Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 29 (2009) 175–180

www.elsevier.com/locate/jeurceramsoc

Synthesis of SiC by silicon and carbon combustion in air

Yun Yang[a,b], Zhi-Ming Lin[a], Jiang-Tao Li[a,*]

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China*

Received 9 January 2008; received in revised form 27 May 2008; accepted 6 June 2008
Available online 31 July 2008

Abstract

Nano-sized β-silicon carbide (β-SiC) powder was successfully prepared using the combustion synthesis method in air in combination with a controlled pre-reaction mechanical activation treatment. For the low-exothermic reaction system Si/C, the effect of the mechanical activation time, one crucial processing variable, on the combustion behavior of Si—C reactant in air was investigated, and the reaction kinetics parameters were measured and calculated to analyze the reaction mechanism of this combustion reaction. Meanwhile, the reaction mechanism was further approved by the thermodynamic calculation.

Keywords: Combustion synthesis in air; Milling; Powders solid state reaction; SiC; Traditional ceramics

1. Introduction

Silicon carbide (SiC) is an important structural ceramic and a candidate for high temperature applications. Many methods could be used to produce SiC powders, such as carbothermal reduction, sol–gel methods, gas-phase reaction method, self-propagation high-temperature synthesis (SHS) and so on.[1–4] Among these methods, SHS was considered to be an attractive method due to its proven advantages: lower energy requirement, simpler and cheaper equipment, higher product purity, and finer and well-sintered starting powders. However, the synthesis of β-SiC from Si and C elements by the SHS process cannot be realized under normal combustion conditions. The reason is that the Si/C system has a low adiabatic combustion temperature which is 1327 °C ~ 1427 °C.[5] Therefore, an additional energy source is required for the Si/C system to realize the SHS reaction. Much research has been done to provide the additional energy source, such as adding chemical promoter,[6] using microwave energy,[7] or carrying out preheating treatment.[8,9]

In this work, the synthesis of nano-sized β-SiC powders was realized, first and successfully in air, by both pre-reaction mechanical activation (named hereafter as MA) treatment of the Si and C reactant mixture and the SHS process. The main objective of this study is to develop a novel low-cost synthesis technology to prepare nano-sized β-SiC powders.

2. Experimental procedure

The raw materials used in this study included Si (purity 99.9%, 325 mesh, General Research Institute for Nonferrous Metals, Beijing, China), carbon black (TianHao Carbon Black Corporation, Tianjin, China), and NH_4Cl (Analytical Reagent, Beijing Chemical Corporation, Beijing, China). The specific surface area (SSA) of Carbon black is 74–90 m^2/g. About 1–3 wt% NH_4Cl was added as milling promoter.

The reactant powders of Si, carbon black, and NH_4Cl were directly put into a stainless steel vessel, and then ball-milled for 2–16 h in air. Subsequently, the milled mixtures of 300 g/batch were loosely loaded into a porous graphite crucible of 200 mm long, 80 mm wide and 50 mm high which was placed in air. The combustion reaction was initiated by igniting a titanium powder compact placed on the top of the reactant.

Two W—Re thermocouples were inserted into the sample to record the temperature history of combustion reactions. To calculate the velocity of combustion wave, the distance between two W—Re thermocouples was exactly kept to be 20 mm.

The effect of the MA on Si—C combustion reaction in air was investigated by modifying the ball-milling time. The combustion temperature histories of each reaction corresponding to different

---

[*] Corresponding author. Tel.: +86 10 82543693; fax: +86 10 82543693.
E-mail address: ljt0012@vip.sina.com (J.-T. Li).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.06.013

MA time were recorded. According to these temperature profiles, the reaction kinetics parameters: the rate of temperature increase, the adiabatic temperature rise, the degree of conversion, and the conversion ratio of reaction, were calculated using the temperature profile analysis method.[10–12]

The crystalline phases of the synthesized powder were identified using X-ray diffraction (XRD; Cu Kα, Rigaku, Japan), and the morphologies of the sample were observed by scanning electronic microscopy (SEM; HITACHI S-4300, Japan).

3. Results and discussion

3.1. The influence of the mechanical activation time

In our previous work, the effect of mechanical activation on the reactant mixtures has been studied through XRD, differential thermal analysis (DTA), and thermo-gravimetric analysis (TGA). The rapid increase in the reactivity and the amorphous degree of the Si and C elements with the increase of milling time has been demonstrated.[13] Therefore, extensive milling of the reactants was carried out to induce the combustion reaction of Si and C elements in air.

For the low-exothermic reaction system of Si/C, in order to identify the feasibility of the Si/C combustion reaction in air, seven experiments with different pre-reaction MA time were performed in air. The composition of the reactant mixtures was Si/C/NH_4Cl = 69.3/29.7/3 (weight ratio), and kept the same in all experiments. The MA times for these experiments were 2 h, 4 h, 6 h, 8 h, 10 h, 12 h, and 14 h, respectively.

The pre-reaction mechanically activated mixtures were all ignited successfully in air, and realized the propagation of combustion waves, except the reactant mixture pre-treated for 2 h. The synthesized products were lumped. In the outer layer of the lump, a thin white product of only 0.5 mm was obtained, which was demonstrated to be SiO_2, residual Si and minor amount of SiC. Fig. 1 shows one of the results of XRD analysis. Shucking off the outer layer of the lump, the rest of the products were loose green powders. Fig. 2 are the XRD patterns of these green powders, in which the products were composed mainly of β-SiC with a minor amount of Si_2N_2O, Si and C peaks were not detected. It means the combustion reactions of the Si–C reactant mixture in air took place and were completed when the MA times reached 4 h.

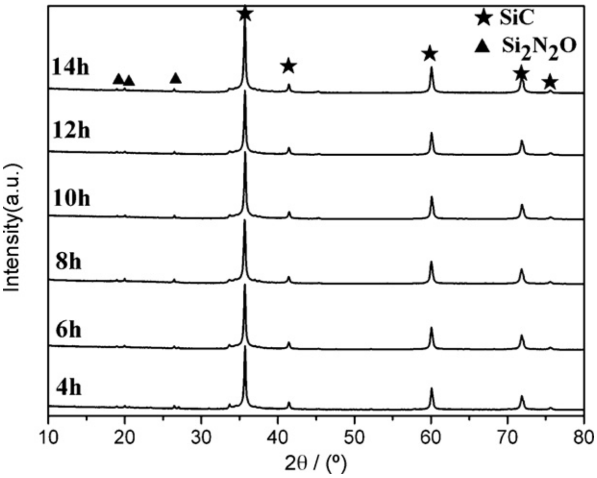

Fig. 2. XRD patterns of the products synthesized from the reactants by different MA treatment.

The typical SEM photograph of the synthesized β-SiC product is shown in Fig. 3. The as-synthesized β-SiC was uniformly equiaxed particles with nanometer size.

It was found that, after ignition, the burning of the Si–C mixtures occurred via two-stage self-propagating regime. In the first stage of combustion, from the ignition point, combustion waves with red wine color propagated through the sample, and the temperature of the combustion region increased rapidly to about 800 °C, but did not reach the maximum value. Soon after the first propagation, the second propagation started from the ignition point through the full volume of the reactant. During the second stage, the temperature of the combustion region increased quickly up to the maximum, the color of the combustion region was white-hot. After that, with the decrease of the combustion temperature, the color of the combustion region gradually changed dim. After about 75 min, the combustion reaction ended. The typical temperature profile of the combustion reaction from Si and C elements in air is shown in Fig. 4. Similar results were also obtained for all of the other experiments. The maximum temperatures of these combustion

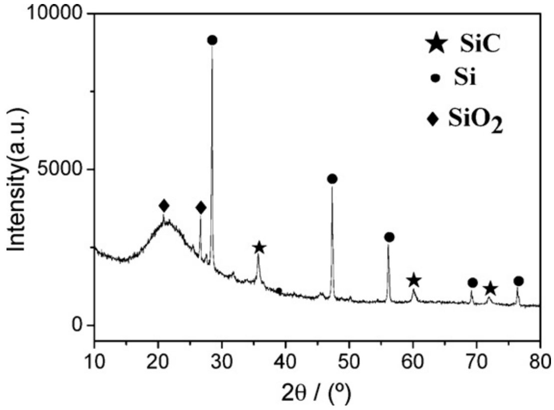

Fig. 1. XRD pattern of the surface product from the combustion reaction of Si and C elements in air.

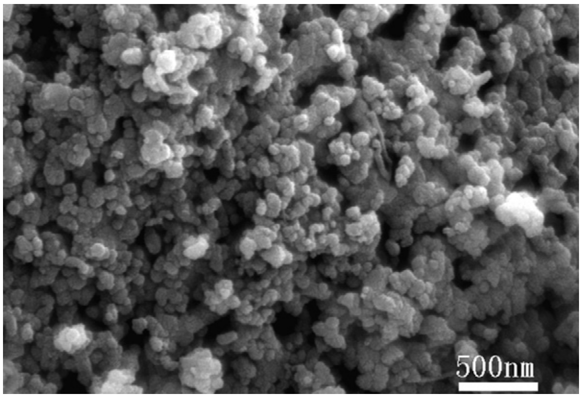

Fig. 3. SEM photo of synthesized product from the combustion reaction of Si and C elements in air.

Table 1
Characteristic kinetics parameters measured and calculated for different experiments

	MA time (h)	The maximum temperature (°C)	The velocity of combustion wave (mm/min)	The adiabatic temperature rise (°C)	The degree of conversion (%)
1	4	1740	8.11	2741.2	90
2	6	1735	9.21	2798.4	90
3	8	1747	12.4	3323.1	98
4	10	1747	12.0	2831.8	90
5	12	1747	11.34	3276.0	95
6	14	1760	11.19	2733.9	95

reactions in air remained almost the same and were all about 1750 °C as shown in Table 1.

Table 1 listed combustion process parameters such as the velocities of combustion wave and the maximum temperature. It is clearly seen from Table 1 that MA leads to the increase in the velocity of combustion wave. Within 8 h of the MA treatment time, the velocity of combustion wave increased from 8.11 mm/min to 12.4 mm/min with the increase of the MA time. However, when the MA treatment time was above 8 h, the velocity of combustion wave decreased. The non-linear relationship of the combustion wave velocity with the MA treatment time indicated that prolonging the MA treatment time over 8 h cannot further increase the reactant's activity.

3.2. The kinetic analysis of the combustion reaction of the Si/C system in air

XRD analysis indicated that the β-SiC could be combustion synthesized in air with Si and C elements. Therefore, the method of temperature profile analysis[10–12] was used to determine the kinetics parameters, and to further identified the feasibility of the Si–C combustion reaction in air.

The combustion wave is assumed to travel along one-dimension. The general heat balance equation for self-propagating reaction is expressed as:

$$k\frac{\partial^2 T}{\partial x^2} - C_p\rho\frac{\partial T}{\partial t} + \Phi'(T, \eta) - h(T - T_0) = 0 \qquad (1)$$

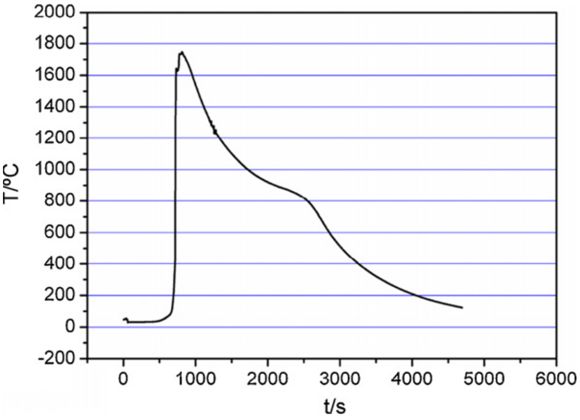

Fig. 4. The temperature profile in the combustion reaction of Si and C elements in air.

In the above equation, k is effective thermal conductivity during the reaction, C_p is the heat capacity of the product, ρ is density, φ is the reaction rate, h is an axial heat transfer coefficient, η is the degree of conversion, T is temperature, t is time and x is the coordinate along which the wave is propagating.

Boddington and co-workers further derived the equation into the following formula:

$$\frac{\partial \eta}{\partial t} = \frac{1}{\tau_{ad}}\left[\frac{1}{t_x}(T - T_0) + \frac{\partial T}{\partial t} - t^*\frac{\partial^2 T}{\partial t^2}\right] \qquad (2)$$

In Eq. (2), $t_x = t_d + t_r$, t_x is the thermal relaxation time, t_d is the inert decay time, t_r is inert rise time during the reaction and τ_{ab} is the adiabatic temperature rise, and

$$\tau = T - T_0, \qquad \frac{1}{t^*} = \frac{1}{t_r} - \frac{1}{t_d} \qquad (3)$$

Ahead and behind of any combustion wave, there are zones in which no chemical reaction takes place. These zones are defined as inert rise zone and inert decay zone. The relationship between $\ln(T - T_0)$ and t in these regions is expected to be linear. Thus, $1/t_r$ and $1/t_d$ could be determined respectively from the slopes of the line, and then, the parameter t^* could be calculated from Eq. (3). The second term $\partial T/\partial t$ and third term $\partial^2 T/\partial t^2$ in Eq. (2) could be obtained from the derivatives of the temperature profile data. Therefore, τ_{ab} could be calculated from the following Eq. (4).

$$\tau_{ad} = \frac{t_r}{t_d - t_r}\tau(t_1) + \frac{t_d}{t_d - t_r}\tau(t_2) + \frac{1}{t_d - t_r}\int_{t_1}^{t_2} \tau(t)\,dt \qquad (4)$$

In Eq. (4), t_1 and t_2 can be selected at random in the inert rise zone and the inert decay zone. The value of $\partial\eta/\partial t$ and η could be obtained respectively from Eqs. (2) and (5).

$$\eta = \int \frac{\partial \eta}{\partial t}\,dt \qquad (5)$$

Based on the calculation procedure listed above, six temperature profile analyses were all performed, and the kinetics parameters of six combustion reactions of Si and C elements in air were calculated and listed in Table 1. And the dependences, obtained by analyzing the temperature profile, of conversion ratio $\partial\eta/\partial t$ and degree of conversion η on the reaction time t were similar in all the experiments. Fig. 5 shows the curves of $\partial\eta/\partial t$ and η vs. t, which was obtained from the combustion reaction in air with the MA 8 h Si–C reactant mixture. From Table 1 and Fig. 5, it is noted that the conversion degree η of the combustion

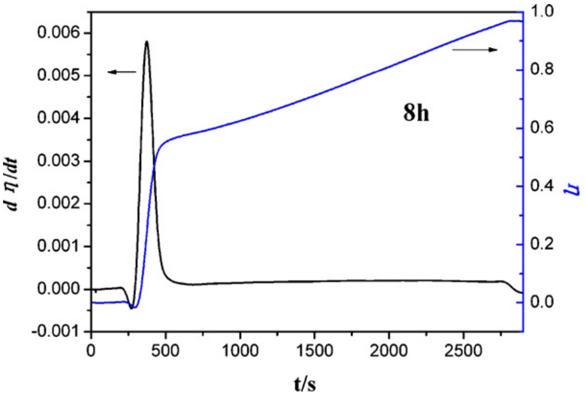

Fig. 5. Dependences of $\partial\eta/\partial t$ and η on the reaction time in the combustion reaction in air with the mechanically activated 8 h Si—C reactant mixture.

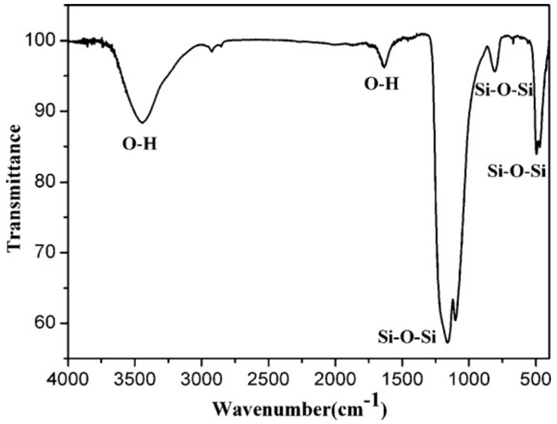

Fig. 6. Fourier transform infrared spectra of the intermediate product quenched before the second propagation.

Table 2
Equilibrium reactions in Si—C—N—O system

	Reaction
1	β-$Si_3N_4 + 3C(s) = 3\beta$-$SiC + 2N_2(g)$
2	4β-$Si_3N_4 + 3O_2(g) = 6Si_2N_2O(s) + 2N_2(g)$
3	β-$Si_3N_4 + 3O_2(g) = 3SiO_2(cr) + 2\ N_2(g)$
4	$2Si_2N_2O(s) + 4C(s) = 4\beta$-$SiC + O_2(g) + 2N_2(g)$
5	$2Si_2N_2O(s) + 3O_2(g) = 4SiO_2(cr) + 2N_2(g)$
6	$SiO_2(cr) + C(s) = \beta$-$SiC + O_2(g)$

reaction of Si and C elements in air are all more than 90% and the maximum is even up to 98%, demonstrating the conversion of Si and C mixtures to SiC in air is near to completion.

Combustion results given in Table 1 indicated that the adiabatic temperature rise τ_{ab} of the Si–C combustion reaction in air were all approach to 2727 °C. That is to say, the mechanically activated Si–C reactant mixture has been changed from the low-exothermic reaction system to the high-exothermic reaction system, which may be the main reason that the combustion reaction of Si and C mixtures could be initiated in air with mechanical activation.

3.3. The reaction mechanism of the Si–C combustion reaction in air

Two contrast experiments were done to deduce the reaction mechanism, in which the same reactant mixtures mechanically activated for 8 h were ignited respectively in the air and argon atmosphere. After ignition, the reactant mixture placed in air underwent combustion reaction, whereas the other reactant mixture quenched in argon atmosphere. This result clearly illustrated that the combustion reaction in air most likely attributed to the oxidation of the Si and C reactant mixtures. Tsuchida et al.[14,15] has also proved that the oxidation reaction could cause the following combustion reaction in air in other reaction system, such as Al/C, Tr/B/C. In order to further confirm this deduction, the combustion reaction in air was quenched before the second combustion propagation, and the intermediate product was obtained. Then the intermediate product was analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectra (FTIR). The XRD pattern was characterized by the presence of Si diffraction peaks only since the carbon black is amorphous. Whereas, in the FTIR spectrum shown in Fig. 6, the absorption bands at 1101 cm^{-1}, 811 cm^{-1}, 495 cm^{-1} are attributed to antisymmetric and symmetric stretching vibrations of Si–O–Si bond, respectively. Therefore, it could be deduced that after ignition, the mechanically activated reactant mixtures firstly took place the oxidation reaction which was the key factor for initiating the following combustion reaction.

Then, how is the product after the second propagation? Inside the lump, the temperature profile showed that, after ignition, the reaction temperature rapidly reached its highest value. Thus, the combustion reaction of Si–C reactant in air may be assumed to take place under near adiabatic conditions. Therefore, the stability of the phases in equilibrium was calculated for the Si–C–N–O system in order to analyze and predict the presence of phases of the synthesized product.[16]

The equilibrium reactions in the Si–C–N–O system in the temperature range concerned in this study are summarized in Table 2. The standard free energies of formation of the solid phase are obtained and listed in Table 3.

When three solid phases and a gas phase are in equilibrium, the number of degrees of freedom determined from the phase rule is two. Combining the equations shown in Table 3, phase stability is calculated at $a_c = 1$ and at temperature 1727 °C (2000 K) which is the maximum value in the combustion of Si/C in air. The carbon is one of the reactants, thus the value of the lever of carbon activity is 1.

The phase stability diagrams were constructed as a function of nitrogen and oxygen pressures for a lever of carbon activity. For example, the $SiC/Si_2N_2O/SiO_2$ phase equilibrium is calculated

Table 3
Standard free energies of formation of condensed phase

Species	ΔG° (kJ/mol)
β-Si_3N_4	$-925.2 + 0.450T$
Si_2N_2O	$-658.3 + 0.131T$
β-SiC	$-72.832 + 0.007T$
SiO_2(cr)	$-900.384 + 0.171T$
Si(l)	$-42.825 + 0.0647T - 0.24 \times 10^{-4}T^2$

Table 4
Invariant points of O_2 and N_2 at given a_c and temperature

a_c	T (°C)	$Si_3N_4/Si_2N_2O/SiC$ (atm)	$SiC/Si_2N_2O/SiO_2$ (atm)
1	1727	$P_{N_2} = 10^{3.95}$ $P_{O_2} = 10^{-17.19}$	$P_{N_2} = 10^{-0.76}$ $P_{O_2} = 10^{-13.05}$

as follows from reactions 5 and 6 in Table 2:

$$\log K_1 - \log(P_{N_2})^2 + \log(P_{O_2})^3 = \frac{-119335.61}{T} - 22.04 - 2\log P_{N_2} + 3\log P_{O_2} = 0 \tag{6}$$

$$\log K_2 - \log P_{O_2} + \log(\mathrm{a_c}) = \frac{-43220.653}{T} + 8.565 - \log P_{O_2} + \log(\mathrm{a_c}) = 0 \tag{7}$$

With known a_c and temperature, the oxygen and nitrogen pressures are calculated for the invariant point. The other invariant point was also calculated and listed in Table 4. The calculated stability diagram was plotted in Fig. 7.

It can be seen from Fig. 7 that, when the value of the log P_{N_2} is -0.102 in air, the presence of phases in the synthesized product was completely dependent on the value of the log P_{O_2}. Combining with the XRD patterns of the products synthesized inside the lump, in which the products were mainly composed of β-SiC with a minor amount of Si_2N_2O, it can be concluded that the value of the log P_{O_2} inside the bulk mixture should be in the range from -13.05 to much lower value. It further indicated that SiC was formed inside the crucible where the reactant mixture was well insulated from oxygen.

Therefore, in view of the analysis listed above, the reaction mechanism of the Si and C elements combustion in air could be described as follows: after ignition, the mechanically activated reactant mixtures proceeded the oxidation reaction in which the O_2 inside the stuff was consumed, and formed the first combustion propagation. During this oxidation reaction, the SiO_x and CO_x, which may be the precursor of the Si_2N_2O existed in the final product, were produced. Meanwhile, the heat evolved by the oxidation of element Si and C was efficiently gathered inside the bulk reactants, and increased the initiative temperature of reactant mixture. According to the thermodynamic formula $\Delta H = \int_{T_0}^{T_{\mathrm{ad}}} C_{\mathrm{P}}\, \mathrm{d}T$, the increase of the initiative temperature of reaction system necessarily led to the increase of the adiabatic temperature rise T_{ab}, and further induced the combustion reaction of Si and C reactant mixture in air.

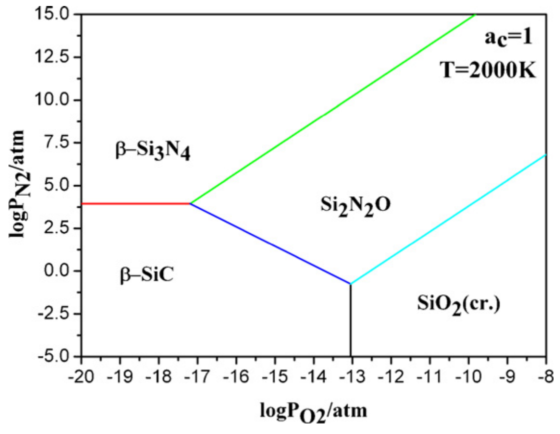

Fig. 7. Phase stability diagram as function of partial pressure of nitrogen and oxygen at $a_c = 1$, $T = 1727\,°C$ (2000 K).

Because of higher rate of temperature increase and higher velocity of combustion wave, the combustion reaction had fast completed before the air outside infiltrated into the bulk reactants. A lump product, which was SiO_2 phase in the outer layer and main β-SiC phase inside the lump, was synthesized and obtained.

4. Conclusions

After mechanically activating Si–C reactant mixture for 4 h or over 4 h, the combustion reactions could be initiated in air. Moreover, this combustion reaction could be steadily repeated. Based on the thermodynamic discussion and reaction mechanism analysis, it can be generalized that the reactant mixture inside the graphite crucible is in the atmosphere of well insulated from oxygen through the combustion process. And the synthesis of the ultra-fine SiC is a dynamically controlled process. Approximately single-phase nano-sized SiC powders were obtained via the SHS process in air. This research result is hopeful to fabricate ultra-fine SiC powders with simplified technology and equipment, and to realize a low-cost manufacture process at large scale.

Acknowledgment

The finance supported from the National Natural Science Foundation of China under the contract No. 50502035 is acknowledged.

References

1. Weimer, A. W., Nilsen, K. J., Cochran, G. A. and Roach, R. P., Kinetics of carbothermal reduction synthesis of beta silicon carbide reactors. *Kinet. Catal.*, 1993, **39**(3), 493–503.
2. Raman, V., Parashar, V. K., Dhakate, S., Bahl, O. P. and Dhawan, U., Synthesis of silicon carbide through the sol–gel process from rayon fibers. *J. Am. Ceram. Soc.*, 2000, **83**(4), 952–954.
3. Leonhardt, A., Liepack, H., Biedermann, K. and Thomas, J., Synthesis of SiC nanorods by chemical vapor deposition. *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2005, **13**, 91–97.
4. Pampuch, R., Stobierski, L., Lis, J. and Raczka, M., Solid combustion synthesis of β-SiC powders. *Mater. Res. Bull.*, 1987, **22**, 1225–1231.
5. Zhang, J., Jeong, J. C., Lee, J. H., Won, C. W., Kim, D. J. and Kim, C. O., The effect of carbon sources and activative additive on the formation of SiC powder in combustion reaction. *Mater. Res. Bull.*, 2002, **37**(2), 319–329.
6. Yang, K., Yang, Y., Lin, Z. M., Li, J. T. and Du, J. S., Mechanical-activation-assisted combustion synthesis of SiC powders with polytetrafluoroethylene as promoter. *Mater. Res. Bull.*, 2007, **42**, 1625–1632.
7. Peng, J. H., Binner, J. and Bradshaw, S., Microwave initiated self-propagating high-temperature synthesis of SiC. *J. Mater. Synth. Process*, 2001, **9**(6), 363–368.
8. Yang, Y., Yang, K., Lin, Z. M. and Li, J. T., Mechanical-activation-assisted combustion synthesis of SiC. *Mater. Lett.*, 2007, **67**, 671–676.

9. Larpkiattaworn, S., Ngernchuklin, P., Khongwong, W., Pankurddee, N. and Wada, S., The influence of reaction parameters on the free Si and C contents in the synthesis of nano-sized SiC. *Ceram. Int.*, 2006, **32**, 899–904.
10. Boddington, T., Laye, P. G., Tipping, J. and Whalley, D., Kinetic analysis of temperature profiles in pyrotechnic system. *Combust. Flame*, 1986, **63**, 359–368.
11. Boddington, T., Laye, P. G., Morris, H., Rosser, C. A., Charsley, E. L., Ford, M. C. *et al.*, A study of pyrotechnic reactions by temperature profile analysis and differential thermal analysis. *Combust. Flame*, 1975, **24**, 137–138.
12. Dunmead, S. D., Munir, Z. A. and Holt, J. B., Temperature profile analysis in combustion synthesis: II. Experimental observations. *J. Am. Ceram. Soc.*, 1992, **75**(1), 180–188.
13. Jin, H. B., Yang, Y., Chen, Y. X., Lin, Z. M. and Li, J. T., Mechanochemical-activation-assisted combustion synthesis of a-Si_3N_4. *J. Am. Ceram. Soc.*, 2006, **89**(3), 1099–1102.
14. Tsuchida, T., Hasegawa, T., Kitagawa, T. and Inagaki, M., Aluminium nitride synthesis in air from aluminium and graphite mixtures mechanically activated. *J. Eur. Ceram. Soc.*, 1997, **17**, 1793–1795.
15. Tsuchida, T. and Yamamoto, S., Mechanical activation assisted self-propagating high-temperature synthesis of ZrC and ZrB2 in air from Zr/B/C powder mixtures. *J. Eur. Ceram. Soc.*, 2004, **24**, 45–51.
16. Wada, H., Wang, M. J. and Tien, T. Y., Stability of phases in the Si—C—N—O system. *J. Am. Ceram. Soc.*, 1988, **71**(10), 837–840.