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Sintering of silicon nitride with Mg-exchange zeolite additive

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The possibility of using Mg-exchanged zeolite as additive for densification of Si_3N_4 ceramic was studied. The zeolitic precursor was previously heated at 800 °C to obtain an amorphous powder with a composition corresponding to $MgO{\cdot}Al_2O_3{\cdot}nSiO_2$. The powder was mixed with Si_3N_4 and the sintering additive was homogenized by attrition milling in the presence of isopropanol and finally compacted by cold isostatic pressure. Pushrod dilatometry was used to measure the shrinkage behaviour of green bodies under a nitrogen atmosphere from room temperature to 1500°C. The chemical reactions and phase evolution during pressureless sintering were also followed by means of X-ray and dilatometric analysis. Results show that the first liquid forms as low as 1070 °C, sharing in a significant reduction of sintering temperature. The final phase composition obtained at 1500 °C consist of crystalline α-Si_3N_4 phase which is emended in oxynitride glassy phase The results show that the Mg-exchanged zeolite is a very effective low–temperature sintering additive for silicon nitride.

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1. Introduction

Silicon nitride based ceramics have excellent chemical, physical, mechanical, and tribological properties [1,2]. Because of its covalent bonding and low diffusivity Si_3N_4 cannot be densified by common dry sintering [3]. Thus, sintering additives are precondition for dense Si_3N_4 ceramics. Common sintering additives contain rare earth oxides (R_2O_3, R = Y, Ce, Yb, Lu), which are expensive and require high sintering temperatures. The applications of silicon nitride ceramics are still limited due to the high cost of both raw materials and production processes [4,5]. Therefore, studies on low-melting and low-cost additives are one main emphasis of ongoing research efforts.

Since melting temperatures are relatively low in the magnesium alumosilicate (MgAS) system, suitable sintering additives may be expected to exist in this system. Moreover, most MgO – Al_2O_3 – SiO_2 glasses can be crystallized under proper heat treatment conditions [6], which may allow ceramics with favorable thermo-mechanical properties to be obtained in spite of the low sintering temperatures. Magnesium aluminum silicates (MgAS) have already been used for sintering of Si_3N_4 ceramics. The procedure described in [7] consisted of a mixture of MgO, Al_2O_3 and SiO_2, which then reacted with silica on the surface of Si_3N_4 to form MgAS liquid. In comparison, several advantages are expected if pre-reacted MgAS is used directly, such as smaller susceptibility to hydrolysis, lower vapor pressure of MgO at high temperature, and less problems with the homogeneity of the powder mixtures. MgAS compositions were successfully used as binders for silicon carbide fibers and in the matrix of silicon carbide-titania composites [8]. MgAS can be prepared from different sources, but the synthesis route used in the present study, which starts from ion-exchanged zeolites, has some benefits [9]. For example, it is a low-cost method leading to an amorphous phase with enhanced chemical reactivity as compared to crystalline phases. While one report on the use of an ion-exchanged barium- and lithium zeolite as a constituent of Si_3N_4 composite materials can be found in the literature [10,11], it seems that no work has been performed to-date on the pressureless sintering of Si_3N_4 with Mg-exchanged zeolite additives.

2. Experimental

For the sintering study a commercial Si_3N_4 (UBE) powder synthesized was used (Japan). Its characteristics, as supplied by the manufacturer, include a specific surface area of 3.2 m^2g^{-1}, mean particle size of D_{50} = 1.2 μm, Si_3N_4 phase composition of $\alpha/(\alpha+\beta)$ = 0.94. The Mg-containing additive powder was produced from a sodium aluminum silicate-type zeolite (A-zeolite, Birach Co., Bosnia and Hercegovina) via the substitution of Na by Li. The substitution was accomplished by a standard ion exchange procedure that was repeated eight times to ensure complete exchange of ions [12]. The phase analysis of the thermally treated material as well as the weight fraction of the α – and β – Si_3N_4 phases on the basis of a method proposed by Gazzara and Messier [13] were evaluated by XRD [12].

Samples were prepared by attrition-milling the Si_3N_4 powder with 10, 20 and 30 wt.% of this MgAS precursor. After 4 h, the isopropanol-based slurry was separated from the silicon nitride milling media by sieving and pre-dried in a rotating vacuum evaporator. After another drying step for several hours in a drying oven at 65 °C, the powders were sieved to obtain granules with a maximum size of 160 μm. Green body compaction was done by cold isostatic pressing at 240 MPa. The green density reached about 57 % of the theoretical density (T.D.) as calculated from the composition of the starting powder by the rule of mixtures. Pushrod dilatometry (Theta Industries, USA) was used to measure the shrinkage behavior of green bodies under a nitrogen atmosphere at a heating rate of 10 K/min from room temperature to 1500 °C.

3. Results and discussion

Densification is limited in silicon nitride ceramics in absence of the liquid phase. The onset of shrinkage is assumed to be related to liquid formation in the compacts. Dilatometric data (Fig. 1 and 2) show the shrinkage and shrinkage velocity. The maximum at 851 °C (point 1) is related to collapse of Mg-zeolite structure. The shrinkage first occurs at 1070 °C and accelerates somewhat at 1170 °C. However it increases dramatically at 1500 °C and levels off at 1500 °C after 55 and 40 minutes of isothermal annealing for samples with 10 and 30 wt% of additives, respectively.

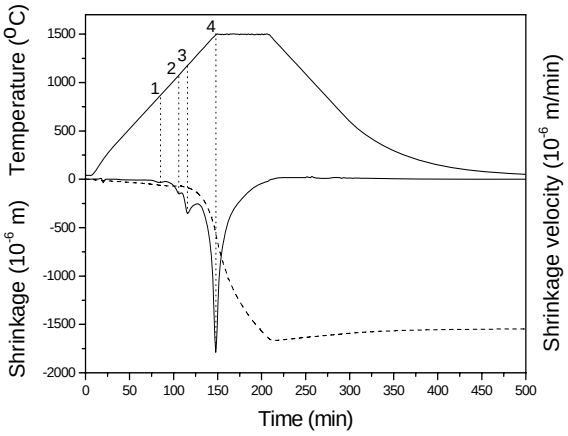

Fig. 1. Shrinkage (full line) and shrinkage velocity (dashed line) of a silicon nitride green body with 10% MgAS additive showing characteristic features at (1) 851 ℃, (2) 1070 ℃; (3) 1169 ℃ and (4) 1500 ℃.

The phase evolution of samples with 10 wt% of MgAS additive after heat treatments at temperatures between 900° and 1500°C for 5 min is shown in Fig. 1. The main crystalline phase is α–Si_3N_4 for all stages of annealing. At 900°C the initial MgAS sintering additive is present in an amorphous state due to collapse of Mg-zeolite structure at 850 °C (Fig. 1 and 2). At 1300°C the β–Si_3N_4 has completely disappeared indicating its dissolution into the liquid phase. Thus, resulting liquid belongs to Mg-Al-Si-N-O system. Also, the presence of a new phase (SiO_2) is associated with excess silica, which had crystallized from the liquid during cooling.

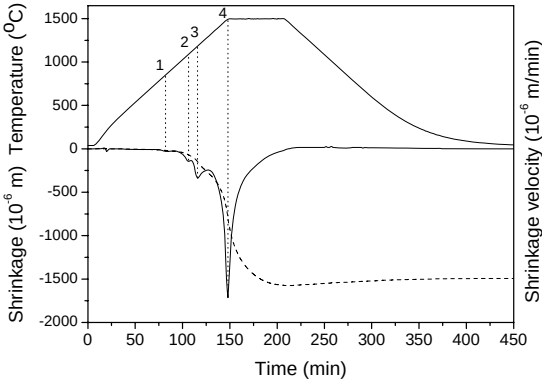

Fig. 2. *Shrinkage (full line) and shrinkage velocity (dashed line) of a silicon nitride green body with 30% MgAS additive showing characteristic features at (1) 850 ℃, (2) 1070 ℃; (3) 1171 ℃ and (4) 1500 ℃.*

According to the phase diagram MgO-Al_2O_3-SiO_2 the lowest eutectic temperature in the system is 1345 °C [14]. However, the overall liquid forming temperature is lower than the nominal eutectic temperature because of the present nitrogen in the liquid phase. This confirms that MgAS acts as a very good solvent for Si_3N_4, which is also a prerequisite for a good sintering additive.

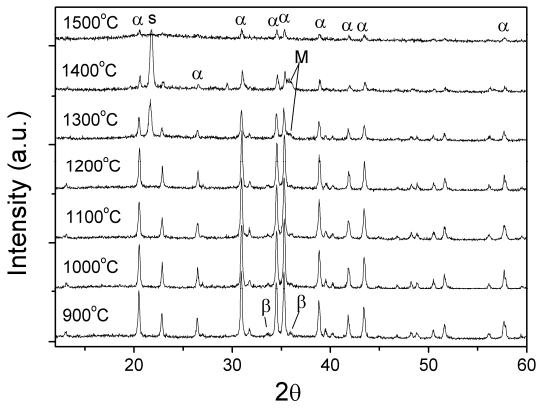

Fig. 3. Phase evolution during heating of mixture (Si_3N_4/MgAS) at different temperature for 5 minutes of soaking time. (α-Si_3N_3, β-Si_3N_3, S-SiO_2, M-Mg-Al-Si-N-O).

XRD pattern shows remarkable decreasing of the diffraction lines intensities, which can be explained by the increasing of liquid amount. Therefore, the total liquid

content increases substantially and at 1500 °C, which upon cooling formed amorphous glassy phase. At this temperature the crystalline α-Si_3N_4 phase, traces of silica as well as, oxynitride glassy phase are the only present phases. This phase compositions indicate that no significant transformation takes place up to 1500 °C. In the other side, having in mind that α–Si_3N_4 has a very high hardness as does magnesium silicon oxynitride glassy phase [2], the final ceramics might have promising mechanical properties in spite of the low sintering temperature.

5. Conclusions

Dilatometric properties of the system Si_3N_4 and of a zeolite-derived magnesium aluminium silicate (MgAS) were investigated. Onset of shrinkage first occurs at 1070 °C what is related to liquid formation in the mixture compacts.

The used additive forms a liquid that acts as a very good solvent for Si_3N_4 resulting in silicon oxynitride glassy phase, which in turn allows decreasing the sintering temperatures at as low as 1500 °C. It was found that the transformation from α-Si_3N_4 to β-Si_3N_4 does not take place before 1500 °C. Composition of material sintered at 1500 °C has potential for enhanced hardness.

Acknowledgments

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References

[1] G. Ziegler, J. Heinrich, G. Wötting, J. Mater. Sci. **22,** 3041 (1987).
[2] G. Petzow, M. Herrmann, in Structure and Bonding, Springer-Verlag, Berlin. **102**, 51 (2002).
[3]
[4] F. L. Riley, J. Am. Ceram. Soc. **83,** 245 (2000).
[5] M. Hermann, I. Schulz, J. Hintermayer, Fourth Euro-Ceramics **2**, 211 (1995).
[6] Y. Pan, L. Baptista, J. Eur. Ceram. Soc. **16,** 1221 (1996).
[7] X. Liu, Z. Huang, Q. Ge, X. Sun, L. Huand, J. Eur. Ceram. Soc. **25,** 3353 (2005).
[8] Z. Panek, J. Mater. Sci. **29,** 5383 (1994).
[9] V. Dondur, R. Dimitrijevic, J. Solid State Chem. **63,** 46 (1986).
[10] S. Boskovic, Dj. Kosanovic, V. Dondur, R. Dimitrijevic, Ceram. Int. **26,** 33 (2000).
[11] B. Matovic, G. Rixecker, F. Aldinger, J. Eur. Ceram. Soc.
[12] V. Dondur, N. Petranovic, R. Dimitrijevic, Mater. Sci. Forum **204,** 91 (1996).
[13] C. P. Gazzara, D. R. Messier, Am. Ceram. Soc. Bull. **56,** 777 (1977).
[14] M. Keith, J. Schairer, J. Geol. **60,** 182 (1952).

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