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Pressureless sintering of silicon nitride with lithia and yttria

B. Matovic, G. Rixecker*, F. Aldinger

Max-Planck Institut für Metallforschung and Institut für Nichtmetallische, Anorganische Materialien der Universität, Heisenburgstrasse 5, Stuttgart 70569, Germany

Abstract

Pressureless sintering of Si_3N_4 with additives from the Li_2O–Y_2O_3 system was investigated. $LiYO_2$ and equimolar mixtures of $Li_2O+Y_2O_3$ were added to Si_3N_4, respectively. The degree of densification, phase transformation, sample shrinkage and weight loss were measured as a function of the type of additives and the sintering temperature. The results revealed that heterogeneity of the liquid phase formed in the case of the separate oxide additions leads to nonuniform densification and lower of $\alpha \rightarrow \beta$ transformation rates in comparison to the $LiYO_2$ additive. Hence $LiYO_2$ is a more effective sintering additive than a mixture of the oxides.

Keywords: Liquid phase sintering; $LiYO_2$; Si_3N_4; Sintering

1. Introduction

Silicon nitride has been investigated intensively due to its promising potential as a high-temperature structural material.[1] However, densification of pure Si_3N_4 powder compacts is inhibited by the strongly covalent character of the Si–N bond, which results in an extremely low self diffusivity of Si_3N_4.[2] Hence, high density Si_3N_4 can only be obtained by addition of sintering additives. Various types of sintering additives have been used which react with the adherent silica on the powder surface of Si_3N_4 to form a eutectic melt and thus promote liquid phase sintering. The liquid acts as a medium for mass transport during densification. The additives, however, remain as glassy or crystalline grain boundary phases that deteriorate the high-temperature properties of the final products.[3] Some of the most common sintering additives are MgO, Y_2O_3 and $Y_2O_3+Al_2O_3$ in combination.[4,5] Y_2O_3 as an additive leads to excellent mechanical properties at room temperature as well as at elevated temperatures.[6] Furthermore, it enhances the growth of elongated β-Si_3N_4 grains.[3] However, yttria is not overly beneficial to the kinetics of densification because of the resulting high melting point and viscosity of the glass. Therefore, pressureless sintering of Si_3N_4 requires the addition of a less refractory oxide. Since the viscosity of the liquid phase becomes very low in the presence of Li_2O, its combination with Y_2O_3 may be an effective sintering additive for Si_3N_4. In comparison to mixtures of lithia and yttria, $LiYO_2$ has some advantages such as smaller susceptibility to hydrolysis and a lower vapor pressure than Li_2O. In addition, less problems with the homogeneity of the powder mixtures are to be expected. Some reports on the use of $Li_2O+Y_2O_3$ as sintering additives for AlN exist in the literature.[7,8] However, no work has yet been done on pressureless sintering in the systems Si_3N_4–$LiYO_2$ and Si_3N_4–Li_2O–Y_2O_3.

2. Experiment

Two different Si_3N_4/additive mixtures, M1 and M2, were fabricated and tested. Each composition was formulated based on an addition of 10 and 15 wt.% of additives from the Li_2O–Y_2O_3 system (Table 1). In the case of mixture M1, the additive consisted of lithia and yttria in a molar ratio of 1:1. Mixture M2 was prepared by using previously synthesized $LiYO_2$ as the sole additive. The $LiYO_2$ was synthesized by mixing as-received Y_2O_3 and Li_2CO_3 powders and calcining at 1400 °C for 4 h.

A commercially available Si_3N_4 powder was used as the starting powder (SILZOT HQ, SKW-Trostberg, Germany; 80% α-phase content, average particle size of 1.7 μm, specific surface area of 3.2 m^2/g, impurities (in wt.%) : Fe <0.04, Al <0.1, O <0.5, SiC <0.4, free Si <0.5).

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* Corresponding author.
E-mail address: rixecker@aldix.mpi-stuttgart.mpg.de (G. Rixecker).

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The mixtures (Table 1) were prepared by attrition milling for 4 h in isopropanol, using Si_3N_4 milling media. After drying, green body compaction was carried out by cold isostatic pressing at 240 MPa. A relative density of about 57% was obtained. Pushrod dilatometry (Theta Industries, USA) was used to measure the shrinkage behavior of green bodies under nitrogen atmosphere at a heating rate of 5 K/min from room temperature to 1500 °C. The pressed samples were placed in a covered BN crucible, and sintering was accomplished in a gas pressure furnace (FCT, Germany) under 0.1 MPa nitrogen atmosphere. A heating rate of 10 K/min was used for all sintering runs. Experiments were conducted from 1550 to 1700 °C with a soaking time of 5 min. Different annealing times in the range of 5–240 min were used at 1600 °C only.

Table 1
Chemical composition of the starting materials (wt.%)

Mixture	Si_3N_4	Li_2O	Y_2O_3	$LiYO_2$
M1	90	1.11	8.89	–
	85	1.67	13.33	–
M2	90	–	–	10
	85	–	–	15

X-ray diffraction (XRD) was used to evaluate the weight fractions of the α-Si_3N_4 and β-Si_3N_4 phases, by a calculation based on the method proposed by Gazzara and Messier.[9] Bulk density was measured by the liquid displacement technique. The mass loss of the specimens was also followed. In the case of mixture M1, the total weight loss upon sintering is calculated after subtraction of the weight loss due to thermal dissociation of Li_2CO_3. Linear shrinkage was recorded by measuring the heights of the green and sintered bodies. Scanning electron microscopy (SEM) analyses were carried out on polished and plasma etched surfaces of samples using a JEOL 6300F microscope at 3 kV accelerating voltage.

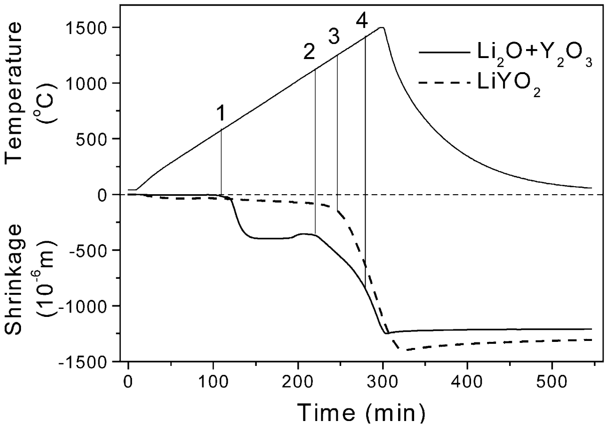


Fig. 1. Length change of Si_3N_4 green bodies with 10 wt.% of additives ($LiYO_2$ and equimolar mixture of $Li_2O+Al_2O_3$, respectively) between room temperature and 1500 °C.

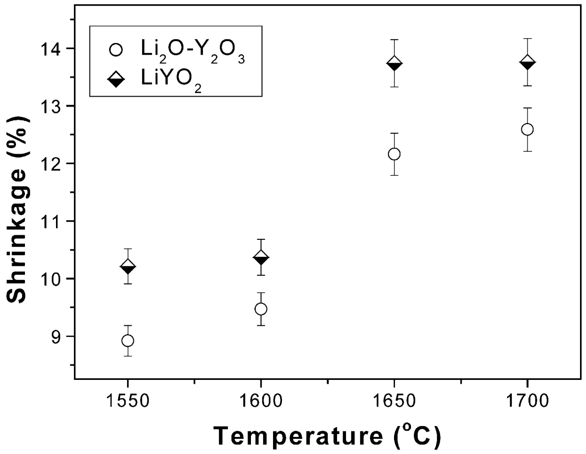
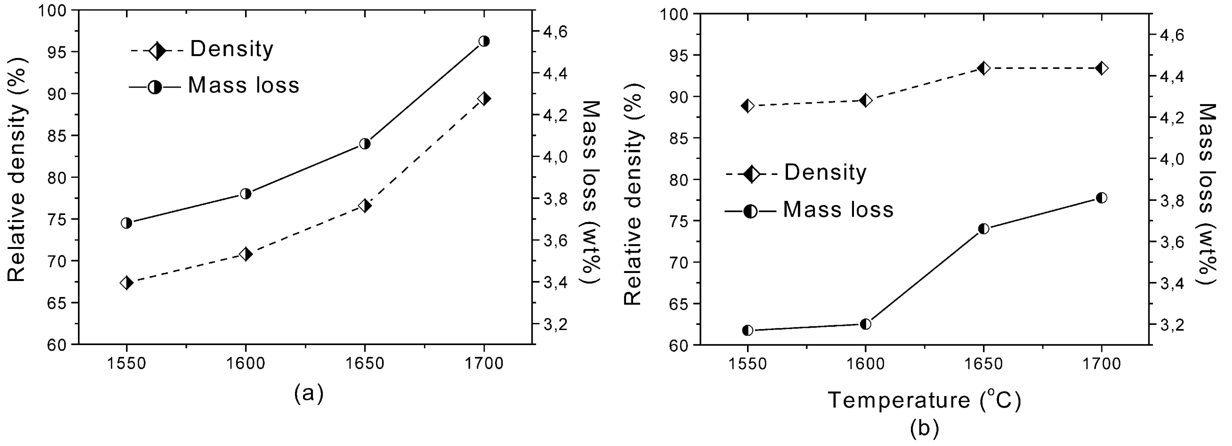


Fig. 2. Linear shrinkage of Si_3N_4 green compacts with 10% of additive (◆-$LiYO_2$, ○-Li_2O–Y_2O_3) after heat treatments at 1550-1700 °C for 5 min.



(a)

(b)

Fig. 3. Plot of relative density and weight loss versus temperature for pressureless sintered Si_3N_4 with 10 wt.% of additives: (a) Li_2O-Y_2O_3 and (b) $LiYO_2$. The soaking time at the temperatures indicated was 5 min.

3. Results

The dilatometric data (Fig. 1) show the densification shrinkage profiles of pressureless-sintered Si_3N_4 using the M1 and M2 additives to be significantly different. In case of the additive mixture M1, shrinkage first occurs at 575 °C (point 1) and, after a plateau, proceeds at 1125 °C. For the $LiYO_2$ additive (M2) the shrinkage curve has a sigmoidal shape. Shrinkage starts at about 1250 °C and proceeds rapidly above 1350 °C. At 1500 °C, the total linear shrinkage is about 9.5% and 11% for M1 and M2 samples, respectively.

Upon short-time sintering at higher temperatures, the length change is also more pronounced in M2 samples (Fig. 2).

Values of relative density and weight loss are shown in Fig. 3. For both M1 and M2 the relative densities increase with temperature up to 1700 °C. Samples with $LiYO_2$ addition (M2) exhibit higher densities than samples with $Li_2O + Y_2O_3$ additions. For sintered Si_3N_4 with additions of $YAlO_3$ and $Y_2O_3 + Al_2O_3$, similar behavior has been reported in the literature.[10] The weight loss, on the other hand, is higher for the additive composition M1.

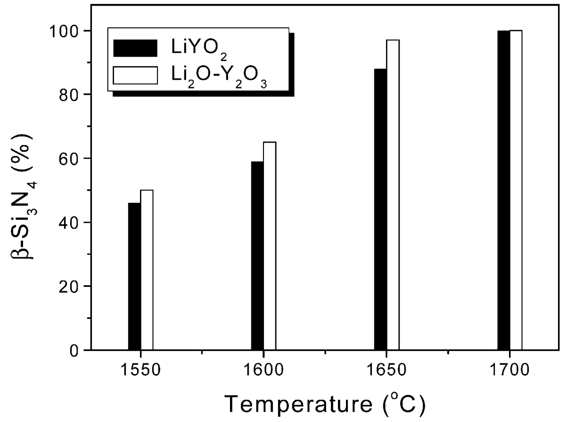


Fig. 4. Evolution of β-Si_3N_4 phase content as a function of sintering temperature and additive composition. The soaking time at the temperatures indicated was 5 min.

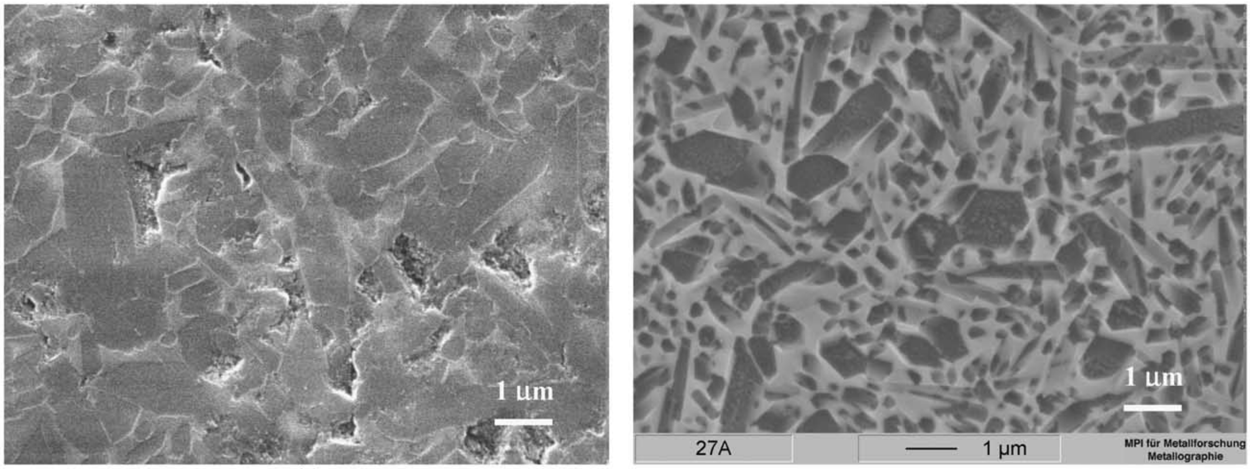
The same trend is obtained for samples sintered isothermally at 1600 °C with different soaking times. The density increase is more emphasized in case of the M2 composition, with 98% of the theoretical density being reached after 1 h of sintering (Table 2).

The transformation of α- to β-Si_3N_4 proceeds along with the sintering temperatures. The ratio $\beta/(\alpha + \beta)$ is shown in Fig. 4. At lower sintering temperatures, the amount of phase transformation is slightly higher for samples made from the M1 mixture.

Different microstructures of the sintered bodies are obtained for the two different compositions. The material produced from mixture M2 has a finer-grained microstructure with higher aspect ratios as compared to the sintered bodies prepared from mixture M1 (Fig. 5).

4. Discussion

The sintering additives determine the onset of liquid formation and the rate of densification during pressureless sintering. They also have an influence on the morphology of the Si_3N_4 grains and on the grain boundary phase. According to the shrinkage profile, the densification process in the case of mixture M1 has two steps. The first step (point 1) is related to the decarbonatization of Li_2CO_3. The second shrinkage step can be attributed to liquid formation (point 2). In the case of M2, the shrinkage starts later (point 3). The difference



(a) (b)

Fig. 5. SEM micrographs of Si_3N_4 materials pressureless sintered at 1600 °C for 4 h with 15 wt.% of additives: (a) Li_2O–Y_2O_3, (b) $LiYO_2$.

Table 2
Densities after sintering M1 and M2 compositions at 1600 °C with 10 and 15 wt.% of M1 and M2 additives (TD-theoretical density)

Time (min)	M1 $Li_2O+Y_2O_3$		M2 $LiYO_2$	
	Density (% TD)		Density (% TD)	
	10 wt.% additive	15 wt.% additive	10 wt.% additive	15 wt.% additive
60	83.8	89.1	90.4	98.0
120	89.5	90.7	93.1	98.3
240	91.4	92.8	95.3	98.1

in densification temperature between M1 and M2 can be explained by referring to the temperature of formation of the first liquid. This temperature is assumed to be lower in SiO_2–Li_2O–Y_2O_3–Si_3N_4 mixtures than in a SiO_2–$LiYO_2$–Si_3N_4 mixture.

Melting occurs at 1255 °C in the Li_2O–SiO_2 and 1650 °C in the SiO_2–Y_2O_3 systems.[11,12] In the Li_2O–Y_2O_3 system the lowest liquidus temperature is 1350 °C.[13] The low melting point in the Li_2O–SiO_2 system leads to the formation of a Li_2O-rich liquid in M1 materials, locally enhancing the densification before Y_2O_3 undergoes melting. This promotes differential sintering. In contrast, the liquid phase that is formed upon melting of the composition M2 is homogenous with an equimolar ratio of Li_2O and Y_2O_3.

The weight loss of Si_3N_4 with the composition M1 is higher as compared to M2. This is due to the high vapor pressure of Li_2O at relatively low temperatures (10^{-1} Pa at 1300 °C, 1 Pa at 1500 °C and 10 Pa at 1600 °C).[14] Li_2O is removed in gaseous form from the specimens at temperatures below 1600 °C, which contributes to the compositional change of the liquid phase during heating. This effect is also deleterious to sintering.

In contrast to the densification behavior, the α-Si_3N_4 to β-Si_3N_4 phase transformation is more rapid in the case of M1. Here the Li_2O-rich liquid reduces the viscosity locally which leads to an enhanced dissolution of Si_3N_4 at moderate temperatures already and to an accelerated solution-diffusion-precipitation process. In the case of composition M2, the improved homogeneity of the liquid leads to a more sluggish but also complete β-Si_3N_4 transformation.

The inhomogenity of the liquid phase results in some residual porosity which is distributed within the material sintered with the additive of composition M1 (Fig. 5a). This is due to the evaporation of the Li_2O-rich liquid. In contrast, samples prepared from composition M2 have a homogeneous distribution of elongated β-grains without porosity.

5. Conclusions

The sintering of Si_3N_4 with $LiYO_2$ and an equimolar mixture of $Li_2O+Y_2O_3$ as sintering additives has been studied. The results show that $LiYO_2$ has a more beneficial effect on sintering than the $Li_2O+Y_2O_3$ mixture. Using $LiYO_2$ leads to higher relative densities and less weight loss, as compared to samples sintered with the $Li_2O+Y_2O_3$ mixture. Also, the α- to β-Si_3N_4 phase transformation is complete in the system $Si_3N_4/LiYO_2$ additive. This leads to a rod-like microstructure which has potential for good mechanical properties.

The difference in sintering behavior occurs because of the heterogeneity of the liquid phase formed in the $Li_2O+Y_2O_3$ mixture-containing samples.

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