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Short communication

Synthesis of pure rod-like α-Si_3N_4 powder with in situ C/SBA-15 composite

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Abstract

Well crystallized pure rod-like α-Si_3N_4 powder (PRSN) without β-Si_3N_4 was successfully synthesized by carbothermal reduction-nitridation (CRN). In situ carbon/mesoporous silica composite (C/SBA-15) was used as a new kind of raw material. Due to in situ composited carbon, the CRN temperature was decreased and the phase transition from α to β-Si_3N_4 was hindered. The sintering temperature was lowered to 1380 °C and the soaking time of the optimal synthesis condition was reduced to 6 h. Moreover, the as-synthesized rod-like α-Si_3N_4, which is induced by SBA-15, was used to enhance the fracture toughness (K_{Ic}) of α-Si_3N_4 based ceramics, which was sintered by spark plasma sintering (SPS). Compared with the undoped ceramics (2.9 MPa $m^{1/2}$), α-Si_3N_4 ceramics doped with 10 vol% PRSN exhibited a higher K_{Ic} value (4.9 MPa $m^{1/2}$), and lower dielectric loss in MHz frequency range. The results demonstrated that the PRSN powder would be promising for toughening α-Si_3N_4 based ceramics.

Keywords: B. Microstructure-final; C. Fracture; C. Dielectric properties; D. Si_3N_4

1. Introduction

In recent years, α-Si_3N_4 based ceramics becomes the research focus in high performance dielectric applications, due to its better dielectric properties compared to β-Si_3N_4 [1,2]. Spark plasma sintering procedure (SPS) with lower temperature and shorter soaking time is considered to be a promising sintering method for sintering of α-Si_3N_4 based ceramics [3,4]. However, the toughness of sintered products is too low (3.0 MPa $m^{1/2}$) due to its equiaxed microstructure [4]. The further development of α-Si_3N_4 based ceramics sintered by SPS is seriously restrained by its fragility. To improve toughness as well as keeping good dielectric properties, adding pure rod-like α-Si_3N_4 powder (PRSN) is a good practice. Firstly, rod-like grains can enhance matrix material through toughening mechanisms like β-phase. Secondly, the similar composition with matrix ceramics will not sacrifice dielectric properties. But pure α-Si_3N_4 powder is difficult to obtain. β-Si_3N_4, which is a detrimental phase to dielectric properties of α-Si_3N_4 powder, always appears as impurity and is hard to be extracted from α-phase [5–7]. The main reason is that, when temperature rises above 1400 °C, which is required in present methods, α-phase converts to β-phase spontaneously. In other words, α-Si_3N_4 can be more stable when temperature is below 1400 °C [8].

To synthesize PRSN, in this work, in situ carbon/ordered mesoporous silica composite (C/SBA-15) was used with carbothermal reduction-nitridation (CRN). Composited carbon in SBA-15 and large specific surface area of SBA-15 [9] are helpful to lower the calcination temperature and time. And the rod-like SBA-15 template may induce α-Si_3N_4 to form the similar morphology. Our research revealed that α-Si_3N_4 has been the only one stable phase without β-phase under lowered reaction temperature. And elongated α-Si_3N_4 grains have the striking similar morphology to that of its parental SBA-15. In addition, the toughness of α-Si_3N_4 based ceramics with 10 vol% PRSN was increased to 4.9 MPa $m^{1/2}$ in K_{Ic}. This value is comparable to that of well-developed β-microstructure [10]. Meanwhile, the dielectric loss ($\tan\sigma$) decreased significantly after adding PRSN. In general, the PRSN powder not only has the excellent performance in toughening α-Si_3N_4 based ceramics, but also has positive effect in dielectric properties of α-Si_3N_4 matrix.

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2. Experimental

2.1. Synthesis of the pure rod-like α-Si_3N_4 powder (PRSN)

SBA-15 and sucrose were used as Si and C source, with a C:SiO_2 molar ratio of 4:1. 1.8 g sucrose and 0.2 g H_2SO_4 were dissolved in deionized water to form solution I at the first stage, then 1.0 g SBA-15 was added in the solution I. The resulting suspension was kept at 80 °C/12 h and 160 °C/12 h. After carbonized under 800 °C for 4 h in a nitrogen flow of 0.3 L/min, SBA-15/C powder (SC) was obtained. Further nitridation of SC was implemented in a graphite furnace with a 0.8 L/min nitrogen flow. The residual carbon was removed by heating at 600 °C for 6 h in air environment.

2.2. Ceramics preparation

α-Si_3N_4 based ceramics was sintered by SPS reported in Reveron's work [4], which introduced LAS ($LiAlSiO_4$) to reduce thermal expansion coefficient. Samples R0, R5, R10 were chosen as the representative samples with different doping contents of PRSN. Related preparation parameters are listed in Table 1.

2.3. Characterization

The surface area of SBA-15 and common SiO_2 was measured by Micromeritics ASAP2010 system (Micromeritics, Norcross, GA). Phase identification was characterized by XRD, and was collected on a D/MAX-γ β X-ray diffractmetor (Rigaku, Japan) by using Cu $K\alpha_1$ ($\lambda = 0.15406$ nm) radiation. The morphology was observed with FSEM (JSM-6700F JEOL, Japan, 10.0 kV), and TEM (JEM2100F JEOL, Japan, 200 kV). The indentation fracture toughness was calculated from indentation fracture lengths based on Anstis's equation [11]. The fracture lengths were measured by Vickers Hardness Tester under 49 N during 10 s. Dielectric measurements were obtained by using Hewlett Packard LCR meter at 150 kHz, 10 MHz and 20 MHz.

3. Results and discussion

Fig. 1 provides XRD patterns of products sintered for 6 h at 1250 °C, 1300 °C, 1340 °C, 1380 °C and 1400 °C. α-Si_3N_4 started forming at 1300 °C, as shown in Fig. 1. As temperature rose, unreacted SBA-15 (indicated by a big "bread" diffraction peak) was gradually transformed to α-Si_3N_4 and crystallinity of

Table 1
Preparation parameters of samples R0, R5 and R10.

Sample	PRSN (vol%)	LAS (vol%)	SPS pressure (MPa)	SPS temperature (°C)	SPS soaking time (min)
R0	0	20	50	1500	5
R5	5	20	50	1500	5
R10	10	20	50	1500	5

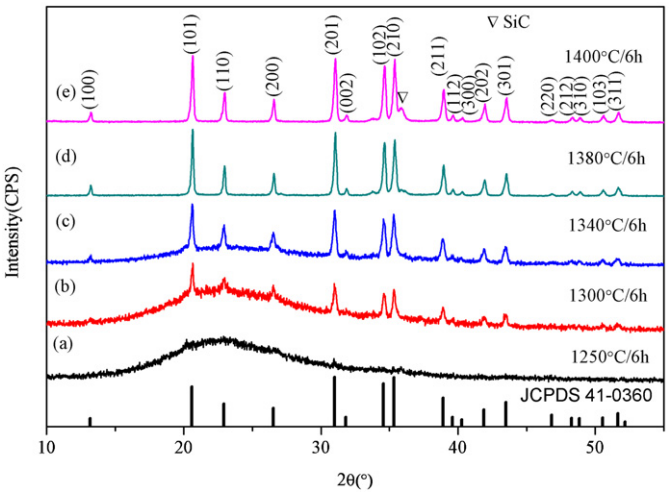

Fig. 1. X-ray diffraction patterns of the products calcinated for 6 h at different temperatures: (a) 1250 °C; (b) 1300 °C; (c) 1340 °C; (d) 1380 °C and (e) 1400 °C.

products increased. Well-crystallized pure α-Si_3N_4 (JCPDS 41-0360) was successfully synthesized at 1380 °C after 6 h. Whereas, less SiC existed as impurity (Fig. 1e) when temperature rose above 1380 °C. Consequently, the optimal sintering temperature should be set in 1380 °C for 6 h in soaking time. Note that β-phase existed in previous methods does not appear because of decreased CRN temperature. Compared to previous work [12], lowered sintering temperatures (1300–1380 °C) inhibit the conversion from α to β and as a result α-Si_3N_4 becomes more stable. We infer the in situ composited carbon may have important role in lowering the CRN reaction temperature.

To confirm the inference mentioned above, controlled experiments on different carbon composited means were implemented. Fig. 2 shows XRD patterns of samples produced by in situ composition method and simple mechanical mixture method. In this work, sucrose was selected to form in situ

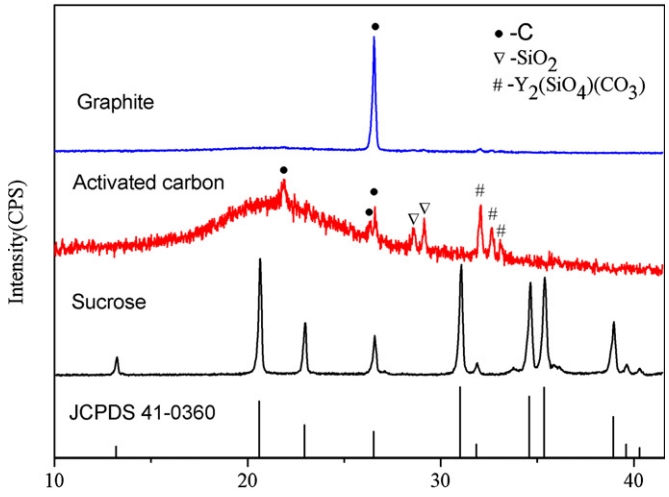

Fig. 2. XRD patterns of products using: (a) sucrose, (b) activated carbon with ball milling for 12 h, (c) graphite mechanical stirring for 12 h, calcinated under same condition at 1380 °C for 6 h.

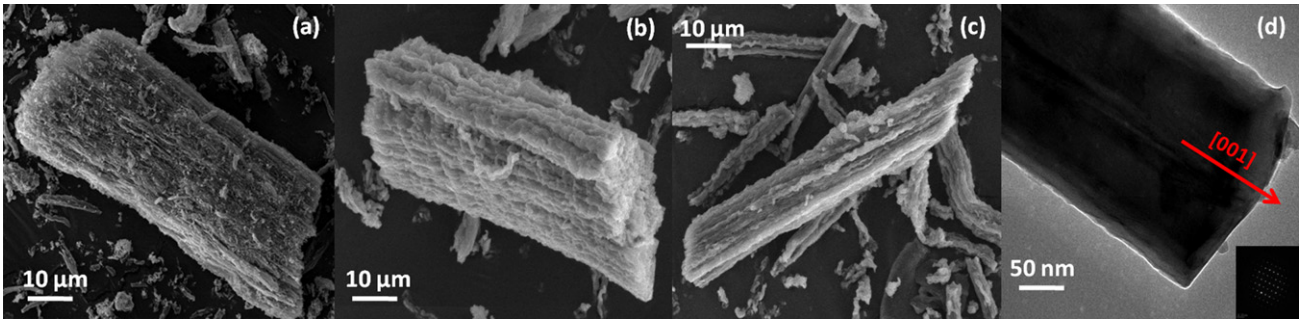

Fig. 3. SEM images of: (a) a single SBA-15 grain; (b) a single α-Si_3N_4 grain calcinated at 1380 °C for 6 h; (c) rod-like α-Si_3N_4 grains; (d) TEM image of a single α-Si_3N_4 grain (1380 °C for 6 h) and its selected area electron diffraction pattern.

Table 2
Relative density, K_{Ic} and dielectric properties of R0, R5 and R10.

Sample	Relative density (%)	K_{Ic} (MPa $m^{1/2}$)	Dielectric constant (ε)			Dielectric loss $\times 10^{-3}$ (tan σ)		
			150 kHz	10 MHz	20 MHz	150 kHz	10 MHz	20 MHz
R0	94.2	2.9	8.6	6.1	6.1	37	3.8	2.8
R5	94.3	4.4	9.5	6.4	6.4	40	1.4	2.1
R10	94.3	4.9	10.2	6.7	6.7	42	0.7	1.9

composited carbon by nanocasting process, while activated carbon and graphite were mixed with SBA-15 by using ball milling and mechanical stirring for 12 h, respectively. All samples were sintered at 1380 °C for 6 h. As reported by Ryoo [13], sucrose with –OH group can be readily impregnated into meso-channels of SBA-15. After carbonization, in situ composited carbon is formed within SBA-15 and certain bonds will exist on the surface of carbon and SBA-15. These bonds are helpful to decrease sintering temperature. As shown in Fig. 2a, by using in situ C/SBA-15 as reactant, well-crystallized α-Si_3N_4 can exist at lower sintering temperature (1380 °C). However, in Fig. 2b and c, there was no indication of formation of α-Si_3N_4, where graphite and activated carbon were mixed in simple mechanical way. These results match our inference well that composited carbon with SBA-15 can lower the reaction temperature.

It is noticed that well-crystallized Si_3N_4 needed shorter soaking time (6 h) than that of previous carbothermal reduction-nitridation methods (16 h) [14]. In the present work, SBA-15 was used instead of traditional SiO_2. We observed that surface area of SBA-15 employed here reaches 493 m^2/g, which is much larger than that of common SiO_2 (3.1 m^2/g). The larger specific surface area supplies more reactive sites to react with carbon and nitrogen in the CRN process, leading to higher reaction efficiency of SiO_2. As a result, the reaction activity will increase. Finally, the increased reaction activity was followed by shorter soaking time.

The SEM images of PRSN (1380 °C/6 h) and original SBA-15 have been shown in Figs. 3a and b. The final α-Si_3N_4 powder has striking similar rod-like morphology to its parental SBA-15. It means the original SBA-15 is responsible for the formation of rod-like morphology. Grains generally grow along the [0 0 1] direction through the observation of TEM shown in Fig. 3d. In Fig. 3c, a great deal of powder appears in a rod-like shape which indicates that the rod-like morphology is not an accidental phenomenon.

Relative density, fracture toughness (K_{Ic}) and dielectric properties (ε and tan σ) of all three samples (R0, R5 and R10) are summarized in Table 2. The relative density results demonstrate that these samples are all nearly densified. The K_{Ic} value of R0 sample (α-Si_3N_4 without reinforcement) was measured to be 2.9 MPa $m^{1/2}$, close to the value (3.0 MPa $m^{1/2}$) reported by Reveron [4]. By adding the PRSN as reinforcement, the ceramics samples exhibited enhanced fracture toughness. Moreover, as shown in Table 2, the fracture toughness is further enhanced with the doping content of PRSN. The K_{Ic} value of R10 sample (with 10 vol% PRSN) is 4.9 MPa $m^{1/2}$, which is about 69% improvement over that of R0 sample. It is at the same levels as that of well developed β-Si_3N_4 ceramics [10]. This improvement is mainly attributed to the rod-like microstructure of PRSN by means of crack bridging/pullout or crack deflection mechanism. As for dielectric properties, no matter what frequency (f) was used between kHz and MHz, ε had no obvious change and still stayed at low values. However, with the doping of PRSN, tan σ has sharp reduction from 0.0038 to 0.0007 when f is 10 MHz and from 0.0028 to 0.0019 when f is 20 MHz. This is desirable result for dielectric applications which prefer low tan σ.

4. Conclusions

In summary, we developed a convenient and effective carbothermal reduction-nitridation (CRN) method to synthesize the pure rod-like α-Si_3N_4 powder (PRSN) by using in situ carbon/mesoporous silica composition (C/SBA-15) as silica source. SBA-15 in this work was used as template. Due to the large specific surface area of SBA-15 (493 m^2/g) and the composited carbon, the carbothermal reduction-nitridation

activity of silica is increased significantly and the nitridation temperature is decreased to the range of 1300–1380 °C, in which α-phase is the thermodynamic stable form (not transformed to β-phase). The pure rod-like α-Si_3N_4 is finally obtained and its morphology is well derived from parental SBA-15. In addition, by doping the as-synthesized PRSN, the fracture toughness of α-Si_3N_4 ceramics is efficiently improved. K_{Ic} value of the doped α-Si_3N_4 ceramics (10 vol% PRSN) can reach 4.9 MPa $m^{1/2}$, which is at the same level as that of well-crystallized β-Si_3N_4 ceramics. Moreover, dielectric loss (tan σ) is reduced after doping PRSN, when frequency is in MHz. In a word, the PRSN powder is a suitable candidate for toughening α-Si_3N_4 based ceramics, which is used in applications requiring low dielectric constant and loss.

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