

High aspect ratio β - Si_3N_4 grain growth

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Abstract

It has been shown by others that high aspect ratio β - Si_3N_4 grains formed in-situ on sintering lead to high fracture toughness in Si_3N_4 ceramics. In this work α - Si_3N_4 powder was sintered at 1750°C for varying times with Y_2O_3 , La_2O_3 , SiO_2 , and CaO additives. The microstructure of the materials was examined by electron microscopy and microanalysis. The β - Si_3N_4 grain growth rate was controlled by diffusion through the liquid phase. A maximum aspect ratio of about 20 was observed for β - Si_3N_4 grains heated for 6 h and was dependent on the chemistry of the liquid phase present. The formation of high aspect ratio Si_3N_4 at a relatively low temperature and short sintering times is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aspect ratio; Grain growth; Microstructure-final; Si_3N_4

1. Introduction

Lange¹ showed that the fracture toughness of polycrystalline β - Si_3N_4 increased with grain length. Elongated grains up to 300 μm in length have been produced by gas pressure sintering at 2000°C for 8 h.² Both these works essentially referred to aspect ratio although they did not specifically state it. The increased aspect ratio of β - Si_3N_4 resulted in increased fracture toughness and a high Weibull modulus. A self-reinforced fibrous microstructure is preferable to one produced by adding, for example, SiC whiskers to increase toughness, because of the inherent hazards in handling whiskers and the high processing costs.³ In previous work,⁴ elongated β - Si_3N_4 grains were obtained in a SiC-containing composite which had additions of Y_2O_3 , La_2O_3 , and SiO_2 , by heating to 1750°C, without any dwell at temperature. This same system has been investigated extensively,^{5–8} and further work has been carried out here to study the formation of elongated grains in this system. The addition of CaO to Y_2O_3 - MgO - Si_3N_4 system has been shown to produce β - Si_3N_4 grains with an aspect ratio of about 5.⁹ Therefore, in the present work additions of CaO to the Y_2O_3 - La_2O_3 - Si_3N_4 system (free of SiC)

were investigated to assess its influence on β - Si_3N_4 aspect ratio. Most of the literature work described above was performed at high temperatures (> 1800°C) either by gas pressure sintering or hot pressing, and in some cases by heat treating (up to 66 h).¹⁰ In the present work pressureless sintering was carried out at 1750°C with dwell times of up to 12 h.

2. Experimental

The compositions investigated are listed in Table 1. Composition C1 has been extensively investigated previously.^{4–8} All starting powders were mixed in iso-propanol in an alumina mortar and pestle for 15 min, dried at 110°C for 4 h and uniaxially pressed into cylindrical pellets of size ≈ 20 mm diameter \times 10 mm, followed by cold isostatic pressing at 200 MPa. The pellets were embedded in an equal volume of a BN/ Si_3N_4 powder mixture placed in a graphite crucible. The crucible was placed in a graphite furnace and sintered in a flowing nitrogen atmosphere. The maximum sintering temperature was 1750°C with a range of dwell times used. The heating and cooling rates were 5°C/min.

Scanning electron microscopic (SEM) examination was performed using a JEOL 6300 SEM on polished and fracture surfaces. Ion-milled thin sections were examined using a JEOL 2000FXI scanning transmission electron

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microscope (TEM). Quantitative energy dispersive X-ray spectrometry (EDS) was performed using both TEM and SEM. The sintered pellets were crushed for powder X-ray diffraction (XRD) analysis using a Siemens D500 diffractometer with $\text{CoK}\alpha$ radiation.

The intercept method¹¹ method used to calculate mean grain size was unsuitable because most of the $\beta\text{-Si}_3\text{N}_4$ grains were acicular. The grain measurement method used was that of Hwang and Tien.¹⁶ The random orientation of the prismatic grains meant that the grain dimensions could be determined by measuring the maximum lengths and widths of appropriately oriented grains in the sectioned plane. The prismatic nature of the $\beta\text{-Si}_3\text{N}_4$ grains permitted those grains which lay parallel to the plane of the polished section to be readily identified by their rectangular shape, and by a corresponding absence of facets on the long axis of the grain. The lengths and breadths of 50–100 $\beta\text{-Si}_3\text{N}_4$ grains from several SEM micrographs were measured and averaged. Also, in selected specimens the maximum aspect ratio was calculated for clearly visible grains.

Table 1
Compositions investigated (wt%)^a

Composition	Si_3N_4	La_2O_3	Y_2O_3	CaO (SiO_2)	Total additives
C1	58.4	15	9	(3)	27
E1	75	15	9	1	25
E2	89	6.25	3.75	1	11
E3	51	30	18	1	49
E4	90	5	3	2	10
E5	80	10	6	4	20

^a For composition C1, SiO_2 was added instead of CaO; it also contained 14.6 wt% SiC. All materials ex-China Building Materials Academy, Beijing, China (typically > 99% purity). For others: Si_3N_4 , LC12SX [impurities (C, Fe, Si) < 0.35%], H.C. Starck, Berlin, Germany; La_2O_3 (99.9% purity), Sigma Chemical Co. Inc., USA; Y_2O_3 (99.99% purity); and CaO added as CaCO_3 , Aldrich Chemicals Inc., USA.

3. Results and discussion

3.1. Microstructure

All the sintered materials are denoted by M as a prefix to the composition. The influence of sintering dwell time on MC1 is shown in Fig. 1, where average grain lengths were $\approx 0.5 \mu\text{m}$ after a 0.1 h dwell [Fig. 1(a)] but 4–5 μm after a 12 h dwell [Fig. 1(b)]. This is in marked contrast to ME4 which showed elongated $\beta\text{-Si}_3\text{N}_4$ grains of length 3–5 μm after no dwell [Fig. 2(a)] at 1750°C and 10–30 μm after a 6 h dwell [Fig. 2(b)]. The grain growth in MC1 is limited probably due to the presence of SiC causing steric hindrance (see below). This effect has also been shown previously,¹² where 20 vol.% of sub-micron SiC additions to Si_3N_4 retarded $\beta\text{-Si}_3\text{N}_4$ growth. SiC will remain inert under the sintering conditions used here.

The elongated grain growth of $\beta\text{-Si}_3\text{N}_4$ is expected to increase fracture toughness. A fracture toughness value of 7.1 $\text{MPa m}^{0.5}$ was obtained for material of an identical composition to C1.⁷ This material was hot isostatically pressed (HIPed) and had a density of 99.7% that of theoretical. The materials which were pressureless sintered here were too porous (10–20% porosity) to enable the fracture toughness to be determined. Subsequent unpublished work by the present authors has shown that this porosity can be eliminated by glass encapsulating the materials, followed by HIPing.

EDS point analysis of the glassy regions near equiaxed grains in ME1 (Fig. 3) showed high SiO_2 contents (Table 2). Similar analyses near elongated grains in ME5 (Fig. 4) which had much higher CaO levels than ME1 showed high CaO contents (Table 2). The composition C1 has been shown to first form a liquid phase at 1390°C.⁶ For the series of compositions E1–5 which contain CaO additions a lower temperature for liquid

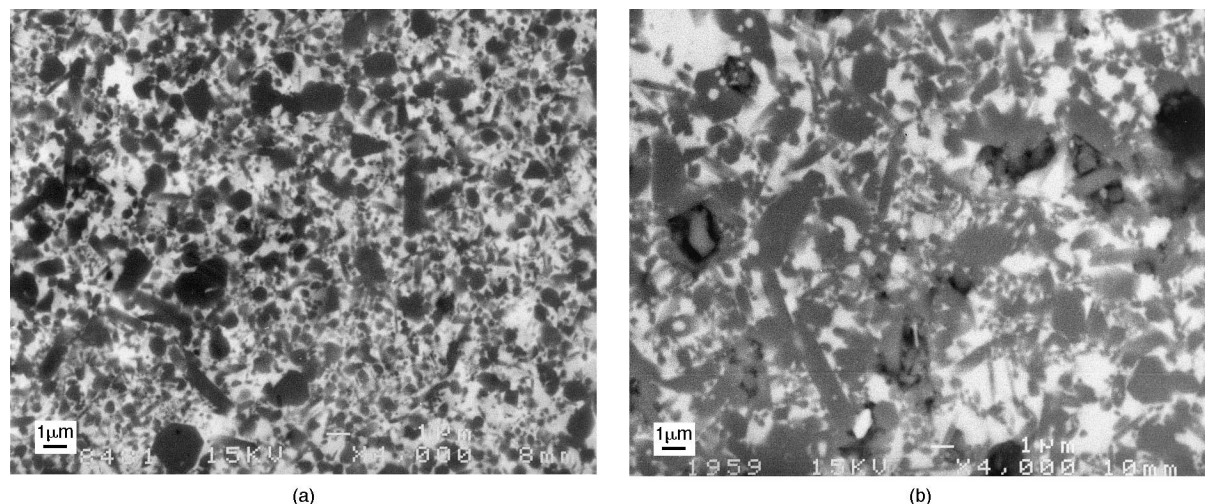


Fig. 1. SEM micrographs of polished sections of MC1 sintered at 1750°C using (a) 0.1 h and (b) 12 h dwell times.

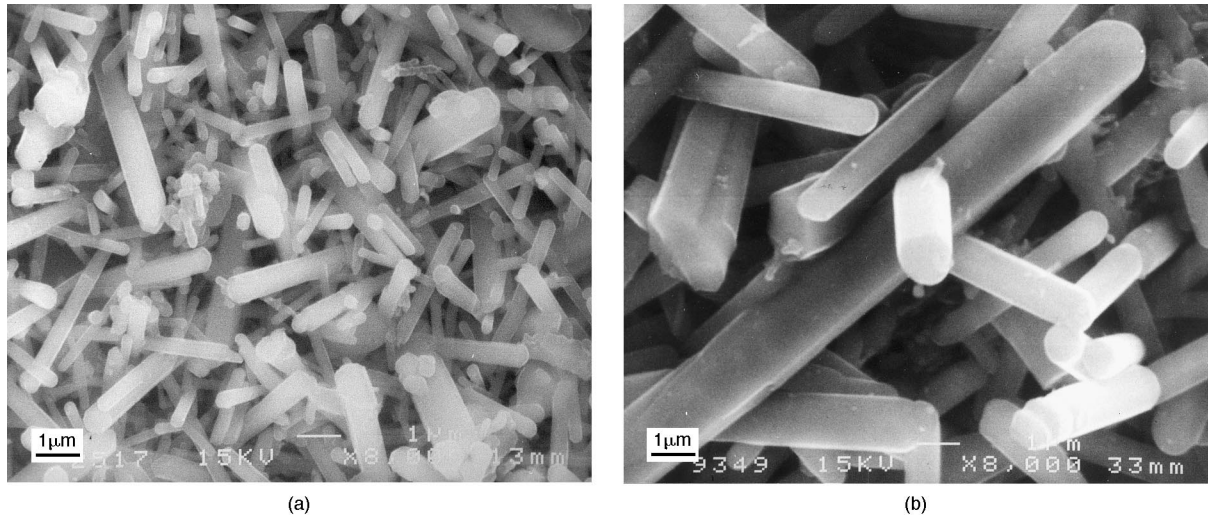


Fig. 2. SEM micrographs of fracture sections of ME4 sintered at 1750°C using (a) 0 h (brought to temperature and then cooled immediately) and (b) 6 h dwell times.

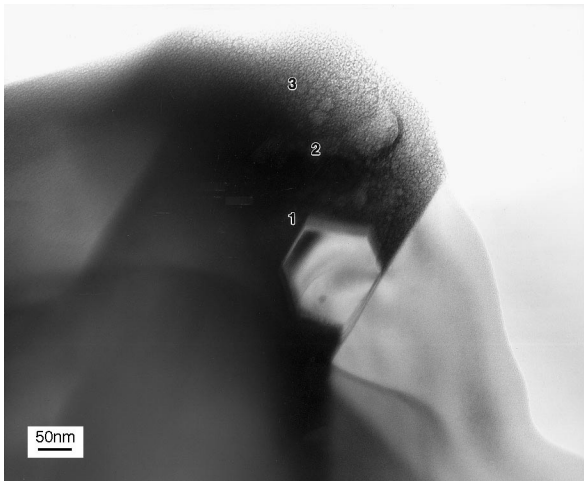


Fig. 3. TEM micrograph of ME1 showing an equiaxed β - Si_3N_4 grain in a SiO_2 -rich glassy phase. Numbers indicate positions of point analysis detailed in Table 2.

phase formation would be expected compared to C1. It has been shown that CaO additions lower the viscosity of oxynitride glass.¹³ The viscosity of a liquid (including melted glasses) decreases with increasing temperature. Therefore, the CaO-containing materials (E1-5) which gives rise to a liquid at a lower temperature (than C1; no CaO) would be expected to have a lower viscosity than that in C1 at the sintering temperature of 1750°C. Since a lower viscosity favours crystal growth¹⁴ the results found here suggest that liquid phase viscosity is reduced by CaO additions, hence facilitating grain growth [compare Figs. 1(a) and 2(b)].

3.2. Grain growth kinetics

The classical equation for grain growth during the latter stages of sintering is given as:¹⁵

Table 2
EDS analysis (at%) of the glassy regions shown in Figs. 3 and 4

Materials	Si	La	Y	Ca
ME1/Regions ^a				
1	78	12	7	3
2	61	19	17	3
3	57	21	18	4
ME5	–	–	–	–
Range	53–66	7–10	9–14	17–24
Mean	57	9	13	21

^a As marked in Fig. 3.

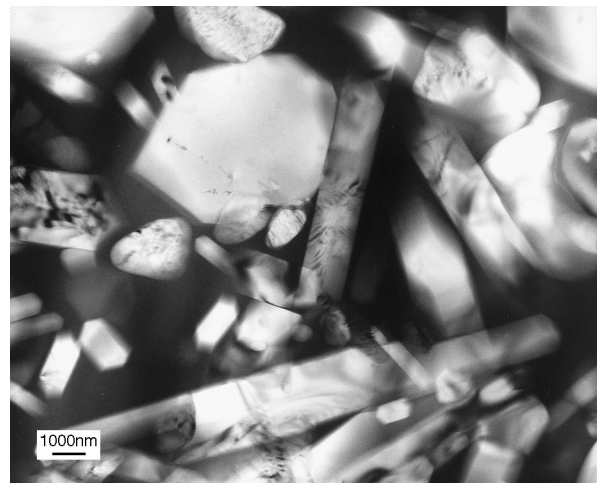


Fig. 4. TEM micrograph of ME5 showing elongated β - Si_3N_4 grains in a CaO-rich glassy phase.

$$G^n - G_0^n = Kt \quad (1)$$

where G is the grain diameter at time t and G_0 is the grain diameter at $t=0$. The exponent n is dependent on the mechanism of grain growth and has a value of 3

when the grain growth rate is controlled by diffusion through a liquid phase.

$K = \exp(-Q/kT)$, where Q is the activation energy for grain growth, T is the absolute temperature and k is Boltzmann's constant. For the current work where the grains are elongated it is more meaningful to obtain an expression for area than diameter.

Eq. (1) can be modified to $A^m - A_0^m = Ct$, where $A = \text{length} \times \text{breadth}$, $m = n/2$ and $C = (\pi/4)^{0.5}K$. A plot of $A^{1.5} - A_0^{1.5}$ (i.e. $n = 3$) against t should yield a straight line passing through the origin. The mean length and breadth of $\beta\text{-Si}_3\text{N}_4$ grains are listed in Table 3 for materials MC1 [Fig. 1(a) and (b)] and ME4 [Fig. 2(a) and (b)]. The plots from these data (mean grain area parameter) are shown in Fig. 5, where a linear relationship with a correlation coefficient of >0.99 was obtained. Thus grain growth rate is controlled by diffusion through a liquid phase, as observed by many workers for $\beta\text{-Si}_3\text{N}_4$ systems (e.g. Hwang and Tien¹⁶). The liquid phase, which was evenly distributed, remains

Table 3
Mean length and breadth of $\beta\text{-Si}_3\text{N}_4$

Length \times breadth (μm)	Area (A) (μm^2)	$A^{1.5} - A_0^{1.5}$ ($\mu\text{m})^{3/2}$	Time (h)
<i>Materials from composition C1</i>			
0.35 \times 0.3	0.1	0	0
0.4 \times 0.3	0.1	0	0.1
1.2 \times 0.4	0.5	0.3	1
2.0 \times 0.5	1.0	1.0	3
2.7 \times 0.6	1.6	2.0	6
4.7 \times 0.5	2.4	3.6	12
<i>Materials from composition E4</i>			
4.8 \times 0.7	3.4	0	0
9.2 \times 0.8	7.4	14.0	2
10.2 \times 1.0	10.2	26.4	5
10.5 \times 1.3	13.6	44.2	6

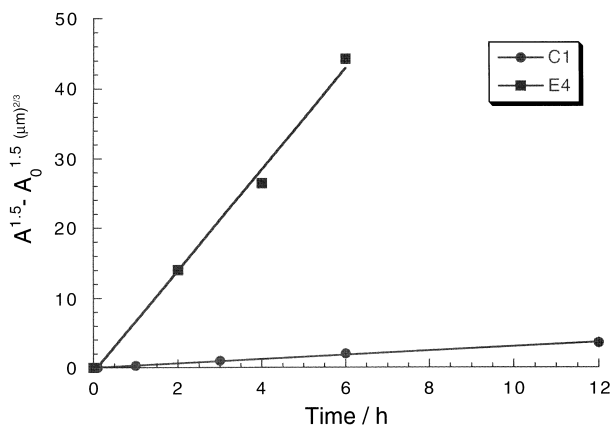


Fig. 5. The mean grain area parameter (see text) of $\beta\text{-Si}_3\text{N}_4$ as a function of sintering time.

as glass in these materials, for example as seen in Fig. 1(a). An increase in aspect ratio of $\beta\text{-Si}_3\text{N}_4$ is seen for both C1 and E4 (Table 3) with increasing sintering time as observed by others for $\beta\text{-Si}_3\text{N}_4$ ^{17,18} and $\beta\text{-SiAlON}$.¹⁶ In fact, Lai and Tien¹⁸ showed a difference in the grain growth exponent against time for length ($n = 3$) and breadth ($n = 5$) for Si_3N_4 sintered with 10 wt % $\text{Y}_3\text{Al}_5\text{O}_{12}$. However, the material in that work was more likely to be a $\beta\text{-SiAlON}$ than the $\beta\text{-Si}_3\text{N}_4$ in the present work, because some Al_2O_3 would have been incorporated in the $\beta\text{-Si}_3\text{N}_4$ structure. They also ignored the grain size at t (time) = 0 in their plots. In the present work grain growth kinetics of both length and breadth yielded exponents closer to $n = 3$.

$\alpha\text{-Si}_3\text{N}_4$ grains are equiaxed and on heating they transform at $\sim 1400^\circ\text{C}$ to $\beta\text{-Si}_3\text{N}_4$ through a solution-precipitation process in the presence of a liquid phase.¹⁶ Most commercial $\alpha\text{-Si}_3\text{N}_4$ contains $\sim 5\%$ $\beta\text{-Si}_3\text{N}_4$ which acts as a nucleating agent for subsequent $\beta\text{-Si}_3\text{N}_4$ grain growth. The viscosity of the liquid plays a prominent role, both in the solution rate of $\alpha\text{-Si}_3\text{N}_4$ and in the diffusion of Si and N to pre-existing $\beta\text{-Si}_3\text{N}_4$ nuclei.¹⁹ In ME4, the viscosity is expected to be lower than that of MC1 because of the presence of CaO (as discussed above). This factor clearly dominates the grain growth kinetics (Fig. 5), whereas the overall level of additives, and therefore the total volume of the liquid phase (Table 1), appears to exert no significant influence. Park et al.²⁰ have shown that even a limited amount of liquid phase could give rise to elongated grains ($\sim 200 \mu\text{m}$) provided it had a low viscosity and good wettability. If there is sufficient liquid phase to form a continuous membrane throughout sintering, then the volume fraction of liquid phase would not be expected to affect grain growth kinetics.²¹ However, where there is insufficient liquid phase to form a continuous membrane, the liquid phase volume fraction would then be expected to influence kinetics.

3.3. Aspect ratio

The maximum aspect ratio (length/breadth) was calculated for the E series of compositions and these ratios are listed in Table 4. Comparison of the maximum aspect ratios for ME4 (Table 4) showed that a 100%

Table 4
Maximum aspect ratio of $\beta\text{-Si}_3\text{N}_4$ grains

Material	Maximum aspect ratios	Dwell time (h)	Total additions (%)	CaO (%)
ME4	10	2	10	2
ME4	20	6	10	2
ME2	7	2	11	1
ME3	8	2	49	1

increase in aspect ratio resulted from increasing the dwell time from 2 to 6 h on sintering at 1750°C. A doubling of the CaO content (similar dwell and total additives) increased the maximum aspect ratio by 43% (compare ME2 and ME4/2 h dwell, Table 4). Pyzic and Beaman³ observed an increase in aspect ratio when as little as 0.5 wt% of CaO was added to a Si₃N₄/Y₂O₃/MgO mixture. In the present work high levels of La and Y additives did not make much of a difference to the maximum aspect ratio for a given amount of CaO (compare ME2 and ME3, Table 4). Consideration of liquid phase formation in the Si₃N₄-Y₂O₃-SiO₂²² and Si₃N₄-La₂O₃-SiO₂²³ systems would suggest that high levels of additives would favour the formation of large amounts of liquid phase. However, large amounts of liquid phase can prevent the growth of large grains because subsequent grain nucleation is homogeneous,²⁰ thereby preventing growth of a smaller number of large grains. It was observed by XRD analysis that there were at least four other phases present in these sintered materials, viz. LaSi₃N₅, (La, Y)₂O₃-Si₃N₄, (Y, La)₁₀(SiO₄)₆N₂ and La₂O₃-Y₂O₃-3.3Si₃N₄, which can also impede grain growth due to steric hindrance.¹⁷

4. Conclusions

Powders containing α -Si₃N₄ and various additives were sintered at 1750°C for a range of times to study the development of β -Si₃N₄. Si₃N₄ sintered with Y₂O₃, La₂O₃ and CaO produced a ceramic containing β -Si₃N₄ grains with the highest aspect ratio (20). However, CaO levels were found to be the key factor influencing β -Si₃N₄ grain growth, with additions of up to 49% by weight Y₂O₃, La₂O₃ and SiO₂ exerting little effect.

Kinetic measurements showed that the growth rate of β -Si₃N₄ was consistent with being controlled by diffusion through the liquid phase. It is believed that the significant effect of CaO on the kinetics stems from the reduction in the viscosity of the liquid phase at the sintering temperature.

Comparison with literature data suggest that CaO additions used in the present work permit the production of quite high aspect ratio (up to 20) β -Si₃N₄ at lower temperatures (1750°C) and shorter dwell times (6 h) than has been achieved previously.

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