

Fracture toughness of Silicon nitride

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Abstract. This paper deals with toughness of Si_3N_4 materials that was pressurelessly sintered with two different additives, LiYO_2 and LiAlSiO_4 respectively. The influence of types as well as additive amounts have been studied on densification, phase transformation and microstructure development in order to clarify their effect on toughness of silicon nitride ceramics.

Introduction

Silicon nitride ceramics are the most promising material for engine components due to high strength and high fracture toughness. Typically Si_3N_4 is densified by employing various mixtures of additives that, in combination with the surface SiO_2 on the silicon nitride particles, results in the densification and phase transformation. The liquid phases formed during densification provide a media for the growth of prism-shaped $\beta\text{-Si}_3\text{N}_4$ grains [1, 2]. These elongated grains, in turn, act as a reinforcing phase that promotes crack bridging processes and toughens the ceramics, contrary to $\alpha\text{-Si}_3\text{N}_4$ which usually has equiaxed grain morphology and as a consequence poor toughness. On the other side, α -structure had much higher hardness (Vickers microhardness) than the β -structure [3], and that is why α -to $\beta\text{-Si}_3\text{N}_4$ transformation during the liquid phase sintering leads to decreasing of hardness of ceramic materials. These facts are the reason why it is very important to control the microstructure that is able to maintain high hardness and at the same time to increase fracture toughness. There is nowadays ongoing searching for production processes on the basis of low-cost Si_3N_4 powder as well as sintering additives that are equally inexpensive and enable low sintering temperatures. Additives that can satisfy this criterion are LiYO_2 and Li-exchanged zeolite because they enable a substantial reduction in the processing temperature while at the same time the intergranular phase can be tailored by a partial evaporation of Li_2O [4,5,6]. In this paper the relationship between additive content, microstructure development and fracture toughness of liquid-phase sintered $\text{Si}_3\text{N}_4\text{-LiYO}_2$ and $\text{Si}_3\text{N}_4\text{-Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ceramics are discussed.

Experimental

The starting material used for 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. 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 additives used in the present work are Li-exchanged zeolite with a composition corresponding to β -eucryptite ($\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) as well as LiYO_2 . The additives were homogenized with the Si_3N_4 powder by attrition milling in isopropanol. Samples composition containing 5, 10 and 15 wt% of both additives were prepared. Green pallets were obtained by applying cold isostatic pressing at 240 MPa. Sintering was accomplished in a (gas pressure) furnace with graphite heating element in a nitrogen atmosphere of 0.1 MPa. The range of sintering temperatures investigated was 1200-1700 °C. Bulk densities were measured by the Archimedes method using distilled water. Microstructural observation of polished and plasma-etched specimens was conducted by scanning electron microscopy (SEM).

Fracture toughness (K_{IC}) was determined by using the indentation method. After polishing to a 1 μm finish, 12 Vickers indentations per specimen are introduced under a load of 50 N. A formula valid for semi-circular crack systems [7] was used to calculate K_{IC} from the lengths of edge cracks and indentation diagonals:

$$K_{IC} = 0.016 \cdot \sqrt{\frac{E}{H}} \cdot F \cdot L^{\frac{3}{2}} \quad (1)$$

where E = Young's modulus, taken as 300 GPa for Si_3N_4 ceramics, H = Vickers hardness (GPa). F = Load (N), L = Crack length (μm)

From the same experiments, the hardness is calculated by the formula given below:

$$H = 1.8544 \cdot \frac{F}{d_H^2} \quad (2)$$

where d_H = diagonals of Vickers indentation (μm).

Results and discussion

The present study shows that the phase transformation and densification do not have a straightforward relationship with each other. This is illustrated in Fig. 1, where the extent of densification and $\alpha \rightarrow \beta$ phase transformation is compared as a function of sintering temperature.

In both systems, there is a lag between densification and phase transformation showing that the major amount of transformation occurs in a later sintering stage. At 1400 °C, almost no transformation is observed, while more than 90 % and 80 % of the theoretical density have already been reached by applying both LiYO_2 and LiAlSiO_4 additive, respectively. At higher temperatures, the differences in the degree of densification and phase transformation become smaller in case of the LiYO_2 additive, while it is still present at 1700 °C in case of the LiAlSiO_4 additive.

Fig.1 depicts the relationships between densification and phase transformation as a function of sintering time for both types of materials. In both cases, the differences in the degree of densification and phase transformation diminish with prolonged heating time. Both processes are particularly fast in the LiYO_2 - Si_3N_4 system where the densification and phase transformation have gone to completion already after 60 minutes.

At higher sintering temperature a less viscous liquid phase is present resulting in faster $\alpha \rightarrow \beta$ phase transformation and higher densities.

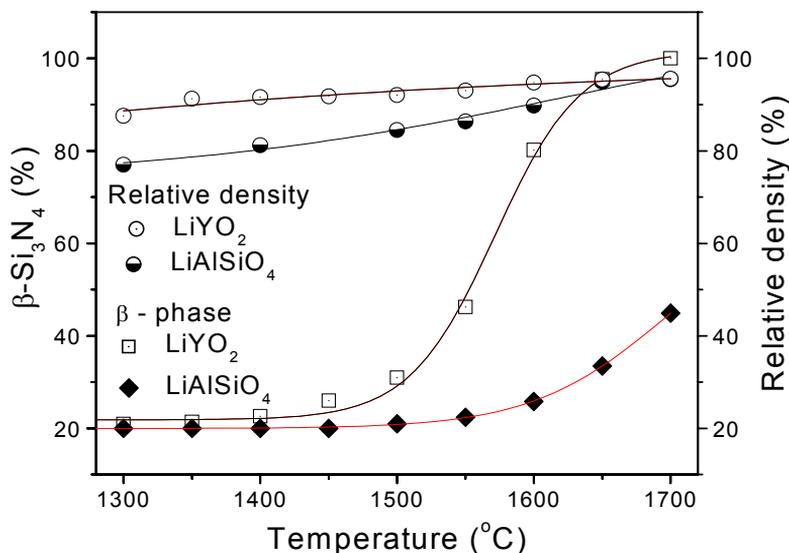


Fig. 1. The relationship between densification and phase transformation as a function of sintering time for $\text{LiYO}_2\text{-Si}_3\text{N}_4$ and $\text{LiAlSiO}_4\text{-Si}_3\text{N}_4$ additive systems (with 15 wt% of additive and at a sintering temperature of 1500 °C).

The hardness and indentation fracture toughness of both types of materials were measured and plotted against the annealing time (Fig.2). In both compositions, the fracture toughness and hardness initially increase with increasing annealing time, whereas decreasing hardness is observed in the case of annealing for at least 4 hours. Further increase of the sintering time leads to constant or decreasing hardness for both LiAlSiO_4 and LiYO_2 additives. The fracture toughness continuously grows with prolonged annealing time for the LiYO_2 additive, while this behavior is less pronounced in case of LiAlSiO_4 additive. In the latter case it becomes constant after 4 hours of annealing. Variations in the fracture toughness of Si_3N_4 materials sintered with LiYO_2 and LiAlSiO_4 additives should be related to the microstructures and glassy phase contents. Fracture toughness is improved when large elongated grains are formed in a fine grained matrix [8,9]. In the case of the LiYO_2 additive the fracture toughness increased with sintering time as a result of the continuous growth of elongated grains (Fig. 3). On the other hand, materials sintered with LiAlSiO_4 additive at 1500° C exhibit fine and predominantly equiaxed $\beta\text{-Si}_3\text{N}_4$ grains which do not change in size and shape during annealing (Fig. 4) resulting in a constant value of fracture toughness.

As mentioned before fracture toughness differs mainly with variations in the microstructure. The grain shape and size as well as the phase composition of the grain-boundary phase have a strong influence on fracture toughness. High fracture toughness of Si_3N_4 based ceramics could be explained on the basis of similar toughening mechanisms as in whisker reinforced composite materials (grain bridging, pull-out, crack deflection, and crack branching [10,11]). However, these toughening mechanisms are only active when the dominant fracture mode is intergranular.

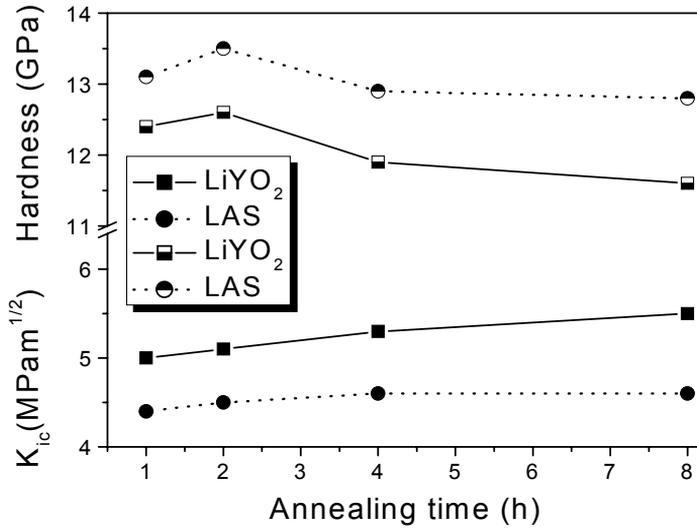


Fig. 2. Variation of fracture toughness and hardness as a function of the annealing time in Si_3N_4 ceramics sintered with LiYO_2 and LiAlSiO_4 additive systems, respectively at 1500°C .

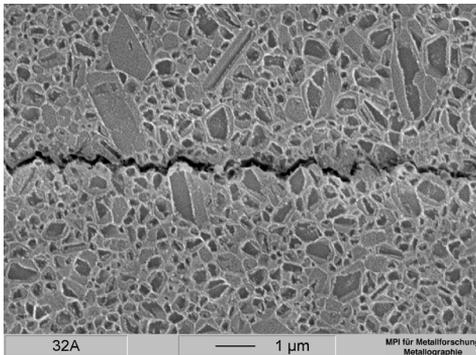


Fig. 3. Microstructure and crack path in Si_3N_4 ceramic sintered with 15 wt% of LiAlSiO_4 additive at 1500°C for 8 h.

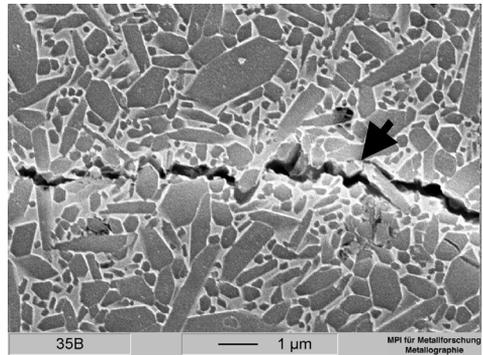


Fig. 4. Microstructure and crack path in Si_3N_4 ceramic sintered with 15 wt% of LiYO_2 additive at 1600°C for 8 h. The crack is bridged by an elongated grain (arrow,) which was pulled out of the matrix on the upper side of the crack as the crack opened.

The ratio of transgranular to intergranular fracture depends on the strength of both intergranular-phase and Si_3N_4 grains. In material with dominant intergranular fracture grain boundary appears to be weaker. On the other side, the strength of the grain-boundary phase is connected with the local residual stresses [12]. When the thermal expansion coefficient of the grain-boundary phase is higher than that of the Si_3N_4 grains, the grain-boundary phase after cooling remains under tensile stress and the fraction of intergranular fracture is high. As a consequence, the fracture toughness increases. In contrast, ceramics with a grain boundary phase under compression have low fracture toughness because of a higher amount of transgranular fracture [13]. The microstructural effects on the fracture toughness are well illustrated by crack paths generated by indentation, as shown in Figs. 3 and 4.

Materials with globular grain structure reveal crack propagation with few signs of toughening mechanisms other than crack deflection. However, the microstructures with elongated grains that can act as a reinforcing phase promote crack bridging mechanism and consequently toughen the ceramics, which was observed at higher temperatures. These mechanisms are operative in both systems with LiYO_2 as well as with LiAlSiO_4 additives, for samples sintered at $1600\text{ }^\circ\text{C}$, due to their similar microstructures.

The maximum values of fracture toughness obtained are 6.8 and $6.2\text{ MNm}^{3/2}$ for the materials sintered with LiYO_2 and LiAlSiO_4 additives, respectively, at $1600\text{ }^\circ\text{C}$ for 8 h .

Conclusions

LiYO_2 and LiAlSiO_4 act as efficient additives that promote densification and the anisotropic grain grow which enhanced fracture toughness. Microscopy studies of crack path in densified silicon nitride ceramics reveal that pullout, crack bridging and crack deflection are the main observed mechanisms. The appearance of toughness mechanisms is attributed to the needle-shaped $\beta\text{-Si}_3\text{N}_4$.

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