Sintering Behavior of Si₃N₄ Ceramics at Low Temperature in Air Atmosphere Furnace

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Abstract: Si₃N₄ ceramics have been densified in air atmosphere furnace at low temperatures of 1600–1650°C with Li₂O-Al₂O₃sintering additives. Molar ratio of 0.4–1.6:1 of Li₂O and Al₂O₃ were used to study the effects of additives on sintering behavior of Si₃N₄ materials. It is found that the densities of sintered samples increased and then decreased with the increase of molar ratio accordingly. Highest densities in excess of 95% of theoretical are obtained with the ratio of 0.7:1. Densification process is accompanied by phase transformation. Therefore, the primarily phases in sintered specimens are β-Si₃N₄ and α-Si₃N₄, with a small amount of Si₂N₂O existed because of minor oxidation of the specimens during sintering. However, relatively low α- to β-Si₃N₄ transformation (~63% β-Si₃N₄) took place in the present densification conditions. The microstructures of the sintered samples exhibited typical β-Si₃N₄ elongated grain morphologies with small amount of homogeneously distributed residual pores. The sintered Si₃N₄ materials have the hardness of 14GPa and fracture toughness of 5.08MPa·m¹/₂, indicating a potential method for low-cost processing of Si₃N₄-based ceramics.

1. Introduction
Si₃N₄ ceramics have excellent chemical and mechanical properties which are widely used for variety of engineering applications[1,2]. Dense Si₃N₄ ceramics are generally obtained by liquid phase sintering at high temperature with proper additives. However, most of the sintering techniques reported are performed at high temperature (1750–1900°C) with high pressure[3-5]. Li₂O has relatively lower melting point and low viscosity, which is used as sintering additives to decrease the sintering temperature of AlN ceramics [6]. Recently, several researches are focused on sintering Si₃N₄ ceramics by the addition of Li₂O, which shows a potential usage as sintering additives. Matovic [7,8] and Lee [9] reported that Si₃N₄ ceramics with high relative density and good mechanical properties could be prepared by the addition of LiYO₂ with pressureless sintering at 1650°C in N₂ atmosphere. Chockalingam [10] fabricated the Si₃N₄ ceramics with relative density of 93% by microwave sintering at 1600°C using LiYO₂ and ZrO₂ as the sintering additives.

In the present work, the densification behavior of Si₃N₄ ceramics with sintering additives of Li₂O-Al₂O₃ was studied. Meanwhile, a low-cost sintering method in air atmosphere furnace was also developed to fabricate dense Si₃N₄ ceramics.

2. Experimental procedure
Commercial α-Si₃N₄ powders with particle size of 0.7μm have been used in present work. Li₂CO₃ and Al₂O₃ submicron powders as sintering additions were firstly mixed and then calcined at 900°C for 4h in
The molar ratios of the two additions were selected as (1) 0.4:1, (2) 0.7:1, (3) 1:1, (4) 1.3:1 and (5) 1.6:1, subsequently referred to R=0.4, 0.7, 1, 1.3 and 1.6 respectively.

Si$_3$N$_4$ powders with 15wt% of calcined sintering additions were then mixed for 24h in ethanol by ball milling. The slurry were dried at 65°C in a drying oven. Completed dried mixture powders were subsequently sieved and pressed by cold isostatic pressing at 150 MPa to obtain the green body compaction. Pressed samples buried with Si$_3$N$_4$ powders in graphite crucible were set in Al$_2$O$_3$-sagger with full filled graphite powders, as shown in figure 1.Sintering was performed in air using a conventional furnace equipped with MoSi$_2$ heating elements at temperature of 1600 and 1650°C for 4h.Densities of sintered specimen were determined by the Archimedes method. Phase identification of the powders and sintered specimens was performed by XRD analysis. Microstructural characterization of the sintered materials was performed by scanning electron microscopy(SEM) and energy-dispersive X-ray spectroscopy (EDS).

![Figure 1. Schematic representation of crucible/sagger arrangements for Si$_3$N$_4$sintering.](image1.png)

![Figure 2. XRD analysis of pretreated sintering additions. (γ: LiAlO$_2$, χ: LiAl$_5$O$_8$, c: Li$_2$CO$_3$)](image2.png)
3. Results and discussion

XRD characterizations of pretreated sintering additions are shown in figure 2. Almost pure LiAlO$_2$ was obtained at the calcining temperature of 900°C for the addition mixture of R=1. LiAlO$_2$ and LiAl$_5$O$_8$ were co-existed in the pre-treated additions when the Li$_2$CO$_3$ content is less. A certain amount of Li$_2$CO$_3$ was residual when the initial Li$_2$CO$_3$ content is excess in the sintering additions.

Figure 3 shows the effects of sintering additions on the relative density of sintered specimens. Densities of 93.7% and 95.2% of theoretical are obtained when R=0.7 at the sintering temperature of 1600 and 1650°C respectively. With the decrease or increase of R value, densities decreased accordingly at both sintering temperatures.

![Figure 3. Relative density of sintered Si$_3$N$_4$ specimens.](image1)

![Figure 4. Weight loss of Si$_3$N$_4$ specimens after sintering.](image2)

Weight loss of the specimens after sintering is shown in figure 4. In the present experimental conditions, it can be considered that the weight loss is primarily caused by the evaporation of Li containing additions. Consequently, the sintered specimens had generally greater weight loss when Li$_2$CO$_3$ content is more in the sintering additions. However, the great growth of weight loss happened when the R value is higher than 1. When R≤1, Li containing compositions are existed in the form of...
LiAlO$_2$ or LiAl$_5$O$_8$ which are much more difficult to evaporate than Li$_2$CO$_3$ or Li$_2$O, leading to much less weight loss after sintering.

As shown in figure 5, the main phases existed in all the specimens after sintering are $\alpha$- and $\beta$-Si$_3$N$_4$ with various R values. The XRD pattern shows remarkable diffraction lines in the regions around 26$^\circ$, which can be associated with the phase LiAlSi$_2$O$_6$. This can be indicated that sintering addition LiAlO$_2$ reacted with SiO$_2$ on the a-Si$_3$N$_4$ powder surface during sintering to form low melting point phases (~1350$^\circ$C) as assistance to lower the densification temperature of Si$_3$N$_4$ materials. Otherwise, it can also indicate that nucleation and crystallization of LiAlSi$_2$O$_6$ took place in the sintering procedure. A lower volume fraction of Si$_2$N$_2$O is noted to form in all specimens. Si$_2$N$_2$O formation occurs because of minor oxidation of the specimens during sintering. It can also be further understood from the predominance area phase diagram of C-Si-O-N (figure 6) that Si$_2$N$_2$O could be formed and existed in the present experimental atmosphere.

![Figure 5. XRD analysis of sintered specimens. ($\alpha$: $\alpha$-Si$_3$N$_4$, $\beta$: $\beta$-Si$_3$N$_4$, O: Si$_2$N$_2$O, L: LiAlSi$_2$O$_6$).](image)

![Figure 6. Predominance area phase diagram of C-Si-O-N.](image)
Understandably, densification process was accompanied by transformation from α- to β-Si₃N₄ (Fig.5). This phase transformation generally occurred at the treatment temperature above 1500°C. Figure 7 shows the β-Si₃N₄ fraction of sintered specimens with various R values. It can be seen that relatively more transformation could take place at higher sintering temperature. The most β-Si₃N₄ fraction appeared with the sintering addition of R=0.7 at both 1600 and 1650°C. However, using LiAlO₂ as sintering addition at present experimental conditions, highest fraction of only 63%β-Si₃N₄ was formed in the sintered specimens comparing to that of rare earth (such as Y₂O₃), which could even obtain the 100% phase transformation at the same temperature[11]. This may be due to the existence of Al₂O₃ as the addition which probably has not obvious promotion of phase transformation.

![Figure 7. β-Si₃N₄ fractions of sintered specimens.](image)

![Figure 8. SEM images of sintered specimens. (a)1600°C, R=0.7, (b)1650°C, R=0.7,(c)1650°C, R=1.6.](image)
SEM observations of the microstructures of the sintered specimens are shown in Fig. 8. As expected from the densification data presented in Fig. 3, obvious residual micro pores are apparent in specimen of R=0.7 sintered at 1600°C (figure8(a)) and for specimen of R=1.6 sintered at 1650°C (figure8(c)). Conversely, the specimen of R=0.7 sintered at 1650°C shows pretty small amount of residual pores (figure8(b)). It is also noted that average pore size in the specimen of R=1.6 (3~5μm) is much bigger than other specimens, which is probably caused by the evaporation of excess Li₂O with this additive composition.

An advantage of the outlined method is indicated that the buried powders and crucibles could be reused after many cycles in the present experimental conditions. In especially, it is found that using the recycled Si₃N₄ powders as buried materials is definitely beneficial for the densification behavior in sintering Si₃N₄ ceramics.

Considering the good mechanical properties with hardness of 14GPa and fracture toughness of 5.08 MPa·m¹/² for the specimen of R=0.7 sintered at 1650°C, the general approach in the present work appears favorable for the preparation of low-cost Si₃N₄ ceramics.

4. Conclusion
For low-cost fabrication of dense Si₃N₄ ceramics, sintering was conducted in air atmosphere furnace at low temperatures of 1600~1650°C with the usage of Li₂O-Al₂O₃ sintering additives. Molar ratio of the two additions had great effects on the sintering behavior of Si₃N₄ ceramics. Highest densities in excess of 95% of theoretical are obtained with the ratio of 0.7:1 at sintering temperature of 1650°C. β-Si₃N₄, α-Si₃N₄ as well as a small amount of Si₂N₂O are observed in the densified specimens. Relatively low fraction of less than 63% β-Si₃N₄ was formed in the sintered specimens. This phenomenon may be due to the existence of Al₂O₃ as the addition which probably has not obvious promotion of phase transformation.

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