Lower Temperature Pressureless Sintering of Si_3N_4 Ceramics using SiO_2 – MgO – Y_2O_3 Additives without Packing Powder

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SiO_2 – MgO – Y_2O_3 助剤添加窒化ケイ素セラミックスのつめ粉不使用低温無加圧焼結

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Si_3N_4 ceramics were sintered at 1873–2023 K (1600–1750°C) with additives from the SiO_2 – MgO – Y_2O_3 system. The degree of densification, α – β transformation, mass loss and microstructure were measured as a function of additives composition, sintering temperature, nitrogen gas pressure, and with/without packing powder. Specimens prepared from 3 mass% SiO_2 , 3 mass% MgO , and 5 mass% Y_2O_3 as the sintering additive could be sintered to almost full density at relatively low temperature as 1923 K for 2 h under ambient pressure of nitrogen atmosphere without using packing powder. The α – β transformation was not completed at this condition. The mass loss was relatively high due to the evaporation of SiO_2 and MgO . However, the resulted materials have high bending strength as 980 MPa, with fracture toughness of $6.6 \text{ MPa} \cdot \text{m}^{1/2}$, Vickers hardness of 18.4 GPa, and thermal conductivity of $34 \text{ Wm}^{-1}\text{K}^{-1}$. [Received February 10, 2006; Accepted July 20, 2006]

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1. Introduction

Silicon nitride (Si_3N_4) based materials are one class of promising structural ceramics for mechanical, high chemical resistance, high-temperature material, and high thermal conductivity material applications.^{1,2)} However, chemically pure and dense Si_3N_4 ceramics could not be obtained by sintering because of its high degree of covalent bonding nature and low diffusion coefficients.^{2,3)} As a consequence, several alternative techniques were developed to enable the densification of Si_3N_4 -based ceramics, but fully dense Si_3N_4 materials can be produced only by presence of liquid phase derived from additives in the sintering process.^{4,5)} Wide range of sintering additives have been explored up to now for Si_3N_4 ceramics. Since the densification rate is directly related to the type and amount of sintering additives, and also microstructural development and thermal and mechanical properties of sintered bodies are strongly influenced by these additives, there has been considerable effort to find and optimize sintering aids for high performance Si_3N_4 materials.

Si_3N_4 can easily be hot-pressed with small addition of metal oxides to give a product with high strength without porosity but the disadvantages of hot-pressing are that it is an expensive process, limited to the formation of simple shapes, and small batches. By other methods such as, with gas pressure assisted approaches, hot isostatic pressing and gas pressure sintering, dense materials are also obtained using several sintering additives such as Y_2O_3 , MgO , Al_2O_3 , La_2O_3 , CeO_2 , etc.,⁶⁾ However, these methods are still expensive for commercial products. Pressureless sintering, hereafter designated simply sintering, as an alternative processing method, usually requires both a high processing temperature at which Si_3N_4 would decompose,^{7,8)} and a considerable amount of sintering additives which degrade the high temperature mechanical properties.

Table 1 summarizes earlier results on pressureless sintering (ambient gas pressure) of Si_3N_4 ceramics using several kinds of additives. In the reports No. 1 to 13, the sintering was done under N_2 atmosphere, whereas in No. 14 and 15, the sintering was done in an air atmosphere furnace.

Y_2O_3 – Al_2O_3 is the most popular additive system for low temperature sintering of Si_3N_4 ceramics, due to its low eutectic temperature. However, the presence of aluminum is not proper for high thermal conductivity as mentioned elsewhere.^{9,10)}

MgO is another famous additive for the sintering of Si_3N_4 ceramics. It was reported recently that the Si_3N_4 ceramics with relatively high thermal conductivity as $90 \text{ Wm}^{-1}\text{K}^{-1}$ could be sintered using MgO co-doped with Y_2O_3 and SiO_2 and gas-pressure-sintering, using 50 mass% Si_3N_4 /50 mass% BN packing powder and subsequently post-sintering heat treatment without packing powder.¹¹⁾ However, the effect of this sintering additive on pressureless sintering without packing powder has not been investigated yet.

In most experiments, Si_3N_4 powders (with BN powder and/or other additives) needed to be used as a packing powder, as shown in Table 1. Without packing powder, Si_3N_4 ceramics containing no porous surface layer could not be easily sintered under ambient pressure.^{7,12)}

However, the cost of packing powder is generally 3–4 times more than that of raw powder for specimens. The packing powder will not be necessary for pressureless sintering only in case of rather low sintering temperature. Recently, more attention has been given to low-temperature sintering of Si_3N_4 ceramics with the aim of reducing manufacturing costs. Motavic et al.¹³⁾ succeeded in sintering Si_3N_4 ceramics at low temperature of 1823 K (1550°C) for 2 h under 0.1 MPa– N_2 gas pressure with addition of 15 mass% LiYO_2 . A full density is attained for the sintered specimens. Li_2O is removed in gaseous form during sintering and thus the liquid phase is tran-

Table 1. A Summary of Earlier Results on Ambient Gas Pressure Sintering of Si₃N₄ Ceramics

No.	Additives		Sintering Condition		Density		Packing Powder	References
	(mass%)	Type	(Temp, K)	(Time)	(g/cm ³)	TD(%)		
Nitrogen atmosphere								
1.	15% LiYO ₂	oxide	1823	2 h	3.18	98	-	Matovic et al. ^{13),17)}
2.	9.8% Y ₂ O ₃ : 6.8% Al ₂ O ₃ : 3.4%	oxide	1923	1 h	3.10	93	40%Si ₃ N ₄ /40%BN/20%mixed	Almeida et al. ¹⁸⁾
3.	19.3% Nd ₂ O ₃ : 2.3% MgO	oxide	1923	2 h	3.2	-	-	Pomeroy et al. ¹⁹⁾
4.	4% Y ₂ O ₃ : 5% MgO*	oxide	1973	1 h	-	99	50%Si ₃ N ₄ /50%BN	Ling et al. ²⁰⁾
5.	4.5% Y ₂ O ₃ : 1.5% Al ₂ O ₃	nitrate salt	2023	2 h	-	99	Si ₃ N ₄	Yano et al. ²¹⁾
6.	8.3% Y ₂ O ₃ : 4.5% Al ₂ O ₃ : 3.3%	nitrate salt	2023	2 h	3.29	-	50%mixed/50%BN	Yang et al. ⁶⁾
7.	6% Y ₂ O ₃ : 4% Al ₂ O ₃	oxide	2023	2 h	3.3	-	50%Al ₂ O ₃ /50%BN	Uno et al. ²²⁾
8.	3% MgO : 1.5% Al ₂ O ₃ : 3.5% SiO ₂	oxide	2053	3 h	-	99.7	50%Si ₃ N ₄ /50%BN	Liu et al. ²³⁾
9.	18.1% La ₂ O ₃ : 5.8% SrO	oxide	2073	1 h	-	89	50%Si ₃ N ₄ /50%BN	Tunaboylu et al. ²⁴⁾
10.	5% CeO ₂ : 5% MgO*	oxide	2073	1 h	-	98.6	50%Si ₃ N ₄ /50%BN	Yang et al. ^{25),26)}
11.	10% (Y _{0.8} La _{0.2}) ₂ O ₃ : 10% AlN	oxide, nitride	2073	3 h	3.44	-	50%Si ₃ N ₄ /50%BN	Huang et al. ²⁷⁾
12.	16% Yb ₂ O ₃ : 4.9% SiO ₂	oxide	2073	4 h	3.55	98.4	70%Si ₃ N ₄ /30%BN	Goto et al. ²⁸⁾
13.	10.1% MgAl ₂ O ₄	oxide	2123	4 h	3.15	96	-	Masaki et al. ²⁹⁾
Air atmosphere								
14.	5% Y ₂ O ₃ : 5% Al ₂ O ₃	oxide	1973	2 h	3.17	95	Si ₃ N ₄	Wada et al. ^{30),31)}
15.	12% Y ₂ O ₃ : 3% Al ₂ O ₃	oxide	2023	2 h	3.43	98	Si ₃ N ₄	Pluchnett et al. ³²⁾

* considerable of WC-6%Co media contamination.

sient. This creates some potential for good high-temperature properties despite the low sintering temperature. However, such kind of additive is still expensive.

In order to reduce the production cost, the present work has therefore focused on densification of SiO₂-MgO-Y₂O₃-added Si₃N₄ ceramics by the much cheaper and more versatile technique of ambient gas-pressure-sintering (pressureless-sintering). This ternary compound produces an eutectic liquid at a rather low temperature as 1673 K (1400°C).¹⁴⁾ It will be a favorable additive for low temperature sintering of Si₃N₄ ceramics under ambient N₂ gas pressure without packing powder.

2. Experimental

Green Si₃N₄ specimens were prepared from a high-purity α -Si₃N₄ raw powder (particle size 0.8 μ m, oxygen content 1.3 mass%; SN-E10 grade, Ube Industries, Japan) with Y₂O₃ (RU, Shin-Etsu Chemical, Japan), SiO₂ (KE-P30, Nippon Shokubai, Japan), and MgO (surface area 31.7 m²/g, Iwatani Chemicals, Japan) as sintering aids. Three kinds of additive systems, 3 mass% SiO₂ + 3 mass% MgO + (1, 3, 5) mass% Y₂O₃-added Si₃N₄, named as 3S3M1Y, 3S3M3Y and 3S3M5Y, respectively, were prepared. Another composition, 5 mass% Y₂O₃ + 3 mass% Al₂O₃ (TMD, Taimei Chemical, Japan), named as 5Y3A, was prepared for comparison. Mixtures were ball-milled for 24 h in a polyethylene bottle with silicon nitride balls (SUN-12, diameter 5 mm, Nikkato Corporation, Japan) and ethanol (99.5%) as a medium. Slurries were dried in a rotary evaporator at a temperature of 333 K and the mixed powder was sieved through a 100-mesh sieve. Dried powder was uniaxially pressed under 20 MPa. The pellet was then isostatically cold-pressed (CIP) under a pressure of 200 MPa. Specimens (10 mm in diameter and 2 mm in thickness) were sintered in a BN crucible without packing powder at the temperature of 1873–2023 K (1600–1750°C) for 2 h under 0.1 MPa of N₂ gas flow (2 l/min).

After sintering, specimens were weighted to calculate the mass loss during sintering process, and bulk density was measured by the Archimedes method using water. Cross-sections of the sintered bodies were observed by SEM after sintering. Specimens were cut, ground using 1 μ m diamond paste, plasma-etched in a CF₄/O₂ gas for 40 s, coated with evaporated carbon, and observed by a field-emission type scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan).

Sintered specimens were ground into powders using a SiC mortar and sieved through a 200-mesh sieve for phase identification. Phase identification was performed by an X-ray diffractometer using monochromated Cu K α (XRD, PW 1700, Philips, Holland) at room temperature. XRD was also used to evaluate the weight fraction of the α -Si₃N₄ and β -Si₃N₄ phases based on the method proposed by Gazzara and Messier.¹⁵⁾

A commercial hot-gas-extraction analyzer (TC-436, LECO Co., USA) was used for determination of total oxygen. About 50 mg of each powder sample was weighted into a graphite crucible (10 mm ϕ × 16 mm), and about 50 mg of graphite powder was added to the sample to accelerate the carbo-thermal reduction. The amount of oxygen was calibrated using a standard specimen.

In addition, the effects of the packing powder (50 mass% Si₃N₄ and 50 mass% BN; SN-E10 and BN-GP (Denka, Japan), respectively) and N₂ gas pressure (0.1 and 1.0 MPa) on the sinterability of the 3S3M1Y, 3S3M3Y and 3S3M5Y specimens at the sintering temperature of 1650°C for 2 h were also investigated.

Sintered specimens were prepared for mechanical properties measurement from approximately 8.5 g of the dried powder, uniaxially pressed under 20 MPa in a square die of 35 mm inside length and subsequently isostatically cold-pressed under a pressure of 200 MPa. Samples were sintered at 1923 K for 2 h under 0.1 MPa of N₂ gas flow (2 l/min) without packing powder. Rectangular bars 3 × 4 × 25 mm were cut and ground

using 1 μm diamond slurry. The edges were chamfered. Mechanical testing was performed using a commercial screw-driven load frame (Instron, Model 1185) with a 3-point bending fixture. Test conditions were as follows; loading with 20-mm span and a crosshead speed of 0.5 mm/min at room temperature. Number of specimen was three for each synthesis condition. Young's modulus was calculated from the stress-strain curve of 3-point bending test with 2 mm strain gage (Kyowa) attached on a tensile surface of the specimens. Vickers hardness was measured using a Vickers hardness tester at room temperature (AVK-A, Akashi). The load and loading time were 49 N and 15 s, respectively. Fracture toughness was deduced from the diagonal length and crack length of Vickers indentations according to JIS R 1607.

3. Results and discussion

During sintering, a part of Si_3N_4 may decompose depending on the conditions such as temperature, N_2 gas pressure, and kind and quantity of sintering aids. In the previous study,¹¹⁾ dense Si_3N_4 specimens were sintered at 2123 K (1850°C) with SiO_2 - MgO - Y_2O_3 additive (3 mass% SiO_2 , 3 mass% MgO , and 1 mass% Y_2O_3) under 1.0 MPa- N_2 atmosphere. The relatively high N_2 gas pressure was applied to suppress the decomposition of Si_3N_4 . SiO_2 and MgO were thought to react with Si_3N_4 at the sintering temperature. Otherwise, liquid phase was generated to enhance the densification. The liquid phase should be composed with the Y_2O_3 - MgO - SiO_2 - Si_3N_4 system (oxynitride glass). However, decomposition of the liquid phase must be considered if the sintering was performed under ambient N_2 pressure.

Mass loss of the specimens sintered at all sintering temperature under ambient N_2 pressure without packing powder was measured and shown in Fig. 1. The mass loss of all specimens increased with increasing the sintering temperature. It indicates that the mass loss reactions should be occurred as a result of the evaporation of SiO , N_2 and/or Mg gas as supposed in the reactions (1) and (2).¹¹⁾ The mass loss of the 3S3M1Y was always highest at the same sintering temperature, due to the highest relative content of volatile components, SiO_2 and MgO .

At high temperature as 2123 K, vapor pressure of SiO gas was calculated to be about 78 kPa (0.77 atm) for the reaction (1) and 34 kPa (0.33 atm) for the reaction (2).¹⁶⁾ The evaporation of gases in the reactions (1) and (2) is a cause of the mass loss in resulted products. The decomposition rate of the liquid phase must be controlled to be as low as possible for keeping the succeeding of densification process. To suppress the mass loss reactions, higher N_2 gas pressure was generally used to force the reactions (1) and (2) backward. Moreover, the use of packing powder is the most popular method for suppressing the mass loss reaction of specimens.

The other way, by decreasing the sintering temperature, to minimize the mass loss reaction was examined in this study instead of the using of packing powder and high N_2 gas pressure. At the sintering of 1923 K, the vapor pressure of SiO gas was estimated to be about 6 kPa (0.06 atm) and 3 kPa (0.03 atm) for the reactions (1) and (2), respectively, which is lower than one-tenth that of during sintering at 2123 K.

However, the suitable sintering additives must be used to promote densification. The higher addition of Y_2O_3 (3 and

Fig. 1. Effect of sintering temperature on mass loss of the 3S3M1Y, 3S3M3Y, 3S3M5Y and 5Y3A-added Si_3N_4 ceramics sintered at 1873–2023 K for 2 h under 0.1 MPa- N_2 gas pressure without packing powder.

Fig. 2. Effect of sintering temperature on relative density of the 3S3M1Y, 3S3M3Y, 3S3M5Y and 5Y3A-added Si_3N_4 ceramics sintered at 1873–2023 K for 2 h under 0.1 MPa- N_2 gas pressure without packing powder.

5 mass%) was used to improve the sinterability. The lower amount of mass loss in the 3S3M3Y and 3S3M5Y specimens may be due to the higher concentration of Y_2O_3 .

Almost full density was obtained in the 3S3M3Y and 3S3M5Y specimens after sintering at 1923 K as shown in Fig. 2. The relative density of the 3S3M5Y specimen increased with the increase of sintering temperature, whereas these of the 3S3M1Y and 3S3M3Y decreased at sintering temperatures higher than 1923 K. In comparison, the 3S3M3Y and 3S3M5Y specimens could be easily sintered than the 5Y3A specimen at temperatures lower than 2023 K. The 5Y3A specimen could not be sintered to full density at temperatures lower than 1973 K.

On the other hand, as shown in Fig. 1, the mass loss was

Fig. 3. SEM micrographs of Si_3N_4 ceramics sintered under 0.1 MPa- N_2 without packing powder, showing a surface porous layer in some specimens.

Fig. 4. SEM micrographs of polished and plasma-etched surface of the 3S3M1Y, 3S3M3Y and 3S3M5Y-added Si_3N_4 ceramics sintered at 1873 and 1973 K for 2 h under 0.1 MPa- N_2 without packing powder.

also observed in the 5Y3A specimens, but the lowest amount, according to the mass loss reaction (1). SiO_2 existed as a surface oxidized layer of the α - Si_3N_4 raw powder. Moreover, the other mass loss reaction (3) was also considered for a higher temperature and longer soaking time sintering due to the Al_2O_3 addition.^{9),11)}

Figure 3 shows low magnification SEM photographs of the sintered specimens. Porous layer indicated by arrows was formed in the 3S3M1Y specimen. Thickness of the porous layer increases with increasing sintering temperature. Only the 3S3M1Y specimen could not be sintered to full density (<95% theoretical density) at any temperature under ambient N_2 pressure. The presence of surface porous layer at

higher sintering temperature in the 3S3M1Y and 3S3M3Y specimens is a cause of the decreasing in relative density.

Figure 4 shows higher magnification SEM micrographs of polished and plasma-etched surface of the sintered specimens. The change in microstructure with the sintering temperature was observed from these figures. At the lower sintering temperature as 1873 K, the average grain size was smaller, and some amount of porosity could be observed in all specimens. Moreover, a small number of elongated-grains recognized as β - Si_3N_4 grains was created at such a low sintering temperature by this sintering additives system. On the other hand, at the higher sintering temperature as 1973 K, the grain growth was observed in all specimens. The amount of elongated β - Si_3N_4 grains increased, that could be confirmed by XRD analysis mentioned later. However, larger amount of porosity was always observed in the 3S3M1Y specimen, which agreed with

the result of its lowest relative density.

The phase evolution of the 3S3M3Y sample after ambient N_2 pressure sintering at various temperatures between 1873–2023 K for 2 h without packing powder is shown in Fig. 5. The main crystalline phases were α - Si_3N_4 and β - Si_3N_4 . The α - β -phase transformation already occurred at the relatively low temperature as 1873 K with SiO_2 -MgO- Y_2O_3 addition. X-ray diffraction patterns of all samples sintered at 2023 K for 2 h show only the presence of β - Si_3N_4 without any secondary crystalline phases. Figure 6 summarizes the α - β - Si_3N_4 phase transformation by the ambient N_2 pressure sintering at the temperature range of 1873–2023 K for 2 h. All specimens show almost full transformation after sintering at 1973 K and the phase transformation saturates with less than 5% α - Si_3N_4 remaining. The higher Y_2O_3 addition seems to be slightly effective to the phase transformation than that of the other additions, but less than that of the 5Y3A specimen at 1873 and 1923 K.

The sintering temperature of 1923 K was selected to compare the effect of packing powder and N_2 gas pressure during the sintering. Table 2 summarizes bulk density, relative density, mass loss and oxygen content of the 3S3M1Y, 3S3M3Y and 3S3M5Y specimens sintered at 1923 K for 2 h. The mass loss of the specimens sintered without packing powder was always higher than that of the specimens sintered with packing

powder. Moreover, the mass loss of the specimens sintered under the lower N_2 gas pressure was always higher than that of the specimens sintered under the higher N_2 gas pressure. The application of packing powder and high N_2 gas pressure suppress the mass loss reactions as expected from the reactions (1) and (2).

Mass gain was observed in all three specimens after sintering with packing powder and under 1.0 MPa- N_2 gas pressure. The mass gain was thought to be due to excess generation of oxynitride glass in the surface region of specimens, probably induced by the next solid-gas reaction (4).¹²⁾

In the reaction, $Si_3N_4(s)$ reacts with absorbed $SiO(g)$ vaporized from the Si_3N_4 /BN packing powder. The oxygen content of the specimens increased about 0.1 mass% after the sintering comparing with that of the raw mixtures. This result supports the absorption of SiO gas and the formation of oxynitride glass. Although crystalline Si_2N_2O was not detected by XRD analysis in this work, it was thought to dissolve into a glassy phase. The generation of excess glassy phase at the surface region suppressed the diffusion of gas species through pores from the inner part of the pellet to the surface, and delayed the densification. As a result, bulk density of the specimens sin-

Fig. 5

Fig. 5. XRD patterns of 3S3M5Y specimens sintered under 0.1 MPa- N_2 at 1873–2023 K for 2 h without packing powder.

Fig. 6

Fig. 6. β - Si_3N_4 phase content as a function of sintering temperature of Si_3N_4 ceramics under 0.1 MPa- N_2 without packing powder.

Table 2. Bulk Density, Relative Density, Mass Loss and Oxygen Content of Si_3N_4 Ceramics Sintered at 1923 K for 2 h under Different Conditions of Packing Powder and N_2 Gas Pressure

Specimen	3S3M1Y				3S3M3Y				3S3M5Y			
	without		with		without		with		without		with	
N_2 gas pressure (MPa)	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0
Bulk density (g/cm^3)	3.01	3.13	2.99	3.02	3.14	3.16	2.99	3.05	3.20	3.19	3.08	3.07
Relative density (%)	94.3	97.9	93.8	94.6	98.0	98.6	93.5	95.1	99.2	98.7	95.4	95.1
Mass loss (mass%)	5.59	1.24	1.94	-0.18	3.98	1.02	0.88	-0.40	3.76	0.85	0.07	-0.56
Oxygen content (mass%)	2.97	3.96	3.61	3.98	3.76	4.23	4.46	4.62	4.19	4.66	4.90	5.08

tered with packing powder was always lower than that of the specimens sintered without packing powder. The oxygen content of all specimens, decreased with increase in mass loss, indicating the reactions (1) and (2) proceeded as main reactions.

The sintering without packing powder is effective to get high density Si_3N_4 ceramic with $\text{SiO}_2\text{-MgO-Y}_2\text{O}_3$ additions at the sintering temperature of 1923 K. Although the mass loss of the sintered bodies was lower than the specimen sintered under 1.0 MPa- N_2 gas pressure, bulk density of the 3S3M3Y and 3S3M5Y specimens sintered under 0.1 MPa- N_2 was not so different from those of higher N_2 gas pressure sintering. The sintering under 0.1 MPa- N_2 gas is more suitable in commercial point of view.

The 3S3M3Y and 3S3M5Y were selected for mechanical properties measurement. The specimens were sintered at 1923 K for 2 h under ambient N_2 pressure without packing powder. Both specimens have the same values of Young's modulus and Vickers hardness as 300 GPa and 18.4 GPa respectively. However, the bending strength and fracture toughness of the 3S3M3Y specimen were 840 MPa and $5.4 \text{ MPa} \cdot \text{m}^{1/2}$, which were lower than those of the 3S3M5Y specimen as 980 MPa and $6.6 \text{ MPa} \cdot \text{m}^{1/2}$, respectively, probably relating to the difference in relative density.

In addition, thermal conductivity of the 3S3M3Y and 3S3M5Y specimens sintered at 1923 K without packing powder under 0.1 MPa- N_2 were measured by a method as reported elsewhere.⁹⁾ The thermal conductivity of the 3S3M3Y and 3S3M5Y was 31 and $34 \text{ Wm}^{-1}\text{K}^{-1}$, respectively. Whereas the relatively high mass loss as about 4 mass% was found in these specimens, there was no porous surface layer.

4. Conclusions

The liquidus temperature in the system $\text{SiO}_2\text{-MgO-Y}_2\text{O}_3$ is about 1673 K (1400°C), which enables liquid-phase sintering of Si_3N_4 at relatively low temperature. Si_3N_4 ceramics prepared with 3 mass% SiO_2 , 3 mass% MgO , and 5 mass% Y_2O_3 as the sintering additives could be sintered to almost full density (99%) by pressureless sintering at relatively low temperature as 1923 K (1650°C) for 2 h in ambient pressure N_2 flow without packing powder. The α - β transformation was not completed at this condition (70% β -phase). The mass loss was relatively high as 3.8 mass% due to the evaporation of SiO_2 and MgO . However, The resulting materials have high bending strength as 980 MPa, with fracture toughness of $6.6 \text{ MPa} \cdot \text{m}^{1/2}$, Vickers hardness of 18.4 GPa, and thermal conductivity of $34 \text{ Wm}^{-1}\text{K}^{-1}$. It is concluded that the pressureless sintering without packing powder at lower temperature than usual is capable for the fabrication of fully dense Si_3N_4 ceramics, if the proper additive system such as $\text{SiO}_2\text{-MgO-Y}_2\text{O}_3$ system is selected.¹¹⁾

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