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SILICON NITRIDE SINTERED BODY

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14. Abstract  Sintered silicon carbide and its production are described. A detailed description of the invention is given. The invention is illustrated by means of six examples.  ORIGIN OF THIS COPY OF POOR QUALITY			
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## Specifications

### 1. Title of Invention

Sintered silicon carbide and its production.

### 2. Scope of Patent Claim

(1) Sintered silicon carbide consisting essentially of fine granules of silicon carbide with aluminum oxynitride crystals present at the granular boundary of the silicon carbide.

(2) The sintered silicon carbide of Claim 1 in which the flexural strength exceeds  $50 \text{ kJ/mm}^2$  at normal temperatures and  $50 \text{ kg/mm}^2$  at the high temperature of  $1400^\circ\text{C}$ .

(3) A method of producing sintered silicon carbide in which a mold consisting of aluminum oxynitride crystals or material which produces aluminum oxynitride crystals during sintering at an amount of 0.2 to 10 wt.% converted to the amount of Al with a remainder consisting essentially of silicon carbide is sintered in a non-oxidizing atmosphere at a temperature of  $1900$  to  $2300^\circ\text{C}$ .

(4) A method of producing sintered silicon carbide characterized by sintering a mold consisting of 0.2 to 10 wt.% converted to the amount of Al of aluminum oxide with a remainder essentially of silicon carbide in an atmosphere containing AlN at a temperature of  $1900$  to  $2300^\circ\text{C}$ .

### 3. Detailed Description of the Invention

This invention concerns sintered silicon carbide, especially dense, strong sintered silicon carbide and its method of production by so-called usual calcination in which molding is followed by sintering without compression.

Silicon carbide is known as useful ceramic material with high hardness, outstanding abrasion resistance, a low coefficient of thermal expansion, a high degradation temperature, great resistance to oxidation, chemical stability and considerable electrical conductivity. In addition to the aforementioned properties, high density sintered silicon carbide has strength at high temperatures, outstanding resistance to thermal shock, and is promising as high temperature structural material. It has been tested in various applications, beginning with gas turbines. Silicon carbide is difficult to sinter alone because it is a compound with strong covalent bonding. A sintering promotor must be added to produce a high density sintered substance. B, B<sub>4</sub>C or AlN are used as sintering promotors in hot pressing. Carbon is added to these in usual pressure sintering. However, the product of normal sintering is inadequate in terms of performance, as discussed below. /350

The inventors have conducted research to discover sintered silicon carbide with superior characteristics to those of the conventional product using ordinary calcination which does not rely on hot pressing, and they have discovered that the use of aluminum oxide as a sintering promotor is effective.

The use of aluminum oxide as a sintering promotor of silicon carbide has been known, but usually,  $\text{Al}_2\text{O}_3$  has been blended in the coarse particle aggregate of silicon carbide and molded, followed by calcination at a temperature of 1200 to 1500°C. The product has had low strength due to the presence of large amounts of a layer of aforementioned or  $\text{SiO}_2$  around the granules of silicon carbide (SiC). The product belonged to the category of refractory brick.

In contrast, a product with outstanding strength is produced through normal pressure (ordinary) sintering because of improvements in various conditions when using the aforementioned aluminum oxide ( $\text{Al}_2\text{O}_3$ ).

The resulting sintered material can be sufficiently used in industry and has already been used in practice, but with recognition of the superiority of this type of silicon carbide sintered ceramic, a product with even better performance has come to be demanded.

The inventors have conducted further research to meet these demands, and they have realized that improvement in the composition is essential.

Accordingly, in considering the composition of sintered silicon carbide, the use of a sintering promotor results in considerable residue of a second phase consisting primarily of the promotor on the silicon carbide granular boundary. This second phase reduces the performance at high temperatures. A

softening phenomenon is induced at high temperatures even when slight amounts of aluminum oxide remain at the granular boundary when using aluminum oxide as the sintering promotor, and this greatly reduces the strength at hgh temperatures. Thus, elimination of sintering promotor at the silicon carbide granular boundary of the sintered material which is present due to degradation and solid solution development is desirable, but complete implementation of this is difficult. Furthermore, there are limits to improvement in the strength even if sintered material could be produced without the presence of a sintering promotor.

Furthermore, the intertwining of the dimensions and shape of the silicon carbide granules which constitute the fine structure is important. They vary with the sintering promotor and the sintering conditions (atmosphere, temperature, presence of pressure). For example, intertwined isometric granules and columnar granules of silicon carbide are desirable.

This invention is the result of research to develop sintered silicon carbide with such a new and effective crystalline structure.

Specifically, this invention provides sintered silicon carbide composed essentially of fine granules of silicon carbide characterized by the presence of aluminum oxynitride crystals at the silicon carbide granular boundary as well as the method of production.



This invention is characterized by the novel presence of Al-O-N-based crystals, aluminum oxynitride, at the silicon carbide granular boundary, thereby suppressing softening at the granular boundary at high temperatures.

Thus, in this invention, the aluminum oxynitride induces an effect without decline in the high temperature strength even when it is present at the silicon carbide granular boundary, but in the sintered material, the switch to material whose minimization is desirable, such as oxides which induce high temperature softening, is best at the granular boundary which occupies a very slight proportion of the total volume. The amount is essentially very slight, and the effect is enhanced with lower amounts.

The aluminum oxynitride in the sintered material of this invention is present on the contact bonding surfaces of the silicon carbide granules, and it is present among the granules in the matrix in very slight amounts in terms of the volumetric proportion of the sintered material. /351

Furthermore, the fine structure in the sintered material of this invention consists of plate shaped granules or columnar shaped granules intertwined when  $\beta$  type silicon carbide is used as the raw material. Furthermore, the structure consists of primarily isometric granules when  $\alpha$  type silicon carbide is used as the raw material. The size of the granules is under 10  $\mu\text{m}$ , and preferably under 2  $\mu\text{m}$ .

The aluminum oxynitride which is present in this invention should be present in the form of one or more compounds consisting of Al, O and N. In the system consisting of AlN-Al<sub>2</sub>O<sub>3</sub>, AlN should be present in the range of 20 to 90 mol%. There are two types of forms, the spinel phase and the X phase. These may be present separately or blended.

The presence of aluminum oxynitride is confirmed through X-ray diffraction or characteristic X-ray spectral analysis and electron energy loss spectral analysis, but quantitative analysis is difficult.

Furthermore, there is a very slight amount of aluminum oxynitride at the silicon carbide granular boundary as the crystals which exist in the sintered material of this invention, but  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, AlN, Sialon, aluminum oxycarbide, and aluminum silicon carbide have also been confirmed.

The method of production of such sintered material is explained below.

First, the use of crystals of silicon carbide (SiC) raw material in either the  $\alpha$ -form or the  $\beta$ -form is desirable. The purity should exceed 98%, but material with purity of 90 to 98% can be used effectively. The grain size is expressed in the specific surface area rather than in the mean granular diameter in the case of extremely fine granules. Material with a specific surface area above 5 m<sup>2</sup>/g, preferably above 10 m<sup>2</sup>/g, is desirable in order to effectively achieve the objectives of this invention.

Next, the sintering promotor used in the silicon carbide raw material is related to the calcination conditions, and material which provides the composition characterized by aluminum oxynitride, which is the objective of this invention, must be selected.

First, the ingredient which most closely matches the objectives of this invention is aluminum oxynitride which exists in sintered material as an additive in the silicon carbide raw material.

This aluminum oxynitride must be synthesized since it does not exist alone naturally.

Synthesis of it is not especially difficult. For example, it is produced by calcination of a blend of AlN and Al<sub>2</sub>O<sub>3</sub> in N<sub>2</sub> at a temperature of 1600 to 2100°C.

The synthesized aluminum oxynitride usually has a melting point above 2000°C, and it has been confirmed to demonstrate the same effects as a sintering promotor as Al<sub>2</sub>O<sub>3</sub>.

The total amount of the synthesized aluminum oxynitride in the silicon carbide should be 0.2 to 10 wt.% converted to Al. That is because densification during sintering does not proceed sufficiently when the amount is under 0.2% while the crystals readily exist in sintered material when the amount exceeds 10%, but sufficiently strong material cannot be produced even if densification occurs following sintering at low temperatures below 1900°C. Furthermore, when an excessive amount is added,

porosity of the sintered material is induced at the temperature range of 1900 to 2300°C which is required to produce the sintered material of the invention.

The optimum amount of addition is 0.5 to 5%. Furthermore, material which exists as crystals of aluminum oxynitride at the silicon carbide granular boundary in addition to aluminum oxynitride which has been synthesized in advance may be used. A means of achieving that would be to suitably select the calcination conditions and the additive as the sintering promotor. A desirable example is illustrated below.

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Specifically, sintering in the presence of AlN as the atmosphere would be conducted when selecting Al<sub>2</sub>O<sub>3</sub> (alumina) as the sintering promotor. Corundum can be used conveniently for aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) in this case, but other crystal forms such as the gamma form may also be used. Furthermore, aluminum hydroxide or aluminum sulfate, which form aluminum oxide upon heating, may also be used. The aluminum oxide of this invention includes these compounds which form aluminum oxide. The purity based on the residue following heating should exceed 98%, and the material should have a low soda content. The grain size should be under 1 μm mean grain diameter, preferably under 0.2 μm.

The proportion of aluminum oxide in the total silicon carbide in this invention is 0.2 to 10 wt.% in terms of Al. That is because densification does not adequately proceed upon sintering when the proportion is under 0.2%, while densification proceeds, but the strength declines even upon sintering at low

temperatures below 1900°C when the amount exceeds 10%. Furthermore, the amount of decomposition increases following sintering at a temperature of 1900 to 2300°C, and porosity develops.

In this invention, the raw material should be compounds whose residue consists essentially of silicon carbide as well as alumina as one feature of this invention, but the silicon carbide raw material may contain slight amounts of other ingredients which are contained or incorporated during pulverization as impurities. Furthermore, comparatively large amounts of one ingredient such as silicon oxide may also be contained, which is an additional advantage.

Suitable amounts of aluminum oxynitride and alumina may be used jointly.

Furthermore,  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  may be used as the sintering promotor in another mode of this invention, and Al-O-N compounds may be produced in the sintered material due to the reaction of  $\text{Al}_2\text{O}_3$  and  $\text{AlN}$  during sintering in an  $\text{N}_2$  gas atmosphere at 1900 to 2300°C.

Next, methods which are used in ordinary molding of ceramics may be used as the method of molding in this invention. Specifically, press molding, slurry pouring molding, injection molding or extrusion molding may be used.

Sintering must be conducted in a non-oxidizing atmosphere regardless of the sintering promotor used. However, the mold

itself need not be subjected to special compression (hot pressing). That is a significant advantage of this invention. Of course, sintering by hot pressing or hot isotatic pressing may also be used.

The sintering atmosphere is explained further here. Nitrogen, argon, helium, carbon monoxide or hydrogen, which form a non-oxidizing atmosphere, may be used when using aluminum oxynitride which has been synthesized in advance, but nitrogen, argon or helium would be most convenient. Nitrogen is especially desirable because it suppresses decomposition of aluminum oxynitride.

Conversely, special measures are required when using  $Al_2O_3$  since aluminum oxynitride, which is the objective, cannot exist only in these atmospheres as the sintering promotor. One measure would be the use of an atmosphere containing AlN. There are numerous ways of producing an atmosphere containing AlN. For example, the following method would be easy and suitable. Specifically, AlN powder could be blended around SiC mold and heated in a non-oxidizing atmosphere to 1900 to 2300°C, thereby producing an atmosphere containing AlN.

There are various means of blending AlN powder around SiC mold, including compression molding of AlN powder followed by setting this mold near a SiC mold or coating the inner walls of a pod set in a SiC mold with AlN powder.

The calcination temperature must be 1900 to 2300°C, preferably 1950 to 2100°C. Densification does not proceed sufficiently and a high density sintered product does not develop when the temperature is under 1900°C, while the mold undergoes excessive decomposition, resulting in porosity, when the temperature exceeds 2300°C. In addition, the granular growth is excessive, which is undesirable. The time must be 1 to 24 hours, preferably 2 to 10 hours. Densification does not occur when the time is too short, and adequate strength is not reached even if densification does take place, while excessive decomposition occurs, resulting in porosity if the time is too long. Furthermore, the granular growth is excessive, which is undesirable. /353

The composition of the sintered material of this invention which is produced in the aforementioned manner has an improved granular boundary composition, and the actual strength is as follows.

Specifically, the flexural strength should be at least 50 kg/mm<sup>2</sup>, preferably 70 kg/mm<sup>2</sup>, and most preferably in excess of 80 kg/mm<sup>2</sup>. The high temperature flexural strength is much better than in the past. For example, strength exceeding 50 kg/mm<sup>2</sup> at 1400°C is easily achieved even in sintering without compression. Strength above 60 kg/mm<sup>2</sup>, and even strength exceeding 70 kg/mm<sup>2</sup>, can be achieved.

Actual examples of this invention are explained below.

### Actual Examples 1-5

$\text{Al}_2\text{O}_3$  powder and AlN exceeding 98% purity with mean granular diameter below  $3 \mu$  were blended at (a) 35:65 mol%, (b) 50:50 mol%, and (c) 70:30 mol% ratios. These blended powders were heated for two hours at  $2000^\circ\text{C}$  in an  $\text{N}_2$  gas atmosphere. The heated powders were then pulverized to a mean granular diameter under  $1 \mu$ . The results were Al-O-N compound powders consisting respectively of the (a) spinel phase, (b) spinel phase + X phase, (c) X phase.

The X phase was hexagonal crystals of Al-O-N compound identical with aluminum oxynitride.

$\beta$  and  $\alpha$ -type silicon carbide powder with purity above 98% and specific surface area above  $13 \text{ m}^2/\text{g}$  were blended with the three types of Al-O-N compound powders (a), (b) and (c) in the proportions illustrated in Table 1. The blends were then subjected to hydraulic molding at pressure of  $2000 \text{ kg}/\text{cm}^2$ , thereby producing molds approximately  $40 \times 20 \times 15 \text{ mm}$ . These were then sintered in an  $\text{N}_2$  gas atmosphere for three hours at  $2050^\circ\text{C}$ . The density and strength of the resulting sintered materials are illustrated in Table 1.

### Actual Example 6

A mold was produced using the same raw materials as were used in actual examples 1-5 and the same method except that only  $\text{Al}_2\text{O}_3$  was added. In addition, compressed powder only of AlN approximately  $20 \times 20 \times 20 \text{ mm}$  was produced. Both SiC mold and



AlN mold were placed in a carbon case fitted with a lid and heated in an N<sub>2</sub> gas atmosphere for 5 hours at 2000°C. The resulting density and strength of the sintered material are illustrated in Table 1.

Actual Examples 7, 8

A mold was produced using the same raw materials as were used in actual examples 1-5 and the same method except that Al<sub>2</sub>O<sub>3</sub> and AlN were added to produce a mold. This was then sintered for five hours at 2000°C. The resulting density and strength of the sintered material are illustrated in Table 1.

Table 1

1 实例例	S i C 主结晶形	3 添 加 剂 4 种	5 量 (wt.%)	6 密 度 (g/cm <sup>3</sup> )	7 曲 折 强 度 (kg/cm <sup>2</sup> )	8 1400°C
1	2,	(a)	5	3.15	805	64.5
2	"	(b)	5	3.10	68.4	65.6
3	"	(c)	5	3.10	75.2	71.3
4	"	"	10	3.13	85.6	76.2
5	α	(a)	5	3.18	62.0	63.5
6	"	Al <sub>2</sub> O <sub>3</sub>	10	3.16	65.3	60.8
7	β	Al <sub>2</sub> O <sub>3</sub> AlN	5 5	3.05	70.2	63.4
8	α	Al <sub>2</sub> O <sub>3</sub> AlN	4 1	3.17	59.2	59.1

1 Actual Example

3 additive

5 amount (wt.%)

7 flexural strength (kg/mm<sup>2</sup>)

2 main crystal form

4 type

6 density

8 chamber temperature

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