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SILICON CARBIDE CERAMIC PRODUCTION

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Translation of Japanese Kokai Patent No. 58-91064; Published, May 30, 1983; Application No. 56-189209; Filing Date, November 7, 1981; Inventors, Keiichiro Suzuki et al.; Assignee, Asahi Glass Co., Ltd., Tokyo, Japan
This invention describes a method to produce sintered silicon carbide ceramics in which powdery carbonaceous components with a dispersant are mixed with silicon carbide powder, shaped as required with or without drying, and fired in non-oxidation atmosphere. Carbon black is used as the carbonaceous component.

**Translation of Japanese Kokai Patent No. 58-91064:**
Published, May 30, 1983; Application No., 56-189209; Filing Date, November 27, 1981; Inventors, Keiichiro Suzuki et al.; Assignee, Asahi Glass Co., Ltd., Tokyo, Japan.
1. Name of the invention

Silicon carbide ceramic production

2. Scope of the patent application

(1) A method to produce sintered silicon carbide ceramics in which carbonaceous components with a dispersant are mixed with silicon carbide powder, shaped as required with or without drying, and fired in non-oxidation atmosphere.

(2) The production method which is listed in para 2 (1) of this application, in which carbonaceous components are used, in this invention uses carbon black.

(3) The production method which is listed in para 2 (1), 2 (2) of this application in which carbon (C) as the carbonaceous component (0.2 - 10 % in weight of silicon carbide), and a dispersant (0.05 - 50 % in weight of carbon) are mixed to be used as silicon carbide mixture.

(4) The production method listed in para 2 (1) and 2 (3) of this application in which silicon carbide mixture containing carbon components and a dispersant are spray dried to form raw material for the production.

(5) The production method listed in para 2 (1) and 2 (4) of this application in which silicon carbide mixture is fired in non-oxidation atmosphere in 1900 - 2300 degrees C temperature.

(6) The production method listed in para 2 (1) and (5)

*Numbers in the margin indicate pagination in the foreign text.*
of this application in which the firing of the silicon carbide mixture is done without applying mechanical pressure.

(7) The production method listed in para 2 (1) and 2 (6) of this application in which boron components or aluminum components are used as agents for promoting sintering.

3. Detailed description of the invention

This invention pertains to a production method of high density silicon carbide ceramics sintering.

Silicon carbide is known to be a useful ceramics material which is high in solidity and dissolution temperature, low in a coefficient of thermal expansion, abrasion-proof and oxidation-proof, chemically stable and generally excellent in electric conductivity. Its high density sintering is, in addition to the above characteristics, shock-proof and superior in rigidity even in high temperature. Its use as high temperature structuring material, e.g., gas turbine etc., is full of promise.

Production method of silicon carbide sintering include hot press sintering, constant pressure sintering, reaction sintering, recrystallization and chemical evaporation methods. The constant pressure method among the ones mentioned above is said to be the most efficient for industrial use. Commonly used methods of forming ceramics material by the constant pressure method are the press method, the mixture casting method, the extrusion method and the injection forming method. These methods are effective in producing complicated, thin and thick, and large and small ceramic products. In addition, these products by this method are higher in performance capacity than any other products of other methods.
However, because silicon carbide, a covalent bond, is difficult in sintering itself by the constant pressure sintering method (same as the hot press sintering method), an agent to promote sintering needs to be added if high density sintering is to be produced. Known sintering agents for hot press sintering method are boron, boron compounds, aluminum and aluminum compounds. The same for the ordinary pressure method are those listed above and carbon.

In case of the constant pressure sintering method, it is difficult to produce a high quality, high density sintering even if the additive agent is used in the production process. It is so because a layer of silica on the surface of the silicon carbide, in particular, is difficult to remove. This problem becomes more severe when complicated shapes, large and thick products must be produced in even density and high quality.

A typical production method of silicon carbide ceramics sintering at present, boron - carbon group additives, is explained here:

Boron (B) components as sintering agents dissolve in silicon carbide during the process of sintering reducing the particle field energy. It also reduces the progress of surface diffusion at low temperature. At the same time, it reacts with the added carbon, thus forming boron - carbon compound layer, which contribute toward the formation of minute texture.

However, in spite of the effect of boron as mentioned above, the attainment of high density sintering material simply by adding boron is not an easy task. That is, in the raw material of
silica amide per exist up to 10 % of surface silica, which represses the acceleration of sintering. The surface silica needs to be removed in order to produce minute, high density, high quality sintering. Carbon components are added just for this reason. It is known that carbon restore and remove silica through the following chemical reaction.

$$S\text{O}_2 + 3C \rightarrow S\text{C} + 2\text{CO}$$

As explained thus far, carbon component additives are effective in the production of silicon carbide ceramics sintering; the proper selection of carbon components and their management are yet to be improved, however.

There are basically two kinds of carbon components generally in use at present - liquid and powder. Liquid components include phenolic resin, polyphenylene, polymethyl phenylene; powder components include carbon black...etc.

Liquid components require solvent such as alcohol and acetone in order to increase the flow, but the solvent must be removed later. In removing solvent, the most effective method is to add heat, however, heating tends to hasten the hardening process of resin, resulting in poor and unevenly textured final product. The fact that spray drying is not possible, from the industrial point of view, is a problem because mass processing becomes impossible. On the other hand, solvent removal by nitrogen gas or freeze drying method without using heat also is possible. Yet, this is a time consuming and costly method with little or no applicability for resin.

The use of carbon black, although no problem exists in
reference to what has been discussed above, has its own shortcoming - the difficulty in dispersing carbon black, below micron in size, evenly in silicon carbide powder; and the relatively low density of silicon carbide due to the remaining carbon black in condensed particles within silicon carbide.

Considering those problems listed above, this invention was made after a long period of studies and discussions to enable the production of high density, high rigidity, and mass produced silicon carbide ceramics sintering.

In this invention, carbon black and other powdery carbon components are mixed with a dispersant and water, further mixed with silicon carbide powder and preferably a sintering promoting agent; the mixture is dried, or left as it is, depending on the situation; after forming the prescribed shapes and forms, the mixture is fired in non-oxidation atmosphere without applying mechanical pressure.

The aim of this invention is to maintain the effects of carbon components added to restore $S, O_2$ formed on the surface of silicon carbide powder which is the raw material for silicon carbide sintering ($S, C$) in high density and rigidity. For this reason, this invention applies to all the other methods of producing the same material by adding carbon components.

In the application of this invention, traditionally used sintering promoting agents such as boron and aluminum group are typical ones.

As boron components, boron in its original form, boron carbide, boron nitride or boron oxide, or even boron compounds such
as boracic acid can be used. The content ratio of these boron components in 100 weight parts silicon carbide should be 0.1 - 5 weight parts, preferably 0.2 - 2 parts.

As aluminum components, aluminum in its original form, non-oxidation components of aluminum such as aluminum carbide, aluminum nitride, or aluminum oxide or even aluminum compounds such as aluminum hydroxide can be used.

The content ratio of these aluminum components in 100 weight parts silicon carbide should be 0.1 - 5 parts, preferably 0.5 - 3 parts.

Other well known sintering promoting agents are beryllium components.

As the raw material of silicon carbide (SiC), both α and β crystallization forms may be used. Its purity should be above 98 %, but 90 - 98 % also may be used effectively. The grain size, in the case of extremely fine grain, is properly shown by the surface area ratio instead of the average particle size. Generally speaking, 5 square meters/g and above, preferably 10 square meters/g should be used.

The silicon carbide components used in this invention are powdery carbon components. Carbon black is the most suitable.

The content ratio of silicon carbide to carbon in this invention is 100 weight parts silicon carbide per 0.2 - 10 parts carbon. Although it may depend on the kind of the raw material of silicon carbide, the usual ratio is 0.5 - 5 parts.

Too much carbon components cause residual carbon particles in the sintering, which cause lower quality products.
The dispersant used with the carbon components in this invention is not specified. The ones used commonly in the other field can be used.

For example, because carbon black is hydrophobic, dispersants which form hydrophile surface such as alkyl sulfate, alkyl allylsulfonate, alkyl amidesulfonate and other anion group, or polyoxiethylene alkyl ether and other non-ionic group are suitable.

The ratio of these dispersants to carbon (C) should be 0.05 - 50 % in weight; the ratio which is too low results in lack of dispersing effect, while the ratio which is too high results in solidification of particles during the process of drying causing unevenly formed product.

One of the advantages of this invention is in the instance of impurities found in silicon carbide raw material, or in case foreign objects are mixed in during the process. Impurity in general do not affect the process of this invention.

As for the method of forming shapes, virtually every method commonly used for ceramics processing, eg. pressing method, mixture casting method, injection method...etc. can be used.

In case the mixture casting method is used with water as a dispersant, the mixture can be processed as is instead of going through the lengthy drying process. If the pressing method is used, additives must be dried and prepared as the material for the pressure forming. Even in this instance, the spray drying method which is suitable for a mass process of mixture can be used because the method of this invention receives little or no harm by heat.
By the same token, if water is used as the dispersant, there is no need to dry the mixture, thus shortening the process.

Next is the explanation of the conditions of firing. First of all, it is necessary to keep the atmosphere oxidation free — argon, helium, carbon monoxide or hydrogen can be used for this purpose.

The sintering temperature should be 1900 – 2300 degrees C, preferably 1950 – 2100 degrees C.

If the temperature is below 1900 degrees C, high density material cannot be produced; if the temperature is above 2300 degrees C, the mixture dissolves too quickly resulting in foaming of the mixture. The time required for firing is usually 1 - 24 hours, preferably 2 - 10 hours. If the time is too short, density or rigidity of the finished product tends to stay low.

One of the great advantages of this invention in the firing process is that no mechanical pressure is required during the process, in other words, there is no need for hot pressing (although it is OK to do so if so desired).

The sintering products by this invention exceed the flexural rigidity of 40 Kg/mm² with ease, and 50 Kg/mm² possibly.

4. Practical applications and a comparison

(#1 - #3)

Silicon carbide powder, above 98 % purity, the surface area above 13 m²/g, a model was mixed with carbon black, average particle size of below 0.1 micron and other agents, a dispersant and water as shown in Fig. 1; after one hour of mixing, the mixture was dried; a 40 x 20 x 15 mm material was formed under
2000 (?) pressure. This material, in Ar atmosphere, was fired in 2050 degrees C temperature for one hour. As the temperature went up, the temperature 1400 degrees C was maintained for two hours under vacuum. The density of the sintering is shown in Fig. 1.

(#4)

The mixture processed in the same manner as the application #1 was cast in a gypsum mold; a 30 x 40 x 5 mm material, shape of a crucible was formed and fired under the same condition as #1. The density of the sintering of this object is also shown in Fig. 1.

(#5)

The mixture obtained under the same condition as the application #1 was spray dried; powdery particles with diameter 0.1 - 0.5 microns were formed. The mixture was pressurized in the same manner as #1, then formed into sintering. Its density is listed in Fig. 1.

(#6)

As an example of comparison, sintering was obtained in the same manner as #1, except that no dispersing agent was used in this case. The density of the sintered object obtained as the result of #6 is shown in Fig. 1.
Key:

a. main crystal form  
b. additives  
c. kind of additives  
d. volume (weight %)  
e. dispersant  
f. kind of dispersant  
g. volume (weight %)  
h. density  
i. naphthalene sulfonic acid ammonium

Note:
1. Additives are per 100 parts in weight of SiC.
2. Dispersants are per 100 parts in weight of carbon black.

SiC, 100 parts in weight, were mixed with water, 100 parts in weight, as dispersants.