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SINTERED SILICON NITRIDE WORKPIECE

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Translation of "Chikka keiso no shohketsu Hohhoh," Japanese patent no. 58-64275, April 16, 1983, pp. 379-381.

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16. Abstract

A description is given of a sintering method for silicon nitride. A detailed explanation of the invention is presented. Four procedures for the sintering process are described.

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SPECIFICATIONS

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1. Name of the invention

Sintering Method of Silicon Nitride

2. Claim

This is a sintering method of silicon nitride which has the following characteristics. Calcine compacted silicon nitride for 30 - 500 minutes at 400-800°C in air, and dip the obtained porous body in a solution including metallic compounds which are chosen from the group of Al, Mg, Si, Y, and Zr.

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*Numbers in margin indicate foreign pagination

Calcine again under the above conditions and later sinter 60-500 minutes at 1500 - 2400°C in an atmosphere of inert gas.

3. Detailed Explanation of the Invention

The subject of this invention is a sintering method of silicon nitride (Si_3N_4) as a ceramic sintered body.

Since silicon nitride is difficult to sinter, sintering is performed by adding a small amount of the proper sintering agent: for example, spinel (Al_2O_3 + MgO), Y_2O_3 + MgO, Al_2O_3, Y_2O_3, MgO or SiO_2 by itself or in combination. In specific terms, silicon nitride as a main component, and the above compounds as sintering agents, are reduced to powders of less than 1 micron. In order for the proportion of sintering agent to silicon nitride to be 2 to 20 mole %, both (silicon nitride and sintering agent) are mixed with the proper amount of organic binder and a small amount of water. Then the desired configuration (for example, a configuration of parts for a gas turbine, etc.) is formed, and later it is sintered at high heat such as about 2000°C.

However, for this type of sintering method both the silicon nitride and the sintering agent are used as powders. By mixing both compounds in the powder form, the mixing becomes insufficient because of differences in specific gravity, differences in chemical adsorption due to different surface energies, and also differences in the particle size distribution, etc. Problems thus arise. For example, as a result density differences occur in the final sintered product. Also the strength of the final sintered product is insufficient.

The purpose of this invention is to produce a final sintered product of silicon nitride which has excellent characteristics by supplying a silicon nitride sintering method in which the sintering agents are used efficiently after being dispersed and mixed. /380

The characteristics of the sintering method of this invention are as follows. Silicon nitride powder is molded by using an organic binder, or by adding the usual sintering agent. After molding, the porous body is dipped in a solution which satisfies the following conditions and is calcined again and sintered. The above solution includes metals which form the above mentioned oxides, which are used as the usual sintering agents, namely, Al, Mg, Si, Y or Zr in the following compounds - for example, carbonates of the said metals, nitrates, or sulfates or organic compounds of the metals. In this case, water or hydroxy compounds, for example, alcohol or phenol, are used for solvents.

The most important characteristic of this invention is to add the substance which acts as sintering agent not in solid form, but in liquid form. In this case the first calcination makes a compact porous body of silicon nitride, and the second calcination converts the impregnated metallic compounds to metallic oxides. The following conditions are used for both of the calcinations:

atmosphere:	air
heating temperature	400 - 800°C
heating time	30 - 500 minutes

Also the calcined material, obtained by these two calcinations, is sintered under the following conditions:

atmosphere:	inert gas
heating temperature	1500 - 2400°C
heating time	60 - 500 minutes

A commonly used organic binder used for molding is polyvinyl alcohol. Water is added if necessary. Following is a detailed explanation of this invention .

Procedure 1

30 parts polyvinyl alcohol are added to 100 parts of Si_3N_4 of 0.5 micron grain size, and molded in the configuration of a gas turbine rotor. This molded body is calcined in an air atmosphere at 600°C for 3 hours and a porous body is obtained. Then the porous body is dippled alternately in an ethanol solution of aluminum acetate and a methanol solution of magnesium oxalate, and it is calcined under the above conditions. The dipping and calcining operations are repeated until Al or Mg become 1 - 10 mole% toward Si_3N_4, namely, until the Si_3N_4 is impregnated. Then the calcinated material is sintered at 2000°C for 5 hours in an atmosphere of argon gas and sintered material (no. 1) is obtained.

Procedure 2

30 parts of polyethylene resin are added to 100 parts of a mixed powder which includes 2 moles each of Al_2O_3 and Y_2O_3 in 100 moles of Si_3N_4 of average grain size of 0.7 microns. This mixture is molded in a plate configuration of a gas turbine engine. This molded body is calcined in an air atmosphere at 450°C for 2 hours and a porous body is dipped alternately in an aqueous solution of aluminum hydroxide and a trimethylphenol (TMF) solution of sodium and zirconium, and calcined under the above conditions. These operations are repeated until the necessary amount of impregnation is reached. Then the sintered material is obtained (No. 2) by sintering the calcined material

in an atmosphere of nitrogen at 2300°C for two hours.

Procedure 3

In procedure 1, sintered material (No. 3) was obtained by using silicon oil instead of aluminum acetate.

Procedure 4

As in procedure 1, sintered material (No. 4) was obtained by molding, not in the form of a gas turbine rotor, but in the form of a gas turbine engine shroud. At the time of molding, slip casting (molding method) was employed.

Comparison Example 1

When this process was performed without the dipping process of procedure 1, a sintered body was not obtained.

Comparison Example 2

In procedure 2, a sintered material (contrast 1) was obtained without a dipping process. /381

(a) hardness and (b) flexural strength were measured for the sintered bodies (No. 1-4 and Contrast 1) which were obtained in each example. In this case, (a) was performed by the micro Vickers method, and (b) was performed by the three point bending method. The following table gives the results of these measurements.

TABLE

Sintered body	Characteristics	
	Hardness	Flexural strength (kg/mole)
1	1570	56
2	1620	63
3	1580	58
4	1500	54
Contrast 1	1320	29

As can be seen in the above table, the sintered bodies (No. 1-4) of this invention have outstanding values for both hardness and flexural strength compared to the past sintered bodies (Contrast 1).

As mentioned in the Procedure, a necessary amount of impregnated metal, which consists of the sintering agent, is in the range of 1 - 10 mole% toward Si_3N_4. To maintain the amount within this range, it is best to adjust the concentration and viscosity properly.

As above, depending on the sintering method of this invention, the sintering agent diffuses homogeneously in the molded body by impregnating the silicon nitride molded body with the material which is to become the sintering agent in liquid form. As a result, silicon nitride sintered bodies which have outstanding characteristics are obtained. This was possible by calcining before impregnation and making the molded body before a porous body, and also by converting metal oxides, which are the usual sintering agents, from liquid substances by calcining after impregnation.

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