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The role of $MgSiN_2$ during the sintering process of silicon nitride ceramic

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Abstract

The reaction process between $MgSiN_2$ SiO_2 and Si_3N_4 was investigated by analyzing the composition change of the powder mixture of 61 wt% $MgSiN_2$, 34 wt% SiO_2 and 5 wt% α-Si_3N_4 after heat treatment at different temperatures. The phase and chemical compositions of the grain boundary phase in the silicon nitride ceramic was analyzed by x-ray diffraction, transmission electron microscope, and energy-dispersive x-ray spectroscopy. The results demonstrated that $MgSiN_2$ reacted with the surface silica and Si_3N_4 to form Mg–Si–O–N liquid phase, which promoted the consolidation densification of silicon nitride powders through liquid-phase sintering mechanism. The amount of Mg–Si–O–N glass boundary phase using $MgSiN_2$ as additives is much less than that using the same amount of MgO additive, owing to the lower oxygen concentration and higher nitrogen content.

Keywords: A. Sintering process; D. Silicon nitride; Ceramic; $MgSiN_2$

1. Introduction

Bulk silicon nitride ceramics have been comprehensively investigated and are widely used for structural application due to their outstanding mechanical and physical properties, including high strength, high fracture toughness, high thermal conductivity, good thermal shock, good oxidation resistance, and negligible creep [1,2]. Because Si_3N_4 is a strong covalent compound and its self-diffusion coefficient is very low, silicon nitride is difficult to consolidate without sintering additives. Generally, metal oxides, such as MgO, Al_2O_3, Y_2O_3, Yb_2O_3, La_2O_3, and Lu_2O_3, were used as sintering additives, which can react with Si_3N_4 and SiO_2 on the surface of Si_3N_4 powder at a high temperature to form M–Si–O–N liquid phase [2–5]. Besides of oxide additives, nitrides, such as AlN, YN, TaN, Mg_3N_2, Be_3N_2, and $BeSiN_2$ have also been adopted as additives to manufacture silicon nitride ceramics [6–9].

$MgSiN_2$, which has orthorhombic crystal structure and can be deduced from AlN by systematically replacing two Al^{3+} ions by a combination of Mg^{2+} and Si^{4+} [10], has also been utilized as a consolidation addition for silicon nitride ceramics [11–13]. In 1976, Inomata et al. [11] reported that densification was rapid when both $MgSiN_2$ and SiO_2 powders were used as aids, yet rapid grain growth took place and the densification in the later stage was hindered with only $MgSiN_2$ addition. Considering the fact that $MgSiN_2$ can supply magnesium ions which could decrease the melting point of silicate glass without increasing the oxygen content. Hayashi et al. [12] firstly employed the concurrent additions of $MgSiN_2$ and Yb_2O_3 to fabricate the β-silicon nitride ceramic, which exhibited high thermal conductivity of 140 W $(m\,K)^{-1}$, owing to both the purification of β-Si_3N_4 grains by a solution-reprecipitation process and the enhanced grain growth.

Our previous works have proved that $MgSiN_2$ was an effective additive to fabricate high-density silicon nitride ceramics by either hot-pressing (HP) or spark plasma sintering (SPS) [14–16]. α/β Si_3N_4 composite with an excellent combination of mechanical properties (Vickers

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indentation hardness of 23.1 GPa, fracture strength of about 1000 MPa, and toughness of 6.3 MPa m$^{1/2}$) could be fabricated by hot-pressing at 1600 °C for 6 h using MgSiN$_2$ addition, and the mechanical properties could be optimized by changing sintering parameters, such as sintering temperature and dwell time [14,15]. MgSiN$_2$ was also applied to prepare high thermal conductivity β-Si$_3$N$_4$ ceramics by SPS, and thermal conductivity of 100 W (m K)$^{-1}$ was achieved after sintering at 1600 °C for 12 min [16]. However, the role of MgSiN$_2$ during the sintering process is still ambiguous. In the present work, the reaction process between MgSiN$_2$, SiO$_2$ and Si$_3$N$_4$ was simulated by using a homogenized powder mixture, and the role of MgSiN$_2$ was studied by XRD, TEM, EDS and TG-DSC.

2. Experimental procedures

α-Si$_3$N$_4$ (SN-E10, UBE Industries, Tokyo, Japan) and MgSiN$_2$ (purity > 99%, prepared by self-propagating high-temperature synthesis in our laboratory [17]) were used as the starting raw materials to prepare silicon nitride ceramics. The raw materials, according to the required mass ratios, were ball milled in absolute ethanol for 24 h with Si$_3$N$_4$ balls. The homogenized slurry was dried in a vacuum oven followed by passing through a 40-mesh sieve to obtain an agglomerate-free powder mixture. All ceramic samples were hot pressed for 1 h under 20 MPa uniaxial pressure in a flowing nitrogen atmosphere and the detailed experimental parameters are shown in Table 1.

61 wt% MgSiN$_2$, 34 wt% SiO$_2$ (4N, Sinopharm Chemical Reagent Shanghai Co., Shanghai, China) and 5 wt% α-Si$_3$N$_4$, were mixed by ball milling, then dried and sieved. The composition of the above-mentioned mixture was designed to be close to the mass ratio of SiO$_2$: MgSiN$_2$ in sample S2. The oxygen content of α-Si$_3$N$_4$ is about 1.50 wt%, analyzed by Nitrogen/Oxygen Determinator (TC436, LECO, USA). All oxygen in α-Si$_3$N$_4$ was postulated existing as SiO$_2$, thus the mass ratio of SiO$_2$: MgSiN$_2$ was fixed at 34: 61. On the other hand, 5 wt% α-Si$_3$N$_4$ was also added into the mixture because α-Si$_3$N$_4$ will dissolve in the liquid phase during the sintering process. The mixture was hot pressed under 5 MPa uniaxial pressure and the detailed experimental parameters are listed in Table 1.

The densities were determined by the Archimedes method using distilled water. The phase compositions were identified by X-ray diffraction analysis (XRD, Rigaku D/max 2550V, Japan) with Cu Kα radiation, operating at 40 kV and 100 mA. Transmission electron microscope (TEM, JEM-2010, JEOL, Tokyo, Japan) was used to observe the microstructure. The chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS, GENESIS, EDAX, America). Specimens for TEM and EDS analysis were prepared by standard procedures of cutting, grinding, dimpling and ion-beam thinning, followed by sputtering with a carbon layer to avoid charging during observation. Differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TG) were carried out with a STA-409PC/4/H Luxx simultaneous TG-DTA/DSC apparatus (Germany) with a heating rate of 10 °C min^{-1} in a flowing nitrogen atmosphere.

3. Results and discussion

The relative density of sample S0, hot-pressed at 1600 °C for 1 h without additives, is about 60%, as a result of applied uniaxial pressure. The relative density increased to 98% with the MgSiN$_2$ content increasing from 0 wt% to 2 wt%. When the MgSiN$_2$ content further increased to 5 wt% α-Si$_3$N$_4$ powders were fully consolidated. The results suggest that MgSiN$_2$ additive does effectively improve the consolidation of silicon nitride powders.

Fig. 1 shows the XRD patterns of sample S2 and S3. Due to the relatively low sintering temperature, there was part a-Si$_3$N$_4$ remained in sample S2, which was hot-pressed at 1600 °C for 1 h. All a-Si$_3$N$_4$ converted to β-Si$_3$N$_4$ when the sintering temperature increased from 1600 °C to 1750 °C. It is also noted that no peaks of MgSiN$_2$ appeared in the XRD patterns of both samples, although it was detected in the green powder mixture. This result is consistent with those results reported by Hirao's group, using the concurrent addition of MgSiN$_2$ and Y$_2$O$_3$/Yb$_2$O$_3$ to fabricate high thermal conductivity silicon nitride ceramics by gas pressure sintering or the sintered reaction-bonded method [12,13]. The microstructure characterizations of sample S3 are presented in Fig. 2. The low-magnification TEM image (Fig. 2a) shows that the amorphous grain boundary phase existed within three- or four-grain junctions. EDS analysis

Table 1
Experimental conditions of different samples.

Sample	Mass ratio α-Si$_3$N$_4$: MgSiN$_2$			Temperature (°C)	Hold time (min)	Pressure (MPa)
S0	100	0		1600	60	20
S1	100	2		1600	60	20
S2	100	5		1600	60	20
S3	100	5		1750	60	20
SiO$_2$: MgSiN$_2$:α-Si$_3$N$_4$						
G1	34	61	5	–	–	–
G2	34	61	5	1400	15	5
G3	34	61	5	1500	30	5
G4	34	61	5	1600	15	5

(Fig. 2b) indicates that the glass pockets contained Si, O and N, but also Mg. Fig. 2c shows that adjacent Si_3N_4 grains are typically separated by an amorphous grain-boundary film.

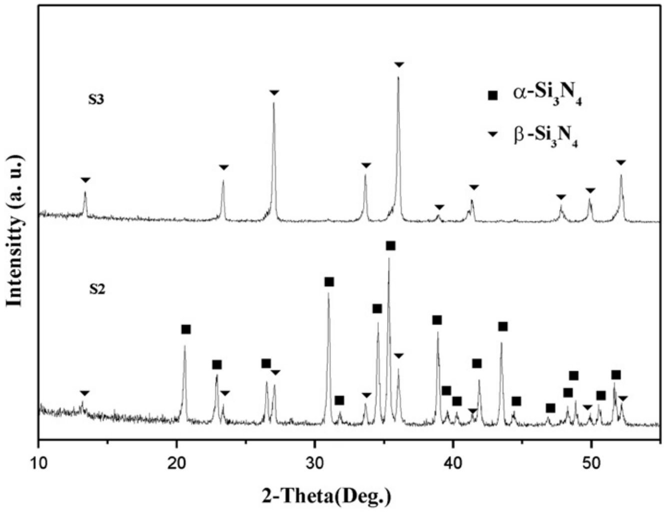

Fig. 1. XRD patterns of samples S2 and S3.

These results suggest that $MgSiN_2$ perhaps reacted with SiO_2 to form Mg–Si–O–N liquid phase, which promoted the consolidation of silicon nitride powders.

The thermal behavior of the powder mixture G1, which consisted of 61 wt% $MgSiN_2$, 34 wt% SiO_2 and 5 wt% α-Si_3N_4, was investigated by TG-DSC in the temperature range from room temperature to 1350 °C, as shown in Fig. 3. The TG and DSC curves show that the weight is almost unchanged and there are no identifiable endothermic or exothermic peaks, demonstrating that no chemical reaction or phase transition took place in the temperature range of RT − 1350 °C. The lowest heat treatment temperature, therefore, was set at 1400 °C.

The X-ray diffraction patterns of sample G1–G4 are given in Fig. 4. Sample G1, as shown in Fig. 4(a), is composed of the main crystalline phase $MgSiN_2$ and a small amount of α-Si_3N_4, and no diffraction peaks of SiO_2 is observed because of its vitreous form. This is in agreement with the composition of the starting mixture, 61 wt% $MgSiN_2$, 5 wt% α-Si_3N_4 and 34 wt% amorphous SiO_2. After the powder mixture was hot-pressed at 1400 °C for 15 min, three new crystalline substances, Mg_2SiO_4,

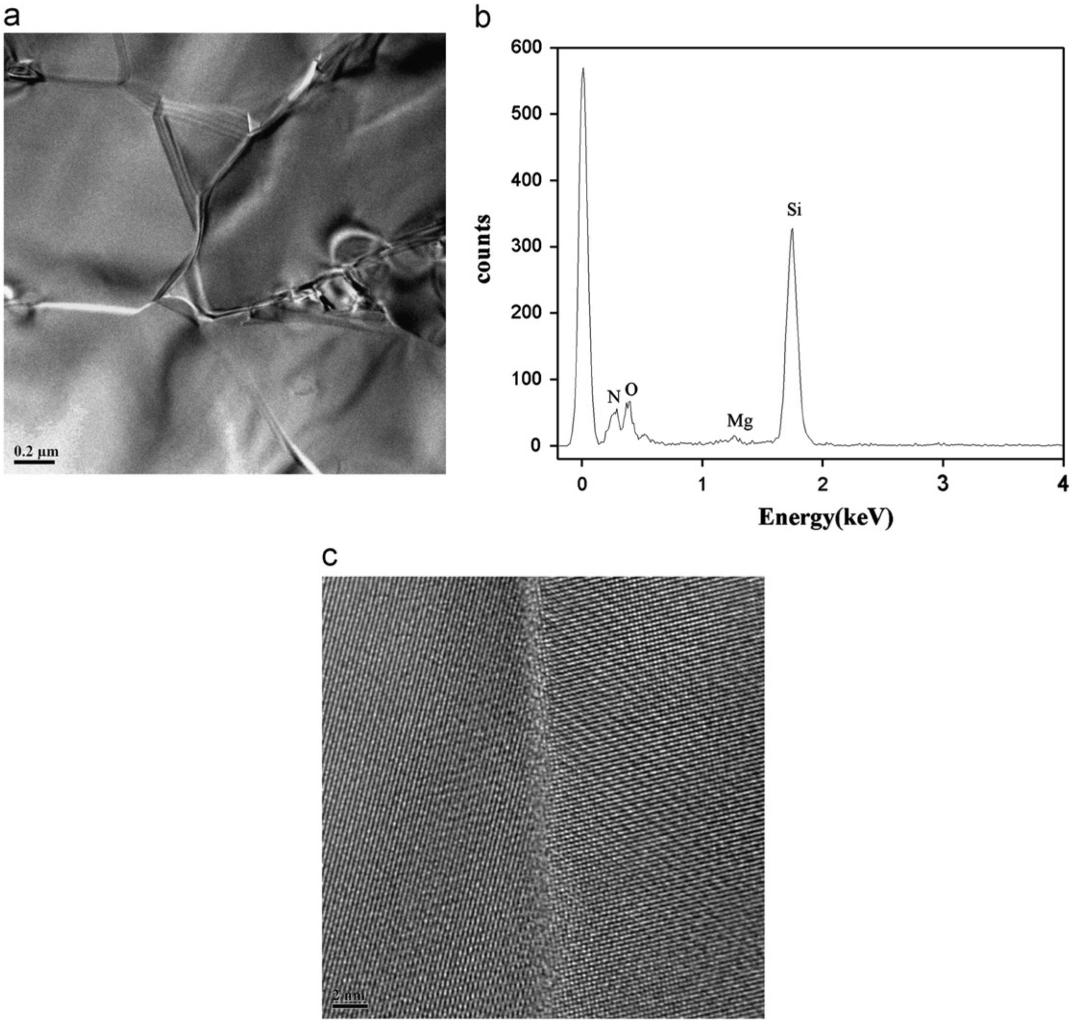

Fig. 2. (a) Typical low-magnification TEM image of sample S3; (b) EDX patterns of three-grains junction of sample S3 and (c) high-resolution TEM image of two-grain boundary in sample S3.

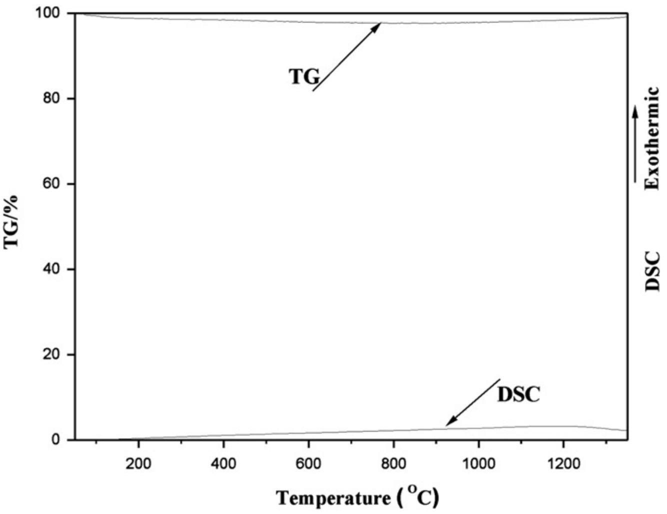

Fig. 3. Differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TG) curves of sample G1.

Si_2N_2O, and SiO_2, came into being. Comparing the relative intensity of α-Si_3N_4 diffraction peaks in Fig. 4(a) and (b), it is clear that the α-Si_3N_4 content of sample G2 obviously increased. The report of Lenčéš et al. showed that $MgSiN_2$ powders are stable up to 1400 °C at 0.1 MPa N_2 pressure [18]. Therefore, the increase of α-Si_3N_4 content in sample G2 is not because of the decomposition of $MgSiN_2$. Based on the foregoing analysis, the following two chemical reactions are proposed to occur in sample G2 at 1400 °C:

$$2SiO_2+2MgSiN_2 \rightarrow Mg_2SiO_4+\alpha-Si_3N_4 \quad (1)$$

$$\alpha-Si_3N_4+SiO_2 \rightarrow Si_2N_2O \quad (2)$$

Sample G3 contains five crystalline phases, α-Si_3N_4, $MgSiN_2$, Mg_2SiO_4, SiO_2 and β-Si_3N_4 (Fig. 4c). There are several differences existing in sample G3 beside sample G2: the main crystalline phase with the highest amount was α-Si_3N_4, not $MgSiN_2$; the $MgSiN_2$ content significantly diminished; there was a small amount of β-Si_3N_4; Si_2N_2O phase disappeared.

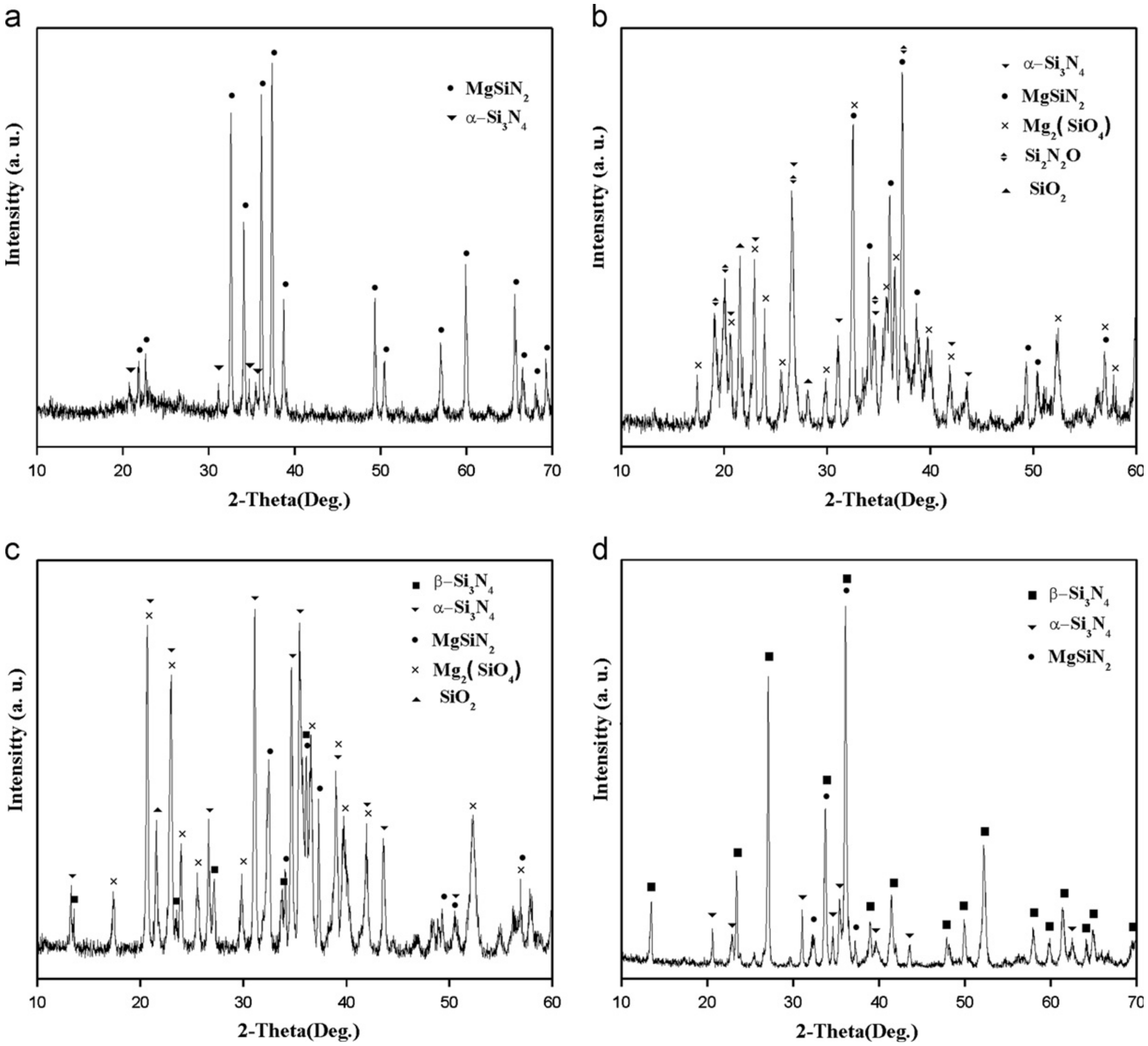

Fig. 4. XRD patterns of samples G1, G2, G3 and G4 (a) G1; (b) G2; (c) G3 and (d) G4.

The mass loss of $MgSiN_2$ powders after heat treatment at 1500 °C for 2 h in 0.1 MPa nitrogen atmosphere was only 4.5 wt% and α-Si_3N_4 was the major decomposition product [18]. Obviously, the formation of α-Si_3N_4 in sample G3 is mainly attributed to the reaction between SiO_2 and $MgSiN_2$ (reaction (1)), not the decomposition of $MgSiN_2$, because the hold time of sample G3 at 1500 °C was 0.5 h, much shorter than 2 h. The drastic shrinkage were also observed when sample G3 was hot-pressed at 1500 °C, indicating that a significant amount of liquid phase had formed in the powder mixture.

There are three crystalline phases, β-Si_3N_4, α-Si_3N_4 and $MgSiN_2$, in sample G4 (Fig. 4d), which was hot-pressed at 1600 °C for 15 min. Note that the concentration of β-Si_3N_4 is much higher than that of α-Si_3N_4 or $MgSiN_2$ and both Mg_2SiO_4 and SiO_2 are not detected in sample G4. In the case of the homogenized powder mixture of 56 wt% $BeSiN_2$+44 wt% SiO_2, reported by Greskovich, a significant amount of β-Si_3N_4 also formed after heat treatment at 1640 °C for 10 min [9]. We also found that a large amount of sample G4 had been extruded out of the die cavity during hot-pressing at 1600 °C, demonstrating that the amount of the liquid phase, formed at 1600 °C, was much more than that at 1500 °C. Thus, it is presumed that three procedures occurred in the process of hot-pressing at 1600 °C: firstly, SiO_2 reacted with $MgSiN_2$ to form Mg_2SiO_4 and α-Si_3N_4; then, Mg_2SiO_4 reacted with unreacted SiO_2 to form a viscous liquid phase and the speed of this reaction was so fast that no Mg_2SiO_4 existing in sample G4; finally, β-Si_3N_4 formed via the $\alpha \rightarrow \beta$ phase transformation. It is well known that the $\alpha \rightarrow \beta$ phase transformation takes place by (a) dissolution of the a-Si_3N_4 phase and saturation of the liquid phase, (b) transport of Si and N ions through the liquid phase and (c) attachment onto existing β-Si_3N_4 particles. The primary requirement of forming β-Si_3N_4 is that the nitrogen content in the liquid phase reaches or exceeds its nitrogen saturation limit. Although the nitrogen solubility in Mg–Si–O–N liquid phase is unavailable, analysis of the oxynitride glasses, e.g. Si-RE-Mg–O–N, Si-RE-Al–O–N, Ln-Si–O–N, confirms that the nitrogen solubility is generally lower than 30 eq% [19–21]. In the present powder mixture, if the overall nitrides, including $MgSiN_2$ and Si_3N_4, dissolve into the liquid phase, the equivalent percent (eq%) nitrogen of the Mg–Si–O–N liquid phase is 70 eq%, which is much higher than the nitrogen solubility of 30 eq% and provides sufficient nitrogen to assume supersaturation. Except for the above-mentioned three procedures, the decomposition of $MgSiN_2$ could not be excluded for the decomposition rate increases with the increase of the temperature. The mass loss of $MgSiN_2$ after heat treatment at 1600 °C for 2 h in 0.1 MPa N_2 was 22.9 wt%, demonstrating that about 50 wt% $MgSiN_2$ decomposed at this condition [18]. In the present work, based on the hold time (15 min) and the diminution of $MgSiN_2$ in sample G4 (less than 61 wt%), about 3.8 wt% or less $MgSiN_2$ decomposed to form about 2 wt% Si_3N_4 (a-Si_3N_4 and β-Si_3N_4), which is a small part of the total Si_3N_4 in sample G4.

$MgSiN_2$ powders annealed at 1550 °C for 2 h had a mass loss of 13.2 wt% [18], that is, about 18 wt% Si_3N_4 existed in the final powder mixture, but no α-Si_3N_4 or β-Si_3N_4 could be detected by XRD in the $MgSiN_2$ ceramic, which had been hot-pressed at 1550 °C for 1.5 h [24]. The results indicate that the decomposition of $MgSiN_2$ can be effectively suppressed by sintering, may well due to the decrease of the decomposition surface. When $MgSiN_2$ was applied as a single sintering aid in the present work, the content of $MgSiN_2$ was low and it disperses among Si_3N_4 powders. The relative density of silicon nitride ceramic, which was hot-pressed with 5 wt% $MgSiN_2$ additives at 1600 °C for 10 min under 20 MPa uniaxial pressure, reached 90%. Therefore, it is reasonable to speculate that the decomposition of $MgSiN_2$ was substantially hindered during the sintering process of Si_3N_4 ceramics.

On the basis of Kingery's liquid phase sintering mechanism [22,23], the densification process of Si_3N_4 ceramic is generally divided into three stages, i.e.: (i) particle rearrangement; (ii) solution-reprecipitation; and (iii) a coalescence stage. It is clear that the liquid phase is the key factor for fabrication of high density silicon nitride ceramics. The requirements for complete densification are: (i) an appreciable amount of liquid; (ii) an appreciable solubility of the solid; and (iii) complete wetting of the solid by the liquid.

Based on the above results of simulative experiments, XRD, TEM and EDX, we deduced that the role of $MgSiN_2$ during the sintering process was similar to that of MgO aid because both reacted with SiO_2 and Si_3N_4, and then formed Mg–Si–O–N liquid phase to promote the densification [25,26]. On the other hand, it should be noted that the difference between $MgSiN_2$ and MgO was that the former introduced much less oxygen than the latter. Thus, the amount of the liquid phase with $MgSiN_2$ as an addition should be much less than that with the same amount of MgO additive, and subsequently, the intergranular amorphous phase should also be much less. This can also be proven by the fact that Si_3N_4 powders (SN-E10, UBE Industries, Tokyo, Japan) is very difficult to be fully consolidated by pressureless sintering with only $MgSiN_2$ as an additive, even if the concentration of $MgSiN_2$ increased to 15 wt%, for the liquid phase amount is insufficient. On the other hand, the high nitrogen content in the $MgSiN_2$–SiO_2 boundary phase also contributed to the reduction of intergranular amorphous phase by the formation of β-Si_3N_4 crystals. The reduction of the amorphous phase content is benefit for the improvement of such properties as thermal conductivity and hardness, because the thermal conductivity and hardness of glassy phase is far lower than that of silicon nitride crystalline particles.

4. Conclusions

Silicon nitride can be fully densified by hot-pressing at 1600 °C with $MgSiN_2$ as an additive, while the relative density of the specimen, hot-pressed at the same conditions without additives, is only about 60%. During the hot-pressing process,

$MgSiN_2$ reacted with the surface layer of SiO_2 and Si_3N_4 powders to form Mg–Si–O–N liquid phase, which promoted the densification through liquid-phase sintering mechanism and remained as glass boundary phase in the resultant silicon nitride ceramic. Compared with MgO addition, the amount of Mg–Si–O–N glass boundary phase using $MgSiN_2$ as an additive is much less because the oxygen content, introduced by $MgSiN_2$ additions, is very low. The partial nitrogen in $MgSiN_2$, which exceeds its nitrogen saturation limit in Mg–Si–O–N liquid phase, precipitates as β-Si_3N_4 crystals.

Acknowledgments

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