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ScienceDirect
Ceramics International 35 (2009) 3371–3374
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Microstructure control and mechanical properties of porous silicon nitride ceramics

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Received 2 January 2009; received in revised form 1 April 2009; accepted 4 June 2009
Available online 7 July 2009

Abstract

Porous silicon nitride ceramics with a fibrous interlocking microstructure were synthesized by carbothermal nitridation of silicon dioxide. The influences of different starting powders on microstructure and mechanical properties of the samples were studied. The results showed that the microstructure and mechanical properties of porous silicon nitride ceramics depended mostly on the size of starting powders. The formation of single-phase β-Si_3N_4 and the microstructure of the samples were demonstrated by XRD and SEM, respectively. The resultant porous Si_3N_4 ceramics with a porosity of 71% showed a relative higher flexural strength of 24 MPa.

Keywords: C. Mechanical properties; Porous; Silicon nitride; Microstructure control

1. Introduction

Porous Si_3N_4 ceramics with rod-like β-Si_3N_4 grains show superior mechanical properties, such as high strength, good thermal shock resistance, and high strain damage tolerance, which makes them become promising candidates for application as molten metal filters, soot collectors, heat exchangers, catalyst carriers, bioreactors, and so on. Porous Si_3N_4 ceramics can be fabricated by using the fugitive substance [1], controlled sintering of Si_3N_4 powder with low sintering aid [2,3], partial hot-press [4], freeze-drying [5]. However, it is difficult to produce the porous Si_3N_4 ceramics with fine pores and high porosity.

In our prevenient studies, we had investigated the effect of SiO_2 particle size, sintering conditions, adding seed and the ratio of carbon and silicon dioxide on microstructure and mechanical properties of porous Si_3N_4 ceramics [6–8]. In the article, we reported on the fabrication of high-porosity Si_3N_4 ceramics with interlocking microstructure by changing starting powders. Effects of different starting powders on their microstructure and mechanical properties were investigated. This reaction ($3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$) can be advantageous because the silicon dioxide and carbon powder are cheaper and easily attainable than the silicon nitride powder. Compared with other methods, porous Si_3N_4 prepared by this method have higher porosity because of a large weight loss of this reaction.

2. Chemical reactions

The overall reactions for the carbothermal synthesis of porous silicon nitride in this study are believed to include [9]:

$$3SiO_2(s) + 6C(s) + 2N_2(g) = Si_3N_4(s) + 6CO(g) \quad (1)$$

$$2SiO_2(s) + 3C(s) + N_2(g) = Si_2N_2O(s) + 3CO(g) \quad (2)$$

$$3Si_2N_2O(s) = Si_3N_4(s) + 3SiO(g) + N_2(g) \quad (3)$$

It was obvious that the carbon needed for reaction (2) was less than that for the reaction (1). Lower molar ratio of C/SiO_2, that is lower carbon concentration, prompts effectively the formation of Si_2N_2O [10]. Si_2N_2O phase occurs at lower sintering temperature by reaction (2), and transforms to β-Si_3N_4 phase with increasing temperature by reaction (3) [8].

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0272-8842/$36.00
doi:10.1016/j.ceramint.2009.06.009

3. Experimental

Quartz SiO_2 (99.3% purity, Fine Chemical Plant, Tianjin, China; mean particle size: 5 μm or 0.2 μm) was used as the starting powder. Activated carbon powder (96% purity, fine chemical plant, Tianjin, China; mean particle size: 10 μm) or nano-meter carbon powder (C(n)) (98% purity, Zhongchao Nanometer Industry Ltd., Haerbin, China; particle size: 30 nm), Y_2O_3 (99.9% purity, Shin-etsu Chemical Co., Ltd., Tokyo, Japan) and α-Si_3N_4 (SN-E10, 99.5% purity, 95% phase content) were used as the carbon source, sintering additive and seed, respectively. The sample designation and their compositions in this paper are shown in Table 1.

The above starting powder mixture were wet-milled with high-purity silicon nitride balls in anhydrous alcohol for 24 h in a plastic bottle. After milling, the slurry was dried, sieved, and uniaxially pressed to form rectangular bars. The green bodies were sintered in furnace (High multi-5000, Fijidempa Co. Ltd., Osaka, Japan) at 1800 °C for 2 h under a nitrogen-gas pressure of 0.6 MPa.

The bulk density of the sintered products was measured by the Archimedes displacement method. Crystalline phases were identified by XRD (D/MAX-2400X, Rigaku Co., Tokyo, Japan) analysis. Microstructure was characterized by SEM (JSM-35C, JEOL, Japan). The three-point bending strength was measured on specimen bars with a span of 16 mm at a cross-head speed of 0.5 mm/min by an instrument (Instron 1195, Instron Co., England). Each final value was averaged over three measurements.

4. Results and discussion

Variations in the weight loss, shrinkage, green porosity and porosity with different carbon sources are shown in Table 2. As is shown in Table 2, the green porosity of the sample increased with a decrease in the size of starting powders, which was in accordance with that small particles result in the low green density.

Table 1
Compositions of the starting powder.

Samples	Composition
A	64.3 wt% SiO_2 (5 μm) + 25.7 wt% C (10 μm) + 5wt% Y_2O_3 + 5 wt% α-Si_3N_4
B	64.3 wt% SiO_2 (0.2 μm) + 25.7 wt% C (10 μm) + 5 wt% Y_2O_3 + 5 wt% α-Si_3N_4
C	64.3 wt% SiO_2 (0.2 μm) + 25.7 wt% C (30 nm) + 5 wt% Y_2O_3 + 5 wt% α-Si_3N_4

As shown in our previous study [8], the theoretical weight loss after complete reaction of β-Si_3N_4 is obviously different for the different reaction process, because the reaction process was different for powder mixtures with different carbon sources. For the nanometer carbon, the reaction proceeds mainly according to reaction (1), with weight loss of 44%, which is similar to the actual value of the sample C. For the large size carbon, the reactions perform mainly according to reactions (2) and (3) separately. The theoretical weight loss of reaction (2) is 36%, and 53% weight loss of reaction (3) was caused by the loss of SiO gas and N_2 resulted from the decomposition of Si_2N_2O. Therefore, the combined theoretical weight loss of reactions (2) and (3) should be 69%, which is near to the actual values of the samples A and B.

Green bodies composed of fine particles tend to shrinkage more easily [11]. However, in this study, in spite of lower green porosity, the shrinkage of the sample A or B was much larger than that of C, which was resulted from much higher weight loss and maybe the formation of a large amount of Si_2N_2O at the initial sintering stages.

The porosity is a combining result from green porosity, shrinkage and weight loss, increasing green porosity or weight loss increases the porosity, and increasing shrinkage decreases it. The lower porosity with A or B was mainly caused by much larger linear shrinkage.

Fibrous β-Si_3N_4 grains are in favor of enhancing the flexural strength of porous silicon nitride by pull-out and bridge of the rod-like grains [3]. Only β-Si_3N_4 phase, and grain boundary phase were detected by X-ray diffraction analysis as shown in Fig. 1B and C. While minor of α-Si_3N_4 phase was detected in Fig. 1A, due to the coarser starting powder lowering the speed of the reaction and phase transformation. The grain boundary phase was identified as a crystalline $Y_8Si_4N_4O_{14}$, which was apparently formed by the reaction between Y_2O_3, SiO_2 and Si_3N_4.

The typical grain and pore morphology obtained from the different starting powders are shown in Fig. 2. As shown in Fig. 2, variation in the starting powders resulted in different microstructures. The sample A occupied the coarse, conglomerated equiaxial β-Si_3N_4 grains (Fig. 2A), due to the large particle size of starting powders. As a comparison, the sample B with smaller particle size for SiO_2 was almost composed of rod-like β-Si_3N_4 grains (Fig. 2B), however, part of the rod-like grains conglomerated together so that pores were not distributed uniformly. The microstructures of A and B was mainly resulted from the reactions (2) and (3), and their large pores came from the loss of the large sized carbon particles. The microstructures of Fig. 2A or B was detrimental to mechanical properties. While the sample C

Table 2
Summary of sintering behavior and flexural strength of porous Si_3N_4 ceramics.

Carbon source	Green porosity (%)	Shrinkage (%)	Weight loss (%)	Porosity (%)	Flexural strength (MPa)
A	66.3	43.5	66.1	36.1	176.3 ± 10.6
B	67.0	38.3	64.0	47.3	108.4 ± 7.3
C	71.2	19.3	44.3	71.2	24.2 ± 1.1

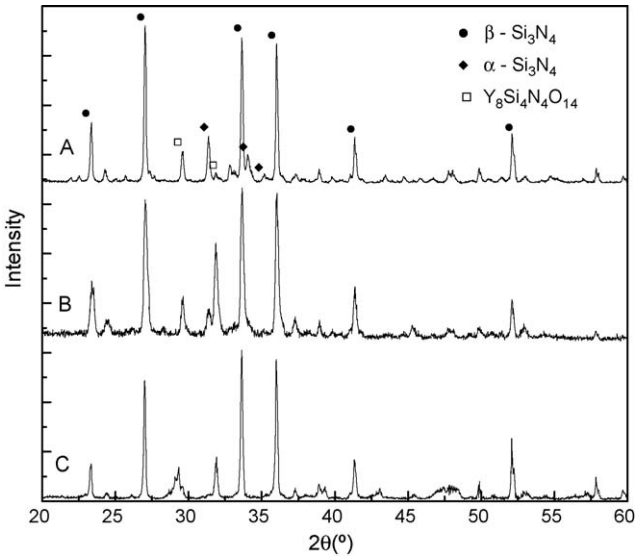

Fig. 1. XRD patterns of different starting powders. A–C represent the sample designation.

with smaller particle size for both SiO_2 and carbon showed ultrafine, rod-like β-Si_3N_4 grains with high aspect ratio and uniform pores (Fig. 2C). It was obvious that the diameter of grains was less than 1 μm and the aspect ratio was more than 6, which was very advantageous for mechanical properties. In a word, with a decrease in the particle of starting powders, rod-like β-Si_3N_4 grains with finer grain size, high aspect ratio, and the uniform pores between the β-Si_3N_4 grains were obtained.

The change of flexural strength as a function of porosity for different starting powders is also shown in Table 2. The flexural strength decreased with the increasing porosity. Although the strength for sample C was lower than the samples A and B, it is difficult to compare each other due to the great difference in the porosity. Compared with the porous Si_3N_4 ceramics obtained from reaction sintering (RSSN) by Rice et al. [12], the sample A exhibited a similar strength at the same porosity because of the larger equiaxial β-Si_3N_4 grains. The sample B showed a slight higher strength because of finer particle size and less conglomerations in comparison with A. While the higher

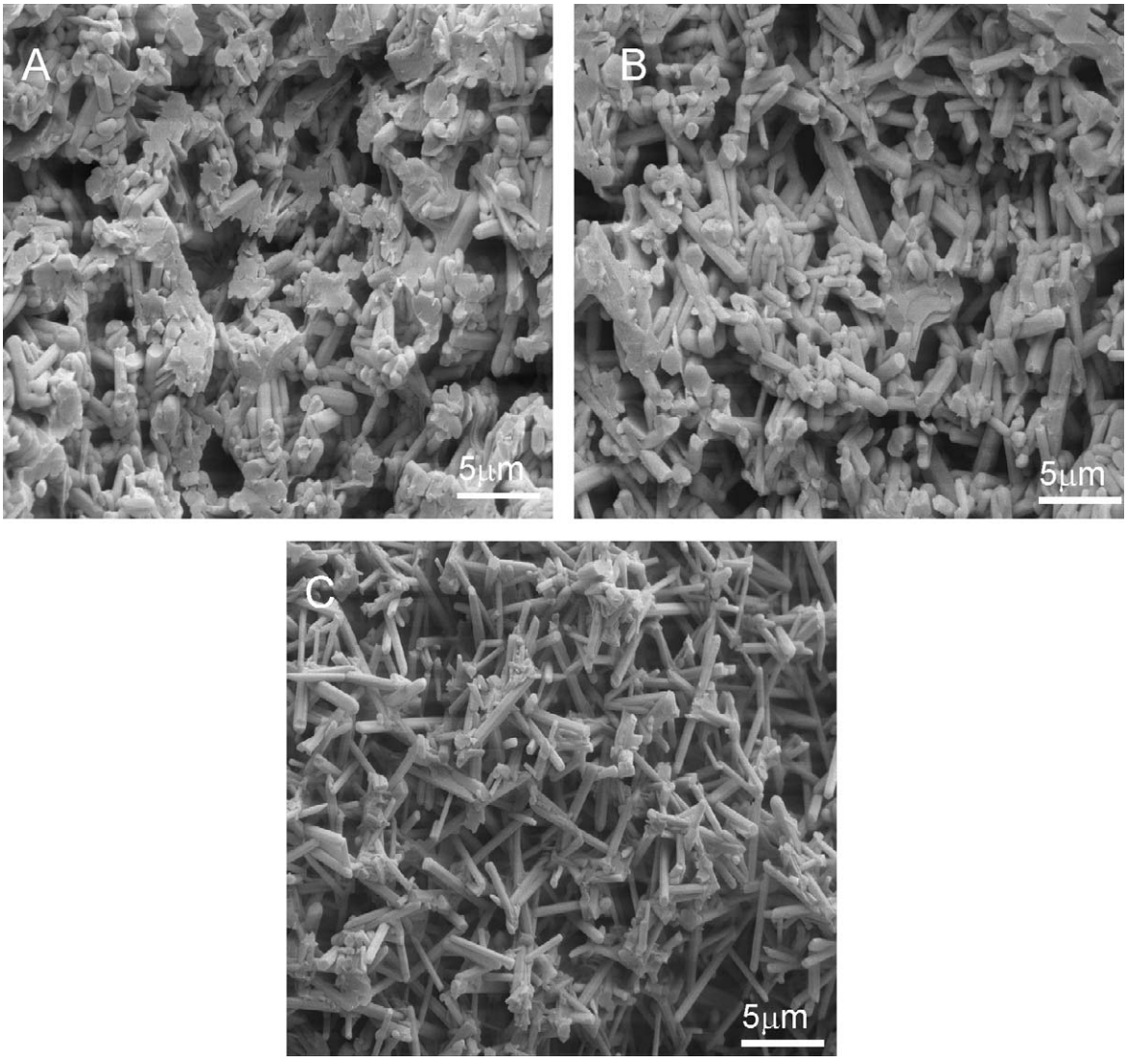

Fig. 2. SEM photographs of the porous Si_3N_4 ceramics with different starting powders. A–C represent the sample designation.

flexural strength of the sintered sample C at the same porosity is because of fine, high aspect ratio β-Si_3N_4 grains and uniform pores between grains. Compared with our previous research results [8], the sintered sample C showed the higher flexural strength at the higher porosity. Compared with the porous Si_3N_4 ceramics obtained by two step centrifuging processing by Pu et al. [13], strength of 3–8 MPa at porosity of 70–80%, the sintered sample C also showed the higher flexural strength. Therefore, the resultant porous silicon nitride ceramics have a good prospect in commercial applications.

5. Conclusions

Highly porous Si_3N_4 ceramics with interlocking microstructure were fabricated by adjusting the starting powders. Using the powder mixture of large sized SiO_2 and C, large weight loss and shrinkage, consequently low porosity, occurred, and β-Si_3N_4 microstructure with low aspect ratio and grain conglomeration were resulted. The porous silicon nitride ceramics using finer starting powder showed finer interlocking microstructure, higher porosity. The resultant porous silicon nitride ceramics obtained from the fine starting powders had high porosity of 71%, and flexural strength of 24 MPa, due to the formation of the fine elongated β-Si_3N_4 grains.

Acknowledgements

This work has been sponsored by State Education Ministry of the People's Republic of China (NCET Program (04-0941), the Personnel Introduction of Kunming University of Science and Technology (2007-18), and Natural Science Fund of Yunnan Province (2008B033M).

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