

Thermal conductivity of pressureless sintered Si₃N₄ ceramics with Li-exchanged zeolite

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Abstract: The effects of temperature on the thermal conductivity of Si₃N₄ sintered with Li-exchanged zeolite were investigated. The highest conductivity was measured for the ceramics sintered with 10 % of additive. The complete $\alpha \rightarrow \beta$ -Si₃N₄ transformation and maximum density (> 98 % TD) were attained with the sample sintered at 1650 °C. However, the results show that Al and O from the additive dissolve into the β -Si₃N₄ structure which act as phonon scattering sites resulting in a lowering of the conductivity and a weaker temperature dependence of the conductivity.

Keywords: pressureless sintering, silicon nitride, thermal conductivity.

INTRODUCTION

The thermal conductivity of Si₃N₄ and its excellent mechanical properties make it a serious candidate for high-temperature energy conversion devices, such as all-ceramic turbines or as replacements for many metallic components in internal combustion engines.¹ Haggerty and Lightfoot were the first to point out that Si₃N₄ is a material with potentially high thermal conductivity at room temperature.² Calculations show that the extrinsic thermal conductivity of single β -Si₃N₄ crystal is 320 W m⁻¹ K⁻¹, similar to the thermal conductivity of SiC and AlN which have been successfully fabricated for commercial use as high thermal conductivity substrates and heat sinks.³ However, relatively poor thermal conductivity values, ranging from 20 to 70 W m⁻¹ K⁻¹, have been reported for Si₃N₄ ceramics fabricated by reaction bonding,⁴ chemical vapour deposition,⁵ hot pressing and hot-isostatic-pressing methods.⁶ Very recently, Watari *et al.*³ fabricated Si₃N₄ with a thermal conductivity value of 155 (W m⁻¹ K⁻¹) by a novel processing technique, grain-orientation technology.

The crystal structure of β -Si₃N₄ is hexagonal. Therefore, it is postulated that heat flow in β -Si₃N₄ is different depending on the crystal axis. Conductivity mea-

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surement of single crystal shows that the conductivity along the c -axis is about three times higher than that along the a -axis.⁷

The thermal conductivity of Si_3N_4 ceramics depends strongly on the amount of impurities and/or sintering additives because the incorporation of Al and O into the β - Si_3N_4 structure reduces the thermal conductivity of the grains due to the reduced free path for phonons.⁸ The object of this study was to investigate the effect of addition of Li-exchanged zeolite as a sintering additive on the parameters affecting the thermal conductivity of β - Si_3N_4 ceramics.

EXPERIMENTAL

Material characterization

The starting material used for the green body fabrication was commercial Si_3N_4 powder, SILZOT HQ (SKW-Trostberg AG). It is a low cost powder produced by a special modification of the direct nitridation method from high purity grade silicon. The chemical analysis of the powder was provided by the manufacturer, characteristic impurity contents being O = 0.5 wt.%, N > 38.5 wt.%, free Si < 0.5 wt.%, SiC < 0.4 wt.%, $\alpha/(\alpha+\beta)$ - $\text{Si}_3\text{N}_4 \approx 0.8$, with a mean particle size of $D_{50} = 1.7 \mu\text{m}$ and a specific surface area of $3.2 \text{ m}^2/\text{g}$.

The sintering additive used in the present work was Li-exchanged zeolite. The ion exchange procedure was repeated eight times to ensure complete substitution of Li for Na in A-zeolite.⁹ After the last exchange step, the product was heated at $800 \text{ }^\circ\text{C}$ to obtain an amorphous powder with a composition corresponding to β -eucryptite ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$). Phase analysis of the thermally treated material was performed using X-ray diffraction, according to which the powder was non-crystalline. XRD was also used to evaluate the weight fraction of the α - Si_3N_4 and β - Si_3N_4 phases on the basis of a method proposed by Gazzara.¹⁰

Samples containing 10 and 15 wt.% of additives were prepared. Green pellets were obtained by applying cold isostatic pressing at 240 MPa. The sintering was accomplished in a (gas pressure) furnace with a graphite heating element in a nitrogen atmosphere of 0.1 MPa. The range of sintering temperatures investigated was $1550\text{--}1700 \text{ }^\circ\text{C}$. Bulk densities were measured by the Archimedes method using distilled water. Micro structural observation of polished and plasma-etched specimens was conducted by scanning electron microscopy (SEM).

Determination of thermal conductivity

The laser-flash method was used for measuring the thermal diffusivity of the Si_3N_4 materials. A disk sample (diameter 1.2 mm and thickness 0.5–1 mm) was tested using self-constructed laser-flash equipment. On the front face of the sample, a laser-pulse (1.06 μm wavelength and pulse duration 1 ms) was homogeneously absorbed. On the rear face, the temperature rise was measured allowing determination of the thermal diffusivity. The equipment uses a longitudinal heat pulse method. The heat source was a pulsed Nd-YAG Laser (max. 55 J/pulse). An In-Sb IR detector recorded the temperature response signal at the rear of the sample. The amplified signal was evaluated by computer software. To protect the sample against heat loss, the specimen holder was installed in a vacuum chamber ($p < 10^{-1} \text{ Pa}$). A Mo-furnace allowed measurements between RT and 2000 K. The method has a standard deviation of 3 % for reference materials.

The thermal conductivity was calculated from the tabulated heat capacity, C_p , of Si_3N_4 ,¹¹ the thermal diffusivity, α as measured by the laser-flash technique, and the bulk density of the material, ρ , according to the equation:

$$K = C_p \alpha \rho$$

RESULTS AND DISCUSSION

Table I shows that the samples sintered with 10 and 15 % of additive content exhibit similar densities for all sintering temperatures as well as for all annealing times. In all cases the density for 10 and 15 % of additives was higher than 98 % of the theoretical density. This degree of densification is very high for low temperature sintering of Si₃N₄.

TABLE I. Sintered density (%TD) as a function of sintering temperature and time

Additive content/wt. %	1550 °C			1600 °C			1650 °C		
	2 h	4 h	8 h	2 h	4 h	8 h	2 h	4 h	8 h
5	90.1	89.7	89.4	89.5	89.2	89.0	89.1	88.8	87.9
10	98.3	98.3	98.3	98.3	98.1	98.1	98.9	98.7	98.5
15	98.3	98.3	98.1	98.3	98.1	98.0	98.2	98.2	98.1

The phase transformation was already completed for bodies with 10 and 15 % of additive. This is very important since the thermal conductivity of the β -Si₃N₄ modification is much higher conductivity than that of α -Si₃N₄.¹²

Figure 1 depicts the typical microstructure of β -Si₃N₄ produced with 10 and 15 % of the additive. The microstructure is characterized by elongated β -Si₃N₄ grains which are embedded in a glassy phase (white area in Fig. 1) located in thin layers at the grain boundaries. Materials with a larger additive content (15 wt.%) exhibit a finer microstructure. The number of coarse elongated β -Si₃N₄ grains decreases with increasing content of additive. It seems that a higher additive content restrains the growth of the Si₃N₄ grains during sintering.

It was noticed that at 1650 °C the amount of residual glass becomes very small, indicating the possibility of aluminum and/or oxygen incorporation into the α -grains (Fig. 2).

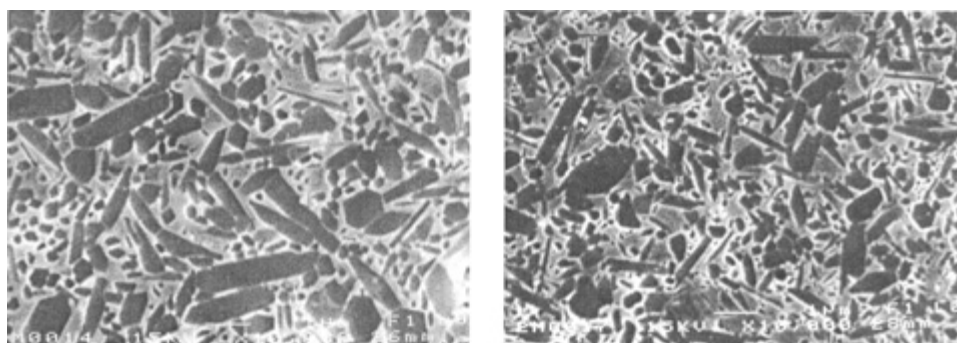


Fig. 1. SEM Micrograph of a polished and plasma etched section of samples sintered at 1600 °C for 8 h with 10 wt.% and 15-wt.% of additive.

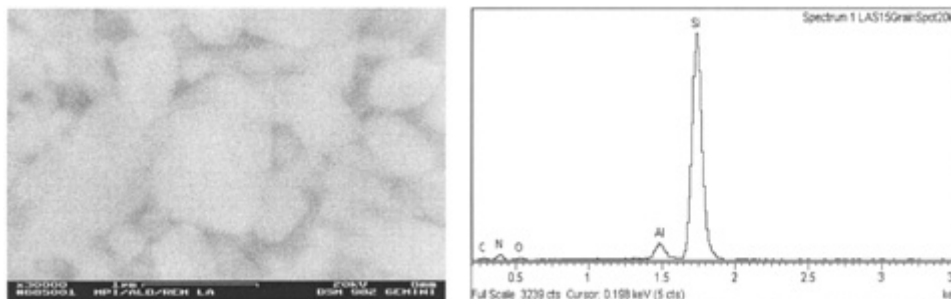


Fig. 2. Backscattered electron images and EDX of β - Si_3N_4 grain. The ample was sintered at 1650 °C for 1 h.

The effect of the amount of additive and the sintering temperature on the thermal conductivity at room temperature are shown in Fig. 3. The thermal conductivity of sintered bodies with 5 % of additive is much lower than those of samples with 10 and 15 % of additive due to the achieved density being lower. That is the thermal conductivity increases because of the increase in the degree of densitication. With increasing sintering temperature, the values of the thermal conductivity decreases. This trend was more emphasized for the higher additive concentration (in the case of 15 % additive, the thermal conductivity drops from 7.1 to 5.3 ($\text{W m}^{-1} \text{K}^{-1}$)).

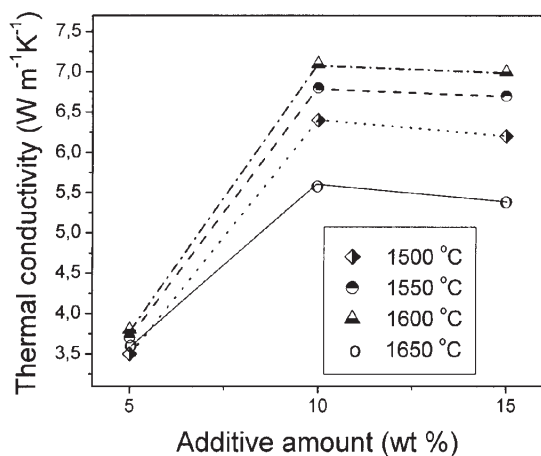


Fig. 3. Thermal conductivity of Si_3N_4 ceramics containing 5–10 wt.% additive sintered at 1500° to 1650 °C (the measurements were performed at room temperature).

Si_3N_4 ceramics can be considered as two-phase materials composed of the Si_3N_4 grains with high thermal conductivity and the intergranular phase with low thermal conductivity. The thermal conductivity of two-phase materials depends on the individual thermal conductivity of the constitutive phases and on their distribution. In the case of higher contents of additive, the amount of glassy phase in the grain-junction is higher which results in a decreasing of the overall thermal conductivity. Thus, the thermal conductivities of samples with 15 % additive are lower than for samples with 10 % additive because of the higher amount of glassy phase in the grain-junction. In addition, the higher the amount of additive is, the higher is

the possibility for dissolution of Al and O into the Si_3N_4 structure. Measurement of the lattice parameter of bodies sintered at 1650 °C shows that pure Si_3N_4 possesses an a -value of 0.759 nm, which increases to 0.7601 and 0.7603 nm for bodies with 10 and 15 % of additive, respectively. The impurity atoms act as scattering centers, lowering the efficiency of phonon motion.

High temperature measurements of the thermal diffusivity for a sample sintered at 1650 °C is shown in Fig. 4. With increasing temperature, the thermal diffusivity decreases. The scattering of the lattice vibrations becomes more pronounced with increasing temperatures; hence the thermal diffusivity diminishes with increasing temperature.

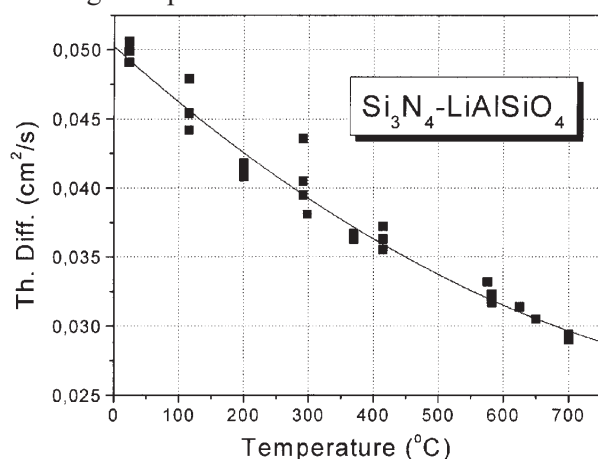


Fig. 4. Temperature dependence of the thermal diffusivity of a Si_3N_4 ceramic sintered with 10 wt.% additive.

red at 1650 °C is shown in Fig. 4. With increasing temperature, the thermal diffusivity decreases. The scattering of the lattice vibrations becomes more pronounced with increasing temperatures; hence the thermal diffusivity diminishes with increasing temperature.

CONCLUSIONS

Pressureless sintered Si_3N_4 ceramics were prepared with a Li-exchanged zeolite additive. The maximum thermal conductivity was obtained for ceramics sintered with 10 % additive. Samples sintered with 10 and 15 % additive obtained a density higher than 98 % of the theoretical density. The material with the lower amount of additive exhibits a slightly coarser microstructure. A higher amount of additive results in higher dissolution of Al and O into the Si_3N_4 structure. According to the obtained results, the dissolution of impurity atoms has a more pronounced influence on the thermal conductivity than on the microstructural differences.

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ИЗВОД

ТОПЛОТНА ПРОВОДНОСТ СИЛИЦИЈУМ-НИТРИДНЕ КЕРАМИКЕ
СИНТЕРОВАНЕ УЗ ПРИСУСТВО Li-ИЗМЕЊЕНОГ ЗЕОЛИТА

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Испутиван је утицај температуре на топлотну проводност силицијум-нитридне керамике синтероване у присуству Li-измењеног зеолиита. Највећа проводност је остварена за керамику синтеровану помоћу 10 % адитива. Постигнута је комплетна фазна трансформација α у β форму силицијум-нитрида на 1650 °C и теоријска густина већа од 98 %. Резултати су показали да се јони алуминијума и кисеоника из адитива растварају у решетки β -силицијум-нитрида и да делују као центри фононоског расипања, и тиме умањује топлотну проводност материјала.

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