Fabrication of Si_3N_4 by Sinter/HIP

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Sinter+HIP which is the most common HIP method is composed of sintering and HIPing processes. Both are performed separately and continuatively in two furnaces. On the other hand, in Sinter/HIP, sintering and HIPing is performed in one furnace. Therefore, Sinter/HIP eliminates extra heating-up, cooling, and handling in Sinter+HIP.

In the present work, a full dense Si_3N_4 sintered body which was added 6 wt% Y_2O_3 and 2 wt% Al_2O_3 as additives was tried to fabricate by Sinter/HIP, whose cycle was composed of the following stages;

- 1) hot evacuation; at 1 400°C, for 2 h, under 70 Pa in vacuum
- 2) gas pressure sintering; at 1 800°C, for 2 h, under 1 MPa of N_2
- 3) HIPing; at 1 750°C, for 3.5 h, under 190 MPa of 0.5 vol% $\text{N}_2 + \text{Ar}$.

At the same time, gas pressure sintering was attempted in which its heating pattern was just the same as that of Sinter/HIP, but its gas pressure which was kept constant was 1 MPa of N_2 .

Three point bending strengths of Sinter/HIPed bodies measured at room temperature and 1 200°C were 1.09 GPa and 605 MPa, respectively. On the contrary, those of gas pressure sintered body were 814 MPa at room temperature and 420 MPa at 1 200°C. Porosity of Sinter/HIPed body was 0.15 % which was much smaller than 0.98 % of porosity of gas pressure sintered body. Large pores of 3~10 μm were observed in gas pressure sintered body, whereas they were eliminated in Sinter/HIPed body. It was concluded that the increase in strength by Sinter/HIP was due to the decrease in porosity and elimination of large pores.

KEY WORDS: HIP; Sinter/HIP; Sinter+HIP; gas pressure sintering; Si_3N_4 ; high strength; image analyzer; Y_2O_3 ; Al_2O_3 .

1. Introduction

Si_3N_4 ceramic has excellent high temperature properties because of its covalent bonding. However, it is very difficult to fabricate a dense body by pressureless sintering. Therefore major methods for fabricating a dense Si_3N_4 are gas pressure sintering, hot pressing and hot isostatic pressing (HIP). It is difficult to fabricate a pore free body by gas pressure sintering. And it is impossible to sinter a large or complex body by hot pressing. On the other hand, HIP is capable of manufacturing a complex and pore free sintered body due to its high gas pressure as pressure transmitting medium.

Two typical HIP methods are known¹⁻³;

- 1) Encapsulation HIP method, and
- 2) Sinter+HIP (Capsuleless) method.

Regarding to capsule HIP method, full densification can be obtained at relatively low temperatures by simultaneous treatment of heating and pressurizing, so grain growth is restrained. However, this process requires the use of expensive capsules.

On the other hand, Sinter+HIP (Capsuleless HIP) method enables us to do HIP treatment without a capsule. This method is a simple and economical way, compared to Encapsulation HIP. At first, by presintering, green compacts are densified to give a sintered body which is impermeable to the pressurizing gas. For successful HIPing, this presintered body must be approximately 90-95 % of theoretical density without surface connected pores. Then this pre-

sintered body is densified fully by HIPing.

Sinter/HIP is new and similar to the Sinter+HIP method, except it combines sintering and HIPing in one furnace.⁴⁻⁶ As shown in Fig. 1, this reduces two steps into one step. Sinter/HIP with a single furnace/pressure vessel allows the immediate application of

Fig. 1. Comparison of Sinter+HIP and Sinter/HIP.

pressure at the end of the sintering. This eliminates extra heating-up, cooling, and handling in Sinter+HIP cycle. As a result, Sinter/HIP is able to reduce its total HIPing time to about 2/3 of that of Sinter+HIP.

In order to perform Sinter/HIP successfully, heating up to 1800°C under low pressure, less than 1 MPa, must be required in former part of Sinter/HIP cycle. Generally it is impossible for ordinary HIP equipment to heat up under such low pressure. NKK-ASEA HIP equipment QIH-15 makes it possible. We tried to fabricate a full dense and high strength sintered body by Sinter/HIP method. Effect of Sinter/HIP on sintered body was studied on this work, with comparing mechanical properties of Sinter/HIPed body to that of gas pressure sintered one.

2. Experiment

2.1. Starting Materials and Processing

High purity powders of Si_3N_4 (Toso Co. TS-7 grade), Y_2O_3 (Shin-etsu Chem. Co.), and Al_2O_3 (Iwatani Chem. Co.) were used. As shown in Fig. 2, Si_3N_4 powder was mixed with 6 wt% Y_2O_3 and 2 wt% Al_2O_3 using attrition mill made of sintered Si_3N_4 balls and pot. The mixing was done for 4 h in propionic acid to avoid oxidation during milling. This mixture was granulated by spray dryer. This granule was uniaxially pressed in a die (25×80 mm) under 29.4 MPa, and then isostatically pressed under 294 MPa. As a result, green compact with density of 1.96 g/cm³ (60 %) was obtained.

2.2. HIP and Gas Pressure Sintering

This green compact was sintered by two methods, (a) Sinter/HIP, and (b) gas pressure sintering, as shown in Fig. 3. Both (a) and (b) have the same heating pattern. But, pressurizing patterns were different. The green compact was placed in Si_3N_4 crucible and covered with $\text{AlN}+\text{BN}$ packing powder.

Sinter/HIP was composed of three stages; (Fig. 3.)

- 1) Hot evacuation: at 1400°C, for 2 h, under 70 Pa of vacuum
- 2) Gas pressure sintering: at 1800°C, for 2 h, under 1 MPa of N_2
- 3) HIPing: at 1750°C, for 3.5 h, under 190 MPa of 0.5vol% N_2+Ar .

Gas pressure sintering has the same heating pattern as Sinter/HIP, but pressure was constant, which was 1 MPa of N_2 gas. The only difference between Sinter/HIP and gas pressure sintering was gas pressure in latter portion of cycle. Thus, effect of HIPing pressure on sintered body was evaluated precisely by comparing mechanical properties.

2.3. Evaluation

Sintered body was evaluated by following points. Bulk density was measured by water displacement (Archimedes method). Porosity and pore size distribution were measured to investigate inner defects in sintered sample in details with image analyzer (NIRECO CO. LUZEX 5000). Three point bend-

Fig. 2. Experimental flow.

Fig. 3. Comparison of Sinter/HIP and gas pressure sintering.

ing strengths were measured at room temperature and 1200°C. Test bar size was 3×4×40 mm, span is 30 mm and, cross head speed is 0.5 mm/min. Fracture surface was observed by scanning electron microscope (SEM). Phase identification and lattice constants were determined by X-ray powder diffractometry using $\text{Cu-K}\alpha$ radiation.

3. Results and Discussion

In Fig. 3, points 1 to 5 are shown. At each point, mechanical properties of sintered samples were ex-

amed. With comparing mechanical properties of point 2 to that of point 4, and point 3 to point 5, effect of Sinter/HIP was evaluated.

3.1. Three Point Bending Strength at Room Temperature

Relationship between time from the start of pressurizing (HIPing time) and three point bending strength is shown in Fig. 4. Both Sinter/HIP and gas pressure sintering have the same heating schedule and almost same pressurizing schedule from start to point 1. At point 1, three point bending strength of gas pressure sintered body was 673 MPa. That of Sinter/HIPed body can be regarded as same value. Then it increased up to 1.09 GPa at point 4, with pressurizing of Sinter/HIP. It was almost constant after point 4. In case of gas pressure sintering, three point bending strength was 814 MPa at point 2, and it was 831 MPa at point 3. Consequently, three point bending strength improved by over 250 MPa by Sinter/HIP.

3.2. Three Point Bending Strength at 1200°C

Relationship between HIPing time and three point bending strength at 1200°C is shown in Fig. 5. Three point bending strength was 325 MPa at point 1. Then, in Sinter/HIP, it increased up to 605 MPa at point 4, and it decreased slightly after point 4. It was 530 MPa at point 6. In case of gas pressure sintering, it was 420 MPa at both points 2 and 3. Therefore, high temperature strength of Sinter/HIPed body was 110–180 MPa higher than that of gas pressure sintered one.

Both Sinter/HIP and gas pressure sintering had the same heating condition, the only difference was gas pressure. Therefore, due to the effect of gas pressure of Sinter/HIP, the strengths at both room temperature and 1200°C of Sinter/HIPed body was improved drastically.

3.3. Density, Porosity, Pore Size Distribution and Grain Size

Density was measured by Archimedes method, and

Fig. 4. Three point bending strength of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering at room temperature.

porosity and pore size distribution were measured by image analyzer (NIRECO Co. LUZEX 5000), in order to investigate the cause of the increase in strength of Sinter/HIPed body.

As shown in Fig. 6, at point 1, density of sintered body was 3.18 g/cm^3 (97.5 % of theoretical density), which had no surface connected pore and was enough dense to do HIP treatment. Then samples became almost full dense, 3.25 g/cm^3 at points 2 to 5 by Sinter/HIP or gas pressure sintering. This increase in density resulted in the increase in strength of both samples. However, no definite difference was found in density between Sinter/HIPed body and gas pressure sintered one.

Residual pores in cut surface of sintered body were shown in Fig. 7. Many residual pores were found, at point 1, but these pores were reduced drastically by Sinter/HIP. On the other hand, the amount of residual pores was also reduced by gas pressure sintering, but large pores still remained. These residual pores were investigated with image analyzer (LUZEX 5000) to know porosity and pore size distribution as shown in Figs. 8 and 9. Residual po-

Fig. 5. Three point bending strength of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering at 1200°C.

Fig. 6. Density of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering. Archimedes method was used.

Fig. 7. Pore distribution in Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering.

Fig. 8. Total porosity of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering.

Fig. 9. Pore size distribution of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering.

rosity was 2.3 % at point 1. And it dropped to less than 0.15 % at points 4 and 5 with Sinter/HIP. However, that of gas pressure sintered body dropped to 0.98 % at most.

Pore size (maximum diameter) distributions at points 3 and 5 were shown in Fig. 9. Pores in the range of 0.5–10 μm were observed in gas pressure sintered body, and 1–3 μm pores were observed most and the number of them were 1 400–1 700/ mm^2 . Large pores of 3–10 μm were about 20 % of all. On

the contrary, 3–10 μm pores could not be found in Sinter/HIPed body. And the number of 1–3 μm pores decreased to less than 1/2 of that of gas pressure sintered body.

Fracture surfaces of each sample were shown in Fig. 10. Grain sizes of both samples, which were almost same, were about 1 μm in diameter. Gas pressure of Sinter/HIP does not affect grain growth.

As a result, the increase in strength by Sinter/HIP

Fig. 10. Fracture surface of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering.

was found to be attributed to following causes;

- (1) Porosity could be reduced from 0.98 to 0.15 %.
- (2) Pores larger than $3 \mu\text{m}$ could be eliminated.

3.4. Phase Identification and Lattice Constants

X-ray diffraction was done to check the change of phase or lattice constants by pressure of Sinter/HIP. As shown in Fig. 11, only $\beta\text{-Si}_3\text{N}_4$ was found at all points. WC was contamination from milling media which was used for preparing specimens for X-ray diffraction. Lattice constants of $\beta\text{-Si}_3\text{N}_4$ were calculated. As shown in Table 1, the values of a -axis and c -axis were almost the same, respectively. From these facts, change of phase or new phase creation did not occur by pressure of Sinter/HIP. With respect to intergranular glassy phase, there was the possibility that Ar or N_2 gas as pressure transmitting medium was dissolved into intergranular glassy phase.^{7,8)} To identify the composition of intergranular glassy phase,⁹⁾ samples were annealed at 1200°C , for 900 s, in air. The new phase of $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$ was found by X-ray diffraction except $\beta\text{-Si}_3\text{N}_4$ in both Sinter/HIPed and gas pressure sintered samples, as shown in Fig. 12. Therefore we may be allowed to decide that there was no definite difference of even intergranular glassy phase in both samples.

In consequence, by effect of pressure of Sinter/HIP,

- (1) new phase creation did not occur,
 - (2) lattice constants of $\beta\text{-Si}_3\text{N}_4$ did not change,
- and
- (3) intergranular glassy phase did not change.

4. Conclusion

(1) A full dense Si_3N_4 sintered body which was added 6 wt% Y_2O_3 and 2 wt% Al_2O_3 as additives could be fabricated by Sinter/HIP, which was composed of these three stages;

Fig. 11. Phase identification of Sinter/HIPed and gas pressure sintered (G.P.S.) bodies by X-ray diffraction.

Table 1. Lattice constants of Si_3N_4 fabricated by Sinter/HIP and gas pressure sintering (G.P.S.).

	Sinter/HIP Point 5	G.P.S. Point 3
a -axis (Å)	7.6023(14)	7.6028(9)
c -axis (Å)	2.9077(14)	2.9073(8)

- 1) Hot evacuation; at 1400°C , for 2 h, under 70 Pa of vacuum
- 2) Gas pressure sintering; at 1800°C , for 2 h, under 1 MPa of N_2
- 3) HIPing; at 1750°C , for 3.5 h, under 190 MPa of 0.5 vol% $\text{N}_2 + \text{Ar}$.

Fig. 12. Phase identification of Sinter/HIPed and gas pressure sintered (G.P.S.) bodies which were annealed at 1 200°C for 900 s in air by X-ray diffraction.

(2) Three point bending strengths of Sinter/HIPed body was 1.09 GPa at room temperature and 605 MPa at 1 200°C. In comparison with gas pressure sintered body, room temperature strength increased by 270 MPa, and high temperature (1 200°C) strength increased by 105–180 MPa.

(3) It was found with image analyzer that porosity of Sinter/HIPed body was less than 0.15 %, and its maximum pore size was 3 μm . On the contrary,

the porosity of gas pressure sintered body was 0.98 %, and the maximum pore size was 10 μm . The increase in strength was due to these drastic decrease in porosity and elimination of large pores by gas pressure of Sinter/HIP.

(4) The grain sizes of Sinter/HIPed and gas pressure sintered bodies were almost the same each other. Therefore, gas pressure of Sinter/HIP did not affect the grain growth of sintered body.

(5) $\beta\text{-Si}_3\text{N}_4$ was only found by X-ray diffraction in both Sinter/HIPed and gas pressure sintered body. Changes of lattice constants or new phase creation did not occur. As a result, gas pressure of Sinter/HIP affected mechanical properties largely, but did not affect the phase of sintered body.

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