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Combustion synthesis of ultra-fine SiC powders in low pressure N_2-atmosphere

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Abstract

Ultra fine SiC nano-powders (100–300 nm) of high purity were successfully produced by combustion of a powder mixture of Si and C, with the addition of poly-tetra-fluoro-ethylene (PTFE) as a chemical stimulator, in a moderately pressurized nitrogen atmosphere (1–10 MPa). The experimental results showed that with the aid of mechanical activation of the starting powders, a small amount of PTFE (1.5 wt%) can effectively stimulate the reaction between Si and C. Both the experimental results and thermodynamic calculations indicate that the formation of Si_3N_4 plays a key role in the process. The optimum conditions for producing the aforementioned SiC fine powders were 1.5 wt% PTFE, 1 MPa N_2 pressure and no addition of diluents of SiC powder.

Keywords: A. Powders: solid state reaction; B. Microstructure-final; D. SiC; Combustion synthesis

1. Introduction

Ceramics made of silicon carbide (SiC) are attractive materials in many high-temperature structural, electrical, and functional applications because of their outstanding properties, such as excellent mechanical properties, high strength and stiffness, good wear and corrosion resistance, chemical resistance to high temperatures, semi-conductivity, high thermal stability, and thermal conductivity [1–5]. Their dielectric properties in the microwave range are also a subject of intensive investigation due to the increase of electromagnetic pollution that results from the vast use of electronic and telecommunication systems [6–8].

Acheson synthesis processing is the conventional production method of SiC powders applied nowadays, whereby a carbothermal reduction of silicon oxide (SiO_2) by carbon takes place at very high temperatures, ranging between 2000 °C and 3000 °C, for about one week [2]. Due to the high temperatures and the long processing time, the SiC powders produced have particles of a large size. Therefore, in order to obtain a powder that is suitable for sintering, the produced powder must be subjected to extensive milling to be converted into a finer powder with particle size ranging from a few micrometers to sub-micrometers. Nevertheless, post milling of the hard SiC particles inevitably contaminates the resultant powder. Accordingly, this method suffers due to the high energy consumption and poor purity of the final powder.

Several other methods have been proposed as alternative ways to produce SiC powders, such as chemical vapour deposition (CVD), carbothermal reduction, plasma, laser and carbon reduction, sol–gel, thermal diffusion, carbon-nanotube-confined chemical reaction, etc. [9–16]. However, in order to apply a production method on a large industrial scale, two main requirements must be satisfied: (a) high purity of products, and (b) low production cost. The latter requirement is directly related to the simplicity of the method, in terms of the apparatus used and the avoidance of expensive preliminary stages, such as preheating. All the aforementioned techniques do not satisfy either one or both of these two requirements.

Combustion synthesis (CS) can be seen as an effective and economic method for producing SiC powders of high purity [11,17]. Production of ceramic powders by the MASHS method, which was employed in this study, combines self-propagating high-temperature synthesis (SHS) and mechanical activation (MA) [18–20]. The MASHS method is gaining increasing interest for producing many inorganic refractory

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powders [18–22] because it features low processing and apparatus costs, high production rate, and high purity of the final products, as well as the possibility of producing novel phases with unique properties [23,24].

The process of CS actually utilizes the heat, released by an exothermic reaction, to sustain the combustion reaction itself, with the aid of a combustion wave that occurs after external ignition. In the case of SiC, the heat of formation at 300 K and 1 atm is only 69 kJ/mol [25]. Thus, additional energy is needed to favour the CS of SiC from a mixture of Si and C powders. An earlier study has demonstrated that a rapid increase in the reactivity and the amorphous degree of the Si reactants can be effectively achieved with an increase in MA time [26]. Besides using metallic catalysts, chemical stimulation was achieved by adding poly(tetrafluoroethylene) (PTFE, $[-C_2F_4-]_n$) as an exothermic promoter in an Ar atmosphere to produce fine SiC powders [27,28]. However, the use of high amounts of PTFE (for instance, the authors of the previous references have used PTFE up to 18 wt%) may give rise to reservations with regards to toxicity and the environmental impact. Addition of NH_4Cl has been also found to effectively enhance the reactivity of the raw powders [26]. Furthermore, it was found that NH_4Cl improves the pulverizing efficiency of milling and prevents the formation of agglomerations in some mixtures during the milling process. Other ways for providing extra energy to the reactants (i.e. the Si/C powder mixture) of the combustion reaction were the rapid preheating of the initial powder of the reactants [29] and the stimulation of the reaction by applying an external electric field [30].

With regard to the importance of the first requirement; i.e. the high purity of the produced powders, it is interesting to notice that the production of Si_3N_4/SiC composite powders by CS has attracted the interest of many papers which have been published for a period spanning more than 25 years [31] until now [32]. The combustion reaction to produce Si_3N_4/SiC composite powders requires no extra stimulation or activation of the reactants, since it easily takes place spontaneously because of the strong exothermic reaction between Si and N_2, which also assists the propagation of the reaction between Si and C. Nevertheless, the separation of pure SiC powder from Si_3N_4 is very difficult.

This paper presents a novel and simple synthesis method of ultra-fine single-phase SiC nano-powders that satisfies both requirements. In particular, the aim of the study was to produce SiC nano-powders via the MASHS method under benign conditions, which means the incorporation of a low amount of PTFE in the Si/C powder mixture with high reactivity due to MA and the application of low pressure of N_2. The influence of the addition of diluents in the raw materials, made of the target-compound, which is SiC in the present study, was also studied. Diluents are usually used in CS to potentially control the extent of metal melting because they can absorb (due to their heat capacity) a portion of the produced energy.

2. Materials and experimental procedure

A mixture of fine Si powder (Shandong Yinfeng Silicon Materials Co. Ltd., P.R. China, 99.5%, <10 μm) and carbon (Shandong Haihua Carbon Black Chemical Co. Ltd., Shandong province, P.R. China, 99.9%, <2 μm), where the molar Si/C ratio was precisely set to 1/1, was mechanically dry-ball-milled for 12 h in a steel jar, using steel balls as the milling media with a ball/powder weight ratio of 10/1. To protect the powders from oxidation, milling took place in an Ar atmosphere (1 atm). Poly(tetrafluoroethylene) (PTFE, Guangzhou Chemical Reagent Factory, Guangdong province, P.R. China) was added as an activator in the mixture in different amounts, up to 2.0 wt% (with respect to 100% Si/C powder mixture). In some samples, fine SiC powder (Beijing Chemical Co. Ltd., P.R. China, 99.9%, <1.0 μm) was added as a diluent in different quantities up to 30 wt% (with respect to 100% Si/C powder mixture). After homogenization (by wet ball-milling in ethanol media), the powder was dried under vacuum at 80 °C. The powder was passed through an 80-mesh sieve and then cold-pressed into cylindrical compacts with dimensions of 50 mm in diameter and 500 mm in height at an apparent density of ~43% of the theoretical density.

The green compact was placed inside the chamber of the CS apparatus. A titanium powder compact (~3 g) was placed on the top of the compact of the reactants, aimed at burning off and igniting the combustion reaction (the triggering of the ignition was done by passing an electric current through the Ti powder-bed via two Ti electrodes). A W–Re thermocouple, protected in a BN tube, was inserted into the centre of the powder compact to record the temperature. The output signal of the thermocouple was transformed with an AC fast converter and recorded on a computer. The CS chamber, suitably connected to a vacuum line, was hermetically sealed. To reduce the partial pressure of oxygen in the chamber, the chamber was evacuated (with the aid of a diffusion pump) and then refilled with pure N_2 (>99.999%). This evacuation-refilling process was repeated three times consecutively. Before ignition, the pressure of N_2 inside the chamber was fixed at certain values; specifically 1, 4, 7 and 10 MPa.

The crystallographic analysis of the phases produced was conducted with X-ray diffraction analysis (XRD, CuK_α, λ = 1.5406 Å). The morphology of the reaction products was observed with a field emission scanning electron microscope (SEM) under secondary electron mode (25 kV acceleration voltage), which was equipped with energy dispersive spectroscopy (EDS) apparatus for chemical analysis. Thermal analysis (DSC/TG) of the reactants was also carried out in an N_2 atmosphere (1 atm = 0.1 MPa) with a heating rate of 15 K/min (using pure alumina powder as reference).

3. Results

The influence of the amount of PTFE on the crystallographic regime of the produced powders after combustion reaction at 1 MPa N_2 is presented in Fig. 1. It is seen that highly crystalline β-SiC was predominantly formed only in the cases of PTFE 1.5% and 2.0%. In the case of 2.0% PTFE, observation of the diffractogram at high magnification (not shown) might also suggest the presence of weak broad peaks attributed to traces of Si and C (that apparently did not react). In the case of the PTFE-free (i.e. 0.0%) samples or those with 1.0% PTFE, the

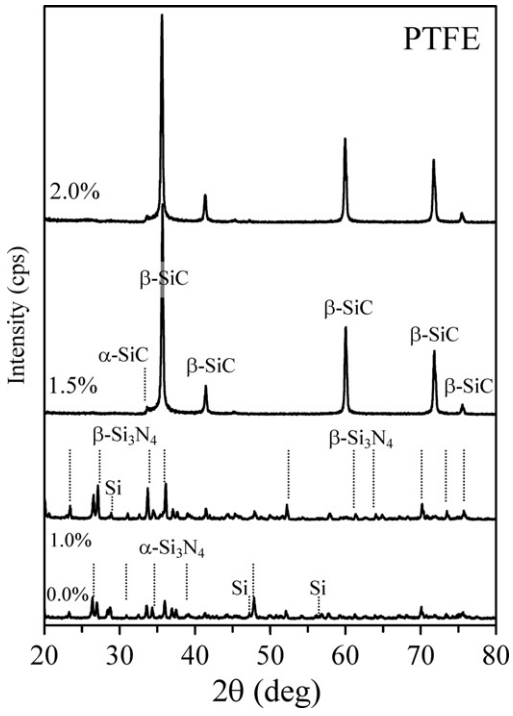

Fig. 1. X-ray diffractograms of powders synthesized in 1 MPa N_2 with different amounts of PTFE (the diffractograms have not been normalized).

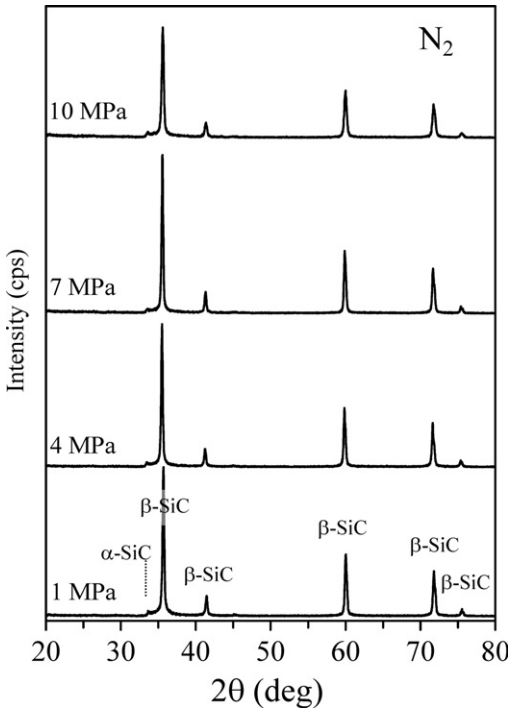

Fig. 2. X-ray diffractograms of powders synthesized with 1.5 wt% addition of PTFE in different pressures of N_2 (the diffractograms have not been normalized).

combustion reaction resulted in production of α- and β-Si_3N_4 while non-reacted Si was also registered. One may also suggest registration of weak peaks of α-SiC in these diffractograms. The addition of 1.0% PTFE in the Si/C powder mixture seemingly favours the formation of β-Si_3N_4 and α-SiC (whose small peaks can be observed, as said before) and suppresses that of α-Si_3N_4. It is also worth noting the pronounced increase of crystallinity of SiC (suggested by the increasing intensity of the diffraction peaks) in the samples with 1.5% and 2.0% PTFE. Therefore, from these experiments, the addition of 1.5 wt% PTFE in the Si/C powder mixture is evidently qualified as the optimum one. Thus, the experiments reported in the following paragraphs were carried out with addition of 1.5% PTFE.

Fig. 2 presents the X-ray diffractograms of the reaction products (all produced with 1.5% PTFE) produced at four different levels of N_2 pressure; specifically 1, 4, 7 and 10 MPa. The main crystalline phase predominantly formed was β-SiC in all cases. Observation of the diffractogram for 10 MPa at high magnification (not shown) might also suggest weak broad peaks attributed to traces of Si and C (that apparently did not react). However, the decrease of the intensity of the diffraction peaks of SiC in the case of 10 MPa is obvious. With regard to the latter case, the micrograph of Fig. 3 corresponds to the central area that was revealed after fracture of the compact of the reaction product produced at 10 MPa N_2 and 1.5% PTFE. Large (5–10 μm) hollowed round particles with walls consisting of many particles of submicron dimensions were found in the core of the compact. The chemical (spot) analysis at the point marked in the main image by EDS (the spectrum is shown in the inset of Fig. 3) suggests that they are residual non-reacted Si.

However, the characteristic microstructure of the reaction products obtained at a low N_2 pressure of 1 MPa and 1.5% PTFE is shown in Fig. 4. Spherical particles with apparently homogenous particle size distribution, in the range of 100–300 nm, were observed. It can also be clearly seen that the SiC particles formed (Fig. 4) are almost 2 orders of magnitude smaller than the Si particles shown in Fig. 3, and are likely to have occurred from the starting powder.

The influence of the 10% and 30% additions of SiC powder, added as diluents, on the crystallographic regime of the synthesized powders is summarized in the diffractograms of Fig. 5 for 10 MPa N_2 and 1.5% PTFE. It can clearly be seen that the presence of SiC in the initial powder mixture favours the

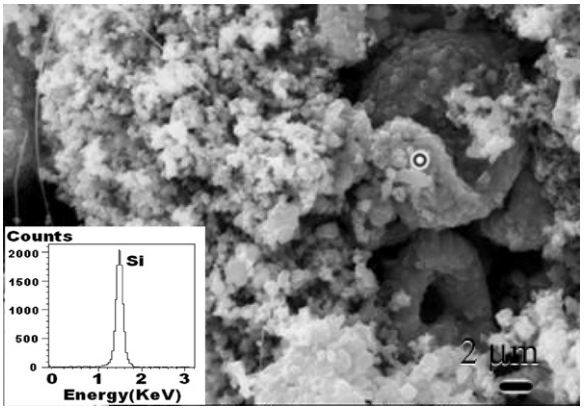

Fig. 3. Morphology observed by SEM at a fracture surface in the core of the product synthesized in 10 MPa N_2 with 1.5 wt% PTFE. The inset shows the EDS spectrum obtained at the point marked in the main image.

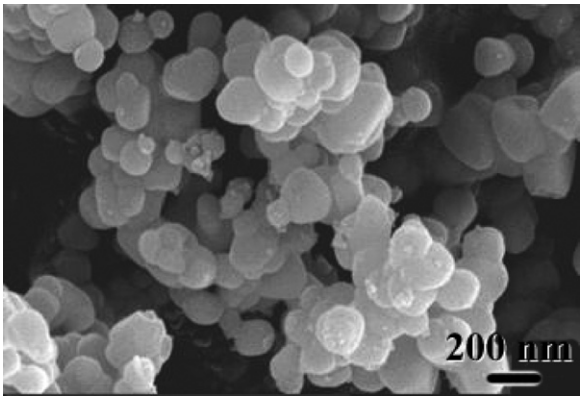

Fig. 4. Morphology of SiC fine nano-powders synthesized in 1 MPa N_2 and 1.5 wt% PTFE.

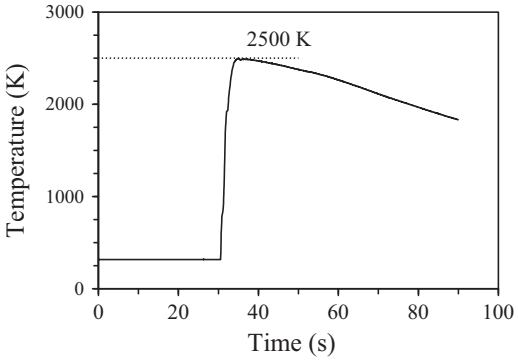

Fig. 6. Evolution of temperature during the combustion reaction for the case of 1 MPa N_2 and 1.5 wt% PTFE.

formation of by-products of Si_3N_4 and does not allow complete consumption of C. Moreover, the crystallinity of SiC, as suggested by the intensity of the peaks, is gradually reduced, and the reduction is more pronounced in 30% SiC than in 10% SiC.

A typical evolution of temperature over time during the combustion is plotted in Fig. 6 (the temperature profile presented in Fig. 6 corresponds to the case of 1.0 MPa N_2 and 1.5% PTFE). The temperature profile features a steep increase, which is attributed to the combustion reaction, and reaches a maximum of ~2500 K. After the main event, there is no evidence of other post-combustion reactions. The experimental results showed that there was no significant influence of the amount of PTFE on the combustion temperature (provided that SiC was formed) or the features of the temperature profile.

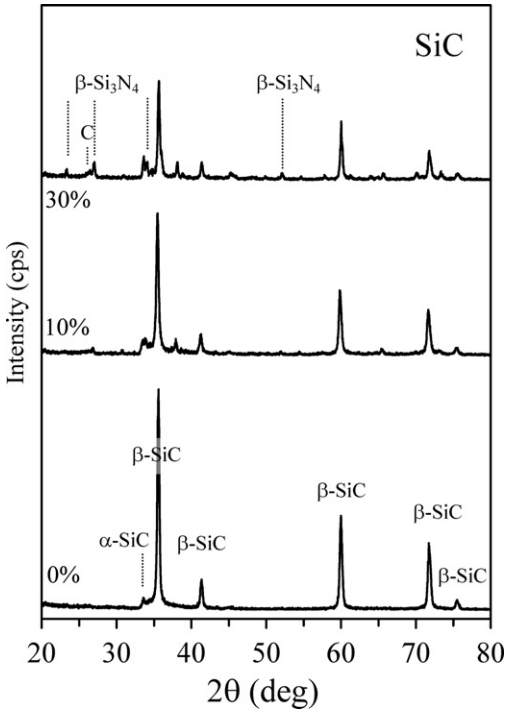

Fig. 5. X-ray diffractograms of powders synthesized in 10 MPa N_2 with addition of 1.5 wt% PTFE and different amounts of diluents of SiC fine powders (the diffractograms have not been normalized).

The curve of Fig. 6 suggests that the entire process takes place very rapidly. Therefore, the results of the DSC/TG analysis for the case of 1.5% PTFE, which are plotted in Fig. 7, shed light on the details and features of the initial stages of the process which occur at low temperatures. The curve of TG suggests that a weight loss starts at 750 K, which can most likely be attributed to PTFE decomposition. That event should result in the first peak of the DSC curve at 773 K. A second peak was recorded at 825 K.

4. Discussion

The experimental results showed that the production method of MASHS successfully overcame the weak exothermic nature of the reaction between Si and C. The combustion reaction took place completely and β-SiC was formed rapidly (Fig. 6) and predominantly (Figs. 1, 2 and 5). The optimum conditions to produce fine SiC nano-powders of high purity and particles with sizes of 100–300 nm (Fig. 4) were: addition of 1.5 wt% PTFE in the mechanically activated powder mixture of Si and C, no addition of diluents of SiC powder, and application of N_2 pressure of 1 MPa.

It is worthy to note that the need for providing extra energy to the system of Si and C powders is evident in the diffractograms of Fig. 1: for PTFE contents of 0% and 1% it

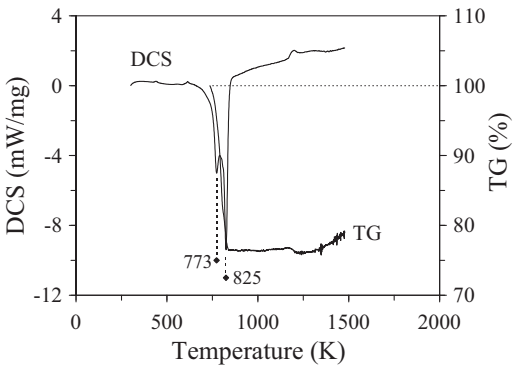

Fig. 7. Thermal analysis (DSC/TG) of Si/C powder mixture with 1.5 wt% PTFE in N_2 atmosphere of 1 atm.

is observed that the powders of Si and C cannot react with each other to produce SiC. In the PTFE-free samples, only nitridation reaction was able to take place resulting in formation of Si_3N_4. Moreover, the amount of 1% PTFE is apparently too little to provide the necessary energy and effectively stimulate the formation of SiC. When the amount of PTFE is sufficient, which seems to be 1.5%, then the reaction products are pronouncedly different (i.e. SiC was formed). Accordingly, the combustion reaction between Si and C powders really needs a chemical activation. The same conclusion is drawn out from the diffractograms of Fig. 5 for 10% and mainly for 30% addition of diluents of SiC powder. The addition of diluents aims to absorb a portion of the produced energy from the combustion reaction. These diffractograms suggest that the reaction between Si and C is considerably suppressed if a portion of the energy of the system is absorbed and dissipated by other factors (such as the powder of the diluents).

Besides mechanical activation, the presence of PTFE seemingly has a multifold effect on providing energy to the system. First of all, at high temperatures, PTFE pyrolyzes exothermally to a variety of fluorocarbon compounds. These compounds are further pyrolyzed to F_2 and the produced F_2 reacts with the superficial passive oxide film, which inevitably forms on the surface of Si particles, to form volatile products. Obviously, the removal of the oxide film from the Si surface facilitates the occurrence of the reaction between the Si and C powders. However, PTFE also seems to have an active and direct role in promoting the reaction between Si and C. This is described in the following paragraphs.

In the present study, two highly exothermic reactions took place. These reactions can be considered as a chemical activation of the CS of SiC, assuming that the weak exothermic nature of the direct reaction between Si and C can hardly sustain a self-propagating reaction. One chemical reaction is the nitridation of Si (ΔH = 198.15 kcal/mol) due to the presence of nitrogen in the combustion chamber. The other one is the direct reaction of Si with PTFE to form SiF_4 [33–35]:

$$n\mathrm{Si}_{(s)} + (-\mathrm{C_2F_4}-)_{n(s)} \rightarrow n\mathrm{SiF}_{4(g)} + 2n\mathrm{C}_{(s)} \quad (1)$$

The results of the thermal analysis (Fig. 7) suggest that the role of PTFE is completed at low temperatures, which are certainly much lower than the combustion temperature (Fig. 6). The second exothermic event registered in the DCS curve with a peak at 825 K could be attributed to the reaction between SiF_4, produced at the first stage of the process (at 773 K), with nitrogen.

However, the chemical equation (1) reveals that the amount of PTFE plays a direct and very important role in the reactions that take place, since the decomposition of PTFE consumes Si and produces C. This immediately implies alterations of the initial stoichiometry between the Si and C of the raw materials. In other words, PTFE is an indirect potential source of C in the combustion chamber after the decomposition of PTFE. Thus, it is necessary to consult the equilibrium phase diagram of the Si–C–N system with respect to the stable phases expected at different conditions.

However, before that, it is worthy to note that the formation of α-SiC, indentified in weak peaks in many diffractograms of Figs. 1, 2 and 5, has also been reported in an earlier study [36], and it has been postulated that it derives from the transformation of β-SiC due to the presence of stacking faults in the crystal [37]. Moreover, the formation of α-Si_3N_4 is usually considered as an index of low combustion temperatures whereas the formation of β-Si_3N_4 is considered as an index of high combustion temperatures.

With the aid of the earlier study of Ref. [38] (and particularly the two phase diagrams of Fig. 5 from that study), the diagram of Fig. 8 was plotted using the available thermodynamic data [39,40]. This diagram is divided into four areas. The curve (a) corresponds to the chemical equilibrium described by the chemical equation (2)

$$\mathrm{Si_3N_4} + 3\mathrm{C} \leftrightarrows 3\mathrm{SiC} + 2\mathrm{N_2} \quad (2)$$

Thus, the area I corresponds to Si_3N_4 + C. According to Ref. [38], if the ratio C/Si > 1, then the areas II, III and IV correspond to SiC + C. If the ratio C/Si < 1, then the chemical equilibrium described by the chemical equation (3)

$$\mathrm{Si_3N_{4(s)}} \leftrightarrows 3\mathrm{Si} + 2\mathrm{N_{2(g)}} \quad (3)$$

is represented by the curve (b). Thus, the area II, defined between the curves (a) and (b), corresponds to SiC + Si_3N_4 and the areas III and IV to SiC + Si. The separation between the areas III and IV is due to the melting of Si (at 1687 K). Thus, the area III corresponds to SiC + $Si_{(l)}$ and the area IV to SiC + $Si_{(s)}$. Similarly, the chemical equation (3) can be correctly written as

$$\mathrm{Si_3N_{4(s)}} \leftrightarrows 3\mathrm{Si_{(l)}} + 2\mathrm{N_{2(g)}} \quad (3a)$$

for the area III, i.e. for temperatures >1687 K; and

$$\mathrm{Si_3N_{4(s)}} \leftrightarrows 3\mathrm{Si_{(s)}} + 2\mathrm{N_{2(g)}} \quad (3b)$$

for the area IV, i.e. for temperatures <1687 K. In this diagram, the points corresponding to the four different N_2-pressures tested, i.e. 1, 4, 7 and 10 MPa, are also marked.

From this diagram, it is concluded that high N_2-pressure and low temperatures favour the formation of Si_3N_4. On the other hand, low N_2-pressure and high temperatures favour the formation of SiC.

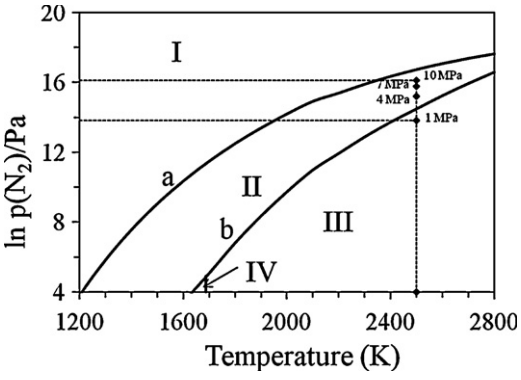

Fig. 8. Equilibrium phase diagram for the Si–C–N system.

Accordingly, the main conclusion of the above discussion is that Si_3N_4 plays a key role in the CS of SiC under an N_2 atmosphere. In other words, the successful formation of SiC greatly depends on the optimum formation of Si_3N_4. Si_3N_4 will inevitably form because the chamber is filled with nitrogen gas. The key point is to develop the correct conditions to favour the spontaneous decomposition of Si_3N_4 to form SiC; for instance by lowering the pressure of N_2. However, since the formation of Si_3N_4 is necessary (because of the highly exothermic reaction of its formation), the presence of N_2 is also necessary. At the same time, the low exothermic nature of the reaction between Si and C always underlines the need for providing extra energy to the system. Otherwise, Si_3N_4 will form. For instance, the addition of diluents of SiC powder, which absorbed a proportion of the heat produced from the combustion reaction, clearly favoured the formation of Si_3N_4 and suppressed the formation of SiC (Fig. 5). Indeed, an earlier study has reported that in the CS of Si_3N_4, diluents are employed to increase the degree of nitridation [41]. The extra energy needed for the CS of SiC is also provided by the PTFE.

According to the diagram of Fig. 8, the point corresponding to 1 MPa N_2-pressure is located in the area III, while the other points corresponding to higher pressures of N_2 are located in the area II. An earlier study on CS of Si_3N_4 has demonstrated that a N_2 pressure up to 10^4 MPa is needed for the formation of stoichiometric Si_3N_4 [42]. That pressure is far higher than those applied in the present study, i.e. 1–10 MPa. If the C/Si $>$ 1 (which is most likely the case in the present study due to the occurrence of Eq. (1)), then the area II (together with the areas II and IV) predicts the formation of SiC + C. Moreover, the actual N_2-pressure in the reaction front should be lower than the initially applied pressure in the chamber because of the continuous consumption of N_2 due to Si nitridation [43]. This approach is consistent with the diffractograms of Fig. 2, where SiC was formed in all cases. In the case of C/Si $<$ 1, the points corresponding to the N_2 pressures of 4, 7 and 10 MPa are located in the area II, which predicts the formation of Si_3N_4 + SiC. The case of C/Si $<$ 1 is apparently approached for 0% and 1% PTFE addition where the formation of extra C (due to Eq. (1)) is zero or very small, respectively. This approach can interpret the findings of the diffractograms of Fig. 1 for 0% and 1% PTFE, where Si_3N_4 was formed.

With regard to the mechanism of SiC formation, the energy released from the decomposition of PTFE is apparently equivalent to a preheating of the reactants that would be done alternatively with the aid of a heating element. However, at high temperatures, extensive melting and coalesce of Si, prior to nitridation, should occur. The heat produced from the exothermic reactions intensifies both Si melting and coalesce. However, Si melting and coalesce significantly decrease the available contacting surface area of Si for reacting with N_2. The addition of diluents is actually aimed at controlling (or suppress) Si-melting in the initial stages of the process. The molten Si quickly coalesces to spherical aggregates due to the action of surface tension. The Si surface is nitrided to a superficial layer of Si_3N_4. The thermal stress developed between the Si_3N_4 film at the surface and the liquid Si in the core, in conjunction with the vaporization of molten Si under the Si_3N_4 layer, causes fracture of Si_3N_4 surface layer and the liquid Si squirts out, which is likely to result in the hollow spherical particles shown in Fig. 3.

The finding that the produced SiC particles (100–300 nm, Fig. 4) are 2 orders of magnitude smaller than the original Si powders (5–10 μm, Fig. 3) suggests that the vapour–crystal mechanism should govern the formation of SiC [25]. Accordingly, more complex phenomena, related to adsorption–desorption of N_2 in the porous powder compact, probably establish local equilibrium conditions with regard to the partial pressure of N_2 and introduce more parameters needed for an explicit quantitative description of the mechanism of SiC formation. For instance, at 2500 K (Fig. 6), the calculated vapour pressure of Si over Si_3N_4 (=2×10^4 Pa) is 2 orders of magnitude higher than that over SiC (=3×10^2 Pa). This is an extra factor that favours SiC formation over Si_3N_4. Certainly, one must apply very carefully the thermodynamics in the case of CS because the rapid occurrence of combustion reaction and the fast cooling rate afterwards (Fig. 6) intrinsically implies deviations from thermodynamic equilibrium.

5. Conclusions

Among the factors that can affect the combustion synthesis of SiC investigated, the addition of PTFE was found to have the most pronounced effect since it effectively activated the reactant powder mixture of Si and C in a relatively low pressure of N_2. The SiC powders, produced under optimized conditions (determined in this study to be 1.5 wt% PTFE, N_2 pressure of 1 MPa and no addition of diluents of SiC powder in the mechanically activated powders of Si and C), featured high purity and fine particles with sizes of 100–300 nm. The combustion synthesis of SiC seemingly occurs in two stages. At low temperatures, vapours of SiF_4, generated due to the reaction between Si and PTFE, predominantly react with N_2 and result in Si_3N_4. At high temperatures, the low N_2-pressure and the carbon produced from the decomposition of PTFE favours the decomposition of Si_3N_4 to form SiC.

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