Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1267–1271
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The influence of mechanochemical activation on combustion synthesis of Si_3N_4

Hai-Bo Jin [a], Mao-Sheng Cao [a], Yi-Xiang Chen [b], Jiang-Tao Li [b,*], Simeon Agathopoulos [c]

[a] School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China
[b] Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100080, China
[c] Materials Engineering Department, University of Ioannina, GR-451 10 Ioannina, Greece

Received 4 December 2006; received in revised form 22 January 2007; accepted 10 March 2007
Available online 24 April 2007

Abstract

This study addresses itself in the performance of Si_3N_4 combustion synthesis, occurred in the presence of Si_3N_4 and NH_4Cl powders in N_2 atmosphere of 6 MPa. Mechanochemical activation of Si powder, achieved via high-energy attrition milling up to 24 h, increases the intensity and the efficiency of the reactions between Si and N_2 as well as combustion temperature. Benign processing conditions, anticipated with lower mechanochemical activation of Si powder, low N_2 pressures, and low combustion temperatures, favor formation of α-Si_3N_4.

Keywords: B. Microstructure final; D. Si_3N_4; Combustion synthesis

1. Introduction

The attractive properties of silicon nitride (Si_3N_4), such as thermal and chemical stability, high mechanical strength and hardness, and good wear, creep, and corrosion resistance, emerge Si_3N_4 as a very important material for high temperature structural applications, such as cutting tools, ball bearings, valves, turbocharger rotors, etc. [1,2]. Powders of Si_3N_4 are commonly produced via direct nitridation, carbothermal reduction, vapor phase reactions, and thermal decomposition processes [3], which, however, generally feature high-energy consumption and poor production rates. Therefore, widening of technological application of Si_3N_4 definitely requires reduction of Si_3N_4 production cost.

The technique of combustion synthesis (CS) [4], whereby the heat generated by an exothermic reaction sustains the reaction itself along a combustion wave after external ignition, attracts an increasing interest for producing many materials. With regard to Si_3N_4 synthesis, CS has been successfully applied in pressurized nitrogen atmosphere [5–8]. With respect to conventional methods of Si_3N_4 synthesis, CS features great energy efficiency, high purity of products, and high production rate. The kinetics of Si combustion in pressurized nitrogen atmosphere is fast and the combustion temperature at the combustion front is far higher than Si melting point. Melting and coalescence of Si can inhibit complete Si nitridation. To suppress such a problem, Si_3N_4 powder is usually incorporated in the initial mixture as a diluent, while ammonium salts, such as NH_4Cl and NH_4F, can enhance nitridation reaction [9–12].

The already acquired experience has shown that combustion nitridation of Si largely results in products with high β-Si_3N_4 content. However, a final product rich in α-Si_3N_4 is rather desirable. Our recent study [13] has successfully tackled that problem reporting the fabrication of rich in α-Si_3N_4 product of CS via a combination of mechanical activation and chemical stimulation at a nitrogen pressure of 1–3 MPa. The interesting results of that work, under the perspective of technology, have motivated the present study, where a course of experiments was planned to shed light in the influence and the impact of mechanochemical activation of Si powder on the CS of Si_3N_4.

2. Materials and experimental procedure

Powders of silicon (purity of 99%, particle size < 44 μm, Shangdong Yinfeng Silicon Materials Co., Ltd., Shandong,

* Corresponding author. Tel.: +86 10 82543695; fax: +86 10 82543693.
E-mail address: ljt0012@vip.sina.com (J.-T. Li).

0272-8842/$34.00
doi:10.1016/j.ceramint.2007.03.020

China), α-Si_3N_4 (93%, <20 μm, Shanghai Junyu High-Technology Ceramic Co., Shanghai, China), and NH_4Cl (Beijing Chemical Co., Beijing, China) were used. Powder mixtures with a weight $Si/Si_3N_4/NH_4Cl$ proportion of 47.5/47.5/4.5 were well homogenized in a ball mill with a weight ratio of powder/steel balls of 1/10. In order to investigate the effect of mechanical activation, the powder mixture was subjected to milling for different times, specifically 8, 12, 16, 20 and 24 h. After sieving, the powder fraction with particles smaller than 200 mesh was collected and loosely packed in a porous graphite crucible of 50 mm in diameter and 350 mm in height. A single load into the crucible was 400 g and the porosity of the green powder compact was about 70–80%.

A compact of high purity Ti powder (99.5%, Beijing Chemical Co., Beijing, China) was placed on the top of the packed reactant mixture, aiming the ignition of combustion. The hermetically sealed chamber (well cleaned from air after three sequential evacuations, down to 10^{-2} mbar, and refilling with pure N_2) was filled with high purity N_2 (99.999%) at a pressure of 6 MPa. The combustion temperature was recorded with a W-Re3/W-Re25 thermocouple of Ø0.2 mm, whose tip was placed at the center of powder compact. Further details of the process have been presented elsewhere [13].

The content of crystalline phases before and after CS was determined with X-ray diffraction (XRD) analysis (Rigaku Geigerflex D/Mac, C Series, Cu Kα radiation, Japan) and according to Gazzara and Messier method [14]. Copper Kα radiation (λ = 1.5406 nm), produced at 30 kV and 25 mA, scanned the range of diffraction angles (2θ) between 10° and 90° with a 2θ-step of 0.02°/s. Microstructure observations were done by field emission scanning electron microscopy (FE-SEM, Hitachi S-4100, Japan; 25 kV acceleration voltage, beam current 10 μA) under secondary electron mode. Differential (DTA) and gravimetric (TGA) thermal analysis of the powder mixture was also carried out in nitrogen atmosphere with a heating rate of 50 K/min (DTA–TG, Labsys Setaram, France).

3. Results and discussion

The influence of milling time on the X-ray diffractograms of the powder mixtures is shown in Fig. 1. The XRD peaks corresponding to Si are specially marked while all the other peaks correspond to Si_3N_4. Evidently, there was a negligible effect on the peaks of Si_3N_4 over prolonged milling but a considerable decrease of the Si XRD peak intensity can be observed, likely attributed to formation of amorphous and nanocrystalline Si. The ratio (in wt.%) of the amount of amorphous Si in the powder mixture produced after certain milling time was calculated by the formula:

$$[(1 - I_{(1\,1\,1)})/I_{0,(1\,1\,1)}] \times 100 \quad (1)$$

where $I_{(1\,1\,1)}$ is the intensity of the strongest Si-peak of the plane (1 1 1) measured from the diffractogram of each milling time and $I_{0,(1\,1\,1)}$ is the intensity measured from the diffractogram of the non-milled (i.e. 0 h) powder mixture. The results

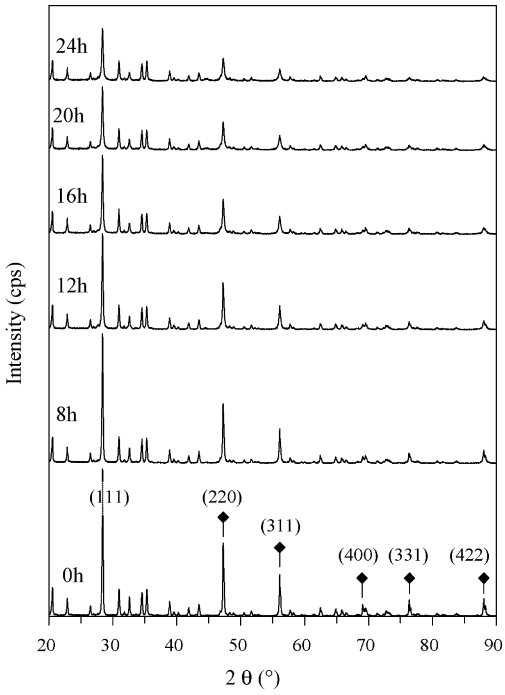

Fig. 1. X-ray diffractograms of powder mixtures, ball milled for different times. The XRD peaks corresponding to Si are marked. All the other peaks correspond to Si_3N_4 (the XRD patterns have not been normalized. Full scale of intensity axis 16,000 cps).

are summarized in Table 1 and confirm an increasing amorphization of Si with increasing milling time.

The increase of amorphous and nanocrystalline Si justifies the term of mechanochemical activation, reached with prolong ball milling of Si. In quantitative terms, it has been reported [15] that the mechanical activation via ball milling of Si to amorphous and nanocrystalline Si leads to an additional free energy of 19.9 kJ/mol when the volume fraction of amorphous Si reaches 15%. That amount of energy is accommodated in various defects of Si, such as dislocations, twins, and stacking faults [16,17].

Two possible mechanisms have been proposed for the amorphization of Si induced by ball milling: Pressure induced amorphization and crystallite refinement induced amorphization. Ammonia halides also play an efficient role during milling since they suppress formation of agglomerates in powder mixture. The enhanced reactivity of Si powder due to the

Table 1
Proportion (in wt.%) of amorphous Si in the milled powders for different milling times

Milling time (h)	I	% Si
0	42,285	0.00
8	34,454	18.52
12	28,544	32.50
16	25,503	39.69
20	23,328	44.83
24	20,527	51.46

The values of I are the integrated areas of the (1 1 1) XRD peaks from the diffractograms of Fig. 1.

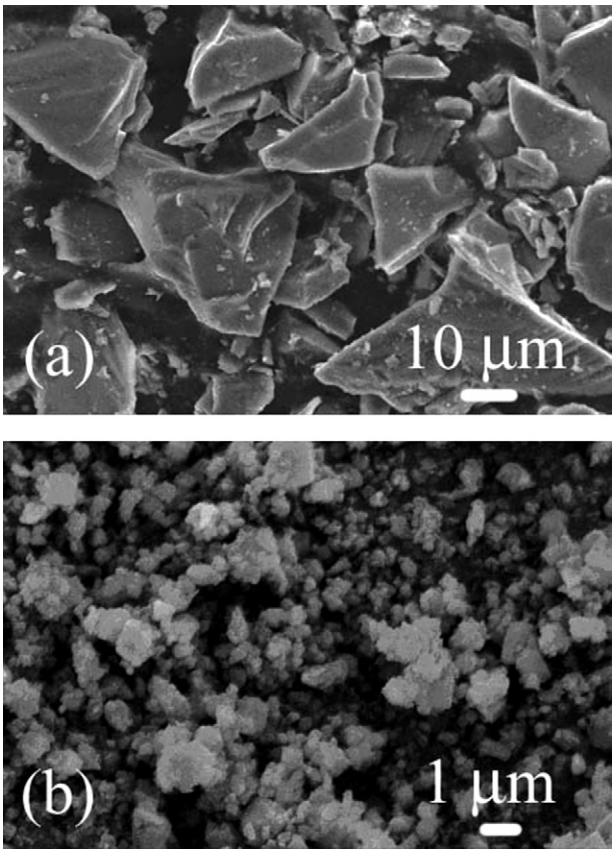

Fig. 2. Prolong ball milling of powder mixture causes significant reduction of the size of Si particles, while the presence of ammonia halides suppresses for formation of agglomerations. (a) Non-milled power and (b) 16 h as milled powders.

reduced size and non-agglomerated particles (Fig. 2), as well as the high concentration of defects, favored by the mechanochemical activation via prolong ball milling, assists CS of Si_3N_4 at low nitrogen pressure [13]. Chemical stimulation is also realized by introducing ammonia halides in the green mixture, which facilitate Si transition to gaseous phase, for instance $SiCl_4$, followed by the reaction with N_2 [9,18]. In that case, the temperature for the reaction between Si and N_2 can be as low as 1000 °C.

The results of thermal analysis (DTA and TGA), plotted in Fig. 3, provide an interesting insight on the influence of mechanochemical activation of the powder mixture, as described above, on the evolution of CS process, although the heating rate of 50 K/min is considerably smaller than the typical rate of CS. The curves of DTA (Fig. 3a) feature a similar general appearance but there is a progressive smooth shift over increasing milling time. Similar features are also seen in the TGA curves (Fig. 3b). Hence, both cases confirm a systematic influence of milling time on thermal behavior of the reactive powder mixture.

The endothermic peak at about 200 °C is attributed to NH_4Cl decomposition:

$$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)} \quad (2)$$

That endothermic effect degrades with increasing the mechanochemical activation (i.e. increasing the milling time) and

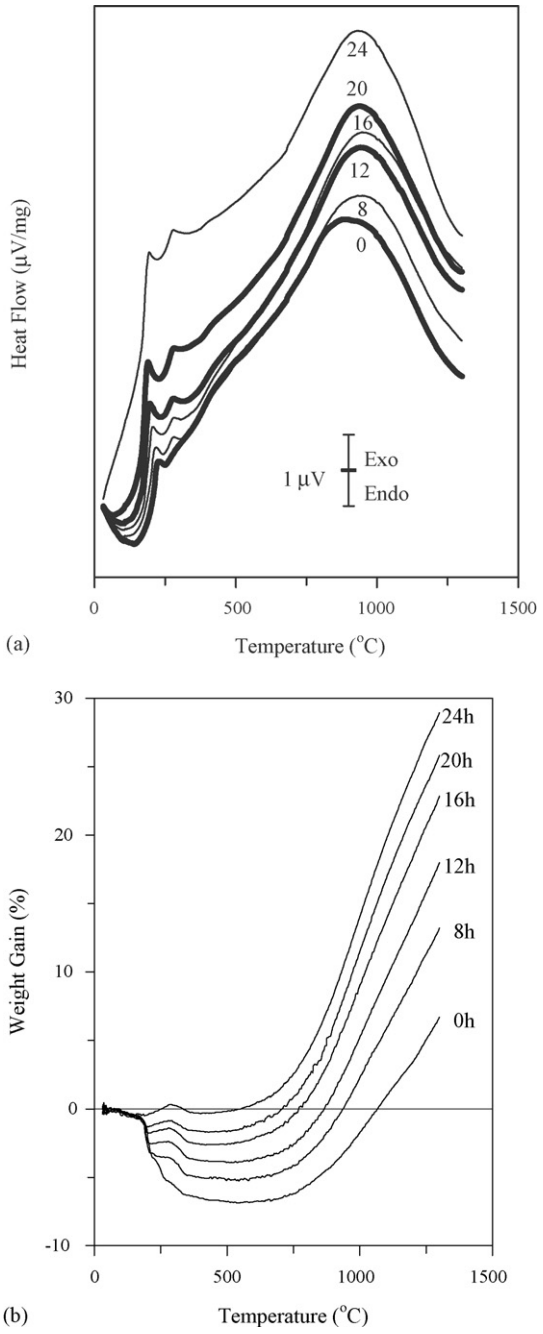

Fig. 3. Thermal analysis of the powder mixtures milled for different times. (a) DTA and (b) TGA (heating rate 50 K/min).

seemingly vanishes after 24 h milling. The two exothermic peaks within the range of 250–350 °C should be due to reactions described by the chemical equations from (3) to (5):

$$Si_{(s)} + 4HCl_{(g)} \rightarrow SiCl_{4(g)} + 2H_{2(g)} \quad (3)$$

$$3SiCl_{4(g)} + 4NH_{3(g)} \rightarrow Si_3N_{4(s)} + 12HCl_{(g)} \quad (4)$$

$$(nx)Si_{(s)} + (ny/3)N_{2(g)} + (ny/3)NH_{3(g)} \rightarrow [Si_x(NH)_y]_{n(s)} \quad (5)$$

The exothermic nitridation reaction of Si in the N_2 atmosphere peaks at ~900 °C, which is considerably lower than the temperature of conventional Si nitridation, confirming the

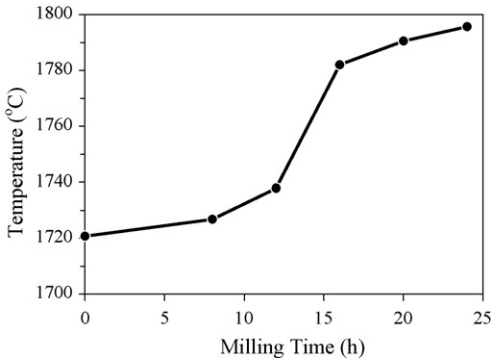

Fig. 4. Maximum combustion temperatures of powder mixtures obtained after ball milling for different times, recorded by the thermocouple.

enhanced reactivity of reactants due to mechanochemical activation.

The TGA curves (Fig. 3b) clearly show the effect of milling time on the weight loss due to NH_4Cl decomposition at the low temperature region of the plot and the significant weight gain due to the reaction of Si at the high temperature region. Accordingly, prolonged milling favors high nitridation conversion rates during CS of Si_3N_4, since, activated Si with energy offered via the mechanochemical activation, as done in this study, reacts at high temperatures more efficiently with nitrogen (increase of weight gain, Fig. 3b).

The above indications, obtained from thermal analysis, were confirmed in the real CS practice, where the combustion reaction of Si spontaneously propagated in the pressurized nitrogen atmosphere of 6 MPa. Fig. 4 plots the maximum combustion temperatures of powder mixtures milled with different times, recorded by the thermocouple. The influence of increasing mechanochemical activation of Si powder on increasing combustion temperature is evident.

The detailed diffractograms (between 20° and 40°) of Fig. 5 show that the reaction was complete since Si_3N_4 was exclusively identified in the reaction products, but no evidence of residual Si or any other byproduct was registered. It is also observed that mechanochemical activation has a strong impact on the proportion of α-Si_3N_4/β-Si_3N_4. The intensities of the peaks of the two phases in the diffractograms of the products from powders milled for different times suggest that longer milling favors formation of β-Si_3N_4 and suppresses formation of α-Si_3N_4 after CS. This finding agrees fairly well with Fig. 4 since it is well known that high combustion temperatures do not favor formation of α-Si_3N_4 [19].

The change of balance between α- and β-Si_3N_4, due to the influence of mechanochemical activation on Si powder, was also obvious in the microstructure of the end products. Fig. 6 shows that pronouncedly different microstructures resulted from combustion of powders milled for 8 h (Fig. 6a) and 24 h (Fig. 6b). In particular, equiaxial Si_3N_4 crystals as shown in Fig. 6a should be largely attributed to α-Si_3N_4, while the combustion of the powder milled for 24 h resulted in long column-like crystals, which, according to Fig. 5, should be predominantly attributed to β-Si_3N_4. With regard to the mechanism of Si_3N_4 formation via nitriding combustion of Si, it has been demonstrated that vapor-crystal growth mechanism

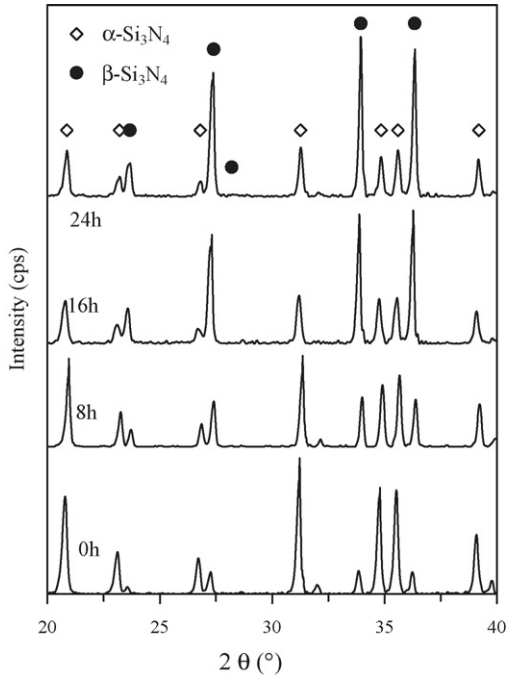

Fig. 5. X-ray diffractograms of products after a combustion synthesis of powder mixtures milled for different times (the spectra have not been normalized. Full scale of intensity axis 800 cps).

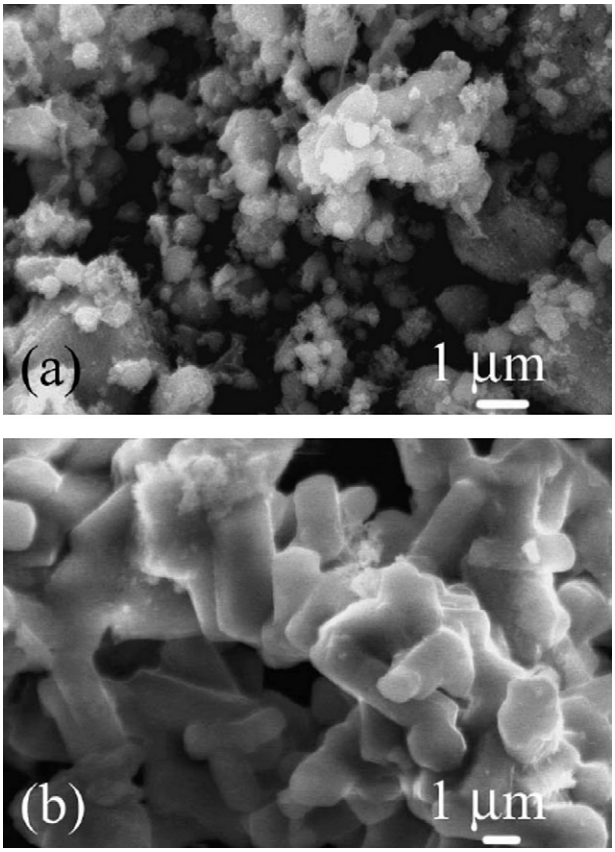

Fig. 6. Typical microstructures of Si_3N_4 products after combustion of powder mixtures milled for (a) 8 h and (b) 24 h.

favors formation of α-Si_3N_4, while vapor–liquid–solid (VLS) mechanism favors formation of β-Si_3N_4 [20,21].

The results of this study, being also considered in the light of our earlier study on CS of Si_3N_4 [3], suggest that formation of α-Si_3N_4 is favored under benign processing conditions, achieved by lower level of mechanochemical activation of Si, or by using low N_2 pressures.

4. Conclusions

The present study has shown that mechanochemical activation is a valuable processing approach to activate the Si powder mixture, by favoring amorphization and reduction of Si particles down to nanosize, and to affect combustion synthesis of Si_3N_4. The results of thermal analysis suggest that longer milling, which implies higher level of mechanochemical activation, results in stronger reactions between Si and N_2 and thus increase of reaction efficiency. The mechanochemical activation causes increase of combustion temperature. Both the combustion temperature and the mechanochemical activation influence the mechanism of Si_3N_4 synthesis, as the results of the analyses of the crystalline structures and the microstructure of combustion products. With regard to the balance between α-/β-Si_3N_4 proportion in the combustion products, it seems that benign processing conditions, anticipated with lower level of mechanochemical activation of Si powder, low N_2 pressures, and low combustion temperatures, favor the formation of α-Si_3N_4.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (contracts 50372074, 50502035 and 50672010).

References

[1] F.L. Riley, Silicon nitride and related materials, J. Am. Ceram. Soc. 83 (2000) 245–265.
[2] T. Abraham, Current US market for advanced ceramics and projections for the future, Ceram. Eng. Sci. Proc. 14 (1993) 25–39.
[3] T. Yamada, Preparation and evaluation of sinterable silicon nitride powder by imide decomposition method, Am. Ceram. Soc. Bull. 72 (1993) 99–106.
[4] Z.A. Munir, A. Tamburini, Self-propagation exothermic reactions: the synthesis of high-temperature materials by combustion, Mater. Sci. Rep. 3 (1989) 277–365.
[5] N.N. Ault, R.L. Yeckley, Silicon nitride, Am. Ceram. Soc. Bull. 74 (1995) 153–155.
[6] M. Skibska, A. Szuls, A.S. Mukasyan, A.S. Rogachev, Microstructural peculiarities of silicon nitride formed by SHS under high nitrogen pressure, Int. J. SHS 2 (1993) 39–47.
[7] K. Hirao, Y. Miyamoto, M. Koizumi, Combustion synthesis of nitride powders under high nitrogen pressure, Adv. Ceram. 21 (1988) 289–300.
[8] I.G. Cano, M.A. Rodriguez, Synthesis of β-silicon nitride by SHS: fiber growth, Scr. Mater. 50 (2004) 383–386.
[9] I.G. Cano, S. Pérez Baelo, M.A. Rodríguez, S. Aza, Self-propagating high temperature-synthesis of Si_3N_4: role of ammonium salt addition, J. Eur. Ceram. Soc. 21 (2001) 291–295.
[10] A.G. Merzhanov, I.P. Borovinskaya, L.S. Popov, N.S. Makhonin, L.V. Kustova, Method of obtaining silicon nitride with high α phase content, WO Patent no. 89/11447, 1989.
[11] J.T. Li, C.C. Ge, Investigation on the microstructural aspects of Si_3N_4 produced by self-propagating high-temperature synthesis, J. Mater. Sci. Lett. 15 (1996) 1051–1053.
[12] Y.G. Cao, C.C. Ge, Z.J. Zhou, J.T. Li, Combustion synthesis of a-Si_3N_4 whiskers, J. Mater. Res. 14 (1999) 876–880.
[13] H.B. Jin, Y. Yang, Y.X. Chen, Z.M. Lin, J.T. Li, Mechanochemical-activation-assisted combustion synthesis of alpha-Si_3N_4, J. Am. Ceram. Soc. 89 (2006) 1099–1102.
[14] X.Y. Yang, Z.W. Hang, Y.K. Wu, H.Q. Ye, HREM observations of the synthesized process of nano-sized-SiC by ball milling of Si and C mixed powders, Mater. Sci. Eng. A 300 (2001) 278–283.
[15] T.D. Shen, C.C. Koch, T.L. McCormick, R.J. Nemanich, J.Y. Huang, J.G. Huang, The structure and property characteristics of amorphous/nano-crystalline silicon produced by ball milling, J. Mater. Res. 10 (1995) 139–148.
[16] W.P. Tong, N.R. Tao, Z.B. Wang, J. Lu, K. Lu, Nitriding iron at lower temperatures, Science 299 (2003) 686–688.
[17] X.Y. Yang, Z.W. Hang, Y.K. Wu, HREM observations of the synthesized process of nano-sized-SiC by ball milling of Si and C mixed powders, Mater. Sci. Eng. A 300 (2001) 278–283.
[18] V.V. Zakorzhevskii, I.P. Borovinskaya, Some regularities of α-Si_3N_4 synthesis in a commercial SHS reactor, Int. J. SHS 9 (2000) 171–191.
[19] K. Hirao, Y. Miyamoto, M. Koizumi, Combustion reaction characteristics in the nitridation of silicon, Adv. Ceram. Mater. 2 (1987) 780–783.
[20] C. Greskovich, S. Prochazka, Observation on the α–β Si_3N_4 transformation, J. Am. Ceram. Soc. 60 (1997) 170–172.
[21] C.C. Ge, J.T. Li, Y.L. Xia, The mechanism of self-propagating high-temperature synthesis of Si_3N_4, Int. J. SHS 5 (1996) 107–117.