Preparing β - Si_3N_4 crystals by freeze-drying and using 10 wt.% $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$ as
flux

Limeng Liu*, Guihong Geng

School of Materials Science and Engineering, Beifang University of Nationalities,
Yinchuan 950021, P. R. China

Abstract: β - Si_3N_4 crystals were prepared by a process of freeze-drying, heat treatment, crushing and leaching. A powder mixture consisting of 90 wt. % α - Si_3N_4 and 10 wt. % $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$ glass powder was blended in water to form a slurry. Freeze-drying of the slurry gave about 85 % porosity in green body and weak strength to the compact after heat treatment at 1700 °C for 2 h in 0.2 MPa N_2 . Needle-like β - Si_3N_4 crystals grew in the pores. After removal of the additive, β - Si_3N_4 grains with a phase purity of > 96% were retrieved.

Keywords: Ceramic; Si_3N_4 ; Celsius; Crystal growth.

1. Introduction

Si_3N_4 has three polymorphs, i.e. the α , the β and the cubic (i.e. c- Si_3N_4) phases [1]. The α - and β - Si_3N_4 are more common in industry relative to the c- Si_3N_4 because c- Si_3N_4 is obtained only at extremely high pressure up to 6.0 GPa [1]. The α -phase is metastable. It transforms to β at high temperatures (> 1450 °C) at presence of a proper liquid [2] while reverse transformation hardly happens. The β - Si_3N_4 starts to decompose at about ~ 1850 °C in 1 atm N_2 [3]. When the N_2 pressure is lowered, the decomposition temperature of the Si_3N_4 compound decreases.

In the Si_3N_4 ceramic industry, α - Si_3N_4 powder is normally used as the starting material [4,5,6,7] due to relatively easy accessibility of the powder. Nevertheless,

*Corresponding author. E-mail: llm681@sina.com; (Liu Limeng);

Tel: +86-951-2066778; Fax: +86-951-2066778

β - Si_3N_4 powder is valuable because (1) β - Si_3N_4 can be used to seed the Si_3N_4 and the SiAlON ceramics or be used to control thermodynamics of the phase transformation taking place in the Si_3N_4 and the SiAlON ceramics to encourage anisotropic growth of the grains in the microstructures [8,9,10], as a reliable approach to increase fracture toughness, and (2) the stability of the β phase should favor its use as a reinforcing agent to highly reactive metals such as aluminum and magnesium [11], in addition to higher reinforcing efficiency by the whisker-like β - Si_3N_4 grains than the equiaxed α - Si_3N_4 particles.

High quality β - Si_3N_4 grains normally grew in ME-Si-Al-O-N liquids (ME = alkali, alkali earth, and rare earth metals) [5,6,12,13,14]. α - Si_3N_4 transformed into β and the β - Si_3N_4 grains grew steadily at temperatures $> 1600^\circ\text{C}$ in the liquid. After the ME-Si-Al-O-N was removed [13,15], β - Si_3N_4 crystals were collected. However, powder compacts containing the Si_3N_4 and the ME-Si-Al-O-N were always sintered to high density. Crushing of the consolidated bulk and leaching off of the additives to retrieve the β - Si_3N_4 crystals were quite time/energy consuming. Herein we report preparation of β - Si_3N_4 crystals by freeze-drying and using 10 wt.% BSAS ($\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$) as the flux. The BSAS was used because it benefited β - Si_3N_4 growth [16,17,18] and easy removal of the flux phase by reaction with molten NaOH or KOH. Freeze-drying was applied because it was capable of producing porous ceramics with high porosities up to 90% [19]. Loose bonding of the β - Si_3N_4 crystals in the porous ceramics facilitated retrieval of the β - Si_3N_4 .

2. Experimental

A BSAS ($\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$) glass powder and α - Si_3N_4 (SN-E10, UBE Industries, Japan) were used as the starting materials. According to the manufacturer's inspection, the Si_3N_4 powder had a mean particle size of $0.4\text{--}0.7\ \mu\text{m}$ and $\sim 94.5\ \text{wt.}\%$

α - Si_3N_4 . About 5.5 wt.% β - Si_3N_4 and ~ 1.27 wt.% surface oxygen were the main impurities. The BSAS powder was synthesized by hydrolysis of alkoxides as described in a previous work [20]. A powder mixture consisting of 5 g BSAS and 45 g α - Si_3N_4 was blended for 4 h in a 200 ml plastic bottle using 85 ml de-ionized water (i.e. about 85 vol% relative to the ceramic phase) and Si_3N_4 balls as the blending media. The slurry was poured into an aluminum container with a diameter and height of 8 cm and 12 cm, respectively, and then froze in liquid nitrogen. After removal of the container, the frozen bulk was put in a ~ 10 Pa vacuum at ~ -70 °C for 2 days. The green body was then heat treated at 1700 °C for 2 h in a 0.2 MPa N_2 atmosphere using a gas pressing furnace (SGM/VB/8-18, Shanxi Bohua Co. Ltd. China).

Surface area of the as-heat treated bulk was measured by nitrogen adsorption. Nitrogen adsorption isotherms (Gemini VII 2390, Micrometics Co., USA) were measured at -196 °C in a relative pressure range of (p / p_0) 0.01 – 0.99. Density was measure by the dimensions and mass of the sample. The porous bulk was crushed by hand with a pestle and mortar, and sieved through a 120 mesh screen. The small scraps were leached in molten NaOH at 450 °C for 10 min and fluxed by water to collect the sedimentation. Phase composition was checked by X-ray diffraction (XRD, Rigaku D/Max 2200 VPC, Japan). Relative content of the β - Si_3N_4 phase was calculated [21]. Particle morphologies were observed by Scanning Electron Microscopy (SEM, Hitachi S-4700 Tokyo, Japan). Grain sizes were determined by image analysis on the micrographs, using a software compact (Image Pro-Plus 5.0.1, Media Cybernetics, Silver Spring, MD). More than 5 hundred grains for each sample were measured.

3. Results and discussions

XRD of the starting powders are shown in Fig. 1. The BSAS glass powder was

amorphous. The average particle size of the BSAS powder was about 0.2 μm , according to SEM as shown in Fig. 2. According to the XRD (Fig. 1), the Si_3N_4 powder was dominated by $\alpha\text{-Si}_3\text{N}_4$ with a very small amount of β , in consistency with the manufacturer's inspection.

XRD of the as heat-treated compact and the retrieved $\beta\text{-Si}_3\text{N}_4$ powder are shown in Fig. 3. The $\alpha\text{-}$ to $\beta\text{-Si}_3\text{N}_4$ phase transformation almost reached completion, with ~ 3.9 wt.% remnant $\alpha\text{-Si}_3\text{N}_4$. Complete transformation of the residual $\alpha\text{-Si}_3\text{N}_4$ needed at least another ~ 30 min at 1700°C which was uneconomically unworthy. Heating the compact at higher temperatures would risk more SiO_2 loss due to evaporation, thus was not tried. A SiO_2 deficient product of $(\text{Ba,Sr})\text{Al}_2\text{SiO}_6$ [PDF 21-0806 for $\text{BaAl}_2\text{SiO}_6$] instead of the stoichiometric BSAS ($\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$) was formed by the BSAS additive in the as-heat treated sample. SiO_2 loss by evaporation at high temperatures could explain the $(\text{Ba,Sr})\text{Al}_2\text{SiO}_6$ formation. It is common that SiO_2 evaporates as SiO species at high temperatures at presence of C which was abundant in the gas pressing furnace. However, the chemistry of the flux phase was not a critical issue as long as it grew the $\beta\text{-Si}_3\text{N}_4$ grains, and it will be leached off in the retrieval step.

No noticeable densification shrinkage was observed to the bulk during the 1700°C heat treatment. A whole density of 0.58 g/cm^3 was estimated by the mass and dimensions method, in consistency with a residual porosity up to 82 vol. %. The high porosity was resulted from the intrinsic nature of the freeze-drying process. When the aqueous slurry froze, the ceramic particles segregated at the grain boundaries of the ice crystals. The pores duplicated the ice crystals after removal of the ice phase in the green body. This meant the ~ 85 vol. % water in the slurry would introduce a porosity of the same volume fraction to the green body. Additionally, in the following heat

treatment stage, materials were transported from the struts to grow the β - Si_3N_4 grains in the pores, causing no significant sintering shrinkage. However, there existed a slight porosity difference between the out surface and the inner part of the bulk. The as-heat treated bulk had a crust up to 2 mm in thickness. The crust had a slightly lower porosity than the center part. The BET revealed aspect surface area of $1.63 \text{ m}^2/\text{g}$ and $3.87 \text{ m}^2/\text{g}$ for the surface layer and the inner part of the as-heat treated bulk, respectively. The existence of the surface layer should not affect yield of the β - Si_3N_4 much due to the small volume fraction of the crust relative to the whole bulk.

Morphology of the β - Si_3N_4 grains in the as-heat treated bulk is shown in Fig. 4a. Perfect needle-like grains were observed, with average diameter and length of $0.32 \pm 0.20 \text{ }\mu\text{m}$ and $25 \pm 11 \text{ }\mu\text{m}$, respectively. The length of the β - Si_3N_4 grains were rather uniform, indicating similar growth rate for each grain.

The as-heat treated material was weak in strength and was easy to crush by hand with a pestle and mortar. After leaching off of the $(\text{Ba},\text{Sr})\text{Al}_2\text{SiO}_6$ phase, the XRD and the morphology of the retrieved β - Si_3N_4 was shown in Fig. 3b and Fig. 4b, respectively. Although damage to the β grains was inevitable, a relatively phase pure β - Si_3N_4 powder was generated. According to the XRD (Fig. 3b), the phase purity of the β - Si_3N_4 was > 96 , with up to 3.9 wt.% α - Si_3N_4 as the main impurity.

4. Conclusions

A highly porous green body was produced by freeze-drying of a homogeneous aqueous slurry consisting of $\sim 85 \text{ vol. } \%$ water and $15 \text{ vol. } \%$ α - Si_3N_4 and $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$. Heat treatment of the green bodies at $1700 \text{ }^\circ\text{C}$ for 2 h in 0.2 MPa N_2 completed the α - to β - Si_3N_4 phase transformation. After removal of the additive, β - Si_3N_4 with > 96 phase purity was prepared.

5. Acknowledgment

Author L.M.L. thanks financial support from the “China National Science Foundation” under Grant No. NSFC 51272053.

6. References

- [1] Zerr A, Miehe G, Serghiou G, Schwarz M. *Nature* 1999; 400: 340–42.
- [2] Ye F, Chen S, Iwasa M. *Scripta Mater* 2003; 48: 1433–38.
- [3] Heuer AH, Lou VLK. *J Am Ceram Soc* 1990; 73 [10]: 2789–803.
- [4] Inoue H, Komeya K, Tsuge A. *J Am Ceram Soc* 1982; 65 [12]: C205–C205.
- [5] Bhatnagar A, Hoffman MJ, Dauskardt J. *J Am Ceram Soc* 2000; 83: 585–596.
- [6] Becher PF, Sun EY, Hsueh CH. *Acta Metal* 1996; 44: 3881–93.
- [7] Rahaman MN. *Ceramic Processing and Sintering*, Second ed., Marcel Dekker, New York, 2003.
- [8] Hirao K, Ohasi M, Brito ME. *J Am Ceram. Soc* 1995; 78 [6]: 1687–90.
- [9] Lu HH, Huang JL. *J Am Ceram Soc* 2002; 85 [9]: 2331–36.
- [10] Chen IW, Rosenflanz A. *Nature* 1997; 389: 701–04.
- [11] Imai T, Mabuchi M, Tozawa Y, Yamada M. *J Mater Sci Lett* 1990; 9 [3]: 255–57.
- [12] Wang L, Tien TY, Chen IW. *J Am Ceram Soc* 2003; 86 [9]: 1586–91.
- [13] Ramesh PD, Oberacker R, Hoffmann MJ. *J Am Ceram Soc* 1999; 82 [6]: 1608–10.
- [14] Satet RL, Hoffmann MJ, Cannon R M. *Mater Sci Eng A*, 2006: 422 [1]: 66–76.
- [15] Zenotchkine M, Shuba R, Chen IW. *J Am Ceram Soc* 2004; 87 [6]: 1040–46.

- [16] Richardson KK. J Am Ceram Soc 1995; 78 [10]: 2662–68.
- [17] Yu F, White KW. J Am Ceram Soc 2001; 84: 5–12.
- [18] Freitag DW. Mater Sci Eng A, 1995; 195: 197–205.
- [19] Yang H, Ye F, Liu Q, Liu S, Gao Y, Liu L. Mater. Lett 2015; 138: 135–38.
- [20] Liu L, Ye F, Zhang H, Yu J, Zhang Z. Scripta Mater 2009; 60: 463–66.
- [21] Messier DR, Riley FL, Brook RJ. J Mater Sci 1978; 13: 1199–205.

7. Figures and figure captions

Fig. 1 XRD patterns of the BSAS ($\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$) glass powder and the α - Si_3N_4 powder used as the starting materials.

Fig. 2 SEM micrograph of the $\text{Ba}_{0.75}\text{Sr}_{0.25}\text{Al}_2\text{Si}_2\text{O}_8$ glass powder.

Fig. 3 XRD patterns of the as-heat treated Si_3N_4 compact (a), and (b) the retrieved β - Si_3N_4 powder after the flux phase was leached off.

Fig. 4 SEM micrographs, showing morphologies of the β - Si_3N_4 grains in the as-heat treated Si_3N_4 compact (a), and (b) the retrieved β - Si_3N_4 powder after removal of the flux phase.