sufficient corrosion resistance and wear can be obtained by adjusting the amount of a boron-containing additive contained therein.



CLAIMS:

1. A method of preparing a silicon carbide sintered body which comprises the steps of: uniformly mixing 100 parts by weight of a silicon carbide powder containing more than 2.0 to 6.0% by weight of SiO_2 with 0.05 to 4.0 parts by weight of either boron or the boron content of a boron compound, 1 to 4 parts by weight of either carbon or the carbon content of a carbon compound, and a forming binder; forming the mixture into a compact body having a bulk density of 1.7 to 2.2 g/cm^3 ; removing the forming binder from the compact body; and sintering the compact body at a temperature of 1100 to 1550°C under a reduced pressure of 5×10^{-1} Torr or less and then in an inert gas atmosphere under atmospheric pressure or under an increased pressure at a temperature of 1550 to 2100°C.
2. A method as claimed in claim 1, wherein the carbon is one of carbon black, charcoal, coke, carbonized chaff, and activated carbon.
3. A method as claimed in claim 1 or claim 2, wherein a phenolic resin is used as the carbon compound and the forming binder.
4. A method as claimed in any one of the preceding claims, wherein the amount of boron or the boron content of the boron compound used is 0.05 to 0.15 part by weight.
5. A method as claimed in any one of the preceding claims, wherein the sintered body is used for wear-resistant sliding part.
6. A method as claimed in claim 1 substantially as hereinbefore described.
7. A method as claimed in claim 1 substantially as hereinbefore described in any one of the specific Examples.



8. A wear-resistant sliding part when formed from a silicon carbide sintered body as claimed in any one of the preceding claims.

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