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Sintering of Si_3N_4 in the presence of additives from Y_2O_3–SiO_2–Al_2O_3 system

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The sintering process of Si_3N_4 in the presence of a liquid phase from the Y_2O_3–SiO_2–Al_2O_3 system was investigated. The starting composition of liquid phase was varied according to data in the phase diagram of the Y_2O_3–SiO_2–Al_2O_3 system, in order to lower the temperature of liquid formation because it might exhibit an influence on the sintering behaviour of Si_3N_4. Densification as well as phase analysis were followed as a function of composition and the amount of liquid phase, both in the sintered and in hot pressed samples.

1. Introduction

It is known [1] that very good quality ceramics can be produced using mixtures of $Y_2O_3 + Al_2O_3$ as a sintering aid. However, there are also data [2] showing that very good materials based on Si_3N_4 can be obtained using mixtures $Y_2O_3 + SiO_2$ and $Y_2O_3 + SiO_2 + Al_2O_3$ to promote densification, during hot pressing. However, there are no data on the sintering course and the possibility of pressureless sintering of the above mentioned materials. We undertook this study to investigate the influence of additives from Y_2O_3–SiO_2–Al_2O_3 and Dy_2O_3–SiO_2–Al_2O_3 systems on the densification during hot pressing and pressureless sintering of Si_3N_4.

2. Experimental details

Starting α-Si_3N_4 powder, LC 12, Starck production was used. To that powder additives designated as 3, 3a, 5, 5a and 8, 8a, were added in the concentration range 10–20%. The additive compositions are given in Table I.

Since the phase diagram of Dy_2O_3–Al_2O_3–SiO_2 is not known, the compositions calculated correspond to molar ratios of components obtained from the Y_2O_3–SiO_2–Al_2O_3 system for each point. Melting points of the additives with Dy_2O_3 are not known.

Homogenization of the host powder with additives was performed in a vibratory WC mill, for 2 h. Isostatically pressed samples under 147 MPa, were sintered and hot pressed at 1780° C.

3. Results and discussion

The common way to enhance densification, from series of published papers, [3–5] is to use a $Y_2O_3 + Al_2O_3$ mixture to enhance rearrangement, whereby, the content of either Y_2O_3 or Al_2O_3 were varied. This variation produces at the sintering temperature not only different amounts of liquid phase but also produces liquid of different composition. We used as additives compositions of invariant points in the Y_2O_3–SiO_2–Al_2O_3 system (Fig. 1) which means that the composition of liquid was the same. It was only its amount which was varied during the sintering. The SiO_2 content in the starting powder ~3 wt %, was taken into consideration during the calculation of the additive compositions.

Al_2O_3 is added to Y_2O_3 usually to lower the temperature of liquid formation [3] in order to enhance densification. Al_2O_3, namely brings about a viscosity decrease of the liquid.

In our case, as can be seen, the Al_2O_3 content of the additives does not vary too much, especially not in additives 5 and 8, while the Y_2O_3/SiO_2 ratio varies from 2.6 to 0.7 respectively for additives 3, 5 and 8. (mol. ratio 0.7–0.2). Melting points of the additives used decrease with decreasing Y_2O_3/SiO_2 ratio (i.e. with increasing SiO_2 content), from 1600 to 1345° C. Besides, these additives were chosen because they offer the possibility to keep the Y_2O_3 level below 13% even if used in maximum concentration, to avoid the formation of $Y_2O_3 \cdot Si_3N_4$ phase, which can be easily oxidized [4].

Hot pressing of samples having 10% of additives was performed at 1780° C. Densities of hot pressed samples do not differ too much, e.g. they are 3.21; 3.23 and 3.20 g cm^{-3} for 3, 5 and 8 additive respectively.

X-ray analysis was used to identify the phases present in these samples (Fig. 2). Only β-Si_3N_4 was

TABLE I Composition of additives (wt %)

Additive	Dy_2O_3	Y_2O_3	Al_2O_3	SiO_2	T_m (° C)	Y_2O_3/SiO_2	Dy_2O_3/SiO_2
3	–	60	16.6	23.4	1600	2:6	–
5	–	45	24.5	30.5	1400	1:5	–
8	–	32	22.0	46.0	1245	0:7	–
3a	71	–	11.9	16.8	–	–	4:2
5a	57.4	–	18.9	23.6	–	–	2:4
8a	43.5	–	18.2	38.3	–	–	1:1

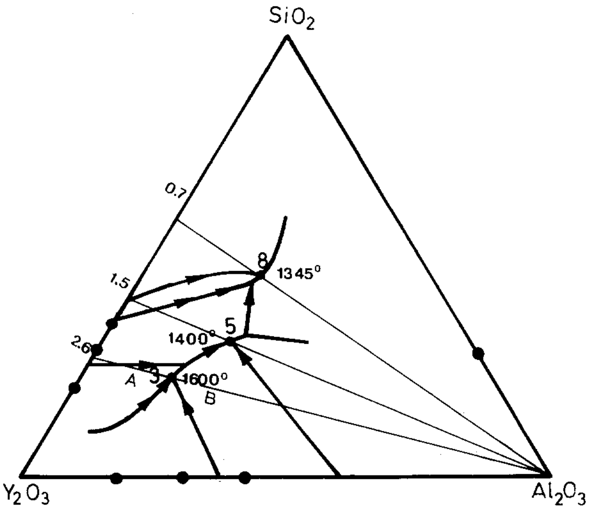

Figure 1 Compositions of additives from Y_2O_3–SiO_2–Al_2O_3 system [6].

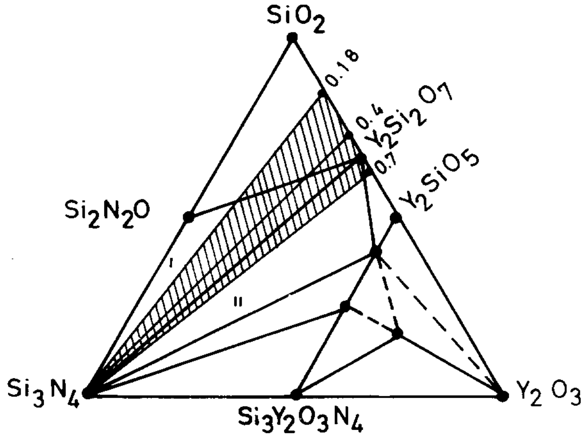

Figure 3 Si_3N_4–SiO_2–Y_2O_3 system [7] with additive range investigated.

present as a crystalline phase within the samples containing additives 3 and 5 with a Y_2O_3/SiO_2 ratio of 2.6–1.5, while with samples containing additive 8 (Y_2O_3/SiO_2 – 0.7), Si_2N_2O was detected in the addition. This is to be expected because, the composition of additive 8 is very close to the Si_3N_4–SiO_2 junction and the composition of the synthesized ceramics lies within the compatibility triangle I (Fig. 3).

Samples with additives 3a, 5a, and 8a, were hot pressed under the same conditions again with 10 wt % of additions. Densities obtained are 3.27; 3.22 and 3.17 for additives 3a, 5a and 8a respectively.

Pressureless sintering was carried out at 1780–1800° C with samples having 10, 15 and 20 wt % of additives. The density change with additive concentration is given in Fig. 4. Maximum densities are obtained with additive 3 having the highest melting temperature and the highest Y_2O_3/SiO_2 ratio. With additive 8 having the lowest melting temperature and the lowest Y_2O_3/SiO_2 ratio densities were very low and the open porosity was still present (Table II). X-ray analysis of sintered samples showed that besides β-Si_3N_4 lines, Y_2SiAlO_5N (N-α-wollastonite) was present. With samples sintered in the presence of additive 8, besides N-α-wollastonite, Si_2N_2O was present. The Y_2SiAlO_5N content is very small, but increases with increasing additive content in all samples. Bearing in mind that this phase (stable up to 1100° C) crystallizes very easily from these liquids, because its composition lies within liquid phase field, the increase of its concentration with increase of additive amount is not unexpected.

The Si_2N_2O content, too, increases with increasing amount of additive 8. This compound is a reaction product between α-Si_3N_4 and SiO_2 from liquid phase [9]. The degree of densification for samples containing additive 8 is low for several reasons. First, reaction of Si_2N_2O involves the starting α-Si_3N_4 component and SiO_2 from the liquid phase, which means that the liquid amount within these sample decreases due to chemical reaction development. This influences densification, as is well known. Besides, the density of the reaction product [–Si_2N_2O–] is lower than the one of Si_3N_4 which brings about the decrease of sintered samples overall density. Besides, judging by the SiO_2 content in the starting additive 8, this liquid may have the highest viscosity, independent of its melting point [8].

In the Fig. 5 one can find another proof that the lower viscosity liquid had a beneficial influence on densification in this case. Namely, these samples were obtained using additives having a constant Y_2O_3/SiO_2

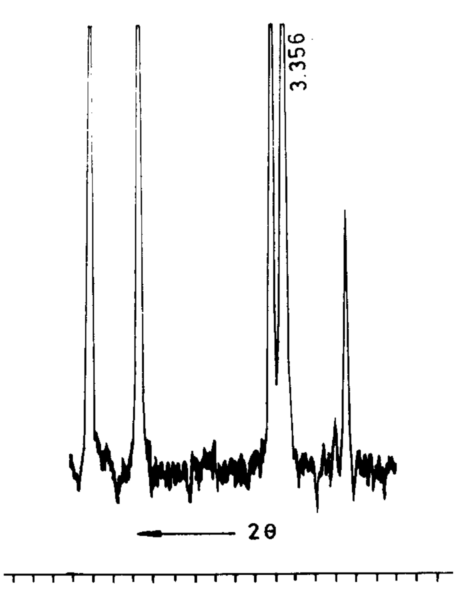

Figure 2 X-ray pattern of hot pressed sample with additive 8.

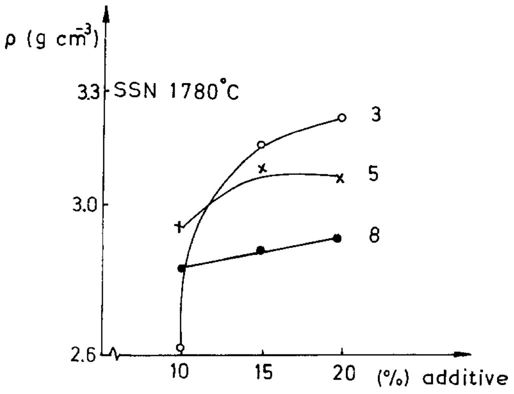

Figure 4 Density change with additive amount variation.

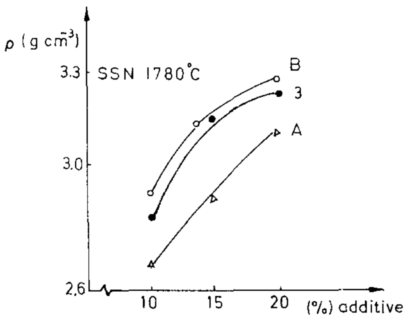

Figure 5 Density dependence on additive amount. Compositions of additives A, 3 and B, lie on the same line connecting Al_2O_3 corner and point 3, as given in Fig. 1.

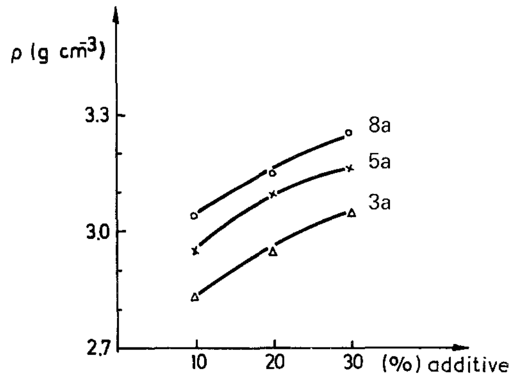

Figure 6 Density dependence on additive amount (3a, 5a, 8a).

ratio but different Al_2O_3 content as indicated in Fig. 1. Samples with additive B attained a higher degree of densification.

Samples sintered with additives 3a, 5a and 8a, achieved slightly higher densities as shown in Fig. 6. However, X-ray data of these samples show besides β-Si_3N_4, the presence of Y_2SiAlO_5N diffraction lines. In samples sintered with additive 5a and 8a, Si_2N_2O was detected in addition. N-α-wollastonite was present in samples in small amounts while the amount of Si_2N_2O increases in samples having additive 8a. This means that both additives 5a and 8a have a high amount of SiO_2 which enabled the formation of Si_2N_2O, contrary to system with Y_2O_3.

Properties of the synthesized materials were measured, and summarized in Table III. According to these data one can see that materials having good properties can be obtained using additives having Y_2O_3/SiO_2 ratio less than 2.6. The difference in properties of pressureless sintered and hot pressed materials are obvious but it is also evident that good quality material can be obtained under the described conditions, using additive 3 as the sintering aid.

Lower hardness comparing with hot pressing materials are the consequence of high liquid content. The very low hardness of sample containing additive 8 is besides, the consequence of open porosity, as well.

4. Conclusion

These results show that it is possible to synthesize materials from this system by pressureless sintering procedure. Keeping the Y_2O_3/SiO_2 ratio within the 2.6 and 1.5 limit one can synthesize single phase ceramics which can subsequently be heat-treated to crystallize the existing glass. Chemical reaction takes place with the additive having the lower Y_2O_3/SiO_2 ratio, which exhibits negative effect on densification during liquid phase sintering. It was found also, that the additive amount can be kept as low as 15% during pressureless sintering because already at 1780° C, open porosity was zero with additives 3 and 5. As far as additive 8 is concerned, one can imagine that good oxidation-resistant materials could be obtained with this liquid composition.

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TABLE II Density (ϱ) and open porosity (OP) in sintered samples

Additive concentration	Additives					
	3		5		8	
	ϱ ($g cm^{-3}$)	OP (%)	ϱ ($g cm^{-3}$)	OP (%)	ϱ ($g cm^{-3}$)	OP (%)
10	2.62	13.8	2.93	0.20	2.83	0.7
15	3.16	0	3.08	0	2.88	0.7
20	3.23	0	3.06	0	2.91	0.6

TABLE III Properties of hot pressed and sintered ceramics

Sample	ϱ ($g cm^{-3}$)	OP (%)	X-ray	H_v (MPa)	K_{IC} ($MN m^{-3/2}$)
HPSN					
10% 3	3.21	0	–	20050	6.7
10% 5	3.23	0	–	20850	6.6
10% 8	3.20	0	Si_2N_2O	20830	7.0
10% 3a	3.27	0	–	20949	6.69
10% 5a	3.22	0	Si_2N_2O	20050	6.8
10% 8a	3.17	0	Si_2N_2O	20318	7.53
SSN					
20% 3	3.24	0	Y_2SiAlO_5N	16000	6.6
20% 5	3.06	0	Y_2SiAlO_5N	13300	7.7
20% 8	2.91	0	$Y_2SiAlO_5N + Si_2N_2O$	10600	6.2

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