Appropriate Sinter/HIP Conditions to Fabricate a High Strength Si₃N₄

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Sinter/HIP is a new and efficient way to fabricate a high strength sintered body, compared to Sinter+HIP. Appropriate Sinter/HIP conditions were determined on this study to fabricate a high strength Si₃N₄ to which 6 wt% Y₂O₃ and 2 wt% Al₂O₃ were added as additives. Sinter/HIP was composed of the following stages; (stage 1) hot evacuation, (stage 2) gas pressure sintering, and (stage 3) HIPing. Important factors among these three stages were (1) N₂ gas pressure at stage 2 and (2) gas, pressure, and time at stage 3.

N₂ gas pressure at stage 2 was found to be the most influential factor on mechanical properties of Sinter/HIPed body, especially its strength. To fabricate a high strength Sinter/HIPed body, N₂ gas pressure at stage 2 must be less than 1 MPa.

Pure N₂ gas is usually used as HIPing gas. However, the mixture gas of 0.5vol% N₂+Ar could be used as HIPing gas. Because three point bending strength of Sinter/HIPed body using 0.5vol% N₂+Ar was almost same as that of sinter/HIPed body using N₂.

HIPing time should be short on the condition that a sample could be densified fully, because high temperature (1 200°C) strength decreased slightly with increasing HIPing time. With regard to HIPing pressure, 120 MPa was sufficient to fabricate a high strength Si₃N₄.

KEY WORDS: Sinter/HIP; HIP; Si₃N₄; gas pressure sintering; three point bending strength.

1. Introduction

Sinter/HIP is a new and similar way to Sinter+HIP, except it combines sintering and HIPing in one furnace. This reduces two steps into one step. Therefore, this eliminates extra heating, cooling and handling in Sinter+HIP. As a result, Sinter/HIP is able to reduce total HIPing time to about 2/3 of that of Sinter+HIP.

Sinter/HIP is a superior method to gas pressure sintering, with regard to fabricating a high strength Si₃N₄ sintered body, as reported. However appropriate Sinter/HIP conditions to fabricate Si₃N₄ were not studied well. Therefore the effect of Sinter/HIP conditions on mechanical properties were studied on this work to establish the appropriate Sinter/HIP condition.

Sinter/HIP used on this work is composed of three stages, shown in Fig. 1.

a) Stage 1: hot evacuation
b) Stage 2: gas pressure sintering
c) Stage 3: HIPing

We evaluated important factors among these as follows.
1) N₂ gas pressure at stage 2
2) HIPing gas, HIPing pressure, and HIPing time at stage 3

Particularly, N₂ gas pressure at stage 2 is very important. Surface connected pores of a sample were enclosed and became impermeable to pressurizing gas at the end of stage 2. However N₂ gas was remaining in enclosed pores. It is thought that this remaining gas prevents the densification of a sample seriously. We examined the effect of gas pressure at stage 2 on mechanical properties of Sinter/HIPed sample.

N₂ is usually used as pressure transmitting medium (HIPing gas) to prevent the decomposition of Si₃N₄. However, the decomposition pressure of Si₃N₄ is about 0.1 MPa at HIPing temperature which is usually 1 600–1 800°C, therefore, 1 MPa of N₂ gas is enough to depress its decomposition. The mixture gas of N₂+Ar is able to use as HIPing gas. Relationship between HIPing gas and mechanical properties were studied, using mixture gas of N₂+Ar and pure N₂ gas.

In case of HIP treatment of cemented tungsten carbide, or iron based alloy powder, it is said that 30 MPa is enough for HIPing pressure. But sufficient pressure to density Si₃N₄ fully was not investigated well. Therefore several pressures were chosen to establish the appropriate HIPing pressure. Simultaneously, HIPing time to obtain fully densified Si₃N₄ was studied, too.

2. Experiment

2.1. Starting Materials, and Processing

High purity powders of Si₃N₄ (Toso Co. TS-7 grade), Y₂O₃ (Shin-etsu Chem. Co.), and Al₂O₃ (Iwatani Chem. Co.) were used. As shown in Fig. 2, Si₃N₄ powder was mixed with 6 wt% Y₂O₃ and 2 wt% Al₂O₃ using attrition mill made of sintered Si₃N₄ 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. Sinter/HIP

This green body was Sinter/HIPed, as shown in Fig. 1. HIP condition was chosen as follows.

Stage 1: Hot evacuation stage

\[ T_0=1400^\circ C, P_0=70 \text{ Pa}, \text{ and } t_0=2 \text{ h} \]

These conditions were not changed.

2.2.1. Pressure of N₂ Gas at Stage 2

The conditions at stages 2 and 3 were chosen as follows to determine the most appropriate pressure of N₂.

Stage 2: \[ T_1=1800^\circ C, t_1=2 \text{ h}, P_1=0.1, 1, 3, \text{ and } 15 \text{ MPa of } N₂ \]

Stage 3: \[ T_2=1750^\circ C, t_2=3.5 \text{ h}, P_2=190 \text{ MPa (1 MPa of } N₂+189 \text{ MPa of Ar)} \]

2.2.2. Gas (HIPing Gas) at Stage 3

N₂ gas (190 MPa) and mixed gas of 0.5vol%N₂(1 MPa)+Ar(189 MPa) were chosen as pressure transmitting medium (HIPing gas). The other conditions were as follows.

Stage 2: \[ T_1=1800^\circ C, t_1=2 \text{ h}, P_1=1 \text{ MPa of } N₂ \]

Stage 3: \[ T_2=1750^\circ C, t_2=3.5 \text{ h} \]

2.2.3. Hiping Time and Hiping Pressure at Stage 3

Three HIPing times and four kinds of pressure were chosen to know the relationship among HIPing time, HIPing pressure and mechanical properties. This HIPing time was counted from start of pressurizing.

Stage 2: \[ T_1=1800^\circ C, t_1=2 \text{ h}, P_1=1 \text{ MPa of } N₂ \]

Stage 3: \[ T_2=1750^\circ C, t_2=2, 3.5, \text{ and } 5 \text{ h}, P_2=1 \text{ MPa (N₂), } 30 \text{ MPa (1 MPa of N₂) } +29 \text{ MPa of Ar), } 120 \text{ MPa (1 MPa of } N₂+119 \text{ MPa of Ar)} \text{ and } 190 \text{ MPa (1 MPa of } N₂+189 \text{ MPa of Ar)} \]

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 (NIRICO CO. LUZEX 5000). Three point bending 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 diffraction using Cu-Kα radiation.

3. Results and Discussions

3.1. Influence of Gas Pressure, \( P_1 \) at Stage 2

Green compact was sintered at this stage to make it impermeable to HIPing gas. Sintered body with the density of 3.18 g/cm³ (97.5 %) was obtained at the end of stage 2. It had no surface connected pores, and N₂ gas was remaining in enclosed pores. Effect of this remaining gas on three point bending strength at room temperature of Sinter/HIPed body was shown in Fig. 3.

Three point bending strength of Sinter/HIPed sample was 1,10–1,08 GPa within the extent that \( P_1 \) was from 0.1 to 1 MPa. It did not depend on \( P_1 \). However it decreased linearly with increasing \( P_1 \) (log \( P_1 \)) in the extent that \( P_1 \) was over 1 MPa. It was 540 MPa in case that \( P_1 \) was 15 MPa.

Residual pores and pore size distribution were
measured by image analyzer to investigate the cause of the decrease in strength. Residual pores in Sinter/HIPed sample in case of \( P_1 = 1 \) MPa and 3 MPa were shown in Fig. 4. They could not be observed in the sample of \( P_1 = 1 \) MPa, on the other hand, a lot of pores observed in the sample of \( P_1 = 3 \) MPa. As shown in Fig. 5, porosity was less than 0.2 % in the range that \( P_1 \) was from 0.1 to 1 MPa. However, it increased rapidly in the range that \( P_1 \) was over 1 MPa. In case of \( P_1 = 3 \) MPa, porosity was 2 %.

Pore size distribution was shown in Fig. 6. This figure showed that the number of residual pores in case of \( P_1 = 1 \) MPa was much smaller than that in case of \( P_1 = 3 \) MPa. Large pores of 3-7 \( \mu \)m were observed in the sample of \( P_1 = 3 \) MPa, on the other hand, they were extinguished in the sample of \( P_1 = 1 \) MPa. The decrease in three point bending strength of Sinter/HIPed sample was due to these facts. Residual gas in enclosed pores affects densification after stage 2 largely. After all, gas pressure of \( N_2 \) at stage 2 (gas pressure sintering stage) must be less than 1 MPa, and must be high to prevent the decomposition of \( \text{Si}_3\text{N}_4 \). Therefore, appropriate pressure is about 1 MPa of \( N_2 \).

### 3.2. Influence of HIPing Gas at Stage 3

We had a lot of experiences that high pressure \( N_2 \) gas gives more damage to a furnace, especially, heating element and thermocouple than high pressure \( \text{Ar} \) gas at elevated temperature. \( N_2 \) gas is dissolved into intergranule glassy phase during HIPping, and affects mechanical properties of \( \text{Si}_3\text{N}_4 \). Therefore, if the mixed gas of \( N_2+\text{Ar} \) was possible to use, it may be favorable for \( \text{Si}_3\text{N}_4 \) and the maintenance of HIP equipment.

\( N_2 \) gas (190 MPa) and mixed gas of 0.5 vol% \( N_2 \) (1 MPa) + \( \text{Ar} \) (189 MPa) were used as HIPping gas, and mechanical properties of Sinter/HIPed body using both gases were evaluated. Table 1 shows bulk density and porosity. Both samples had 99% of theoretical density, but, porosity of Sinter/HIPed body using 0.5 vol% \( N_2+\text{Ar} \) was a little higher than that of Sinter/HIPed body using \( N_2 \). Three point bending strength of Sinter/HIPed body using 0.5 vol% \( N_2+\text{Ar} \) at both room temperature and 1200°C were almost

<table>
<thead>
<tr>
<th>HIPing gas</th>
<th>Bulk density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
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<tbody>
<tr>
<td>( N_2 ) (190 MPa)</td>
<td>3.23 (99%)</td>
<td>0.26</td>
</tr>
<tr>
<td>0.5 vol% ( N_2+\text{Ar} ) (1 MPa)</td>
<td>3.25 (99%)</td>
<td>0.79</td>
</tr>
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</table>

Fig. 3. Relationship between pressure of \( N_2 \) gas at stage 2 (gas pressure sintering stage) and three point bending strength of Sinter/HIPed \( \text{Si}_3\text{N}_4 \).

![Pore distribution in \( \text{Si}_3\text{N}_4 \) fabricated by Sinter/HIP.](image)

Fig. 4. Pore distribution in \( \text{Si}_3\text{N}_4 \) fabricated by Sinter/HIP.

Fig. 5. Relationship between pressure of \( N_2 \) gas at stage 2 (gas pressure sintering stage) and total porosity in \( \text{Si}_3\text{N}_4 \) fabricated by Sinter/HIP.

Fig. 6. Pore size distribution in \( \text{Si}_3\text{N}_4 \) fabricated by Sinter/HIP.
the same as that of Sinter/HIPed body using N₂, as shown in Fig. 7.

Phases were identified in both samples by X-ray diffraction. Only β-Si₃N₄ were found, as shown in Fig. 8. Both samples were annealed at 1200°C, for 900 s, in air to crystallize the intergranular glassy phase in order to investigate its composition. \((\text{No. 10})\) β-Si₃N₄ and γ-Y₂Si₂O₇ \((\text{No. 11})\) were found in both samples, as shown in Fig. 9. But the shape of peaks of γ-Y₂Si₂O₇ was a little different each other, the composition of intergranular glassy phase might be a little different.

Fig. 10 shows fracture surface of both samples by SEM. Both had almost same morphology and almost same grain size (about 1 μm in diameter). After all, clear differences could not be found. Therefore, it was found at least that 0.5vol% N₂+Ar could be used as HIPing gas for Si₃N₄ sufficiently.

3.3. Influence of HIPing Time at Stage 3

Fig. 11 shows relationship between HIPing time and three point bending strength. Three point bending strengths at room temperature were 1.0-1.08 GPa. It was almost constant regardless of HIPing time. At the end of pressurizing, three point bending strength was highest. With regard to three point bending strength at 1200°C, the highest value was obtained at the end of pressurizing, too. However, high temperature strength decreased slightly with increasing HIPing time. Therefore, some change might happen in composition of intergranular glassy phase, because high temperature strength decreased with increasing HIPing time in spite that room temperature strength was constant. Weight reduction ratio of these samples are shown in Fig. 12. Generally, weight reduction ratio increases with increasing sintering time in gas pressure sintering. However, in Sinter/HIP, it decreased with increasing HIPing time, as shown in Fig. 12. This opposite phenomenon shows the pos-
International Sinter/HIP 14, room Influence w/o HIPing follows: pressurc same 120 at should fabricate 0.5 vol%',j,N2(1 u'
short Figs. The be fabricated depress since bending time MPa bend-pure at and Si3N4, oo at HIPing 598 and 6 gas appropriate facts, HIPing pressure as samples the should Sinter/HIP (A) gas about at 200'C as 190MPa to on for -e the 4 sintering. less surfacc well and three HIPing fabricated using 1 of HIPing Pressure d' the I that Effect pressure was I - their three strengths than pressure, tperature point !O gas lo and intergranular were 30 and Sinter/HIPed bending densificd HIPing of temperature pressure, as pressure high on Sinter/HIPed 120 sintering phase. of sample was obtained. These fact, HIPing time should be short, on the condition that a

Fig. 10. Fracture surface of Si₃N₄ fabricated by Sinter/HIP and gas pressure sintering.

Fig. 11. Relationship between HIPing time and three point bending strength of Si₃N₄ fabricated by Sinter/HIP.

Fig. 12. Effect of HIPing time on weight reduction ratio of Si₃N₄ fabricated by Sinter/HIP and gas pressure sintering.

sample could be densified fully.

3.4. Influence of HIPing Pressure

Appropriate HIPing pressure was not well known for successful HIPing of Si₃N₄. Figs. 13 and 14 show the relationship among HIPing pressure, HIPing time, and three point bending strength. Samples were fabricated on the condition shown in Figs. 13 and 14, and their three point bending strengths are shown above the open marks. 120 MPa is enough for HIPing pressure, since three point bending strength of Sinter/HIPed body was 1.11 GPa at room temperature and 598 MPa at 1200°C, which was almost same value of Sinter/HIPed sample at 190 MPa. However, 30 MPa was not enough for HIPing pressure, since three point bending strengths at both room temperature and 1200°C were much lower than those of Sinter/HIPed sample at 120 MPa. Therefore, appropriate HIPing pressure is about 120 MPa on the condition that HIPing temperature is 1750°C.

4. Conclusion

Appropriate Sinter/HIP conditions to fabricate a high strength Si₃N₄ to which 6 wt% Y₂O₃ and 2 wt% Al₂O₃ were added as additives were as follows:

(1) To fabricate a high strength Si₃N₄, N₂ gas pressure at stage 2 (gas pressure sintering stage) must be less than 1 MPa on the condition that it is enough high to depress the decomposition of Si₃N₄.

(2) The mixture gas of 0.5vol%N₂+Ar could be used as HIPing gas. A full dense Sinter/HIPed body was obtained. Three point bending strength of Sinter/HIPed body using the mixture gas was almost the same as that of Sinter/HIPed body using pure N₂ gas.

(3) HIPing time should be short on the condition that samples could be densified fully, because three point bending strength at 1200°C decreased slightly with increasing HIPing time.

(4) 120 MPa was enough for HIPing pressure to fabricate a high strength Si₃N₄.
Fig. 13. Effect of HIPing time and HIPing pressure on three point bending strength at room temperature.

Fig. 14. Effect of HIPing time and HIPing pressure on three point bending strength at 1200°C.

REFERENCES