Development of SHS azide technology of silicon carbide nanopowder

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Abstract. The possibility of increasing the purity and yield of the SiC nanopowder using an intermediate synthesis of silicon nitride (Si3N4) by azide technology of self-propagating high-temperature synthesis based on the use of a powder of sodium azide (NaN3) as a nitriding reagent was investigated. As a result of combustion of the initial mixture of powders ‘19Si + 6NaN3 + (NH4)2SiF6 + 20’, a powdery product was obtained, consisting almost entirely of SiC (about 90%) with an admixture of Si3N4 and Si (about 5% each), and representing nanoparticles (80-150 nm) combined into agglomerates with the size up to 50 µm.

1. Introduction
Silicon carbide (SiC) is an important ceramic nonoxide material used in mechanical engineering, because of the unique set of properties: low density, high hardness, high-temperature strength and high chemical resistance [1]. For many years, the silicon carbide powder has been used as an excellent abrasive ‘carborundum’ in the free state and in the various abrasive and cutting tools in the bound state [2, 3]. The SiC powder is used also to sinter high-quality technical ceramics for a structural purpose with very good mechanical properties. This ceramics is used to produce two groups of components: wear – and corrosion-resistant components (mechanical seals, bushings, shafts and bearings of pumps) and high-temperature components (combustion chambers, rotors and blades of gas turbines, heat exchangers and fans) [1]. Recently, much attention has been paid to the development of nanostructured ceramics, which is sintered from nanopowders and its properties markedly exceed the properties of traditional technical ceramics [4].

The main part of SiC is produced by a simple and cheap Acheson method based on the reduction of SiO2 by carbon in core-type electric resistance furnaces at 2200-2700°C with a process time of about 40 h. The resulting blocks of crystals larger than 10 mm are then ground and sieved, but the product is not enough quality in composition and structure and requires additional treatment [5]. SiC manufactured by this method generally has a coarse grain, with a mean particle size of 5 µm at best [1]. These coarse powders are mainly used as abrasives, for the manufacture of electric heaters, refractories and structural ceramics, partially. Smaller and pure SiC powders, necessary for the production of structural ceramics, can be obtained by the Acheson method from the more homogeneous mixture of small and pure Si and C powders at a low temperature of 1500-1800°C. Since the eighties of the last century, it is known that the smallest submicron and nanosized SiC
powders (less than 0.1 µm) can be synthesized by methods of vapour phase reactions of SiH₄ or SiCl₄ with hydrocarbons CH₄ and C₃H₈ or thermal decomposition of complex chemical compounds CH₃SiCl₃, (CH₃)₄Si or carbosilane, as well as the evaporation of solid-phase reagents Si and C in the atmosphere of a mixture of inert gas with H₂ or N₂ [1]. Then these methods were supplemented by the sol-gel method, plasma and microwave methods [6-8]. However, all these methods are high energy-consuming, prolonged, complicated, resulting in high cost of nanopowders, therefore, attempts are made to date to develop new methods for the preparation of SiC nanopowders.

Among the new methods, the method of combustion synthesis or the method of self-propagating high-temperature synthesis (SHS) of silicon carbide is of undeniable interest, because it is characterized by low energy consumption, short duration of the process, high purity products, simple equipment, wide possibilities of regulation of dispersed structure of powders: from single crystal grains to nanosized particles [9]. However, the problem is that the reaction of direct synthesis of silicon carbide from elements

\[ \text{Si} + \text{C} = \text{SiC} + 73 \text{kJ/mole} \]  

(1)
does not have sufficiently high heat liberation, and, thus, has a relatively low adiabatic combustion temperature (1173 K). Hence, this binary system (1) fails to implement a self-sustaining combustion process. Therefore, for the synthesis of SiC in the SHS mode, different types of the ‘activation’ process are used, among which are pre-heating the initial mixtures [10], addition of chemical activators [11], the use of intermediate high-exothermic synthesis of Si₃N₄ by combustion of a mixture of Si+C in a nitrogen atmosphere or air [12, 13], mechanical activation of the initial mixture [14].

Since 1970, in Samara State Technical University, the azide technology of self-propagating high-temperature synthesis (SHS-Az) has been developed, which allows us to obtain micro- and nanopowders of nitrides and compositions on their basis with the use of a powder of sodium azide (NaN₃) as a nitriding reagent and halide salts [15]. The SHS-Az method was used for the preparation of nanopowder of SiC through intermediate synthesis of Si₃N₄ using energy additive of aluminum [16]:

\[ 14\text{Si} + 3\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 15\text{C} + \text{Al} = 15\text{SiC} + \text{Na}_3\text{AlF}_6 + 5\text{N}_2 + 4\text{H}_2. \]  

(2)

As the result of burning this mixture of powders, a powdery product was obtained based on silicon carbide nanopowder of composition: β-SiC – 48.6 wt. %, α-Si₃N₄ – 27.0%, β-Si₃N₄ – 5.8%, Na₃AlF₆ – 18.6%. The particle size of silicon carbide was in the range of 50-150 nm, and whiskers of silicon nitride had a diameter of about 100 nm. Although the yield for the silicon carbide was about 50%, this composite nanopowdery product was successfully used for modification of aluminum alloy [17].

This work is a continuation of the research initiated in [16], with the aim of increasing the purity and yield of SiC nanopowder during the synthesis by SHS azide technology without the use of energy additive of aluminum.

2. Materials and methods of investigations

For preparation of more pure silicon carbide and elimination of Na₃AlF₆ impurity, it was necessary to exclude the addition of aluminum to the initial mixture of powders and to investigate the influence of the carbon content in the initial mixture by bringing it to 20 moles, when all initial silicon Si is bound into silicon carbide SiC, and the nitride Si₃N₄ is not contained in the final product:

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 15\text{C} = 5\text{Si}_3\text{N}_4 + 5\text{SiC} + 6\text{NaF} + 4\text{H}_2, \]  

(3)

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 8\text{C} = 4\text{Si}_3\text{N}_4 + 8\text{SiC} + 6\text{NaF} + 4\text{H}_2 + 2\text{N}_2, \]  

(4)

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 11\text{C} = 3\text{Si}_3\text{N}_4 + 11\text{SiC} + 6\text{NaF} + 4\text{H}_2 + 4\text{N}_2, \]  

(5)

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 14\text{C} = 2\text{Si}_3\text{N}_4 + 14\text{SiC} + 6\text{NaF} + 4\text{H}_2 + 6\text{N}_2, \]  

(6)

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 17\text{C} = \text{Si}_3\text{N}_4 + 17\text{SiC} + 6\text{NaF} + 4\text{H}_2 + 8\text{N}_2, \]  

(7)

\[ 19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 20\text{C} = 20\text{SiC} + 6\text{NaF} + 4\text{H}_2 + 10\text{N}_2. \]  

(8)

For a preliminary analysis of the temperature of combustion of the starting components and the composition of the synthesis products, the thermodynamic calculations were performed using the ‘Thermo’ program [18].

The following powders were used in the experimental study as starting raw materials: silicon
powder of KR0 brand (purity ≥ 98.8 wt. %, particle size < 10 µm), carbon black of P701 brand (88%, 0.2 µm), sodium azide NaN₃ (98.7%), ammonium hexafluorosilicate (NH₄)₂SiF₆ (99.0%). The methodology of experimental investigations in reactor SHS-Az of constant pressure with a volume of 4.5 l was described in [15]. The cylindrical samples (30 mm diameter, 45 mm height) of initial powders mixture of bulk density were burned. Phase composition of the powdery combustion product was determined on automated X-ray diffractometer ARL X TRA ‘Thermo Scientific’. Shooting X-ray spectra was performed using Cu-radiation with continuous scanning in the range of angles 2θ = 20°÷80° at a speed of 2 deg/min. The obtained spectra were processed using a special software package WinXRD. Quantitative phase analysis was carried out by full-profile analysis (Rietveld method) using the software PDXL 1.8.1.0 using the crystallographic open database (COD). The study of the morphology and chemical element composition of powder particles was performed on the scanning electron microscope JSM-6390A ‘Jeol’ with the EDS attachment JED-2200 ‘Jeol’. The specific surface of powders was determined by the adsorption method on the device ‘Sorbetometr’.

3. Results and discussion

Figure 1 presents the results of thermodynamic calculations showing values of the adiabatic combustion temperature, the enthalpy change of the system in the reaction and the composition of the synthesis products with different contents of carbon in the initial mixture.

![Figure 1](image)

Figure 1. The results of thermodynamic calculations of combustion parameters (a) and composition of synthesis products (b).

The significant reduction of heat liberation and adiabatic temperature of combustion is seen with the increasing content of carbon black in the initial powder mixture (see figure 1 (a)). Referring to figure 1 (b), when the carbon content is near 5 moles, the reaction products contain silicon carbide, silicon nitride, sodium fluoride and hydrogen. With increasing content of carbon black to 20 moles, the products of synthesis become free of silicon nitride. The obtained results of thermodynamic analysis are consistent with equations (3)-(8). Thus the results of thermodynamic calculations show that the initial mixture ‘19Si+6NaN₃+(NH₄)₂SiF₆+20C’ is optimal for the synthesis of silicon carbide by SHS azide process because the combustion of this mixture gives rise to the target silicon carbide and by — products (nitrogen, hydrogen and sodium fluoride), which are easily removed and do not contaminate the final product.

The results of experimental determination of temperature and velocity of combustion is presented in figure 2.
Figure 2. Combustion parameters of mixture 19Si + 6NaN3 + (NH4)2SiF6 + xC.

The figure shows that the temperature and velocity of combustion reduce with increasing carbon black content (x) in the initial mixture which is consistent with the results of thermodynamic calculations. Let us note that the experimental values of the combustion temperature are below the theoretical ones. This is because, the heat of combustion is partially consumed for heating the environment. In addition, the real composition of the combustion products differs somewhat from the composition in accordance with the thermodynamic calculations, that is seen in table 1 and figure 3 from the results of X-ray phase analysis of the products of chemical reactions (3)-(8).

Table 1. The phase ratio in washed products of combustion.

| Carbon content in initial mixture x, mole | SiC | α-Si3N4 | β-Si3N4 | Si | SiO2 |
|------------------------------------------|-----|---------|---------|----|------|
| 5                                        | 8.40| 66.56   | 23.80   | 0  | 1.24 |
| 8                                        | 10.80| 62.10   | 26.00   | 1.10| 0    |
| 11                                       | 50.30| 27.40   | 21.40   | 0.90| 0    |
| 14                                       | 64.70| 19.50   | 14.00   | 1.80| 0    |
| 17                                       | 70.70| 24.70   | 4.60    | 0  | 0    |
| 20                                       | 89.40| 5.50    | 0       | 5.10| 0    |

It follows from the presented data that the increase in carbon content in the starting material leads to the change of the ratio of the phases in the products of combustion. The washed products of the combustion of mixtures with a carbon content up to 17 moles contain three main phases: β-SiC, α-Si3N4, β-Si3N4 and impurities of Si or SiO2 in small proportion. (Sodium fluoride (NaF) due to its good solubility is completely removed as a result of washing in distilled water.) The maximum yield of silicon carbide of about 90% is observed with 20 moles of carbon black, as a result of the combustion; combustion products also contain side products: about 5% Si3N4 and 5% Si. An increase of the content of carbon black above 20 moles did not make sense, since this would have led to the increase in the content of free silicon in the final product of combustion.

Figure 4 shows the morphology and the results of EDS analysis of the powder particle synthesized from two mixtures with 5 and 20 moles of carbon black. Figure 4 (a) demonstrates the shape of columnar crystals with a diameter of from 100 to 200 nm which is typical for silicon nitride. The presence of carbon in these crystals marked with numbers 1-6 can be explained by the fact that the penetration depth of the electron beam is larger than a single crystal of Si3N4 (table 2). Silicon carbide is synthesized in the form of equiaxed particles in the size range of 80 to 150 nm, combined into agglomerates with the size up to 50 µm. The specific surface of the powder of silicon carbide synthesized from ‘19Si + 6NaN3 + (NH4)2SiF6 + 20C’ mixture is 19.16 m²/g.
Figure 3. XRD patterns of combustion products of mixture $19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + x\text{C}$ after washing: (a) $x = 5$ moles, (b) $x = 11$ moles, (c) $x = 20$ moles.

Figure 4. SEM image and EDS analysis of powders synthesized from mixtures: (a) $19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 5\text{C}$, (b) $19\text{Si} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 20\text{C}$. 
Table 2. Content of chemical elements at points marked in figure 4, wt. %.

| Chemical element | 001 | 002 | 003 | 004 | 005 | 006 | 007 | 008 | 009 | 010 | 011 |
|------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C                | 34.62 | 19.47 | 27.72 | 17.07 | 14.84 | 10.39 | 59.21 | 67.51 | 58.12 | 75.54 | 66.63 |
| N                | 23.32 | 8.37 | 13.77 | 20.23 | 36.40 | 9.32 | 12.47 | 12.47 | 12.47 | 12.47 | 12.47 |
| F                | 0.48 | 0.62 | 0.51 | 0.27 | 0.47 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 | 0.53 |
| Na               | 0.29 | 0.31 | 0.08 | 0.19 | 0.13 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 | 1.09 |
| Si               | 64.61 | 56.59 | 63.10 | 68.81 | 60.67 | 52.54 | 30.38 | 31.17 | 28.47 | 23.75 | 32.29 |

4. Conclusion

Application of azide technology of SHS has allowed us to obtain from the initial powder mixture ‘19Si + 6NaN3 + (NH4)2SiF6 + 20C’, a powdery product consisting almost entirely of β-SiC (89.4%) with an admixture of α-Si3N4 (5.5%) and Si (5.1%), and representing nanosized particles (80-150 nm) combined into agglomerates with the size up to 50 µm.

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