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Influence of LiF on the Sintering of Si_3N_4 Ceramics Containing SiO_2–CaO–Al_2O_3: Densification, Microstructure, and Mechanical Properties*

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Abstract

This study investigates the influence of LiF on the sintering behavior of Si_3N_4 ceramics with SiO_2–CaO–Al_2O_3 at the eutectic composition. Compositions containing 90 wt.% Si_3N_4 were sintered at 1650–1815 °C for 1 hour. The ceramics were characterized in terms of density, microstructure, and hardness. At 1650 °C, the $\beta/(\alpha+\beta)$-Si_3N_4 ratio rose from 28.4 % (0 wt.% LiF) to 63.7% (2 wt.% LiF), exceeded 98 % at 1700 °C, and reached 100 % at ≥ 1770 °C. In LiF-free samples, higher sintering temperatures resulted in a higher relative density (95.6 ± 0.4%) and hardness (12.99 ± 0.42 GPa). LiF improved densification and hardness at low content and sintering temperature, yielding 89.4 ± 0.3 % relative density and 9.71± 0.42 GPa hardness (1 wt.% LiF) compared to 84.1 ± 0.5 % and 6.78 ± 0.29 GPa (0 wt.% LiF), both at 1650 °C. At higher temperatures, LiF decreased both properties, likely due to its tendency to evaporate.

Keywords: silicon nitride, sintering, LiF

INTRODUCTION

Silicon nitride (Si_3N_4) ceramics are used in structural applications that demand high thermal, mechanical, and corrosion resistance [1-3]. However, their densification is challenging due to low self-diffusivity and decomposition at high temperatures. As a result, sintering aids are required to promote liquid phase sintering [3]. The selected sintering aids play a critical role in determining characteristics of the liquid phase formed during sintering, such as its temperature of formation, volume, and viscosity [4]. A promising strategy involves the use of systems capable of forming low-temperature eutectic liquids, which enable sintering at reduced temperatures.

Additives as CaO are effective in sintering silicon nitride [5]. Al_2O_3, in turn, contributes to high thermal stability and improves hardness and strength [6]. The combination of CaO and Al_2O_3 with SiO_2 becomes advantageous, as these additives form a low-temperature eutectic (1170 °C, $61SiO_2$–24CaO–$15Al_2O_3$ wt.%) [7], optimizing the sintering process. Studies on silicon nitride with SiO_2, CaO, and Al_2O_3 additions confirm their potential to improve densification and mechanical properties. The incorporation of 10 wt.% calcium aluminates, for example, has been shown to promote strength values around 850 MPa and stability against air oxidation up to 1300 °C, associated with densely packed grains and a uniform distribution of intergranular phases [8]. Even non-eutectic CaO–SiO_2–Al_2O_3 compositions are effective in promoting densification [9], while TiO_2-modified CaO–SiO_2 systems further improve density and fracture toughness by lowering liquid-phase viscosity [10].

Lithium fluoride (LiF) has also shown potential to improve Si_3N_4 sintering. It accelerates particle rearrangement and dissolution–precipitation kinetics [11], as fluorine depolymerizes silicate networks, lowering the liquid viscosity [12,13]. LiF-assisted sintering also promotes homogeneous microstructures and enhances strength, hardness, fracture toughness, and thermal properties [14]. Its effects are strongest in multicomponent systems containing oxides such as Y_2O_3, Al_2O_3, and MgO [15].

Given these findings, this work is motivated by the need to explore whether LiF can further improve the sintering efficiency and final properties of Si_3N_4 ceramics with a low-temperature eutectic SiO_2–CaO–Al_2O_3 system. Therefore, this study investigates the effect of LiF addition on the sintering behavior, microstructure, and properties of Si_3N_4 ceramics containing SiO_2, CaO, and Al_2O_3 in the eutectic composition.

EXPERIMENTAL

Starting materials were Si_3N_4 (UBE, 95 wt.% α-Si_3N_4), SiO_2 (Sigma-Aldrich, 99.9% purity), $CaCO_3$ (Merck, 99.98% purity), Al_2O_3 (Almatis, CT3000), and LiF (99.9% purity). The used CaO–SiO_2–Al_2O_3 ratio was based on the eutectic composition of ~1170 °C [7]. LiF was added at 1 and 2 wt.%. The compositions were: $90Si_3N_4$-$6.1SiO_2$-2.4CaO-$1.5Al_2O_3$ (wt.%), $90Si_3N_4$-$5.5SiO_2$-2.2CaO-$1.3Al_2O_3$-1LiF (wt.%), and $90Si_3N_4$-$4.9SiO_2$-1.9CaO-$1.2Al_2O_3$-2LiF (wt.%), coded as A000, A100, and A200, respectively. These correspond to $89.3Si_3N_4$-$7.3SiO_2$2.3CaO-$1.2Al_2O_3$-0LiF (vol.%), $89.2Si_3N_4$-$6.5SiO_2$-2.1CaO-$1.0Al_2O_3$-1.2LiF

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(vol.%), and $89.1Si_3N_4$-$5.8SiO_2$-$1.8CaO$-$0.9Al_2O_3$-$2.4LiF$ (vol.%), respectively. Powders were milled (24 h, isopropanol, alumina media), dried (80 °C), and pressed (50 MPa uniaxial, 200 MPa isostatic). Pressureless sintering was performed under nitrogen, in a graphite resistance furnace (Thermal Technology) at 1650, 1700, 1770, or 1815 °C for 1 h (10 °C/min). Five samples were prepared for each group.

The relative density was calculated based on the apparent and theoretical densities of each composition, determined by the Archimedes method and rule of mixtures, respectively. X-ray diffraction (XRD) patterns were studied using a Bruker D8 diffractometer. The β/(α+β)-Si_3N_4 phase ratio was quantified through Rietveld refinement (Profex-BGMN) [16]. Fractured surfaces of the samples were analyzed by scanning electron microscopy (SEM) (Hitachi TM-3000). Vickers hardness (Buehler VMT-7) was measured at 100 N on one specimen per group (≤ 10 indentations).

RESULTS AND DISCUSSION

Relative densities are in Table I. LiF-free samples exhibit increasing density with sintering temperatures, indicating the oxide additives promoted solution-reprecipitation during sintering. For LiF-containing samples, the increase in density at 1650 °C suggests that this compound may influence the densification of ceramics with the CaO–SiO_2–Al_2O_3 eutectic composition. This effect is attributed to the ability of LiF to lower the liquid-phase viscosity and temperature required for the formation of a dense microstructure. However, the decrease in density observed as LiF concentration increases from 1 to 2 wt.%, along with the density reduction between 1650 and 1700 °C followed by stabilization at higher temperatures, suggests that the densification-enhancing effect of LiF is more significant at lower sintering temperatures. This is likely due to its low melting point [17], which must have led to partial volatilization of the liquid phase at elevated temperatures, reducing its effectiveness in enhancing densification.

Table I - Relative density (ρ) of the silicon nitride.

	RD (%) of the samples sintered at different temperatures (ºC) for 1 hour			
Code	1650	1700	1770	1815
A000	84.1±0.5	89.4±0.2	94.7±0.3	95.6±0.4
A100	89.4±0.3	88.8±0.6	91.5±0.7	90.4±2.1
A200	88.0±0.4	86.7±0.7	89.2±0.3	89.7±0.4

XRD results (Figure 1) display the presence of α-Si_3N_4 peaks, indicating that at 1650 °C, the transformation to β-Si_3N_4 was incomplete. At 1700 °C, α-Si_3N_4 peaks are detectable (Figure 1b) in LiF-containing samples; however, their intensity is reduced compared to that observed in samples sintered at 1650 °C. In Figures 1c and 1d, only β-Si_3N_4 peaks are observed, demonstrating complete phase transformation at 1770 and 1815 °C, irrespective of the composition. This behavior correlates with the β/(α+β)-Si_3N_4 phase ratio determined by Rietveld refinement. At 1650 °C, the β-phase content rose with increasing LiF content: A000 (28.42%), A100 (38.34%), and A200 (63.69%). Near-complete α-to-β transformation occurred in samples at 1700 °C, with residual α-Si_3N_4 increasing with LiF content: A000 (100%), A100 (99.52%), and A200 (98.80%). Complete transformation was achieved at 1770 °C and above. These results indicate that the additive system promoted α-Si_3N_4 dissolution and β- Si_3N_4 reprecipitation. However, the presence of LiF increased the temperature required for complete transformation above 1700 °C. This behavior is related to the competition between LiF volatilization, which reduces the amount of liquid phase, and the diffusion mechanisms that become activated at higher temperatures. The α/β phase ratio is critical for balancing mechanical properties: α-Si_3N_4 produces equiaxed grains that maximize hardness, while β-Si_3N_4 forms elongated grains that improve fracture toughness and strength through toughening mechanisms.

Figure 2 illustrates SEM images of the fractured surfaces of the samples. The samples exhibit rough fracture surfaces, attributed to crack deflection (blue arrows) and grain pull-out (green arrows) mechanisms. Micropores (red arrows),

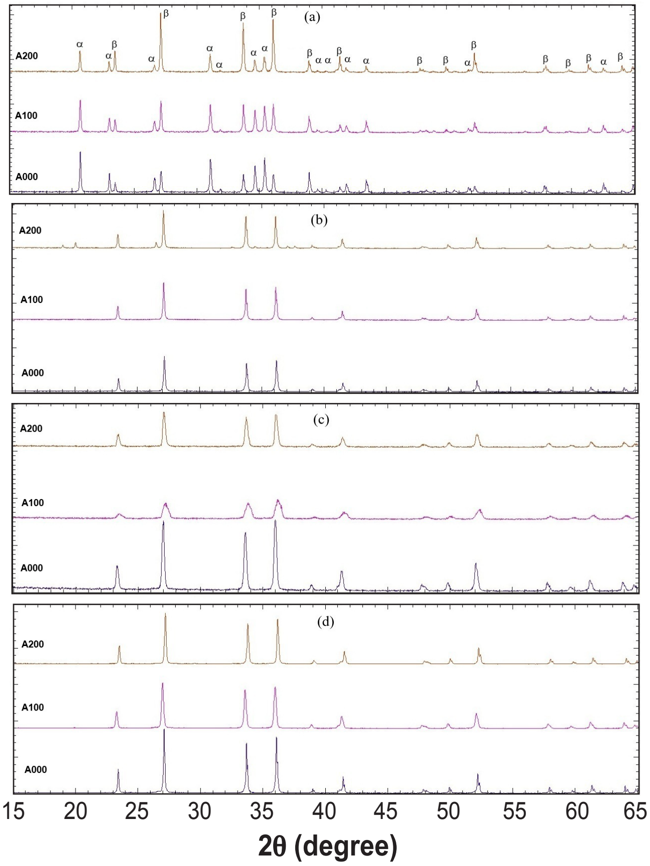

Figure 1: X-ray diffraction patterns of samples sintered at (a) 1650 °C, (b) 1700 °C, (c) 1770 °C, and (d) 1815 °C. α is α-Si_3N_4 and β is β-Si_3N_4.

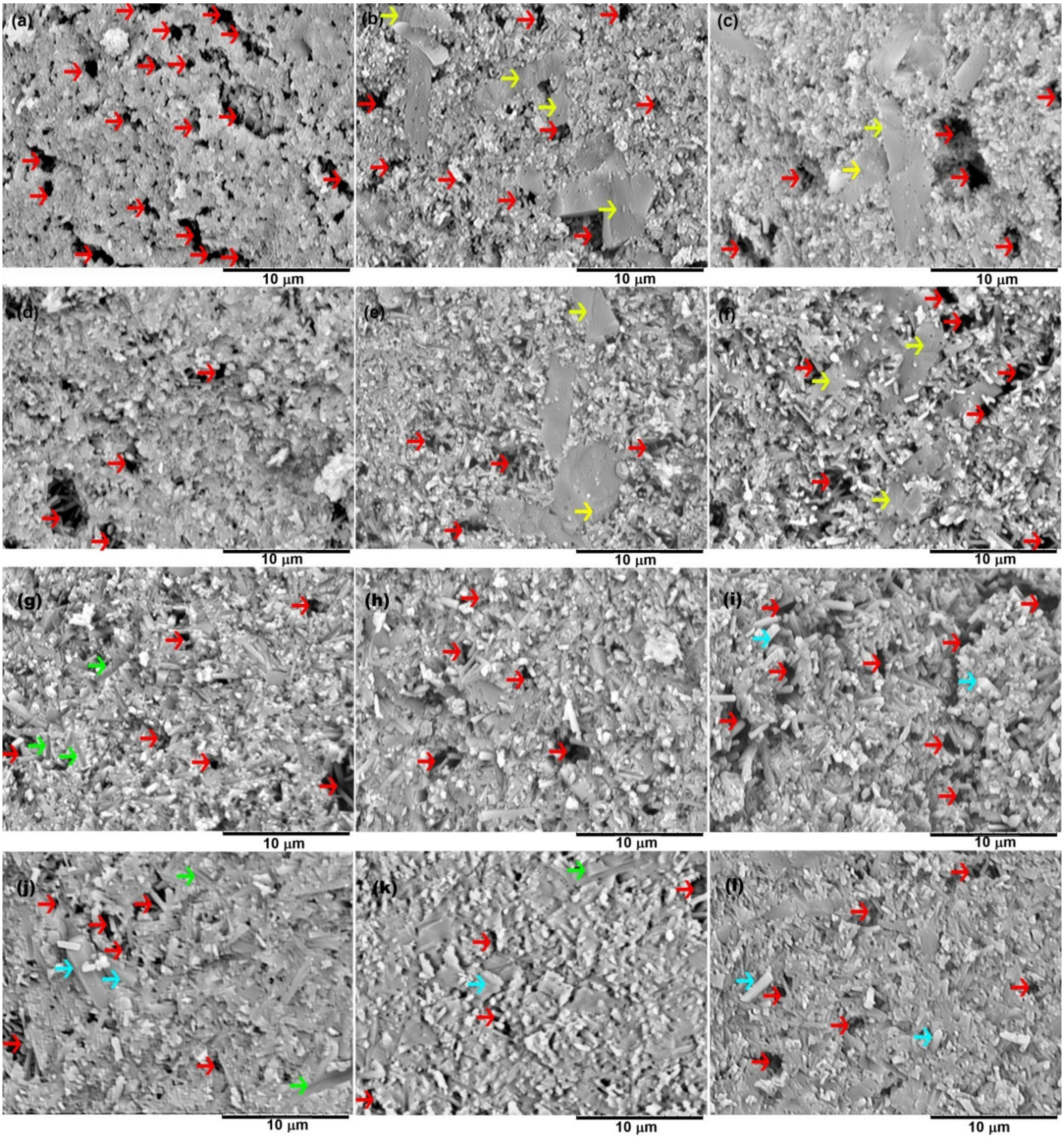

Figure 2: Scanning electron micrographs of the fractured surfaces of samples sintered at different temperatures: (a) A000–1650 °C, (b) A100–1650 °C, (c) A200–1650 °C, (d) A000–1700 °C, (e) A100–1700 °C, (f) A200–1700 °C, (g) A000–1770 °C, (h) A100–1770 °C, (i) A200–1770 °C, (j) A000–1815 °C, (k) A100–1815 °C, (l) A200–1815 °C.

with a higher concentration in samples sintered at lower temperatures, are present. At 1650 °C, in the LiF-free sample (Figure 2a), coalescence of micropores is observed. The microstructure of the samples sintered at 1650 °C (Figure 2a-c) features equiaxed and elongated grains, corresponding to the α-Si_3N_4 and β-Si_3N_4, respectively. Furthermore, an increase in the fraction of β-Si_3N_4 grains is observed with increasing LiF content, as confirmed by XRD results. At higher temperatures, the microstructure is dominated by β-Si_3N_4 grains. However, large β-Si_3N_4 grains are present in samples sintered at 1650 °C and 1700 °C, indicative of abnormal grain growth during the 1-hour dwell time. It was likely due to the combined effects of reduced liquid-phase viscosity caused by the presence of LiF and high porosity, which provided space for grain development. Abnormal grains showed transgranular fracture, indicated by ridged and ribbed fracture surfaces (yellow arrows).

The Vickers hardness (Table II) increased with

Table II - Vickers hardness (HV) of silicon nitride samples as a function of sintering temperature.

Code	Hv (GPa) of the samples sintered at different temperatures (°C) for 1 hour			
	1650	1700	1770	1815
A000	6.78±0.29	10.81±0.39	12.99±0.42	12.31±0.40
A100	9.71±0.42	9.64 ±0.71	11.03±0.31	11.45±0.59
A200	9.36±0.57	9.10 ±0.50	8.57 ± 0.72	9.47 ±1.20

sintering temperature in the A000 composition, stabilizing above 1770 °C. This behavior is linked to the increase in sample density. Similarly, at 1650 °C, LiF addition increased hardness, mainly due to improved densification. Furthermore, higher hardness in LiF-containing samples may have resulted from increased α-Si_3N_4 content and the effect of LiF on the intergranular glassy phase, since α- α-Si_3N_4 is harder than β. In samples with 1 wt.% LiF, hardness tended to increase with temperature, also showing the effect of LiF on the glassy phase. However, increasing LiF content from 1 to 2 wt.% led to decreased hardness, likely due to LiF volatilization, as discussed earlier.

In summary, LiF enabled efficient sintering and improved mechanical performance at reduced temperatures. At 1650 °C for 1 hour, LiF enhanced densification, raised the β/(α+β)-Si_3N_4 phase ratio, and improved hardness. At higher temperatures or higher LiF contents, volatilization limited its effect and induced abnormal grain growth.

CONCLUSION

The $CaO–SiO_2–Al_2O_3$ eutectic system was effective for sintering silicon nitride. LiF addition improved densification, α→β phase transformation, and hardness at lower temperatures. However, it promoted abnormal grain growth and transgranular fracture. At higher temperatures, LiF volatilization impaired densification and reduced hardness, mainly at 2 wt%. LiF. The β- Si_3N_4 phase was favored above 1700 °C, and intergranular fracture dominated, with crack deflection and grain pull-out observed. Maximum relative density and hardness were reached at 1815 °C without LiF (95.6±0.4 %, 12.31±0.40 GPa), at 1770 °C with 1 wt% LiF (91.5±0.7 %, 11.03±0.31 GPa), and at 1815 °C with 2 wt% LiF (89.7± 0.4 %, 9.47 ±1.20 GPa).

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DATA AVAILABILITY STATEMENT

Research data are only available upon request.

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