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SILICON NITRIDE POWDER

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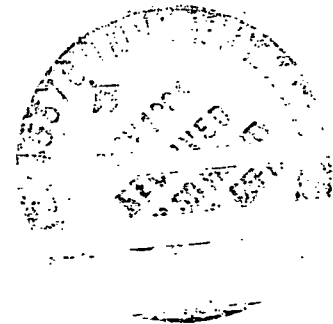
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## Silicon Nitride Powder

Masaaki Mori, Katsutoshi Komeya, Akihiko Tsuge and  
Hiroshi Inoue

\* /834

### 1. Introduction

Silicon nitride,  $\text{Si}_3\text{N}_4$ , makes up the type of ceramics which are mainly constituted of covalent bonds with a low specific weight, low thermal expansion coefficient, high elasticity and high heat resistance rate.

In recent years so-called engineering ceramics which include silicon nitride, silicon carbide and zirconium, have collected attention as materials with high strength, high heat resistance, high anti-corrosion rate, high density, and high anti-abrasion rate, especially when resource and energy conservation or the difficulty of resource acquisition is being considered. The development of these materials, including the application for the high temperature machinery, has been actively conducted. Particularly there is a strong hope to create new machines, such as diesel engines or gas turbines having a lower weight and higher efficiency operating temperature, by utilizing heat resistant ceramics. This idea, stimulated by a national project of the U.S. since the beginning of the 1970's, is an effort to overcome the failure of the Cermet Project, an attempt to combine the advantage of ceramics with that of metals, by means of development of heat resistant ceramics. However, it is extremely difficult to use ceramics, typically brittle material, as machine parts. A technological breakthrough is needed in order to realize this formidable task.

For this reason, close examination of raw materials of ceramics, which are to become the basic component of the machine

\*Numbers in the margin indicate pagination in the foreign text.

parts, is one of the most critical problems that need to be resolved before engineering ceramics are put to practical use. The problems that need to be resolved include; (1) firm establishment of parts manufacturing technology, (2) improvement of parts reliability and establishment of evaluation techniques, (3) improvement of techniques related to practical application of ceramics parts. It has been a while since the period of controversy in regard to the choice between  $\alpha$  and  $\beta$  phase as more suitable raw material in developing silicon nitride ceramics, yet no progress has been made since. Lately, however, silicon nitride has become an issue again because of the items (1) and (2) listed above. Reflecting upon the current trend, which rather seems a natural outcome of the course that has been taken, we will discuss raw material of silicon nitride, particularly focusing our attention on the important points of the production processes starting from the raw material in powder form, followed by its treatment and finally sintering process of ceramics products.

## 2. Nature of Silicon Nitride

Silicon nitride, man-made metal belonging to the hexagonal system, exists in  $\alpha$  and  $\beta$  crystal phases. At the time of the initial discovery of these two phases,<sup>1)</sup> they were considered to take a single transformation pattern from  $\alpha$  to  $\beta$  at temperature between 1400 - 1600 C. However, a new view was presented by Jack et al. whose<sup>2)</sup> diligent research revealed that  $\beta$  phase was made of oxynitride of certain composition and contained O in its structure ( $\text{Si}_{11.5}\text{N}_{15}\text{O}_2$ ),

while  $\beta$  was a nitride containing no O. However, controversies still exist in regard to the crystalline chemistry of silicon nitride, among which is a report stating that  $\alpha$  phase can exist as pure  $\text{Si}_3\text{N}_4$ .<sup>3)4)</sup> We could safely conclude that  $\alpha$  phase is the type of material which contains solid solution oxygen within its crystalline structure. (Tab. 1)

Tab. 1 with keys:

1. Tab. 1: Crystallographic nature of silicon nitride<sup>5)</sup>
2. Crystalline phase
3. Composition
4. Space group
5. Measured density
6. Calculated density

表 1 窒化ケイ素の結晶学的性質<sup>1)</sup>

| 結晶相 2                      | $a$                                                                 | $\beta$                 |
|----------------------------|---------------------------------------------------------------------|-------------------------|
| 組成 3                       | $\text{Si}_3\text{N}_4 \sim \text{Si}_{100}\text{N}_{99}\text{O}_1$ | $\text{Si}_3\text{N}_4$ |
| $a_0$ (Å)                  | 7.76                                                                | 7.61                    |
| $c_0$ (Å)                  | 5.62                                                                | 2.91                    |
| $c_0/a_0$                  | 0.724                                                               | 0.765/2                 |
| $d_0$ (g/cm <sup>3</sup> ) | 3.16                                                                | 3.192                   |
| $d_r$ (g/cm <sup>3</sup> ) | 3.183                                                               | 3.192                   |
| 空間群 4                      | $P31c$                                                              | $P6_3/m$                |

$d_0$ : 密度測定値,  $d_r$ : 密度計算値  
5 6

Tab. 2 with keys:

1. Tab. 2: Physical properties of silicon nitride<sup>6)</sup>
2. Melting point
3. Sublimation decomposition
4. Density
5. Heat expansion coefficient
6. Young's coefficient
7. Thermal conductivity
8. Specific heat
9. Hardness
10. Electric resistance
11. (a) ...depends on manufacturing process
12. (b) ...is different among researchers

表 2 窒化ケイ素の物理的性質<sup>1)</sup>

|             |                                               |
|-------------|-----------------------------------------------|
| 融点 2        | = 1900°C (昇華分解 3)                             |
| 密度 (a 4)    | 2.2~3.2 g/cm <sup>3</sup>                     |
| 熱膨張係数 (d 5) | 2.46~4.1 × 10 <sup>-4</sup> /°C (R.T.~1000°C) |
| ヤング率 (a 6)  | < 3.2 × 10 <sup>4</sup> kg/mm <sup>2</sup>    |
| 熱伝導率 (a 7)  | < 36 W/m·K                                    |
| 比熱 8        | 0.17 cal/g·°C                                 |
| 硬度 9        | 1600~1800 Vickers VPN (> 9 Moh)               |
| 電気抵抗 10     | > 10 <sup>10</sup> Ω·cm                       |

(a) 製造方法に依存する. 11  
(d) 研究者間で異なる. 12

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Tab. 3 with keys:

1. Tab. 3: Materials with high Young's coefficient/ specific gravity\* 7)
2. Materials
3. Young's coefficient/ specific gravity
4. Melting point or decomposition temperature
5. C whisker
6. Steel, glass, wood

表 3 高ヤング率/比重の物質<sup>7)</sup> 1

| 物 質 2                          | ヤング率/比重 3<br>(10 <sup>6</sup> lb/in <sup>2</sup> ) | 融点又は 4<br>分解温度<br>(°C) |
|--------------------------------|----------------------------------------------------|------------------------|
| AlN                            | 15                                                 | 2450                   |
| Al <sub>2</sub> O <sub>3</sub> | 13                                                 | 2050                   |
| BeO                            | 18                                                 | 2530                   |
| C ホイスカー 5                      | 61                                                 | 2500                   |
| SiC                            | 25                                                 | 2600                   |
| Si <sub>3</sub> N <sub>4</sub> | 17                                                 | 1900                   |
| 鋼, ガラス, 木材 6                   | 4                                                  |                        |

Typical physical properties of silicon nitride as a material or ceramic are shown in Tab. 2. Silicon nitride takes covalent bonds and carries a large number of bonding electrons. It accordingly shows high bonding strength, low heat expansion coefficient, high melting point (sublimation decomposition), and high elasticity. Tab. 3 shows Young's coefficient/ specific gravity and the melting point of typical ceramics of various types.\* Aluminum nitride has low acid-resisting quality; beryllia has strong toxicity; carbon is extremely weak when oxidized. Considering these facts, it may be safe to speculate that silicon nitride and silicon carbide are excellent candidates as heat-resisting engineering ceramics. The most important qualification required of high strength ceramics is its quality to withstand high level of stress per a unit stress; in other words, high strength ceramics material is required to have the high coefficient of elasticity. Furthermore, ceramics material which is light weight is more desirable. Viewing ceramics materials from the engineering standpoint, mechanical parts made of ceramics material which have higher strength/ weight ratio are desirable.

Accordingly, it is preferable that the ratio between Young's coefficient and specific gravity of mechanical parts made of ceramic material is as high as possible. It is apparent, from Tab. 3, that silicon nitride and silicon carbide are superior to steel, glass and wood in this aspect.

### 3. Synthesizing Silicon Nitride Powder

Tab. 4 shows typical synthesizing processes of silicon nitride powder. The most widely used process in industry today is the direct nitrifying process, which is characterized by its relative simplicity. However, a technique to control the heat is required in this process because the metal powder when reacted upon  $N_2$  gas generates an intense heat.

Tab. 4 and keys:

1. Synthesizing process of silicon nitride
2. Synthesizing process
3. Reaction formula
4. Direct nitrifying process of silicon
5. Silica reduction process
6. Gas phase synthesizing process
7. Heat decomposition process

| 表 4 窒化ケイ素の合成法 1 |                                                     |
|-----------------|-----------------------------------------------------|
| 合 成 法 2         | 反 応 式 3                                             |
| シリコンの直接窒<br>化法  | 4 $3Si + 2N_2 \rightarrow Si_3N_4$                  |
| シリカ還元法          | 5 $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$    |
| 気相合成法           | 6 $3SiCl_4 + 16NH_3 \rightarrow Si_3N_4 + 12NH_4Cl$ |
|                 | $3SiCl_4 + 4NH_3 \rightarrow Si_3N_4 + 12HCl$       |
| 熱分解法            | 7 $3Si(NH)_2 \rightarrow Si_3N_4 + 2NH_3$           |
|                 | $3Si(NH)_2 \rightarrow Si_3N_4 + 8NH_3$             |

One of the examples of such techniques under development is to conduct the synthesizing process under controlled reaction temperature of 1300-1400 C in a mixed atmosphere of  $N_2$  gas and  $H_2$  or  $NH_3$  gas. The product through this method generally contains a mixture of  $\alpha$  and  $\beta$  phases; the most desirable sintering material,  $\alpha$  phase, can be obtained in higher quantity as synthesizing



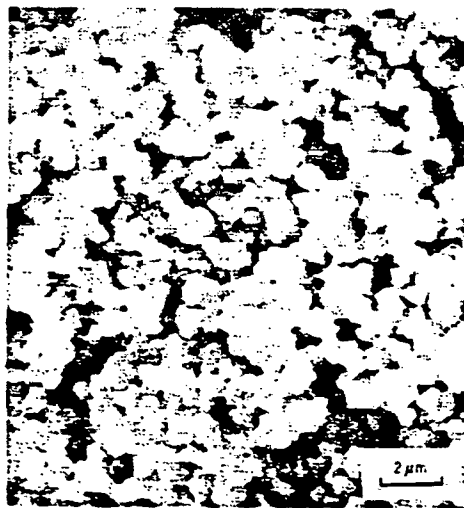
<sup>11) 12)</sup>  
temperature is lowered.\* After the synthesizing process, a grinding process is generally introduced. Problems awaiting solution in the future include an advanced purification process of the basic raw material, silicon, and a purification process of the previously synthesized powder.

Silica reduction method is used to nitrify silica by resolving silica with carbon in an atmosphere of nitrogen. The advantage of this process in the industrial use is that the reaction control is relatively easy because it is an endothermic reaction and that highly pure basic raw materials, silica and carbon, can be purchased at relatively low prices. Even the use of rice hull as a source of  $\text{SiO}_2$  has been attempted in a research program in the US.<sup>13)</sup>\* This is an indication that a variety of resources is possible as SiO resources. The reaction process of the synthesizing process is complex and consists of the following two primary reactions: Generation of SiO and CO gases through the solid to solid reaction between  $\text{SiO}_2$  and C; generation of  $\text{Si}_3\text{N}_4$  through a phase reaction of SiO and N gases in the presence of C. Although the  $\text{SiO}_2$ -C reaction is considered to be the rate determinant step<sup>14)~16)</sup>\*, it is also required /836 to control the partial pressure of CO by extracting the byproduct, CO gas, out of the system. Consideration must be given to the generation of SiC and  $\text{Si}_2\text{N}_2\text{O}$  from the reaction of  $\text{SiO}_2$ -C- $\text{N}_2$ ; the generation of SiC, in particular, is dependent upon the synthesizing temperature, atmosphere and C/ SiO ratio. There are several reports which indicate that temperature between 1400 C and 1500 C is the very maximum temperature in generating  $\text{Si}_3\text{N}_4$  and SiC,

however, these reports should not be regarded as conclusive because the generation of these substances is affected by the quality of the reactants, silica and carbon, as well as the reaction conditions. The thermodynamics aspect of this reaction is not discussed any further, yet, indeed the silica reduction process may become a promising synthesizing method in industry if some improvements are made in the areas of the basic raw material and the synthesizing condition. The technology that has been watched carefully lately involves a technique in which a mixture of silica and carbon powder added with silicon nitride in fine powder form is used as the basic raw material.<sup>20)</sup> This technique has an excellent effect in promoting the reaction and controlling the form and size of silicon nitride particles. Fig. 1 illustrates a SEM photograph of the typical silicon nitride powder synthesized through this process. The powder is uniform in terms of grain size and is sharp in its particle distribution. An additional characteristics of this process are that the product is high in  $\alpha$  phase and that no grinding process is required after the synthesizing process. The only additional requirement is that the remaining carbon after the reaction must be burnt out.

FIG. 1

Silicon nitride powder by a silica reduction process.



The main step of the gas phase synthesizing process is the gas phase reaction between silicon halogenide (primarily  $\text{SiCl}_4$ ) or silane group silicon (primarily  $\text{SiH}_4$ ) and ammonia at high temperature (1000 C and above). The characteristic of this process is that high purity gases can be used as the basic raw material. In this method a reactant gas feeding device as well as a device to process the byproduct, chloride, are as important as a reactor, but these factors are within the domain of chemical engineering. The synthesized silicon nitride is generally non-crystalline and is crystallized through a heat treatment.\*<sup>21) 22)</sup> The crystallization process often causes the generation of high temperature  $\text{Cl}_2$ , which tends to create equipment corrosion problems. The crystallized silicon nitride is characterized as a highly pure and superfine powder. A gas phase synthesizing process assisted by laser beams is being studied at MIT in the U.S. recently.\*<sup>23)</sup> In this new method gases of monosilane ( $\text{SiH}_4$ ) and ammonia are brought in  $\text{CO}_2$  laser in order to synthesize silicon nitride. Superfine non-crystalline powder can be obtained through this process.

Another method to synthesize silicon nitride is to thermally decompose silicon imide ( $\text{Si}(\text{NH})_2$ ) or silicon amide ( $\text{Si}(\text{NH}_2)_4$ ).\*<sup>24) 25)</sup> In general, silicon imide is synthesized by silicon tetrachloride and ammonia, from which ammonia is removed and crystallized in a

non-oxidizing atmosphere at high temperature before silicon nitride powder is produced. Other silicon imide synthesizing processes in developmental stages include a gas-liquid phase reaction between  $\text{SiCl}_4$  and  $\text{NH}_3$  in a solution<sup>25)</sup>, a liquid surface reaction process<sup>26)</sup>, and a gas phase reaction process near room temperature. These thermal decomposition processes will require future improvements such as prevention of clogging of a reactor tube, prevention of oxidation of and moisture absorption by the reaction intermediaries, and removal or lowering of impure Cl contents. The synthesized silicon nitride is reportedly a highly pure, superfine powder with a high content of  $\alpha$  phase.

#### 4. Sintering and Characteristics of the Raw Materials of Silicon Nitride Ceramic.

Ceramics products are produced through sintering, which has a variety of techniques such as normal pressure sintering, hot press sintering, HIP, reaction sintering and CVD.

Because silicon nitride is high in covalent bonds and difficult to sinter, a sintering promoting agent is usually used as an additive prior to sintering process in order to densify the finished product. Most commonly used sintering methods with the additive are normal pressure sintering and hot press sintering. The sintered product, a result of a variety of chemical reactions, conversions and shifting of materials during the sintering process, is obtained through a complex process due mainly to the additive mentioned above. The critical point is how to most effectively

control this process. Because the sintering process develops kinetically, the material cannot be prepared by determining its composition only. The quality of the raw material in a powder form is particularly important because the sintering process is greatly affected by it. Accordingly, so-called characterization must be conducted to the fullest extent.

#### 4.1 The Effect of Crystalline Phase

It is commonly understood that  $\alpha$  phase is a more suitable raw material of sintered silicon nitride because the use of  $\alpha$  phase prompts  $\alpha \rightarrow \beta$  conversion, which is believed to result in significantly improved sintered material high in material density and strength.<sup>27)</sup> It is also known that the sintered material is mostly composed of the collection of column type grains in its structure when  $\alpha$  phase is used. Such particle anisotropy is lost when  $\beta$  phase is used.<sup>28)</sup> It has become clearer recently that the strength of the sintered material is closely related to anisotropic growth of crystalline particles. Fig. 2<sup>29)</sup> shows an example.<sup>29)</sup> The fact that the breaking tenacity rate of the sintered material improves as the ratio of  $\alpha/(\alpha+\beta)$  is increased seems to support the point that anisotropic growth of crystalline particles is closely related to the breaking tenacity rate of the sintered material.

Fig. 2: The effect of the content rate of phase on the breaking tenacity rate. (Lange)\* 29)

- Keys:
1. Breaking tenacity rate
  2.  $\alpha/(\alpha+\beta)$  volume ratio in the raw material

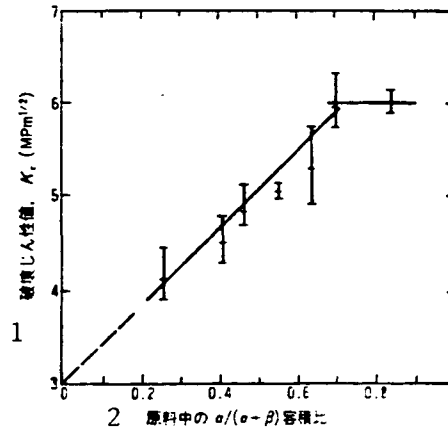
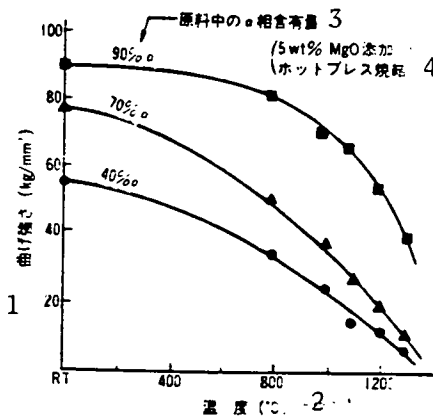


Fig. 3: The effect of the content rate of  $\alpha$  phase on hardness. 30)

- Keys:
1. Flexural strength
  2. Temperature
  3. Content of  $\alpha$  phase in the raw material
  4. Hot press sintering with 5 wt % MgO added



As shown in Fig. 3, 30) flexural strength of the sintered material tends to increase as the ratio of phase content increases. There is no definitive thesis established to explain this phenomenon yet. It probably requires more researches in the area of crystalline morphology to sufficiently explain this phenomenon. Yet, some researchers believe that the use of  $\beta$  phase does not necessarily

lower the quality of a sintering process.\*

#### 4.2 Impurities in Raw Materials and Their Effect

Raw materials generally contain a variety of impurities. Fig. <sup>32)</sup> 4\* shows some examples of impurities, among which Ca, Fe, Al, Mg, Mn and W are considered to be important elements in the research of silicon nitride ceramics. These elements affect the material properties in many ways, particularly in the high temperature strength and acid-proof quality of the sintered material. Fig. <sup>33)</sup> 5\* shows the effect of concentration of impurities converted to high temperature strength. Fig. 6 also shows examples of the relation <sup>34)</sup> between the size of each impurity and strength.

These impurities exist in the intergranular field in almost all cases and are considered to be the determinative factors in promoting softening of the intergranular field or oxidizing the sintered material in high temperature. These impurities also influence the formation of defective sintered material in low temperature.

The choice between high and low purity powders as raw material must be determined by the functions of the machine parts for which the sintered material is produced; it is not proper to consider that raw material powder should always be high in purity. Machine parts in industry are often used in an environment where relatively low stress and temperature is applied to the machine parts. It is important to consider different environment in which ceramic machine parts are to be used and to manufacture the kind of

finished products which is most suitable for the environment.

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FIG. 4: Impurities in various types of raw materials of silicon nitride\* (Analysis of mass by a spark technique, A spark type mass analyzer with an ion source, JMS-01BM, manufactured by Nihon Denshi Co., Ltd. was used.)

Keys:

1. Trace elements in silicon nitride
2. Manufacturing method
3. Interfered by SiO or Si<sub>2</sub>
4. The position was changed due to a scale over.

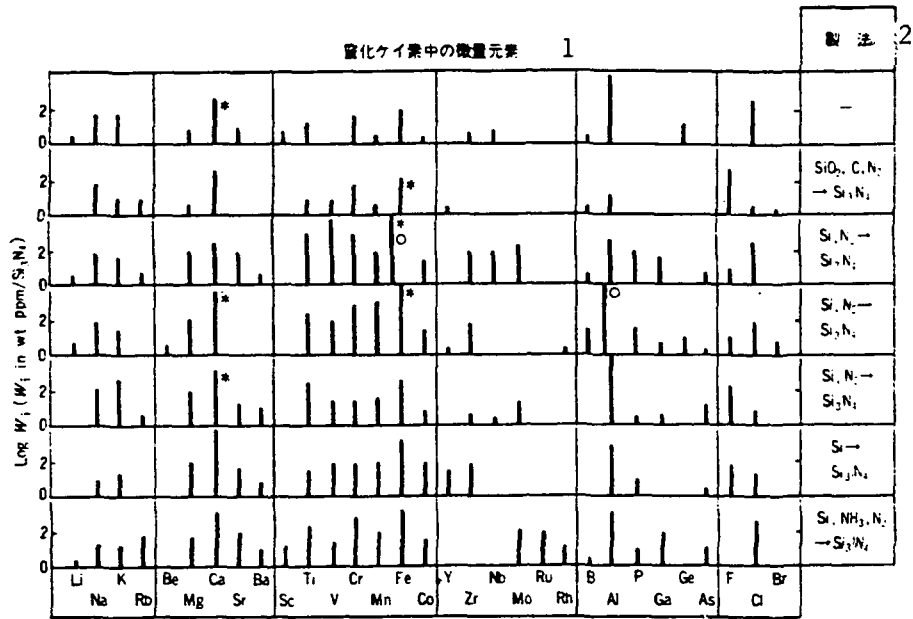




Fig. 5: The effect of various impurities on high temperature strength (Richardson)\*<sup>33)</sup>

Keys:

1. Bending pressure
2. Impurities

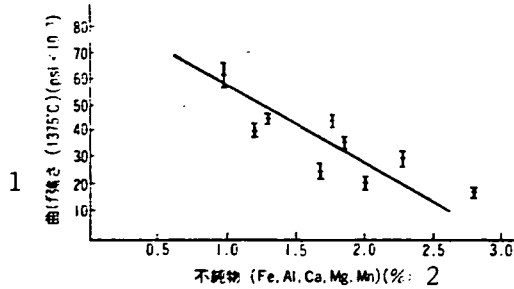
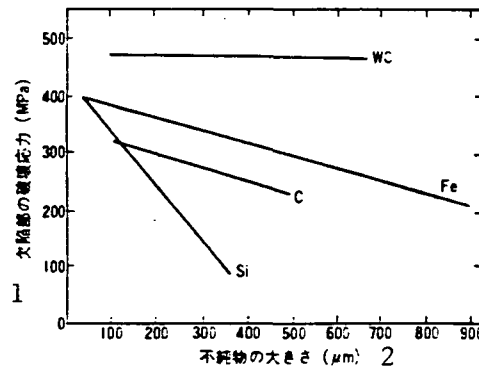


Fig. 6: The effect of impurities on room temperature strength (Evans)\*<sup>34)</sup>

Keys:

1. Fracture stress on the defective parts
2. Size of impurities



#### 4.3 Effects of Oxygen Contained in Raw Material

As mentioned earlier, approximately 1% of solid solution oxygen is usually contained in  $\alpha$  phase silicon nitride crystals. It is also generally known that 1 - 3% of  $\text{SiO}_2$  is also contained in the form of an oxydized layer on the surface of silicon nitride particles.\*<sup>35)</sup> Fig. 7 shows the strength of the surface silica and its effect on the densification process of a hot press sintered

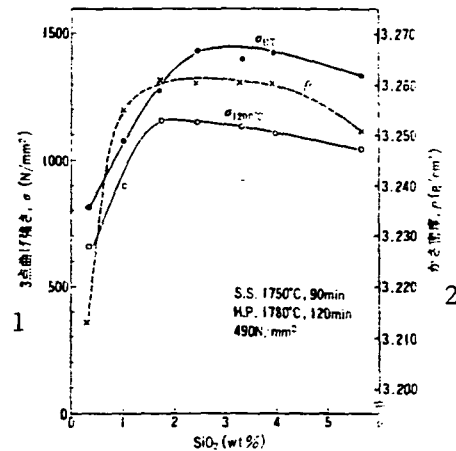
## OXIDATION EFFECT OF POOR QUALITY

material. It is clear from Fig. 7 that the oxygen contained in the raw material gives a subtle effect on the sintered material. It may be due to a qualitative change in the sintering process. Such effect is not expressed in the chemical formula,  $\text{Si}_3\text{N}_4$ . The oxygen contained in silicon nitride powder will be a focus of future research efforts.

Fig. 7: The strength of the surface (and/ or separate)  $\text{SiO}_2$  in the silicon nitride raw material and its effect on densification.\*36) (S. S.: Semi-Sintering, H. P.: Hot Pressing)

Keys:

1. Three points flexural strength
2. Bulk density



#### 4.4 Effects of Particle Shapes of the Raw Material Powder

The crystalline silicon nitride usually assumes the forms of sphere, column, needle or band. Up to this date, no established theory exists concerning the most suitable form among those listed above. It is not totally impossible, however, to attempt to correlate the powder synthesizing process and particle forms based on available data. Due mainly to a grinding process which is included in the direct nitrifying process after the synthesizing

process, powder particles do not show the same characteristics in their shape, instead, powder particles take irregular shapes. Although the samples used in Fig. 1 primarily show short hexagonal column or quasi-cube shapes, other shapes, band or needle, also can be formed depending upon the reaction conditions. Many particles grown through a gas phase synthesizing process show sphere or grain shapes, except occasional long column or needle shapes.

Concerning the effect of a variety of shapes on a sintering process, an interesting thesis appeared in which the originator maintains that "...if all particles are isometric (spheres, cubes...etc.), an environment in which each particle is in contact with each other can be assumed. Accordingly, an ideal sintering process can be made possible without using sintering promoting agents..."<sup>23)</sup>\* The technique of the gas phase process utilizing laser beams mentioned earlier apparently aimed to have this effect, but the result of the experiment has not been made public yet.

#### 4.5 Requirements for the Ideal Raw Material Powder

The research group of MIT in the U.S. including Prof. K. Bowen pointed out the following requirements for the ideal powder:

- (1) Small particle,
- (2) Free of oxygen,
- (3) Narrow particle size distribution,
- (4) Equi-axis particle,
- (5) Phase control,
- (6) Composition (purity, stoichiometry).

As we put together what has been discussed so far, the above requirements seem to be appropriate in all probability. These requirements will be confirmed to be correct as they are examined through positive researches and more requirements may be added in the future.

## 5. Postscript

The center of the discussion has been the characteristics of the raw material in powder form in the production of heat-proof ceramics machine parts through a sintering process. This process seems simple at a glance but involves extremely complex and difficult problems, which are felt keenly by all researchers including myself.

In any case, the day when engineering ceramics are put to practical use is right around the corner although their development will be step by step. The crucial question, before we can reach the objective, is whether or not reliable machine parts can be supplied. To that end, the raw material characterization will become more and more important.

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