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Journal of the European Ceramic Society 28 (2008) 289–293

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PTFE, an effective additive on the combustion synthesis of silicon nitride

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Received 3 February 2007; received in revised form 30 May 2007; accepted 15 June 2007
Available online 27 August 2007

Abstract

Combustion synthesis (CS) of Si_3N_4 with the addition of polytetrafluoroethylene (PTFE) was carried out at a relatively low N_2 pressure of 2 MPa. It was found that the additive PTFE promoted the nitridation of Si. The α-Si_3N_4 contents in the periphery of the combustion-synthesized products showed great dependence on the contents of PTFE added in the reactants, which reached 77.7 wt.% with 4 wt.% PTFE addition. The residual silicon in the center of the combustion-synthesized products could be completely nitrided by further heat treatment at 1300 °C for 1 h in N_2. The temperature difference between the center and the edge of the samples was responsible for the discrepancy in both phase composition and morphology of the products.

Keywords: PTFE; Low nitrogen pressure; Si_3N_4; Combustion synthesis

1. Introduction

Silicon nitride (Si_3N_4) based ceramics are used in a variety of structural applications such as engine component, heat exchanger, pump seal materials, ball bearings, cutting tools and so on, owing to their excellent mechanical properties at both room and elevated temperatures, high resistance to thermal shock and chemical attack, outstanding creep resistance and very good tribological properties.[1] The demands for the Si_3N_4 powders as raw material are constantly growing, therefore simpler and cheaper methods for its production are required. Conventional processes of Si_3N_4 powder production, such as direct nitridation, carbothermal reduction and the decomposition of silicon imide, were characterized by high temperatures and long production periods and complicated technological cycles.[2–4] Thus, the cost of production is very high, which inevitably impedes the application of Si_3N_4 in large scale.

The combustion synthesis (CS) method presents some unique advantages such as cost-effectiveness, self-purification, simple processes, which has been applied to synthesis of various high-temperature materials including ceramics, intermetallic compounds and composites.[5,6] For the fabrication of Si_3N_4 powder, one problem commonly encountered was the agglomeration of Si melted at elevated temperatures which inhibited the diffusion of N_2 due to collapse of the pore openings. It is possible to prevent the coalescence of the melted Si by adding Si_3N_4 diluent ranging from 20 to 60 wt.% into the reactant mixtures to decrease the maximum combustion temperature.[6–10] However, in the point of view of cost-effective production, higher ratio of Si_3N_4 diluent employed in the reactants is not expected. On the other hand, a high pressure of N_2 was usually employed in order to get high degree of Si nitridation by preventing the decomposition of the as-synthesized Si_3N_4 within the combustion wave zone.[6–10] Whereas, the high-pressure process is not desired because of high facility cost and safety production.

In our previous work, the maximum combustion reaction temperature could be lowered by reducing the pressure of N_2 and/or by increasing the content of Si_3N_4 diluent added.[11,12] Hirao et al. reported a critical nitrogen pressure of 3 MPa, below which CS of Si_3N_4 could not be accomplished.[10] The breakthrough of the minimum nitrogen pressure for the CS of Si_3N_4 was realized with the mechanochemical activation of the Si reactants, which was reported by our previous study.[11,12] However, long periods of mechanochemical activation not only leaded to

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doi:10.1016/j.jeurceramsoc.2007.06.008

Table 1
Compositions of the starting powder mixtures

Sample	Si (wt.%)	NH_4Cl (wt.%)	PTFE (wt.%)
S0	95	5	0
S1	94.05	4.95	1
S2	93.1	4.9	2
S4	91.2	4.8	4
S8	87.4	4.6	8

higher energy consumptions but also brought impurities into the reactants.[13]

In the present paper, PTFE was explored as an effective additive to fabricate Si_3N_4 by CS. This work will provide a feasible approach to the production of Si_3N_4 at a low cost.

2. Experimental procedure

The reactants were powder mixtures containing Si (98 wt.% pure, particle size <44 μm), polytetrafluoroethylene (PTFE, 99 wt.% pure) and NH_4Cl (99 wt.% pure). The mass of Si and NH_4Cl were 190 and 10 g, respectively, together with the weight ratio fixed as to 95:5 in all the samples. The starting compositions listed in Table 1. The samples were briefly designated as S0, S1, S2, S4 and S8, respectively, according to the amount of PTFE added to the samples.

All the reactants were attrition milled for 1 h using steel balls as the milling media with a ball/charge weight ratio of 8:1. The mixed powders were sieved through a 200 mesh screen and packed in a porous graphite crucible which was 35 mm in diameter and 150 mm in length. The porosity of the green mixture was about 70–80%. The crucible was then placed into a stainless steel pressure vessel 5 L in volume and 150 mm in diameter. The reaction chamber was evacuated to a vacuum of 10^{-1} Pa and then high-purity N_2 was backfilled to 2 MPa. The combustion reaction was ignited by burning a titanium powder compact placed on the top of the packed reactant using an electrically heated tungsten coil.

The reaction temperatures were recorded with two W Re/3-W Re/25 thermocouples (0.5 mm in diameter) protected by a BN tube 2.5 mm in diameter and 0.3 mm thick, which were attached to the surface or inserted into the center of the packed reactant. The phase compositions of reaction products were determined by XRD (Cu Kα, Rigaku, Japan) and quantitative analysis was carried out according to Gazzara and Messier method.[14] The morphologies of the samples were observed by SEM (JSM-6460LV, JEOL, Japan). Thermogravimetric and diffraction scanning calorimetry (TG-DSC) (STA 409C, Netzsch Co., Germany) were performed in N_2 at a heating rate of 10 °C/min.

3. Results and discussion

CS of Si_3N_4 was accomplished for all the samples except for S0 (without PTFE added) under a nitrogen pressure of 2 MPa. In this work, the period for mechanochemical activation treatment of reactants was only 1 h and, no Si_3N_4 diluent was used. The results showed the effective catalysis of PTFE for the CS of Si_3N_4.

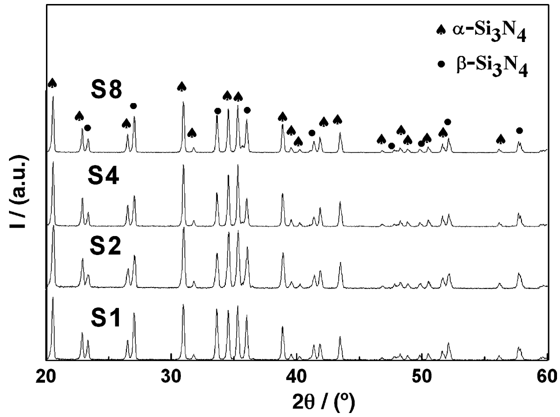


Fig. 1. X-ray diffraction patterns of the CS products without black core from samples S1, S2, S4 and S8.

The reaction products were grey and slightly hard, which kept the same shape as that of the starting powder compacts without obvious expansion or contraction. But the observations of the longitudinal cross-section of the products showed that every CS product consisted of a black core with the dimensions 5 mm in diameter and 130 mm in length in the center. The X-ray diffraction patterns of the combustion-synthesized products with the black core removed are shown in Fig. 1. According to Fig. 1, the CS products consisted of α-Si_3N_4 and β-Si_3N_4, while no diffraction peak of residual Si was found, demonstrating that complete nitridation of Si was achieved. Table 2 shows the surface reaction temperature (T_s) of the powder compact and the measured temperature difference (ΔT_{max}) between the center and the surface for different samples. The α-Si_3N_4 contents of the corresponding products calculated according to Gazzara and Messier method are also shown in Table 2. The values of the α-Si_3N_4 content first increased and then decreased with the increase of PTFE content, whereas the values versus T_s show the inverse trend. It can be concluded that the decrease of T_s may be benefit to form α-Si_3N_4.

The X-ray diffraction patterns of the combustion-synthesized products took from the black core of sample S1and S8 are shown in Fig. 2a and b, respectively. It was found that the dominant phase was β-Si_3N_4 with some diffraction peaks of residual Si and α-Si_3N_4. The presence of residual Si should be attributed to the high temperature in the center of the reactant compact.[6,7] All the black cores of combustion-synthesized products were milled and then heat treated at 1300 °C for 1 h in N_2 atmosphere with

Table 2
Characteristic parameters measured or calculated for the samples

Sample	Surface temperature, T_s (°C)	T_{max} (°C)	α-Si_3N_4 content except for black core (wt.%)
S0	–	–	–
S1	1518	378	67.4
S2	1480	338	75.2
S4	1469	–	77.7
S8	1495	355	72.2

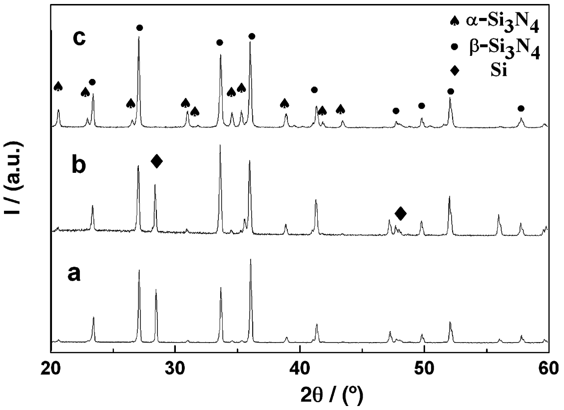


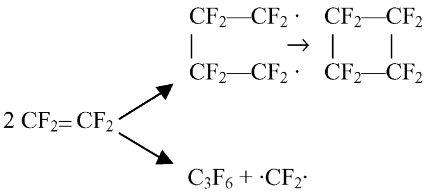
Fig. 2. X-ray diffraction patterns of the black core of CS products from samples (a) S1, (b) S8 and (c) the heat-treated sample.

a pressure of 0.1 MPa in a protective gas furnace. Fig. 2c shows the X-ray diffraction pattern of the heat-treated sample. It can be seen that no diffraction peak of residual Si was found, and the diffraction peaks of α-Si_3N_4 increased markedly than that in Fig. 2a and b. It demonstrated that the residual Si existing in the black core was completely nitrided and converted into Si_3N_4.

Fig. 3a–d shows the scanning electron micrographs of the samples S1, S2, S4 and S8, respectively, with the black core removed. Large columnar particles was observed in Fig. 3a, which was consistent with the higher β-Si_3N_4 content in sample S1 due to the higher combustion temperature reached.[7–11] The variation of reaction temperature was responsible for the discrepancy of the product morphologies.

The decomposition of PTFE is supposed to occur at the high temperature caused by the Si–N_2 exothermal reaction, which is endothermic in nature,[15,16] which is responsible for the decrease of the combustion temperature with the increase of the PTFE content from S1 to S4. The decomposition of PTFE at high temperature can be expressed by the following three step sequent reactions.[17]

$$R{-}CF_2{-}CF_2{-}CF_2^{\bullet} \rightarrow R{-}CF_2^{\bullet} + CF_2{=}CF_2 \quad (1)$$



(2)

$$CF_2{=}CF_2 + {}^{\bullet}CF_2^{\bullet} \rightarrow C_3F_6 \quad (3)$$

Subsequently, the reaction between Si and PTFE could be expressed as[18]:

$$Si + ({-}C_2F_4{-})_n \rightarrow Si + SiF_x + C \quad (4)$$

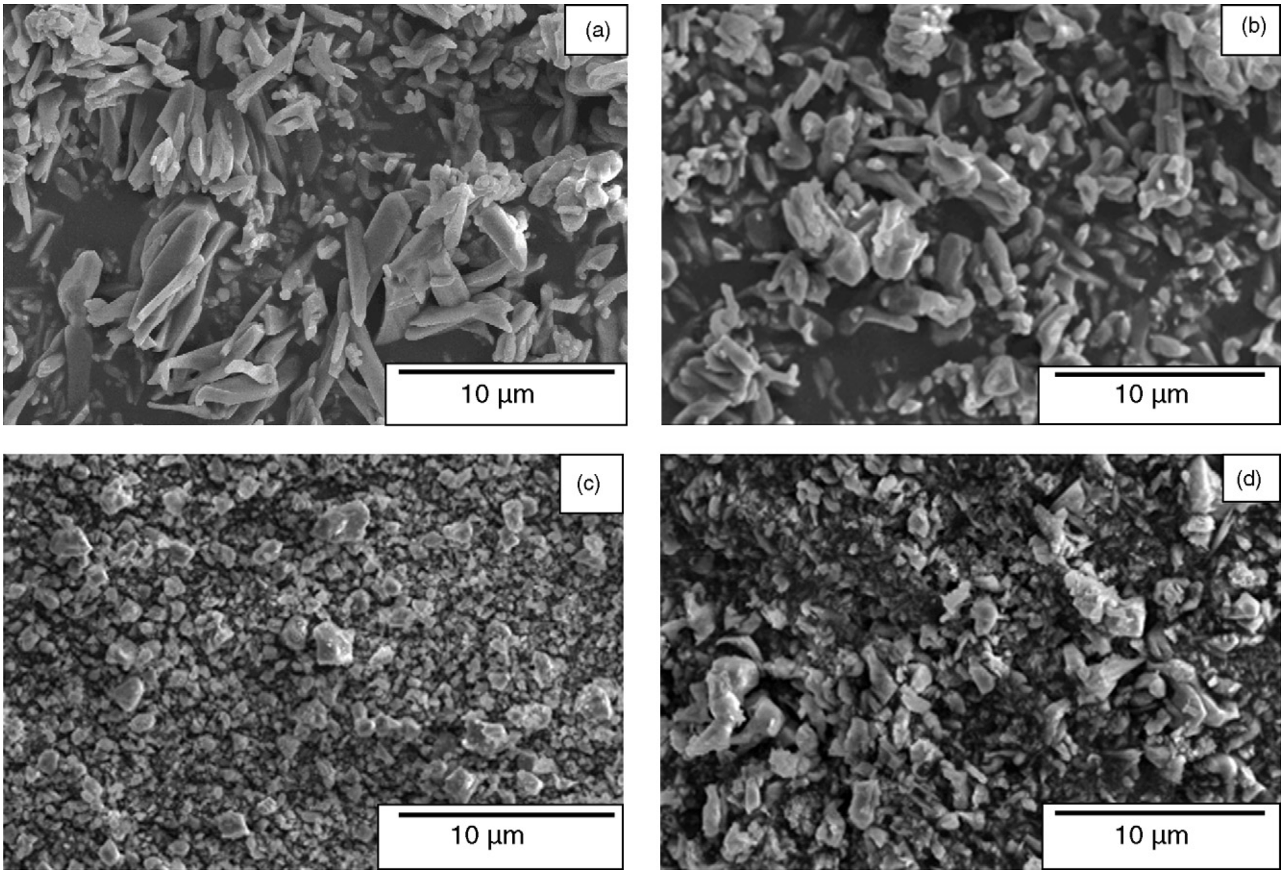


Fig. 3. Scanning electron micrographs of the typical morphologies of the CS products without black core from samples (a) S1, (b) S2, (c) S4 and (d) S8, respectively.

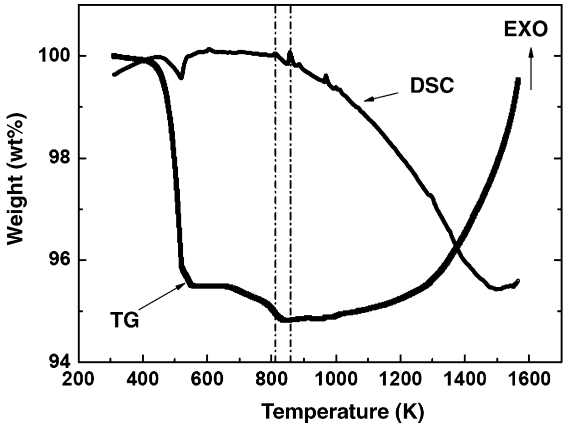


Fig. 4. TG-DSC curves of S1.

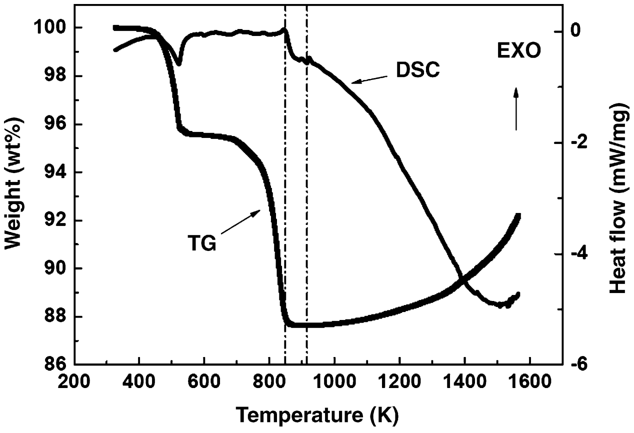


Fig. 5. TG-DSC curves of S8.

Meanwhile, the decomposition of NH_4Cl took place at high temperature via the following reactions.[19,20]

$$NH_4Cl\,(s) \rightarrow NH_3\,(g) + HCl\,(g) \tag{5}$$

$$NH_3\,(g) \rightarrow N_2\,(g) + H_2\,(g) \tag{6}$$

$$HCl\,(g) \rightarrow H_2\,(g) + Cl_2\,(g) \tag{7}$$

During the CS process of the $Si/NH_4Cl/PTFE/N_2$ system, the following reaction mechanisms for synthesizing Si_3N_4 may exist[19,20]:

$$Si + HCl\,(g) \rightarrow SiCl_x + H_2\,(g) \tag{8}$$

$$\begin{aligned} &SiCl_x\,(g) + N_2 + NH_3\,(g)/H_2\,(g) \\ &\quad \rightarrow [Si_x(NH)_y]_n\,(s) + HCl\,(g) \end{aligned} \tag{9}$$

$$\begin{aligned} &SiF_x\,(g) + N_2 + NH_3\,(g)/H_2\,(g) \\ &\quad \rightarrow [Si_x(NH)_y]_n\,(s) + HF\,(g) \end{aligned} \tag{10}$$

$$[Si_x(NH)_y]_n\,(s) \rightarrow Si_3N_4\,(s) + NH_3\,(g) \tag{11}$$

$$Si + N_2 \rightarrow Si_3N_4\,(s) \tag{12}$$

TG-DSC experiments for S1 and S8 were carried out to demonstrate the above analysis, as illustrated in Figs. 4 and 5, respectively. The mass losses of samples in both TG curves at 170 °C and 547 °C corresponds to the decompositions of NH_4Cl and PTFE respectively.[15,16] In S8 with 8 wt.% PTFE addition, a sudden decrease of the heat flow with the increase of temperature was clearly seen at 842 K in the DSC curve, indicating an endothermal reaction occurred at this temperature, which was attributed to the decomposition of PTFE.[15,16] Subsequently, a small exothermic peak appeared at 921 K, indicating the exothermic reaction between Si and free radicals yielded by the decomposition of PTFE was induced.

Therefore, with the increase of PTFE content up to 4 wt.% in samples S1, S2 and S4, the endothermic decomposition of PTFE played the dominate role in determining the combustion temperature reached in the samples. The lower reaction temperature leaded to higher content of α-Si_3N_4 together with higher ratio of equiaxed particles. This is in agreement with the mean particle size decrease from 6 to 1.5 μm with the increase of PTFE content from 1 to 4 wt.%. While, in the case of PTFE content over 4 wt.%, large amounts of SiF_x containing free radicals formed by the decomposition of PTFE exhibited higher reactivity which enhanced the exothermic reaction between SiF_x and N_2,[17–20] regardless the endothermic reaction of PTFE decompo-

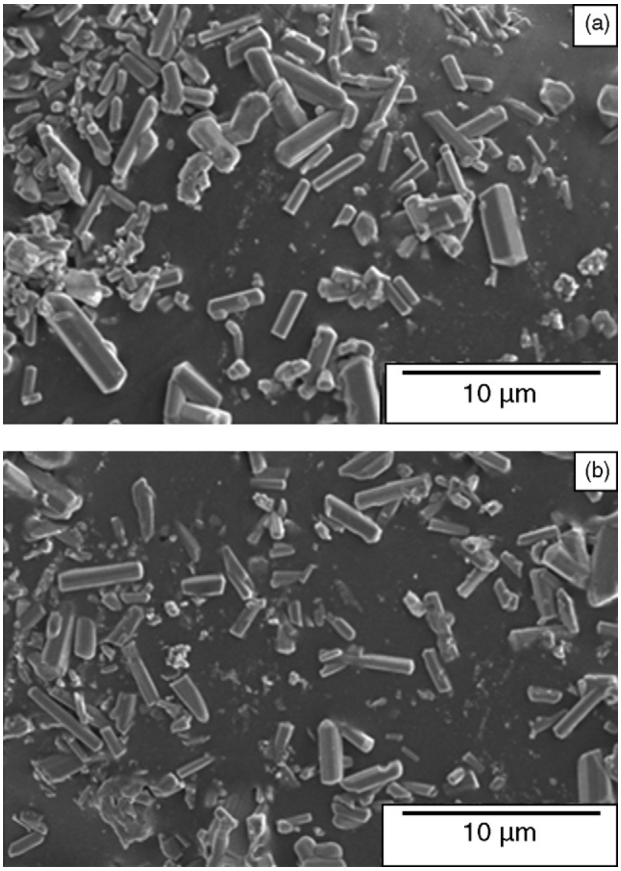


Fig. 6. Scanning electron micrographs of the black hard core from samples: (a) S1 and (b) S8, respectively.

sition at high temperature still existed. Therefore, the measured combustion temperature increased with the increase of the PTFE content from 4 to 8 wt.%, and larger particles were obtained due to the higher temperature in S8.

The SEM photographs of the black cores of S1 and S8 are shown in Fig. 6a and b, respectively. Such large well-developed columnar crystals are expected to find their applications in industry. The mechanism for its formation will be reported elsewhere.

It is noted that the phase compositions and the microstructures of reaction products at different locations of the sample are quite different, as shown in Figs. 1–3 and 6. The discrepancy of the phase compositions as well as the morphology of the as-synthesized product depends strongly on T_s and ΔT_{max}, that is, the decrease of T_s leads to the increase of the α-Si_3N_4 content in the periphery of combustion-synthesized products and the equiaxed particles are easily formed. Assisted by the effective catalysis of PTFE, the complete nitridation of Si was achieved in the periphery of the reactant compact although the T_s was low.

4. Conclusions

(1) CS of Si_3N_4 was accomplished by burning Si powders with PTFE as additive at a relatively low nitrogen pressure of 2 MPa, which would benefit the cost-effective production of Si_3N_4.

(2) PTFE enhanced effectively the nitriding combustion of Si under the lower nitrogen pressure. The content of PTFE additive had a strong effect on the content of α-Si_3N_4, which reached 77.7 wt.% with 4 wt.% PTFE addition.

(3) A small amount of residual Si in the center of the combustion-synthesized products could be completely nitrided after heat treatment at 1300 °C for 1 h in flowing N_2 atmosphere.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (NNSFC) under the Grant numbers 50372074 and 50502035.

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