

## One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

(NASA-TM-77601) TREATING SILICON CARBIDE  
SINTER BY HEATING IN NITROGEN (National  
Aeronautics and Space Administration) 10 p  
HC A02/MF A01 CSCL 11D

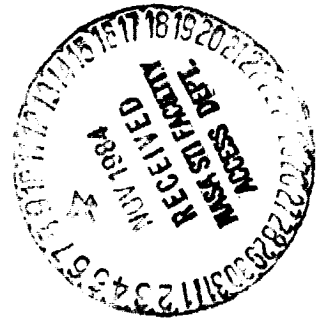
N85-10130

Unclas  
G3/24 24174

TREATING SILICON CARBIDE SINTER BY HEATING IN  
NITROGEN

S. Takahata

Translation of "Tanka keiso shoketsu tai  
no seizo Hohhoh," Japanese patent no. 58-64284,  
April 16, 1983, pp. 423-426.



1. Report No. NASA TM-77601	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle TREATING SILICON CARBIDE SINTER BY HEATING IN NITROGEN		5. Report Date AUGUST 1984	
		6. Performing Organization Code	
7. Author(s) S. Takahata		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address SCITRAM Box 5456 Santa Barbara, CA 93108		11. Contract or Grant No. NASA 3542	
		12. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
		13. Supplementary Notes  Translation of "Tanka keiso shoketsu tai no seizo Hohhoh," Japanese patent no. 58-64284, April 16, 1983, pp. 423-426.	
16. Abstract  A description is given of treating silicon carbide sinters by heating in nitrogen. A detailed explanation of the invention is presented. Two procedures to be followed in the invention are described.  ORIGINAL PAGE IS OF POOR QUALITY			
17. Key Words (Selected by Author(s))		18. Distribution Statement  Unclassified and Unlimited	
19. Security Classification (of this report) Unclassified	20. Security Classification (of this page) Unclassified	21. No. of Pages 10	22. Price

TREATING SILICON CARBIDE SINTER BY HEATING  
IN NITROGEN

S. Takahata

- 19 Japan Patent Office (JP)
- 12 Patent Disclosure Official Report (A)
- 11 Patent Application Disclosure 1983 - 64284

Identification No. 101

Patent Office No. 8216-4G

- 43 Disclosure April 16, 1983
- No. of inventions: 1
- Auditing Request: not claimed

(total: 4 pages)

- 
- 54 Method of manufacturing a silicon carbide sintered body
  - 21 Special claim 1981 - 161540
  - 22 Application date: October 9, 1981
  - 72 Inventor: Shigeru Takahata, Masago 2-15, Chiba city
  - 71 Shinetsu Chemical Industry Co., 6-1, 2-chome,  
Ohtemachi, Chiyoda-ku, Tokyo
  - 72 Attorney: Katsuichi Yamamoto

SPECIFICATIONS

/423\*

1. Name of the invention

Method of Manufacturing a Silicon Carbide Sintered Body

2. Claim

1. This method of manufacturing a silicon carbide sintered body makes the metallic silicon in the surface layer of the silicon carbide, which consists of silicon carbide and metallic silicon, into silicon nitride by reacting it with nitrogen gas at a temperature greater than 900°C.

2. This is a method of manufacturing a silicon carbide sintered body described in the first item in the claim. The method consists of an etching process on the silicon carbide sintered body with chemicals that dissolve metallic silicon and, after that, nitrogen gas reacts with it at a temperature above 900°C.

### 3. Explanation of the Invention in Detail

This invention concerns a method of manufacturing a silicon carbide sintered body, especially one which has a surface layer consisting of silicon carbide and silicon nitride. The following method of producing a silicon carbide-silicon sintered body is well known.

Silicon carbide and carbon are mixed with an organic type binder and molded. After calcination, machining is performed if necessary. Then metallic silicon in the molten form or gaseous form is put in contact with it, and the carbon in the calcined body is made into silicon carbide, and a silicon carbide-silicon sintered body is produced. (Refer to American patent No. 2,938,807 and No. 3,495,935). Compared to the hot press method for manufacturing this kind of silicon carbide sintered body, and the method in which silicon carbide powder of less than 1 micron is heated at 1900-2300°C, the reaction temperature is good in the range of 1400°C -1700°C, which is the melting point of metallic silicon. A sintered body produced by this method has an advantage in that there is no deformation at the time of sintering, as the dimensional change at the time of molding and sintering is less than 1-2%, Thus a homogeneously sintered body can be obtained.

However, since this method makes metallic silicon a /424 catalyst in a silicon carbide calcined body, unreacted metallic silicon remains in the silicon carbide sintered body as the

specified substance. Also this metallic silicon attaches to the surface, and this attachment also occurs by surface effusion caused by cubic expansion, which occurs when the metallic silicon remaining in the sintered body solidifies. It is necessary to eliminate this metallic silicon from the surface of this sintered body. Also, the elimination of the metallic silicon is performed by a mechanical method such as sandblasting. This method is very expensive, if mass production is applied to a small extent. There is also a disadvantage in that the accuracy of the dimensions of the body might be lost. Regarding the elimination of the metallic silicon, chemicals which do not affect silicon carbide, and dissolve only metallic silicon have been tried - for example, methods in which the sintered body is processed by a fluoric acid-nitric acid mixture, or by a warm aqueous solution of caustic soda at over 50°C. However, in this case a very great deficiency occurs. The surface of the sintered body changes to a yellowish-green color, and the hardness declines greatly. This is a disadvantage, as the surface layer which has become a yellowish green color, must be processed by machines, such as sandblasting and barreling.

Regarding this silicon carbide sintered body, if this is used as a melting crucible for high purity metals, the metallic silicon begins to melt and contaminates the specified substance. Thus it has been proposed to process the sintered body beforehand at a high temperature in air to make the metallic silicon into SiO<sub>2</sub>. But the SiO<sub>2</sub> is reduced and becomes metallic silicon in a reducing atmosphere, and under a high temperature vacuum the SiO<sub>2</sub> contaminates the atmosphere. Since SiO<sub>2</sub> dissolves in the molten solid when the crucible process is the melting of a ferrite oxide, the oxidation process is not always useful.

The invention concerns a method of manufacturing a silicon carbide sintered body in which the above disadvantages were solved. Under this invention, the metallic silicon which exists in a silicon carbide sintered body consisting of silicon carbide and metallic silicon, reacts with nitrogen gas at a temperature over  $900^{\circ}\text{C}$  and made into silicon nitride.

The inventor and others studied how to improve the quality of the reaction sintered type silicon carbide, which consists of silicon carbide and metallic silicon. Consequently, if the metallic silicon which exists on the surface of the silicon carbide sintered body is made into silicon nitride by nitriding, the heat resistance becomes  $1900^{\circ}\text{C}$ , which is the decomposition temperature of silicon nitride, instead of  $1400^{\circ}\text{C}$ , which is the melting point of metallic silicon. Even if this is used as a crucible for melting metals, the metal is not contaminated by the decomposition of silicon nitride. Also it was found that silicon nitride was not reduced, and it did not evaporate in a reducing atmosphere or in a ferrite oxidation process. Also the formation of silicon nitride occurs only on the surface layer, and the internal layers do not change from a SiC-Si sintered body. It was thus confirmed that this could be widely used for various uses as non-oxide ceramics and the invention was completed.

The reaction sintered type silicon carbide sintered body which is used for the initial material in this invention has been previously known to be good. If the case of silicon carbide and carbon powder is considered, it is mixed with a binder: for example, methyl cellulose, phenolic resin, silicium resin, or tarred pitch. This is molded in the desired configuration by a rubber press or extrusion molding, and after that it is made into a calcined body by heating between  $500$  and  $1000^{\circ}\text{C}$  in an inert gas such as nitrogen, argon, neon, etc. Next it is heated at over  $1400^{\circ}\text{C}$  in an inert gas or in a vacuum, and the reaction

sintered type silicon carbide sintered body can be obtained by placing it in contact with metallic silicon in the molten or gaseous forms. In this case the greater part of the metallic silicon becomes silicon carbide by reaction with carbon, and the residue remains inside of the silicon carbide calcined body as it is. However, as mentioned before, a part of it effuses from the outer layer by cubic expansion at the time of cooling.

The method proposed by this invention nitrifies the metallic silicon which exists in the outer layer of the silicon carbide sintered body. This is done by heating the silicon carbide sintered body, obtained by the above method, at over  $900^{\circ}\text{C}$  in an atmosphere of nitrogen gas, or favorably from  $1,250^{\circ}\text{C}$  to  $1,450^{\circ}\text{C}$ . Since the structure of the silicon carbide sintered body is minute, the reaction does not reach the internal layers. Only 425 the metallic silicon of its surface layer is nitrified. For the nitrifying reaction, it is better to eliminate substances which might harm the configuration of the formed body or the stability of its dimensions. This can be done by a mechanical method such as sandblasting, or by a mixed solution of fluoric and nitric acids, or by caustic soda in warm water which dissolves metallic silicon. However, if this is performed by the fluoric acid - nitric acid mixed solution or caustic soda methods, as mentioned before, the surface becomes a yellowish green color and hardness decreases. In this case it is better to process the metallic silicon and silicon carbide calcined body before reaction with a synthetic resin such as phenol resin, any kind of fat or oil, liquation including paraffin or polycarbosilane and, depending on the process, this disadvantage can be prevented and nitrifying can proceed efficiently.

The nitrifying reaction is performed with the well known fluoric material, iron powder, etc. as nitrifying catalysts.



Mixing from 0.01 to 20% hydrogen in the nitrogen gas is an option, and, depending on this, the nitriding can proceed more efficiently. A silicon carbide sintered body which is obtained by the method of this invention has a surface layer which consists of silicon carbide and silicon nitride. Since metallic silicon does not exist in the surface layer, there are no problems under  $1900^{\circ}\text{C}$ , which is the decomposition temperature of silicon nitride. Since it also becomes chemically stable and is not disturbed even by a mixed solution of fluoric and nitric acids, it will be widely used as a ceramic agent.

Following are the procedures of the invention.

#### Procedure 1

200 grams of commercial silicon carbide powder of average grain size of 9.5 microns, 120 g of artificial graphite of average grain size of 1.0 microns, and 160 g of silicon resin KR-260 (manufactured by Shinetsu Chemical Industry) were added to 200 ml of methylbenzene in a ball mill. The methylbenzene was removed and a powder mixture under 100 mesh was made.

Next a column with a diameter of 50 mm, length of 70 mm was formed by using a hydrostatic press, and it was calcined at  $800^{\circ}\text{C}$  in an atmosphere of nitrogen gas. After that it was formed into a crucible form with an outer diameter of 45 mm, inner diameter of 35 mm length of 60 mm, and bottom thickness of 5-6 mm. This was reacted with metallic silicon in a vacuum furnace at  $1600^{\circ}\text{C}$ , and the surface was processed by sandblasting, and a crucible, consisting of a silicon carbide-silicon sintered body was produced.

Next the crucible was put in a furnace at  $1100^{\circ}\text{C}$  in a 4:1 nitrogen gas-hydrogen gas mixture. The temperature of the furnace was up to  $1,400^{\circ}\text{C}$  at  $50^{\circ}\text{C}$  per hour, and was maintained

for 4 hours. After that, the temperature was cooled down to room temperature, and the composition of the surface was studied by X-ray analysis. The X-ray analysis confirmed that metallic silicon did not exist, but the surface was silicon carbide and silicon nitride.

When 30 g of metallic aluminum was put in the crucible and heated and melted at 850°C in the vacuum furnace, the metallic silicon in the aluminum was 10 ppm. The amount of metallic silicon, when a crucible was used for which the above mentioned nitriding was not performed, was 200-400 ppm.

### Procedure 2

A ring with outer diameter of 76 mm, inner diameter of 65mm, and length of 6 mm was made from the same raw material as for Procedure 1. It was heated at 850°C in an atmosphere of nitrogen gas and made into a calcined body. It was then impregnated with 50% polycarbosilane in a methylbenzene solution, and it was reacted with metallic silicon in a vacuum furnace at 1600°C, and a ring was produced consisting of a silicon carbide-silicon sintered body.

It was then dipped in a 30% solution of caustic soda which was heated at 70°C for 8 hours, and the silicon existing on the outer surface was eliminated. It was then put in a furnace in an atmosphere of a 4:1 mixture of nitrogen gas and hydrogen gas at a temperature of 1,300°C, and evacuation-gas charging was performed every hour. These conditions were maintained for 8 hours. It was then cooled to room temperature. The product obtained by specular finishing was X-ray analyzed on its surfaces, and no metallic silicon was detected.

When the product was dipped in aqueous solution of 3%

fluoric acid-nitric acid (1:1), no weight change was found. The product which was not nitrated continued to lose weight, and 85% of its metallic silicon was dissolved in 200 hours.

Patent Applicant: Shinetsu Chemical Industry Co.  
Attorney : Katsuichi Yamamoto