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REACTIONS RESPONSIBLE FOR MASS LOSS DURING PRESSURE LESS SINTERING OF Si₃N₄ CERAMICS WITH LiYO₂ ADDITIVE

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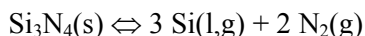
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Abstract

The reactions were investigated with emphasis on the mass loss during pressureless sintering of Si₃N₄ ceramics without powder bed. A Si₃N₄ powder compacts with LiYO₂ additive were heat-treated at different temperatures under the pressure of N₂ of 0.1 MPa. The mass loss increased with increasing temperature as well as with increasing additive content. It is expected that the major mass loss should be caused by volatilisation of lithia due to its high vapour pressure. However, the results of the chemical analysis of the samples are in contradiction with this assumption.

Introduction

Since silicon nitride is a covalently bonded solid compound, the self-diffusivities of Si and N in pure Si₃N₄ are very small [1], therefore it cannot be sintered to full density without additives which form liquid phase upon firing [2]. Thus, liquid-phase sintering is the only method applied for densification of Si₃N₄ ceramics. However, during sintering loss of mass occurs, which is common phenomenon with Si₃N₄ [3]. Si₃N₄ is not getting melt; it decomposes under 0.1 MPa N₂ at 1880° C. The reaction during decomposition according to the formula [4]:



is of increasing importance above 1500° C. In addition, it should be born in mind that sintering additives, which form silicate or oxinitride liquid during the sintering evaporate, as well [5]. The mass loss leads unavoidably to composition change. Moreover, it disturbs the consolidation, causes creation of pores and hence degrades the mechanical properties of the ceramics [6]. For these reasons it is very important to decrease mass loss as much as possible.

The objective of the present work is to examine the mass loss during the pressureless sintering of Si₃N₄ ceramics with LiYO₂ additive.

Experimental

The starting powders were commercial Si₃N₄ (Silzot HQ) and homemade LiYO₂ powder. Si₃N₄ powders with 5, 10, 15 and 20 wt% LiYO₂ were prepared. Sintering was accomplished in a graphite-heated furnace (FCT, Germany) under 0.1 MPa nitrogen atmosphere, in the temperature range from 1550° to 1700°C, with a heating rate of 10 K/min. Chemical analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES, Spectro, Germany) was used to quantify

the Li content of samples after various heat treatments. Mass loss (Δm) of the specimens was calculated according to the following formula: $\Delta m = [(m_G - m_S) \div m_G] \cdot 100$, where m_G = mass of the green body.

Results and Discussion

The mass loss upon sintering with different amounts of LiYO_2 additive is shown in Fig. 1. The loss increased with increasing temperature, as well as with increasing additive content. Larger amount of additive means the larger amount of the liquid phase which in turn, leads to more intensive evaporation. At 1550°C total amount of additive is converted into liquid forming Si-Li-Y-O-N melt. It can be assumed that the vaporization of liquid originates from the vaporization of each of its constituents. Also, reactions between Si_3N_4 and the glassy phases are responsible for the instability of Si_3N_4 ceramics at elevated temperatures. However, Y_2O_3 is stable based on thermodynamic calculations [7]. In contrast, the high vapour pressure of lithia causes its easy evaporation as mentioned earlier.

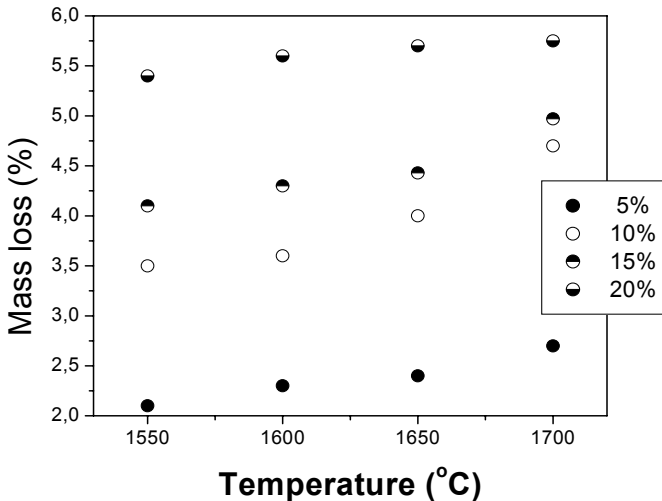
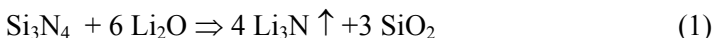


Fig. 1. Mass loss as a function of temperature for Si_3N_4 compacts with different amounts of LiYO_2 additive during sintering with a holding time of 5 min.

It is expected on the basis of the vapour pressure data for Li_2O [8] that lithia should volatilise completely at higher temperatures. However, the results of the chemical analysis of the samples are in contradiction with this assumption (Fig.2). With increasing the LiYO_2 additive the Li_2O content decreases significantly with temperature. However, Li_2O is still present after long annealing times, at all sintering temperatures.

It is known that lithia reacts with Si_3N_4 to give a very volatile lithium nitride (Li_3N) according to the reaction [9]:



The silica formed in reaction (1) combines with unreacted Si_3N_4 [10] according to the reaction (2)



This reaction is well known from thermodynamics and experimental work on the Si-N-O system [11].

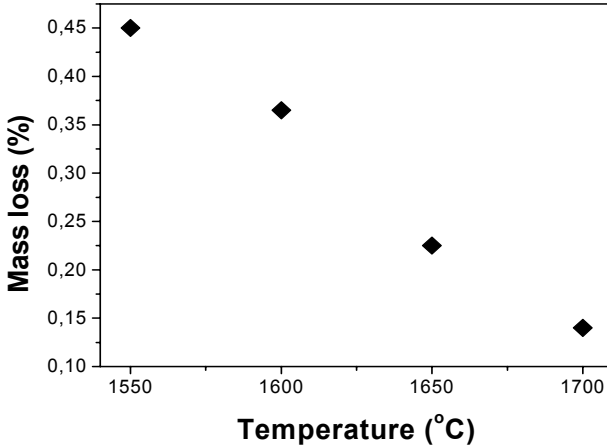


Fig. 2. Mass loss of lithium in Si_3N_4 samples sintered at various temperatures; annealing time is 4 h.

Conclusion

On the basis of the experimental results, it is to be concluded that the major part of the mass loss of the Si_3N_4 ceramics during sintering is a consequence of interaction of silicon nitride with silica, according to the reaction (2).

Acknowledgement

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