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FABRICATION AND CHARACTERIZATION OF Si_3N_4
CERAMICS WITHOUT ADDITIVES BY HIGH PRESSURE HOT PRESSING

Masahiko Shimada, Atsuhiko Tanaka, Tetsuo Yamada
and Mitsue Koizumi

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16. Abstract High pressure hot pressing of Si ₃ N ₄ without additives was performed using various kinds of Si ₃ N ₄ powder as starting materials, and the relation between densification and alpha-beta phase transformation was studied. The temperature dependences of Vickers microhardness and fracture toughness were also examined. Densification of Si ₃ N ₄ was divided into three stages, and it was found that densification and phase transformation of Si ₃ N ₄ under pressure were closely associated. The results of the temperature dependence of Vickers microhardness indicated that the high-temperature hardness was strongly influenced not only by the density and microstructure of the sintered body but also by the purity of the starting powder. The fracture toughness values of Si ₃ N ₄ bodies without additives were 3.29 - 4.39 MN/m to the 3/2 power and independent of temperature up to 1400°C.					
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Masa'iko Shimada,* Atsuhiko Tanaka,** Tetsuo Yamada,**
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1. Preface

1967***

In recent years, from the point of view of the preservation of energy and resources, the development of engineering ceramics has been anticipated, ceramics which have superior characteristics as a substitute for a former heat-proof alloy. Thus carbide and nitride ceramics such as SiC , Si_3N_4 , and AlN draw our attention as potential candidates. These materials possess many excellent heat-resistant impact properties, as well as anti-corrosion and low specific gravity.

However, because these materials have a small self-diffusion coefficient [2], it is difficult to fabricate these elaborate and strong ceramics by themselves [3]. Therefore, in the case of Si_3N_4 , fabrication by the high density hot-pressing method is done by adding an additive such as MgO [4], Al_2O_3 [5] and Y_2O_3 [6] using the hot-pressing sintering method, the atmospheric pressure sintering method or no pressure sintering method. However, in the sintered body obtained by these methods the additive is mainly deposited as a glass form in the particle sphere. It is known that under high temperature the mechanical properties deteriorate considerably because of the particle sphere slippage accompanying the softening of the glass forms [8].

On the other hand, in a sintered body made by non-additive high pressure hot-pressing, there is no deposit in the second constituent in the particle sphere except impurities which were contained in the starting materials. Therefore it is expected that, compared to the sintered body containing an additive, the

*Institute of Scientific and Industrial Research, Osaka University, Ibaraki.

**Central Research Laboratory, Ube Industries, Ltd., Ube

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deterioration of the mechanical and thermal properties is smaller than in the latter.

In this report concerning the densification process of Si_3N_4 ceramics without additives by high pressure hot-pressing, we mainly examine the relationship between densification and phase transformation. We also refer to the results of measurement of the obtained sintered body's temperature dependence on Vickers microhardness and the fracture toughness in the characteristic evaluation.

2. Plan of the Experiment

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2.1. Starting Materials

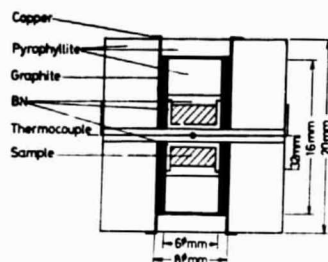
The characteristics of the six powders of Si_3N_4 used as starting materials in the experiment are shown in Table 1. SN-A is the nitride of metal silicon powder and SN-B is the synthesis which is formed by the gaseous reaction of titanium, silicon, and ammonia gas. The materials from SN-C to SN-E are powders synthesized by the thermal decomposition of $\text{Si}(\text{NH})_2$. SN-F is a powder which is SN-E heated to 1850°C at 5 MPa nitrogen pressure.

2.2. High Pressure Hot-Pressing

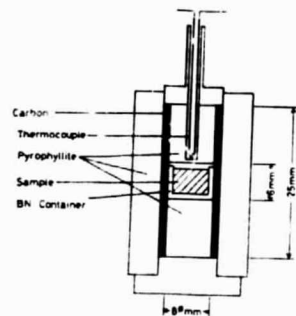
We applied the solid compression method and the heat interval hydrostatic pressure pressing method for high pressure hot-pressing. First of all, for high pressure hot-pressing using the solid compression method, we used a cubic high pressure producing device (henceforth termed "cubic") and a piston cylinder form high pressure producing device (henceforth termed "PC"). For preforming the powder at room temperature we used a gold mold and a fabricated molding for each cubic and PC whose size is $\varnothing 5 \times 4$ mm for the former and 7×5 mm for the latter. We baked this pressed powder body at 1200°C in a nitrogen atmosphere and removed impurities on the surface of the particles. After putting it in the BN container we set it in a high pressure cell shown in Fig. 1 (a) and (b). The pressure applied was 3.0 GPa in the

Table 1. Characteristics of Si_3N_4 powders.

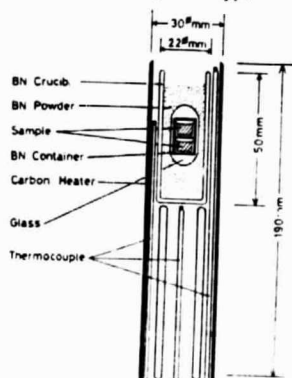
Powder	Manufacturer	Phase (wt. %)		Contents of elements (wt. %)						Specific surface area (m^2/g)	
		α	β	N	O	C	Cl	Al	Ca		Fe
SN-A	H.C. Starck H-1	96	4	31.2	1.1	0.48	—	0.09	0.04	0.03	8.3
SN-B	GTE Sylvania SN-502	57	3	8.0	1.4	—	<0.04	0.002	0.0006	—	4.2
SN-C	Laboratory synthesis	44	6	38.0	1.6	—	<0.01	—	<0.001	<0.001	23.7
SN-D	Laboratory synthesis	86	12	38.1	0.87	0.1	<0.01	0.03	0.003	0.01	4.5
SN-E	Laboratory synthesis	86	14	39.0	1.59	—	<0.01	0.03	0.01	0.03	6.9
SN-F	Laboratory synthesis	0	100	37.5	—	—	—	—	—	—	0.05



(a)
(a): Cubic type.



(b)
(b): Piston-cylinder type.



(c)
(c): HIP.

Fig. 1. High pressure cell assembly.

cubic device and 1.5 GPa in the PC device in the pressure range. Both devices recorded 1500-1800°C over 30-60 minutes for the hot pressing temperature, and the speed of increase and decrease in the temperature was about 300°C/min. In the case of the hot pressing experiment by heat interval hydrostatic pressure pressing (HIP), the operation from forming the pressing powder body to setting it into the BN container is carried out in the same manner as in the case of a solid pressing method as stated above. After this process was completed, the sample was wrapped in the BN container with a tantalum sheet (0.05 mm), and we inserted it in a pyrex tube (diameter 9 mm) and provided a vacuum packaging for it. Further, in the case of HIP use with high temperature (1850°C), we provided a double vacuum package by inserting the sample in the BN container in a pyrex tube which was previously vacuum packaged in a quartz glass tube. This was placed into a high pressure furnace. For the pressure transmission atmosphere, we used argon gas

which is very fluid and has large thermal capacity in a unit under high pressure. Then we applied 170-200 MPa at 1700-1800°C for 60-90 minutes. The high pressure cell is shown in Fig. 1 (c).

2.3. Measurement of Density, Identification of Crystal Phase and Scanning Electron Microscope (SEM) Observation /969

We performed measurement of high density by the Archimedes method after we sealed the surface of the sample of the obtained sintered body by hand in order to close the ventilation holes. Moreover, grinding a part of the sample, we performed the identification of the crystal phase by the powder x-ray diffraction method using $\text{CuK}\alpha$ as the line source. We used the value of the structural factor which was calculated by Gazzara and Messier [9] for the identification of each phase and determined the rate of each phase (201), (102) and (210) of the α -phase, and (201), (101) and (210) of the β -phase from the peak height of each diffraction.

Further we ground the rest of the sample to bulk form and performed hot etching in HF-HNO_3 (50:50 vol.%) for 5-30 minutes. Subsequently we cleaned it by ultrasonic cleaning. After it was dried, 20 Å thickness of gold was applied to the sample surface by a direct current sputter steam applicator and it was submitted to SEM observation.

2.4. High Temperature Hardness

We modified the sample surface to a successive specular surface using boron carbide grind grains #600, #1500 and diamond paste 10 μm , 2 μm . We used the Nikon QM model Vickers hardness meter to measure microhardness. We reduced the pressure of the heated sample part to under 4 Pa and carried out the measurement of the Vickers hardness at every 100°C of the temperature range from room temperature to 1200°C by using a Vickers diamond pressure implement (weight 200 g) in order to prevent the sample and the diamond pressure implement from oxidizing. The hardness measurement was performed by calculating the microhardness from the average value which was calculated from ten pressure mark diagonals on the sample surface at each temperature stage.

2.5. Fracture Toughness Rate (Critical Stress Magnification Coefficient; K_{Ic})

We applied the method of A.G. Evans and E.A. Charles [10, 11] to the measurement of the fracture toughness rate using the Vickers meter. After we reduced the pressure of the heated sample part to under 4 Pa in the same manner as in the measurement of high temperature hardness, we performed ten measurements for each sample at room temperature. We observed the one-second length (a) of diagonals (2a) of the produced pressure marks and the length of cracks which extended from each marked pressure peak by an optical microscope ($\times 400$). Further, in order to verify reproducibility of pressure marks or crack forms, we set the weight of the Vickers pressure implement to 1 kg. We also examined the temperature dependence of fracture toughness in the temperature range from room temperature to 1400°C for a particular sample.

3. Results

3.1. Phase Transition and Densification

Figure 2 shows the relationship between relative density and phase transition ratio of SN-C and SN-E which are hot pressed by a

PC device at 1.5 GPa and SN-E which is hot pressed by a cubic device with 3.0 GPa. We were able to assume that the Si_3N_4 densification under high pressure is classified by three stages from these results of hot pressing.

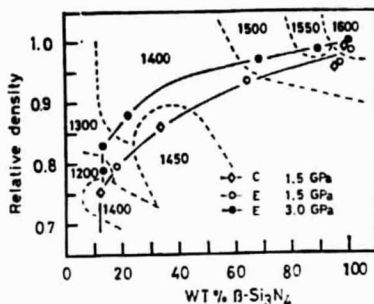


Fig. 2. Relation between relative density and β -phase contents of Si_3N_4 without additives.

The first stage: This is the stage when the relative density is less than 0.83. Phase transition does not occur, and the densification proceeds by the fracture and rearrangement of particles.

The second stage: This is the stage when the relative density is from 0.83 to 0.93. Sudden densification occurs at the early stage of the phase transition.

The third stage: This is the stage when the relative density is more than 0.93. Although the densification is slow, the phase transition proceeds markedly. As stated above, under high pressure, the phase transition and densification proceed in close relation.

It is noted particularly that most of the densification occurs at the early stage or before the phase transition.

3.2. High Temperature Hardness of Si_3N_4 Ceramics Without Additives

Examples of the temperature dependence of Vickers microhardness are shown in Figs. 3, 4, and 5. Figure 3 shows the relationship of the Vickers microhardness and the temperature of the sintered body. The sintered body is produced by a HIP device which treats SN-A, -B and -C at 200 MPa, 1700°C, 90 minutes. We have indicated the example of Y_2O_3 , 3.2 eq.% additive sintered body for comparison.

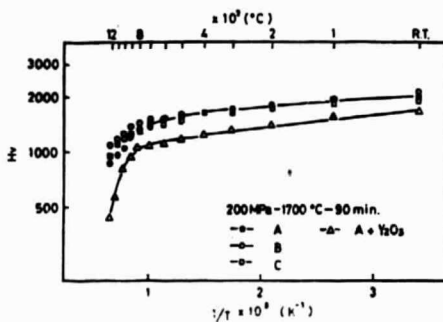


Fig. 3. Temperature dependence of Vickers microhardness.

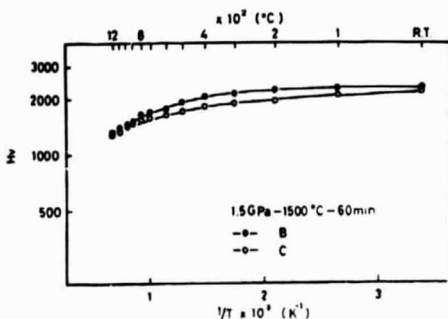


Fig. 4. Temperature dependence of Vickers microhardness.

We observe in this figure that evidently different behavior exists in the sintered bodies with and without additive in the high temperature range of more than 700-800°C.

On the sintered body to which Y_2O_3 is added, yttrium silicate glass [12], which deposits in the particle sphere

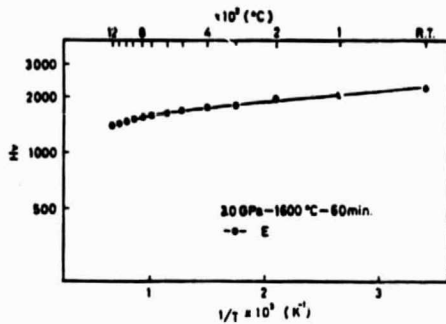


Fig. 5. Temperature dependence of Vickers microhardness.

in the high temperature range of more than 900°C , softens, and as the result of particle sphere slippage, it causes a sudden and substantial decrease in hardness.

Further, because the magne- '970
sium silicate glass which is formed at high temperature (around 1550°C) [4] has less viscosity

than yttrium silicate glass and is apt to cause particle sphere slippage, if we add MgO as the additive, it leads to a substantial decrease in hardness.

The general characteristics [14] of the additive sintered body on the $1/T-H_v$ curve can be observed in a clear bend on the curve bordering the softening temperature of the formed glass in the particle sphere. The other characteristic is that the degree of decrease in hardness depends greatly on the amount of additive, i.e. the amount of glass forms in the particle sphere.

On the other hand, on the non-additive sintered body, the hardness slowly begins to decrease at more than $700-800^{\circ}\text{C}$ temperature and the degree of decrease is much smaller than with the Y_2O_3 sintered body. In this case the estimated amount of SiO_2 with impure oxygen which is contained in the starting materials is 2.1-3.0 wt.% (3.5-4.1 vol.%) and it is assumed that after HIP this is deposited in the particle sphere as starting materials. However, since this glass form has a higher viscosity ratio and occupies less space in the particle sphere than yttrium silicate glass, the effect of Si_3N_4 particle slippage in the particle sphere accompanying the softening of the particle sphere is rather small and the drop in microhardness is also expected to be small.

Figure 4 shows the change in high temperature hardness of a sintered body which was produced by the PC device treating

SN-B and -C at 1.5 GPa, 1500°C, 60 minutes. For the high pressure hot-pressing in the PC device, the pressure action is much higher than for the HIP device. The hot-pressing temperature for about the same density as for the HIP sintered body is about 200°C less than when using the HIP device. When a high pressure such as 1.5 GPa was applied, generally the hot-pressing reaction occurs at 1700-1800°C, a lower temperature than the common hot-pressing temperature. As a result, the microstructure of the sintered body is even and composed of fine particles. It is also expected to have a higher densification ratio than the regular sintered body which is hot pressed using the regular method at both room temperature and high temperature.

Figure 5 shows the change in high temperature hardness of the sintered body which is produced by the cubic device which treats the starting material SN-E with 3.0 GPa, 1600°C, 60 minutes. This sintered body is fabricated with the powder of the highest purity using six starting materials, and its density reaches the theoretical rate. Further, it is observed by SEM that the sintered body is composed of fine polyhedral particles whose average size is 0.5 μm and the bonding of the particles is well advanced. As you can see in the figure, on this sintered body a bend which is thought of as the effect of the particle sphere slippage accompanying the softening of the particle sphere glass form or a slow decrease in hardness is hardly observed in the high temperature range and high temperature hardness is maintained.

As stated above, it is assumed that the characteristics of the high temperature hardness of the Si_3N_4 sintered body depend greatly on the microstructure, the relative density, the particle sphere glass form viscosity and its amount.

3.3. Fracture Toughness Rate (Critical Stress Magnification Coefficient; K_{Ic})

There are several methods for the measurement of K_{Ic} such as the double torsion (DT) method, notched beam (NB) method, and indentation induced flaw (IIF) method. However, a large number of

Table II. Fracture toughness of Si_3N_4 ceramics
without additives.

Sample No.	Density (g/cm^3)	H_V (kg/mm^2)	c/a	K_{Ic} ($\text{MN}\cdot\text{m}^{-3/2}$)
1	3.15	1710	1.71	4.39
2	3.17	1930	2.68	3.29
3	3.15	2120	2.69	3.39
4	3.13	1500	1.71	4.19
5	3.18	1880	2.50	3.49
6	3.18	1750	2.32	3.64
7	3.02	1930	2.06	4.24
8	3.00	2150	2.60	3.54
9	3.01	1710	1.91	4.17
10	2.99	1630	1.82	4.27

samples are needed for these methods, and we cannot apply these methods to this sintered body which has only a few samples. For this reason, we performed the measurement of K_{Ic} adopting the indentation method using a Vickers meter which A.G. Evans and E.A. Charles [10, 11] proposed.

Table II shows the K_{Ic} rate of non-additive Si_3N_4 ceramics at room temperature. The result of the measurement indicates that the K_{Ic} rate varies from $3.29 \text{ MN}/\text{m}^{3/2}$ to the highest rate of $4.39 \text{ MN}/\text{m}^{3/2}$. It is said generally that the higher the hardness of the material, the lower the K_{Ic} rate. It seems that a similar relationship exists in the result of this experiment. In fact, the K_{Ic} rate which is indicated in this graph is similar to that of many other reports [15-17] on additive Si_3N_4 ceramics. Therefore the fracture toughness is hardly affected by the existence of a hot-pressing additive, at least at room temperature.

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Figure 6 shows the change of pressure marks or cracks on the sample surface when indentation is performed by the Vickers diamond pressure implement from room temperature to 1400°C .

At approximately 800°C , which is assumed to be the brittle range of the materials, each side of the pressure mark is clear and the cracks are straight. At over 1000°C , they are apt to exhibit ductility. Each side of the pressure mark depresses into a curve, and a raised portion can be seen on the outside, which is formed by a plastic transformation. The cracks are not

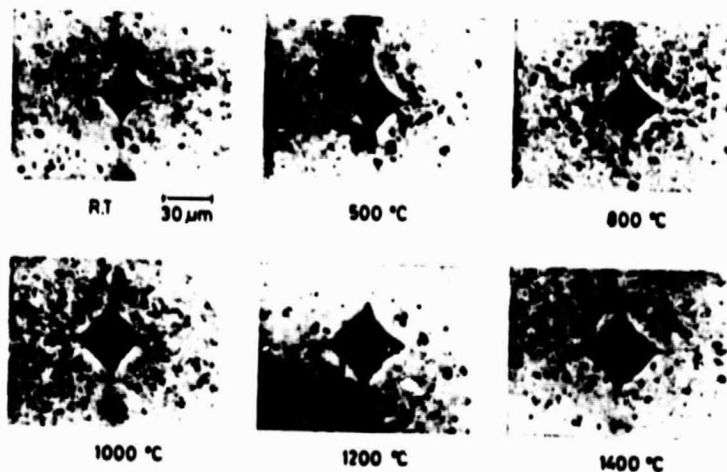


Fig. 6. Photographs of indenter impression produced on the polished surface with Vickers test.

straight at this point. As the temperature rises, the sample marks made by indentation on the sample surface enlarge in size and as a result the c/a ratio, which is the length of the crack (c) to one second (a) of the pressure mark diagonals ($2a$) becomes smaller.

Figure 7 shows the comparison between the additive sintered body and the non-additive sintered body in regard to the temperature dependence of fracture toughness.

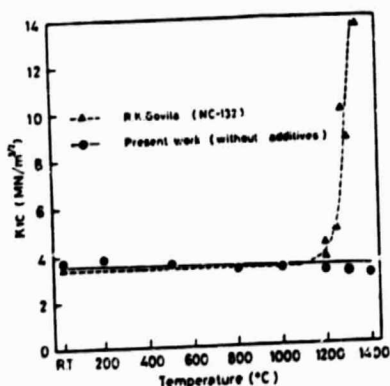


Fig. 7. Temperature dependence of K_{1c} .

at which materials transfer from the brittle range to the semi-ductility or the ductility range. At this point it is known that the fracture toughness of the materials begins to drop more quickly [18].

On the other hand, the high pressure hot-pressing sintered body, which has no additive, seldom possesses other constituents except impurities (such as SiO_2 which is on the surface of Si_3N_4 particles) contained in the starting materials and the constituent which forms in the particle sphere glass forms. The amount of glass forms made by SiO_2 is expected to be very small. As stated above, the sintered body which does not contain the additive is not affected by the particle sphere slippage of Si_3N_4 particles caused by the softening of the particle sphere glass forms even in the high temperature range. Therefore, the fracture toughness does not depend on temperature and it maintains a stable rate.

The non-additive sintered body has a smaller deterioration rate of mechanical properties at 1400°C and is a highly reliable material with respect to a material design when it is compared with the additive sintered body, whose fracture toughness rate greatly depends upon temperature and the deterioration rate of the mechanical properties is conspicuous. In the future, it will be necessary to study the microstructure which affects greatly the fracture toughness and to examine the relationship of size and distribution of internal defects.

4. Conclusions

High pressure-hot pressing of Si_3N_4 without additives was performed using various kinds of Si_3N_4 powder as starting materials and the relationship between densification and phase transformation was studied. It was found that densification and phase transformation of Si_3N_4 under pressure were closely associated. The results of the temperature dependence of Vickers microhardness indicated that the high temperature hardness was strongly influenced not only by the density and microstructure of the sintered body, but also by the purity of the starting powder.

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The fracture toughness values of Si_3N_4 bodies without additives were $3.29\text{--}4.39 \text{ MN/m}^{3/2}$ and were independent of temperature up to 1400°C .

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