

Silicon Nitride Ceramics with High Thermal Conductivity and Excellent Mechanical Properties Fabricated with MgF₂ Sintering Aid and Post-Sintering Heat Treatment

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Abstract

Si₃N₄ ceramics were prepared with MgF₂+Y₂O₃ as sintering aids by means of SPS, assisted by post-sintering heat treatment; these ceramics exhibited high thermal conductivity and excellent mechanical properties. The effect of the introduced MgF₂ content and post-sintering heat treatment on the properties of Si₃N₄ ceramics was investigated in detail. It was found that the introduction of MgF₂ had a positive impact on the growth of large elongated grains and the grain size of the Si₃N₄ ceramics. Compared to Si₃N₄ ceramics with Y₂O₃+MgO as sintering aids, the thermal conductivity, flexural strength and fracture toughness of the Si₃N₄ ceramics with Y₂O₃+MgF₂ as sintering aids were increased by ~ 19 %, 9 % and 12.7 %, respectively. After post-sintering heat treatments, the thermal conductivity and fracture toughness of the Si₃N₄ ceramics were increased by ~ 29.9 % and 16.2 %, respectively. However, the flexural strength of the Si₃N₄ ceramics was reduced by ~ 10 %. The resulting Si₃N₄ ceramics exhibited possessed thermal conductivity of 82.5 W·m⁻¹·K⁻¹, flexural strength of 911 MPa and fracture toughness of 8.47 MPa·m^{1/2}.

Keywords: MgF₂ sintering aids, silicon nitride, thermal conductivity, mechanical properties

I. Introduction

Ceramic materials are widely applied in electronic packaging substrates. Compared with organic polymer counterparts, ceramics boast significant advantages, such as good thermal conductivity, high insulation performance and chemical stability. The most commonly used heat conduction ceramic substrates at present are Al₂O₃, BeO, SiC and AlN, etc.¹ However, there are still some challenges limiting their wider application. For instance, AlN ceramics may be an excellent substrate candidate, with thermal conductivity usually over 150 W m⁻¹ K⁻¹, however, their poor mechanical performance (such as a flexural strength of 300 ~ 400 MPa) severely hinders their commercial application. Si₃N₄ ceramics possess outstanding mechanical properties as well as high intrinsic thermal conductivity (200 ~ 320 W·m⁻¹·K⁻¹), rendering them one of the most promising electronic substrate materials^{2,3}.

Metal oxides and rare earth oxides (e.g. MgO, Al₂O₃, Y₂O₃, CeO₂, La₂O₃, Yb₂O₃) are generally employed as sintering aids to facilitate the sintering process of Si₃N₄ ceramics. These sintering aids were able to generate liquid phase by reacting with Si₃N₄ and SiO₂, forming a coating on the surface of Si₃N₄ powder at high temperature, which had distinct impact on the performance of Si₃N₄ ceramics^{4,5,6}. Kitayama *et al.* reported that the thermal

conductivity of Si₃N₄ ceramics was increased along with the decrease in lattice oxygen content in the Si₃N₄ grains⁷. Hayashi *et al.* reported that using MgSiN₂ as an additive rather than MgO improved the thermal conductivity of Si₃N₄ ceramics (~ 15 %)⁸. These results indicated that, regardless of the fact that the introduced metal oxides promoted sintering, the extra oxygen atom could be easily transferred into the lattice of Si₃N₄ ceramics, which reduced their thermal conductivity. Accordingly, non-oxide sintering aids could be more effective in preventing the extra oxide invading the lattice of Si₃N₄ ceramics, which could consequently improve the thermal conductivity of Si₃N₄ ceramics. Like MgSiN₂, MgF₂ is a non-oxide sintering aid that can supply magnesium ions without increasing the oxygen content in the liquid phase. The presence of alkaline earth ions such as Mg²⁺ usually leads to a decrease in the melting point of silicate glass phase. Compared with MgO, the common oxide sintering additive used for sintering Si₃N₄ ceramics, MgF₂ has another unique characteristic of a low melting point (e.g. the melting points of MgO and MgF₂ are 2800 and 1261 °C, respectively). Hence, the liquid phases can be formed at lower temperature in Si₃N₄ ceramics when MgF₂ is used as a sintering additive compared to in Si₃N₄ ceramics with added MgO. However, there have been only few studies on the fabri-

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cation of Si_3N_4 ceramics with high thermal conductivity using MgF_2 as a sintering aid.

Spark plasma sintering (SPS)^{9,10} is an efficient sintering technique that enables the fast densification of ceramics over short time scales. Compared with conventional sintering, spark plasma sintering can result in densification at much lower sintering temperatures. The sintering temperature with SPS is usually about 100–200 °C lower than that with conventional sintering¹¹.

In the present work, we report on the fabrication of Si_3N_4 ceramics with high thermal conductivity and high excellent mechanical properties by means of SPS, assisted by post-sintering heat treatment. Commercially available α - Si_3N_4 powder was used as the raw material, and a mixture of Y_2O_3 and MgF_2 was used as the sintering additive. The effect of MgF_2 and the post-sintering heat treatment on the thermal conductivity and mechanical properties of the resulting Si_3N_4 ceramics was investigated in detail.

II. Experiments

(1) Raw materials

A commercial α - Si_3N_4 powder (α - $\text{Si}_3\text{N}_4 > 95\%$, $d_{50} = 0.5 \mu\text{m}$, oxygen content $< 1.4 \text{ wt}\%$, Jinsheng ceramics technology Co., Ltd., Jiangsu, China) was used as the starting raw material. MgF_2 (Sinopharm Chemical Reagent Beijing Co., Ltd.), MgO (Sinopharm Chemical Reagent Beijing Co., Ltd.) and Y_2O_3 (Sinopharm Chemical Reagent Beijing Co., Ltd.) were employed as the sintering aids.

(2) Experiment procedure

The α - Si_3N_4 powder was mixed with 5 wt% of Y_2O_3 and certain amount of MgF_2 or MgO in absolute ethyl alcohol, as shown in Table 1, and ball-milled with Si_3N_4 ceramic balls for 12 h. The obtained mixture was dried in an oven at 50 °C for 6 h, and then sieved through an 80-mesh nylon fine screen. The resultant powders were placed into a graphite mold (30 mm in diameter), and sintered by means of SPS (1050T, Japan) at 1600 °C with a dwell time of 5 min. The samples were then placed into a graphite crucible covered with a powder mixture of Si_3N_4 (50 wt%) and BN (50 wt%), and maintained at 1850 °C for 3 h under 1 MPa nitrogen atmosphere in a furnace (HIGH-MULTI 5000, Japan).

Table 1: The compositions of the samples (wt%)

Samples	Y_2O_3	MgF_2	MgO
Y5F0	5	0	0
Y5F2	5	2	0
Y5F4	5	4	0
Y5F6	5	6	0
Y5O4	5	0	4

(3) Characterization methods

The bulk density of the samples was determined with the Archimedes method. The phase compositions were analyzed by means of X-ray diffraction (D8-Advance, Bruker, Germany). Quantitative analysis of α - and β - Si_3N_4 phases was performed with an X'Pert Highscore report program. The samples were polished and then plasma-etched with CF_4 gas for 30 s in plasma etching apparatus (L-451D-L, Anelva reactive ion etching system). The microstructures were observed under a field emission scanning electron microscope (SEM; MERLIN VP Compact, Germany). The thermal conductivity (k) at room temperature (RT) was calculated according to:

$$k = a \rho C_p \quad (1)$$

where ρ is the bulk density. The thermal diffusivity (a) was measured with a laser-flash method (LFA-447, NETZSCH, Germany). The specific heat (C_p) was measured with a physical property measurement system (PPMS-9T, Quantum Design, USA). The chemical composition of the as-fabricated samples was measured by means of X-ray fluorescence analysis (XRF-1800, SHIMADZU, Japan). The fracture toughness was determined with the indentation method under the condition of a load of 5 kg and a dwell time of 10 s. The reported fracture toughness is based on an average of eight indentations. For measurement of the flexural strength, the sintered disks were cut into bars. The rectangular bars with dimensions of 1.5 mm \times 2 mm \times 25 mm (height \times width \times length) were tested using a 20 mm support span and a crosshead speed of 0.5 mm/min. The reported flexural strength is an average of ten test pieces.

III. Results and Discussion

(1) Effect of the sintering additives on the sintering behavior

Table 2 shows the bulk density, true porosity, thermal conductivity, flexural strength and fracture toughness of the samples with different sintering additives. It seems that, with the increase of the MgF_2 content (Y_2O_3 is fixed at 5 wt%), the thermal conductivity, flexural strength and fracture toughness of the samples are firstly increased and then decreased. When the introduced MgF_2 reaches 4 wt%, the thermal conductivity is the highest at 63.5 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. At the same time, the flexural strength and fracture toughness are also reached the highest values, which are 1015 MPa and 7.29 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. Fig. 1(a-d) show typical SEM images of the polished and plasma-etched surface of sample Y5F0, Y5F2, Y5F4 and Y5F6, respectively. It can be observed that relatively small grains and obvious pores exist within the sample Y5F0. It is known that in the sintering of Si_3N_4 ceramics the sintering aids react with Si_3N_4 and SiO_2 coated on the surface of Si_3N_4 powder to generate the liquid phase at high temperatures. If a small amount of the sintering aid is added, the gaps between the Si_3N_4 grains cannot be fully filled by the liquid phase formed, which hinders the diffusion and growth of silicon nitride crystal grains⁵. With the increase of MgF_2 content, ample liquid phase is generated and gradually fills the pores completely. The size

of the grains is increased, which leads to a larger fraction of large elongated grains and improved contact between the Si₃N₄ grains, making the samples fully dense without obvious pores (Fig. 1(b) and(c)). Accordingly, the thermal conductivity, flexural strength and fracture toughness of

the samples are profoundly enhanced. However, when the amount of MgF₂ reaches up to 6 wt%, the excessive addition of sintering aid favors a lot of glassy phase at the grain boundary, which could reduce the thermal conductivity and mechanical properties of the ceramic^{13, 14}.

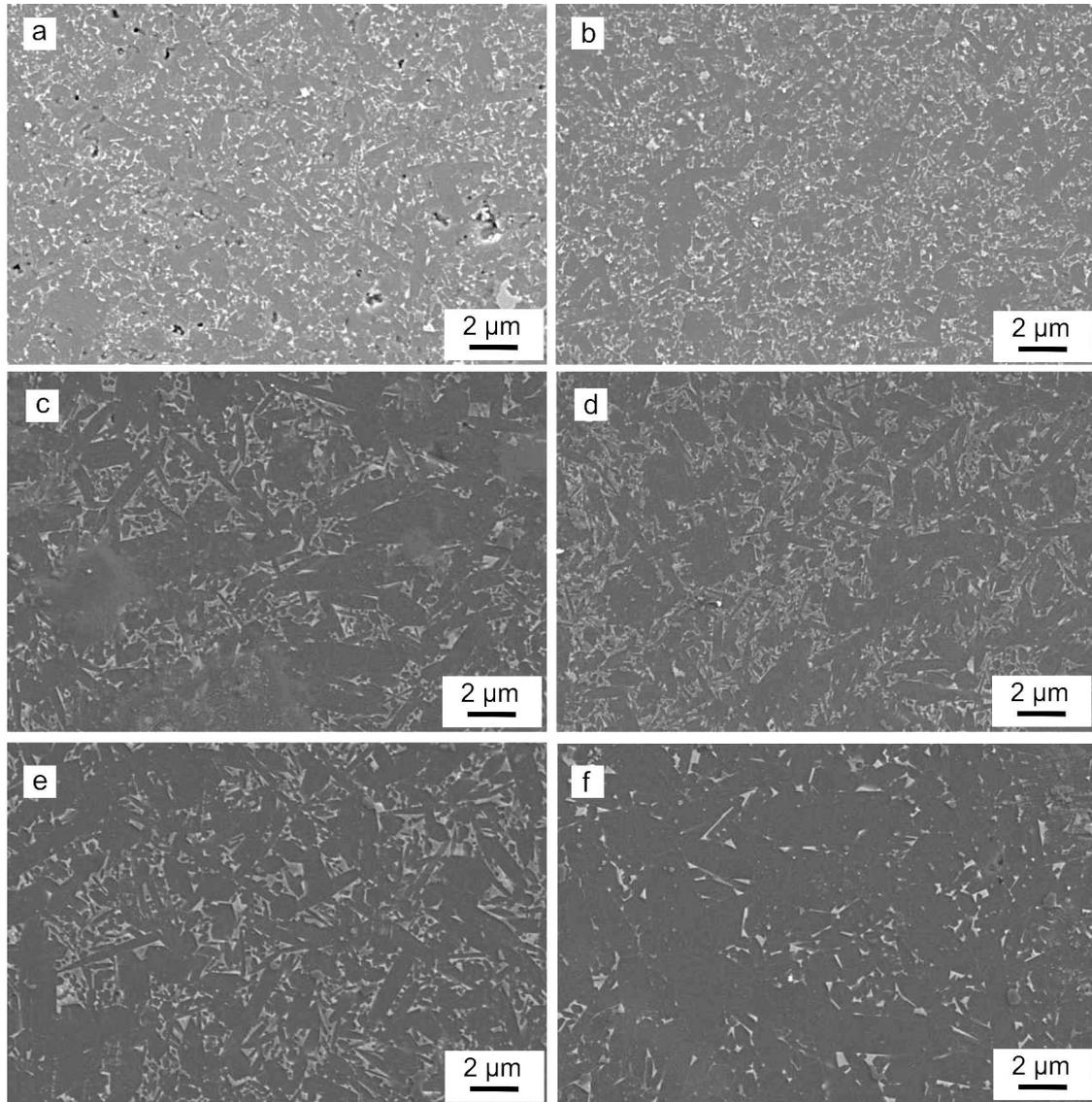


Fig. 1: Representative SEM images of the polished and plasma-etched surface of different samples: (a) sample Y5F0, (b) sample Y5F2, (c) sample Y5F4, (d) sample Y5F6, (e) sample Y5O4, (f) sample Y5F4 after post-sintering heat treatments.

Table 2: The typical performances of the as-prepared samples.

Samples	Bulk density (g·cm ⁻³)	True porosity (%)	Thermal conductivity (W·m ⁻¹ ·K ⁻¹)	Flexural strength (MPa)	Fracture toughness (MPa·m ^{1/2})
Y5F0	3.04±0.07	6.4±2.1	26.5±3.2	456±45	5.54±0.27
Y5F2	3.13±0.02	3.6±0.6	43.2±1.9	902±79	6.29±0.19
Y5F4	3.19 ±0.02	1.3±0.6	63.5±3.2	1015±87	7.29±0.21
Y5F6	3.17±0.01	2.1±0.3	55.6±3.9	989±92	6.98±0.33
Y5O4	3.15±0.02	3.3±0.6	53.2±2.9	930±81	6.47±0.25
Y5F4H	3.22±0.01	0.6±0.3	82.5±3.1	911±47	8.47±0.31

* Y5F4H: the sample Y5F4 after post-sintering heat treatments

In comparison, MgO is used as the sintering aid to substitute MgF₂ in the sample Y5F4, and corresponding results are shown in Table 2. The experimental results show that the bulk density, thermal conductivity and mechanical properties of sample Y5F4 are higher than those of sample Y5O4, indicating that the MgF₂ sintering aid is more beneficial to the grain growth and performance improvement of Si₃N₄ ceramics than MgO.

Fig. 2 shows the typical x-ray diffraction (XRD) pattern of samples Y5O4 and Y5F4, revealing the major phase of β -Si₃N₄ with a small amount of α -Si₃N₄. The grain boundary existed in the sample in the form of glass phase. The quantitative analysis revealed that the β : α ratio of sample Y5F4 was 98.1 : 1.9, which was higher than the β : α ratio (96.8 : 3.2) of sample Y5O4. These results indicated that the MgF₂ is also an excellent sintering additive compared to the traditional sintering additive of MgO. It is well known that lattice oxygen is regarded as the dominant extrinsic factor governing the thermal conductivity of Si₃N₄ ceramics, and the sintering additive is also the main source of lattice oxygen. Hence, compared to the as-fabricated samples with oxide sintering additives, fewer extra oxygen atoms coming from the sintering additives are introduced into the lattice, resulting in a higher thermal conductivity of the Si₃N₄ ceramics⁷.

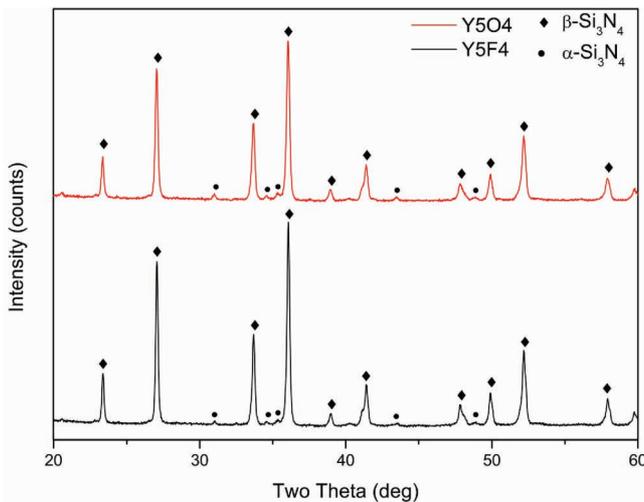


Fig. 2: The typical XRD pattern of samples Y5O4 and Y5F4.

Compared with other common oxide sintering additives used for sintering Si₃N₄ ceramics, the MgF₂ has another unique characteristic of a low melting point (e.g. the melting points of MgO and MgF₂ are 2800 and 1261 °C, respectively). The displacement as a function of temperature during SPS for sample Y5F4 and sample Y5O4 are shown in Fig. 3. It seems that shrinkage occurs at 1200 °C and at 1350 °C for the samples with MgF₂ and MgO as the sintering aids, respectively, verifying that the MgF₂ facilitates the formation of liquid phase at a lower temperature. Above these temperatures, the sample containing MgF₂ reached a plateau at 1500 °C with a displacement of 5.2 mm whereas the sample containing MgO only reached a displacement of 2.86 mm. This shows that the MgF₂-containing sample densified much faster than that containing the MgO additive. The bulk density of the sintered samples is presented in Table 1. The higher bulk den-

sity of 3.1697 g·cm⁻³ was obtained for the sample containing MgF₂. The lower bulk density of 3.1453 g·cm⁻³ was obtained for the sample containing MgO. Thus, the sample containing MgF₂ has higher density than the equivalent MgO-containing samples. Furthermore, the fluorine-containing liquids allow a higher solubility of the nitrogen with regard to oxide-containing liquids. Hanifi *et al.* have reported on the effect of fluorine content on the solubility of the nitrogen in Ca-Si-Al-O-N compositions and found that the maximum nitrogen content of 40 eq% can be obtained at 1 eq% F. Hence, the tiny fluorine content coming from MgF₂ still contributes to the increase in solubility of nitrogen^{15,16}. Table 3 details the fluorine content of the as-prepared samples. The grain boundary existed in the samples in the form of glass phase. With the increase in MgF₂ content, the fluorine content is also increased in the grain boundary glass phase. The effect of fluorine addition on the structure of silicate glasses has been investigated¹⁷ and it has been shown that fluorine can bond to silicon as Si-F¹⁸, in glasses containing both F and N, the network terminating effect of fluorine induces significant reductions in both glass melting temperatures and glass transition temperatures¹⁶. Consequently, the formed liquid using MgF₂ as a sintering additive provides more time for completion of the phase transformation from α to β than that with MgO. A longer transformation process from α to β phase would promote grain growth, which results in the purification of Si₃N₄ and increase of Si₃N₄-Si₃N₄ contiguity^{19,20} (shown in Fig. 1(c) and (e)), offering higher thermal conductivity in the samples with MgF₂ than with MgO as a sintering additive.

Table 3: The fluorine content of the as-prepared samples.

Samples	Fluorine content (wt%)
Y5F0	0
Y5F2	0.63±0.16
Y5F4	1.73±0.18
Y5F6	2.25±0.21
Y5F4H	0.32±0.12

* Y5F4H:

the sample Y5F4 after post-sintering heat treatments

Table 2 lists the typical flexural strength and fracture toughness of sample Y5F4 and Y5O4, suggesting that sample Y5F4 exhibits higher fracture toughness than sample Y5O4, which could be mainly attributed to the fact that the MgF₂-doped sample has a larger fraction of elongated grains than MgO-doped counterparts. These large elongated grains can improve the fracture toughness by facilitating toughening mechanisms such as crack deflection and crack bridging. The flexural strength of sample Y5F4 is also higher than that of sample Y5O4, which could be mainly ascribed to the fact that the MgF₂-doped sample has a higher bulk density than MgO-doped counterparts^{21,22}.

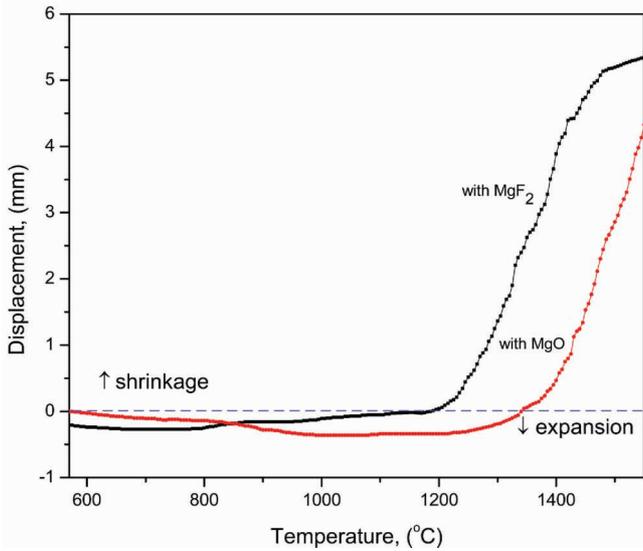


Fig. 3: Displacements as a function of sintering temperatures of the samples with MgF_2 and MgO as the sintering aids.

(2) *The effect of post-sintering heat treatment*

Although SPS exhibits certain advantages, such as accelerating the diffusion of atoms in the sintering process, the short sintering time generally leads to some structural defects in the ceramics. To obtain a better performance, post-sintering heat treatment is necessary²³. The properties of sample Y5F4 before and after post-sintering heat treatment are shown in Table 2. This suggests that the density, thermal conductivity, flexural strength and fracture toughness of sample Y5F4 have been profoundly improved after the post-sintering heat treatment. The thermal conductivity is enhanced up to $82.53 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, with an increase of $\sim 29.9\%$ caused by the post-sintering heat treatment.

Fig. 4 shows typical SEM images of the fractured surfaces of sample Y5F4 before and after post-sintering heat treatment, revealing that sample Y5F4 possesses a larger fraction of elongated grains and sharper grain boundary edges

after post-sintering heat treatment. This result indicated that tiny $\beta\text{-Si}_3\text{N}_4$ grains dissolved constantly and then re-precipitated at the surface of larger $\beta\text{-Si}_3\text{N}_4$ grains during the process of post-sintering heat treatment. As a result of this solution-precipitation mechanism, the $\beta\text{-Si}_3\text{N}_4$ grains become larger and the number of defects can also be reduced²⁴. It is well known that phonons play a dominant role in the heat transport of Si_3N_4 at room temperature. Phonon scattering arising from lattice defects is widely believed to be a major factor in degrading the thermal conductivity of Si_3N_4 ceramics²⁵. Fig. 1(c) and (f) show representative SEM images of polished and plasma-etched surfaces of sample Y5F4 before and after post-sintering heat treatment, revealing the amount and distribution of grain boundary phases within these two samples. The sample after post-sintering heat treatment has fewer grain boundary phases and a higher number of $\text{Si}_3\text{N}_4\text{-Si}_3\text{N}_4$ contacts. The weighing results show that the weight loss of sample Y5F4 after post-sintering heat treatment is 0.75%. The x-ray fluorescence analyses reveal that the magnesium content in the inside of sample Y5F4 before and after post-sintering heat treatment is 1.2 wt% and 0.44 wt%, respectively. According to the report by Y. Zhou, the grain boundary phase can diffuse to the surface of Si_3N_4 ceramics, accompanied with grain growth, and evaporate during the long post-sintering time at 1900°C ². After the post-sintering heat treatment, only a few grain boundary phases covered the grain, while the majority of grain boundary phases resided at multigrain junctions. Hence, the reduced defects caused by grain growth and fewer grain boundary phases are the reason for the significant increase in the thermal conductivity of sample Y5F4 after the post-sintering heat treatment. Owing to the larger amount of elongated grains in the samples induced by the post-sintering heat treatment, the fracture toughness is improved by toughening mechanisms of the large elongated grains. After the post-sintering heat treatment, the flexural strength is decreased by $\sim 10\%$, which is 910.52 MPa , owing to the coarsening of the microstructure²².

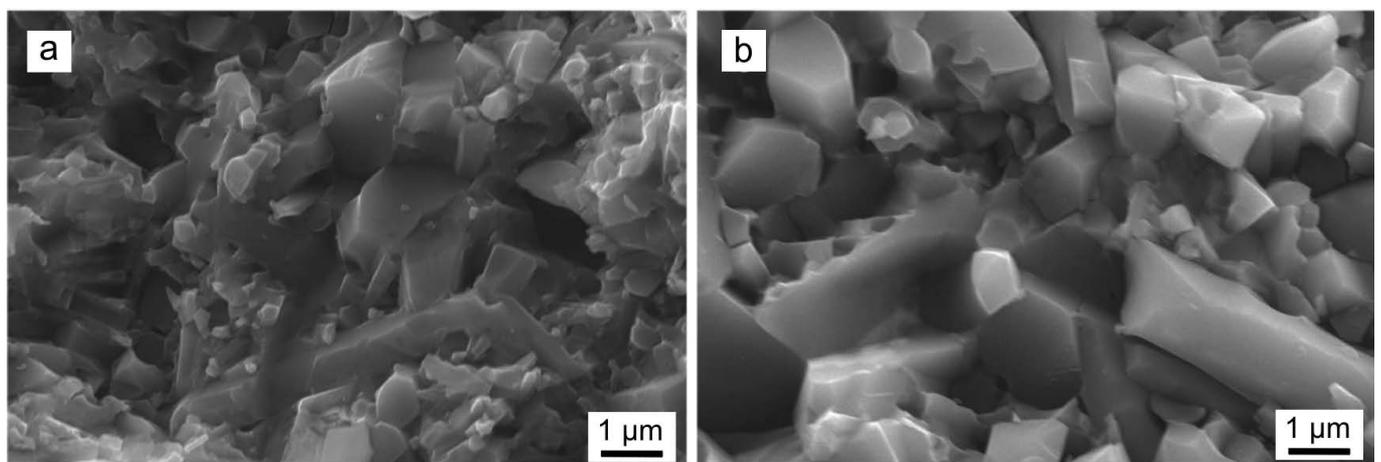


Fig. 4: Representative SEM images of the fractured surfaces of sample Y5F4 before and after post-sintering heat treatments. (a) sample Y5F4 before post-sintering heat treatments. (b) sample Y5F4 after post-sintering heat treatments.

At present, the highest value of thermal conductivity of silicon nitride has been reported at $177 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ by Y. Zhou². In this work, the silicon nitride was fabricated via a route of sintering of reaction-bonded silicon nitride (SRBSN), using $\text{Y}_2\text{O}_3/\text{MgO}$ as additives. Although the value of thermal conductivity is high enough, the lengthy post-sintering time (60 h) and the poor flexural strength (460 MPa) lessen the prospect of application. Hence, the silicon nitride ceramics with high thermal conductivity and excellent mechanical properties fabricated with $\text{Y}_2\text{O}_3/\text{MgF}_2$ sintering aids possess an enormous advantage.

IV. Conclusions

The MgF_2 introduced as a sintering aid plays a significant role in the fabrication of Si_3N_4 ceramics with improved performance. The thermal conductivity, flexural strength and fracture toughness of Si_3N_4 ceramics reach $\sim 63.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, 1015 MPa and $7.29 \text{ MPa}\cdot\text{m}^{1/2}$, respectively, which are increased by 19 %, 9 % and 12.7 % compared to the values of the counterparts with MgO as a sintering additive.

The post-sintering heat treatment has an important effect in improving the performance of Si_3N_4 ceramics, giving them more elongated grains with sharp grain boundary edges. The thermal conductivity and fracture toughness of Si_3N_4 ceramics after the post-sintering heat treatment reached $82.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ and $8.47 \text{ MPa}\cdot\text{m}^{1/2}$, respectively. The flexural strength was 911 MPa, i.e. a ~ 10 % decrease after the post-sintering heat treatment.

Acknowledgements

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