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SILICON CARBIDE MATERIAL SINTERED BODIES MANUFACTURING

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16. Abstract This invention describes a method for producing a high density silicon carbide sintering substance which contains aluminum oxide. The sintering is done in CO gas atmosphere, which is kept at 2-20 atmospheric pressures.			
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1. Name of the invention

\*/379

Silicon carbide material sintered bodies manufacturing

2. Scope of the patent application

(1) A method to produce silicon carbide sintering substance which contains aluminum oxide in CO gas atmosphere.

(2) The production method listed in para 2 (1) in which the mentioned CO atmosphere is kept at 2 - 20 atmospheric pressures.

(3) The production method listed in para 2 (1) or (2) in which 20 weight % of aluminum oxide  $Al_2O_3$  and the remaining silicon carbide mixture are fired in an atmosphere of CO gas.

(4) The production method listed in para 2 (3) in which aluminum oxide and 1 - 10 weight % of silicon carbide molding substance are used for the production.

(5) The production method listed in para 2 (1) and (4) in which silicon carbide molding substance containing aluminum oxide is fired in an atmosphere consisting of CO and silicon and/or carbon excluding CO.

(6) The production method listed in para 2 (1) and (5) in which the firing is done in an atmosphere which contains an inert gas in addition to CO, silicon and carbon.

(7) The production method listed in para 2 (1) and (6) in which the silicon carbide molding substance is fired in 1900 - 2300 degrees C temperature without mechanical pressurizing.

3. Detailed description of the invention

This invention is in regard to a method to produce high

density silicon carbide sintering substance.

Silicon carbide is known to be highly abrasion-proof, oxidation-proof, and have a high dissolution temperature, while having a low coefficient of thermal expansion. It is chemically stable and possesses good electric conductivity. In addition to all the good qualities listed above, the high density sintering substance of the silicon carbide family maintains rigidity even in high temperature. In addition, it has an excellent shock-proof quality. Its practical use in the future could be for various high temperature structures including gas turbines. Silicon carbide sintering substance is produced using hot press sintering, constant pressure sintering, reaction sintering, recrystallization and chemical evaporation methods. The most efficient production method for industrial use among those mentioned above is the constant pressure method. Some of the commonly used methods of forming ceramic material by using the constant pressure method are the mixture casting method, the extrusion method and the injection molding method. These methods are effective in producing ceramics products of thin and thick, large and small and the most complicated shapes. In addition, the products by this method compared to ones by the reaction method or the recrystallization methods are higher in quality.

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However, because silicon carbide is a compound that is high in a covalent bond, sintering silicon carbide alone is rather difficult. In order to produce high density sintering substance by means of the constant pressure method as well as the hot press method, one or two agents must be added to the silicon carbide

mixture to promote sintering. In the case of the hot press sintering method, boron, boron compounds, aluminum, and aluminum compounds are the known additives. The additives for the constant pressure method are the same as the ones for the hot press method, except that carbon should be included in addition to the ones listed above.

It is difficult, however, to produce a high quality, high density sintering substance even if the sintering promotion agents are added. The problem is that at the time of sintering, the silicon carbide mixture could easily dissolve, resulting in a less than desirable level of density in the finished products. This problem arises during the test production of a small sintering substance as well as larger, more complex products for which the problem is more severe.

This invention provides a method to produce high density sintering substance during the process of sintering the silicon carbide mixture containing aluminum by means of the constant pressure sintering method by preventing the promotion agents from becoming neutralized.

This invention requires a compound containing aluminum oxide to be added to silicon carbide as a sintering promoting agent. By an ordinary method (without this invention), aluminum oxide and silicon carbide evaporate, dissolve and are likely to be removed from the mixture; high density sintering substance can not be expected in this manner.

A series of attempts was made to solve this problem until the solution - aluminum oxide - was found. By sintering silicon

carbide mixture containing aluminum oxide in an atmosphere composed of CO (carbon monoxide), sintering substance of higher density can be produced. In this method, the contents of aluminum oxide decrease during the sintering process; the amount of aluminum oxide to be added can be very small; high density, high quality sintering substance can be produced by using this method.

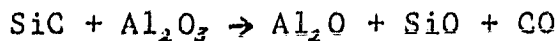
The CO atmosphere is effective because of the following reason: Silicon carbide begins its dissolution at the sintering temperature of the silicon carbide mixture. In other words, silicon carbide does not dissolve under atmospheric pressure, begins to sublime above 2000 degrees C temperature, and dissolves to form carbon and silicon-rich vapor at higher temperatures. The sintering temperature of the silicon carbide mixture necessary for the attainment of a high density sintering substance is generally 1900 - 2300 degrees C; silicon carbide within this temperature range begins to sublime and dissolve, generating Si and Si<sub>2</sub>C vapor. Accordingly, if the silicon carbide mixture is fired in an atmosphere which contains Si and Si<sub>2</sub>C, sublimation and dissolution of silicon carbide in the silicon carbide molding substance can be controlled. However, in practice, dissolution of silicon carbide is not that simple, i.e., reciprocal chemical reactions among aluminum oxide, a layer of silica on the surface of silicon carbide particles, and other impurities within the molding substance or a minute volume of oxygen within the atmosphere could take place.

It is desirable to maintain the partial pressure of these gases above the pressure level of the pressure of gases generated by dissolving sintering substance and also to prevent the mixture

from dissolving during the process of firing.

Although it is rather difficult to examine what kind of vapor is generated, or what chemical reactions take place during the sintering process of the sintering molding substance containing aluminum oxide, it has been revealed that the sintering substance with the highest density and the most even composition is produced by sintering silicon carbide molding substance containing aluminum oxide in an atmosphere consisting of CO, and/or silicon, and/or an atmosphere containing carbon other than CO, and moreover an atmosphere consisting of CO and inert gas. /381

It is thought that the dissolution of sintering molding substance takes place according to the following chemical reaction:



Accordingly, if the partial pressure of  $\text{Al}_2\text{O}$ , SiC and CO in the atmosphere at the time of sintering is kept above the pressure level of equilibrium vapor pressure generated by the dissolution of the molding substance, the dissolution of the molding substance is controlled resulting in a higher density of sintering substance. This invention effectively utilized this discovery.

Next is the explanation of the practical application.

In this invention, both  $\alpha$  and  $\beta$  crystallization forms can be used for silicon carbide (SiC) raw material, although  $\beta$  form is superior to  $\alpha$  form as a raw material. As for its purity, 90 - 98 % pure material can be effectively used, although above 98 % pure material is the most desirable. The grain size, in the case of extremely fine grains, is properly indicated by the surface area



ratio instead of the average size of particles. Generally speaking, 5 square meters/g and above, preferably 10 square meters/g should be used. As for aluminum oxide to be used as the sintering promoting agent, corundum can be conveniently used; gamma forms or other crystallization forms are also acceptable. Also, aluminum hydroxide and aluminum sulfate that change to aluminum oxide by heating can be used. Aluminum oxides in this invention include those compounds that change to aluminum oxide. Their suitable grain size is below 1 micron, preferably 0.2 micron.

The ratio of aluminum oxide in the mixture of silicon carbide and aluminum oxide should be 0.5 - 20 %, preferably 1 - 10 %; it can even be below 5 %. Below 0.5 % is not acceptable because high density substance cannot be expected by such a low aluminum oxide content. On the contrary, the ratio of 20 % and above would result in sintering substance exceedingly low in rigidity even if the sintering temperature was kept below 1900 degrees C. Sintering temperatures of 1900 - 2300 C bring about increased dissolution which result in foaming of the substance. One of the advantages of this invention is that a small amount of  $Al_2O_3$  is needed.

On the subject of raw material of this invention, a mixture of compounds consisting of silicon carbide as well as aluminum oxide are enough to achieve the desired result; moreover, 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 the molding substance during the process. Impurities in general do not affect the sintering process of this invention. Also, the content of some substance such as

silicon carbide can be more than specified. As for the methods of forming the molding substance, virtually every method, the molding casting method, the injection method, the extrusion method can be used. The sintering temperature should be 1900 - 2300 degrees C, preferably 1950 - 2100 degrees C, without mechanical pressures applied within CO gas atmosphere. If the temperature is below 1900 degrees C, high density substance cannot be expected; if the temperature is above 2300 degrees C, the molding substance dissolve too quickly resulting in foaming in the finished product. The time required for sintering is 1 - 24 hours, preferably 2 - 10 hours. If the time is too short, density or rigidity of the finished product will be low; if the time is too long, hyper-dissolution could take place resulting in foaming of the finished substance.

Speaking of the CO gas atmosphere, both a total CO gas atmosphere and a mixture of a partial CO gas/inert gas are effective. (Needless to say, the molding substance during the process of sintering generates gases.) One of the mixtures can be silicon (Si) and/or an atmosphere containing carbon other than CO, moreover, an atmosphere containing an inert gas. Of course, the atmosphere may consist of CO gas, inert gas and silicon (Si).

For example, the gas which contains silicon can be Si,  $\text{SiCl}_4$ ,  $\text{SiH}_4$  and SiO; the gas which contains carbon can be hydrocarbon. Either way, it is effective as long as sintering is done within an atmosphere which contains CO gas. The partial pressure of CO within the atmosphere should be above 50 %.

It has been revealed that the most favorable gas pressure

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is 2 - 20 atmospheric pressures. The introduction of CO gas into the sintering furnace can be easily accomplished by a pipe leading directly to the furnace from the pressurized container. Careful attention must be paid to preventing/avoiding gas explosion.

In this manner, excellent, high density sintering substance can be produced by this production method which uses  $Al_2O_3$  sintering promotion agent, and the constant pressure method (different from the hot pressure method). The composition of the sintering substance produced through this method is briefly explained next.

In the sintering substance produced through the method of this invention, the particle growth of silicon carbide within the sintering substance is suppressed, resulting in the average particle size, below 3 - 5 micron, of silicon carbide.

Although an observation of the sintering substance through an electron scanning microscope revealed the presence of aluminum oxide particles among silicon carbide particles, particularly at the triple point of the particles, the second phase layer of the same substance could not be found among silicon carbide particles adjacent to the triple point. This is an indication that through the method of this invention, the growth of silicon carbide particle is suppressed to form sintering substance which is superior in microscopic composition and high in density and rigidity. The industrial value of this invention is immeasurable.

#### Practical application

As indicated in Fig. 1,  $\alpha$  or  $\beta$  form silicon carbide powder,

98 % purity, comparative square measure of above 13 square meters/g, and aluminum oxide, 98 % purity, comparative square measure of above 5 square meters/g are mixed well; the mixture was liquid pressure formed under a pressure of 2000 \* ; the mixture was formed as molding substance, 40 x 20 x 15 mm. The molding substance was processed by heat at a fixed sintering condition and the density of the sintering substance was measured. The result is shown in Fig. 1.

#### Comparison

The same condition as the practical application, except the atmosphere of the sintering condition, was applied in producing sintering substance. Its density was measured and recorded in Fig. 1.

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\* Translator's Note: illegible notation

Fig. 1

a	bic Al <sub>2</sub> O <sub>3</sub> wt %	Al <sub>2</sub> O <sub>3</sub> wt %	b Firing Temp (C)	g Time (h)	c Density (g/cm <sup>3</sup> )	
1	ρ	2	CO <sub>2</sub> atm	1950	2	3.15
2	ρ	5	"	"	"	3.22
3	ρ	2	CO <sub>2</sub> atm	1975	6	3.21
4	α	1	"	2000	2	3.21
5	ρ	5	CO <sub>2</sub> atm Ar <sub>2</sub> atm	1950	"	3.22
6*	ρ	2	Ar <sub>2</sub> atm	"	"	2.75

注 1) 6 \* は比較用

2) Al<sub>2</sub>O<sub>3</sub> 添加量は bic 100 重量部に対する割合

KEY LIST

Fig. 1

- a. Al<sub>2</sub>O<sub>3</sub> added
- b. sintering condition
- c. density
- d. crystal form (α or β)
- e. volume (% in weight)
- f. atmosphere
- g. temperature (C)
- h. time (h)

Note (1) 6 \* is a comparison

(2) the volume of Al<sub>2</sub>O<sub>3</sub> is per 100 parts in weight of

SiC.