



## Self-Propagating High-Temperature Synthesis Самораспространяющийся высокотемпературный синтез



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Research article

Научная статья



# Self-propagating high-temperature synthesis of highly dispersed $\text{Si}_3\text{N}_4$ -TiC composition using sodium azide and various carbon sources

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**Abstract.** The main properties of the highly dispersed  $\text{Si}_3\text{N}_4$ -TiC composition are presented, demonstrating the potential for using nitride-carbide composite materials across various industries. An *in-situ* process was employed to synthesize composite ceramics by chemically producing nitride and carbide nanoparticles directly within the composite volume. The study details the development of the technology for synthesizing the highly dispersed  $\text{Si}_3\text{N}_4$ -TiC composition using the azide SHS method during the combustion of mixtures of Ti, C, and sodium azide ( $\text{NaN}_3$ ) powders with polytetrafluoroethylene (PTFE,  $(\text{C}_2\text{F}_4)_n$ ) serving as an activating and carbiding additive. Thermodynamic calculations of these reactions showed that the adiabatic temperatures were sufficiently high to sustain a self-propagating combustion mode. Experimental investigations into the microstructure and phase composition of the combustion products are also presented. The synthesized compositions consist of highly dispersed equiaxed particles, which include a mixture of nanosized (less than 100 nm) and submicron (100–500 nm) particles of titanium carbide and nitride, as well as silicon nitride fibers with diameters of 50–200 nm and lengths of up to 5  $\mu\text{m}$ . The use of PTFE as a partial replacement for carbon in the mixture during azide SHS eliminated, in most cases, the limitations of traditional approaches for achieving various ratios of target phases of  $\text{Si}_3\text{N}_4$  and TiC. This enabled the synthesis of highly dispersed  $\text{Si}_3\text{N}_4$ -TiC powder compositions with a phase composition closely aligned with theoretical calculations. Thus, the application of the azide SHS method proved effective for obtaining highly dispersed ceramic powder compositions, including  $\text{Si}_3\text{N}_4$ -TiC and  $\text{Si}_3\text{N}_4$ -TiN-TiC.

**Keywords:** silicon nitride, titanium carbide, composite ceramics, self-propagating high-temperature synthesis, sodium azide, polytetrafluoroethylene, halide salts, combustion, composition

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# Самораспространяющийся высокотемпературный синтез высокодисперсной композиции $\text{Si}_3\text{N}_4$ –TiC с использованием азида натрия и различных источников углерода

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**Аннотация.** Исследованы основные свойства композиции  $\text{Si}_3\text{N}_4$ –TiC, которые показывают перспективы использования нитридно-карбидных композиционных материалов в различных отраслях промышленности. Применен *in-situ* процесс получения композиционной керамики путем проведения химического синтеза нитридных и карбидных наночастиц в объеме композита, так как известно, что полученные заранее очень мелкие частицы различных фаз не могут быть равномерно распределены в объеме композита путем механического смешивания порошков (*ex-situ* процесс). Представлены результаты развития технологии получения композиции  $\text{Si}_3\text{N}_4$ –TiC методом азидного СВС при сжигании смесей порошков Ti, C,  $\text{NaN}_3$  с активирующей и карбидизирующей добавкой политетрафторэтилена  $(\text{C}_2\text{F}_4)_n$  (ПТФЭ). Результаты термодинамических расчетов этих реакций показали, что адиабатические температуры достаточно высоки для реализации самоподдерживающегося режима горения. Представлены экспериментальные исследования микроструктуры и фазового состава продуктов горения. Синтезированные композиции состоят из высокодисперсных частиц равноосной формы, представляющих собой смесь наноразмерных (менее 100 нм) и субмикронных (от 100 до 500 нм) частиц карбида и нитрида титана, а также волокон нитрида кремния диаметром от 50–200 нм и длиной до 5 мкм. Применение ПТФЭ с частичной заменой углерода в составе смесей в азидном СВС позволило устранить в большинстве случаев недостатки традиционного подхода для различных соотношений целевых фаз  $\text{Si}_3\text{N}_4$  и TiC и синтезировать высокодисперсные порошковые композиции  $\text{Si}_3\text{N}_4$ –TiC с фазовым составом, значительно более близким к рассчитанному теоретическому составу. Таким образом, рассмотренное применение метода азидного СВС позволило получить высокодисперсные композиции керамических порошков  $\text{Si}_3\text{N}_4$ –TiC и  $\text{Si}_3\text{N}_4$ –TiN–TiC.

**Ключевые слова:** нитрид кремния, карбид титана, композиционная керамика, самораспространяющийся высокотемпературный синтез, азид натрия, политетрафторэтилен, галлоидные соли, горение, состав

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## Introduction

Silicon nitride ceramics exhibit excellent mechanical and thermal properties, making them an ideal material for high-temperature applications such as aerospace structural components and turbine engines [1]. Their microstructure after sintering resembles that of composites reinforced with  $\beta$ - $\text{Si}_3\text{N}_4$  whiskers, which act as reinforcing elements [2–4]. Adequate fracture toughness, high hardness, and good wear resistance are critical characteristics for advanced ceramics, which find applications in cutting tools and automotive components such as cam rollers and ball bearings in diesel engines [5–7]. Recently, silicon nitride ceramics have attracted significant interest due to their high mechanical properties, wear resistance, and corrosion resistance [8–12]. Thermal shock resistance is a key property for their high-temperature applications. However, most studies on silicon nitride nanocompo-

sites focus on optimizing fracture toughness and flexural strength. To expand the application areas of silicon nitride ceramics, improvements in shock resistance and high-temperature creep resistance are essential [13].

Considerable efforts have been made to improve the mechanical properties of  $\text{Si}_3\text{N}_4$  by controlling the microstructure or creating various types of composites. During the densification process,  $\beta$ - $\text{Si}_3\text{N}_4$  fibers significantly increase fracture toughness as cracks interact with these large grains [14].

Tensile strength is widely recognized as one of the most important factors for enhancing the thermal stability of ceramics [15; 16]. Incorporating second-phase particles into a ceramic matrix can enhance the mechanical properties of ceramics. Studies have also shown that the addition of a secondary phase can improve crack initiation and propagation resistance in various ways [17–20]. For example, adding TiC par-

ticles to a silicon nitride matrix enhances mechanical performance, thermal shock behavior, and fatigue resistance, with an optimal TiC content of 10 wt. % [13]. Other researchers [21–23] have also reported the influence of TiC particles on the Si<sub>3</sub>N<sub>4</sub> matrix.

Moreover, silicon nitride is extremely hard and non-conductive, making machining with conventional diamond tools challenging and costly, significantly increasing the final cost of ceramic components. Consequently, new electrically conductive composites based on silicon nitride have been developed for more cost-effective electrical discharge machining by incorporating certain amounts of electrically conductive particles such as TiC, TiN, or TiCN into the ceramic matrix [24; 25]. For instance, a Si<sub>3</sub>N<sub>4</sub> + TiN composite with critical TiN content can be machined using inexpensive electrical discharge machining [26].

A Si<sub>3</sub>N<sub>4</sub>–TiC nanocomposite with high mechanical properties was obtained by hot pressing with the addition of 10 wt. % nanosized Si<sub>3</sub>N<sub>4</sub> particles and 15 wt. % TiC to a submicron Si<sub>3</sub>N<sub>4</sub> matrix, using Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> as sintering aids. Layered composites demonstrated high strength, fracture toughness, and wear resistance due to the presence of compressive surface stresses in the layers. A ceramic nanocomposite Si<sub>3</sub>N<sub>4</sub>–TiC was fabricated using a Si<sub>3</sub>N<sub>4</sub> micro-matrix with nanosized Si<sub>3</sub>N<sub>4</sub> and TiC particles. Cutting tools made from this ceramic exhibited better wear resistance than those made from sialon. Wear occurred mainly through abrasion and adhesion, whereas sialon cutting tools predominantly experienced abrasion, adhesion, thermal cracking, and delamination [27; 28].

The addition of secondary phases, namely the production of composites with ceramic matrices, offers many significant advantages, such as improved fracture toughness compared to unreinforced ceramics [29; 30]. Moreover, recent studies have shown that *in-situ* phase formation provides additional opportunities compared to composites produced using traditional *ex-situ* methods. The main advantages of *in-situ* manufacturing methods include enhanced mechanical properties, the ability to achieve unique microstructures, process simplicity, and inexpensive raw materials [27].

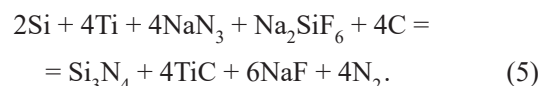
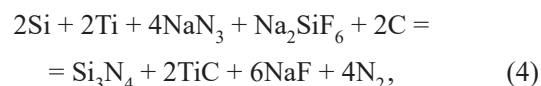
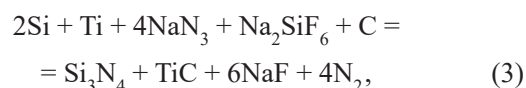
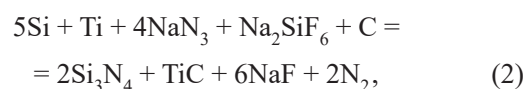
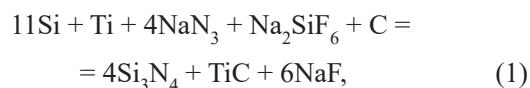
One promising *in-situ* technology is the self-propagating high-temperature synthesis (SHS) process, which enables the production of a wide range of refractory compounds, including nitrides and carbides, by utilizing the heat released during combustion in simple, compact equipment with short processing times [30].

To produce highly dispersed ( $d < 1 \mu\text{m}$ ) Si<sub>3</sub>N<sub>4</sub>–TiC powder compositions, the authors of this article investigated the use of azide synthesis, a variation of SHS where sodium azide (NaN<sub>3</sub>) powder serves as the nitrid-

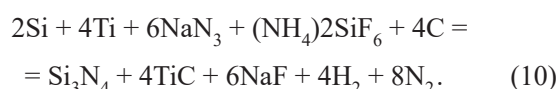
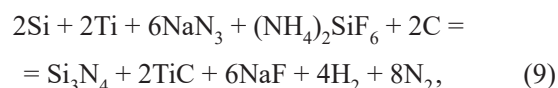
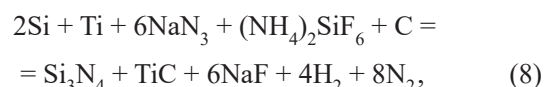
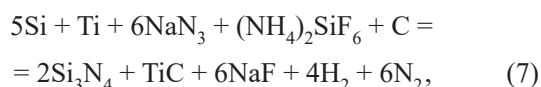
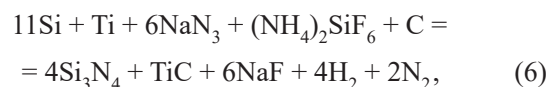
ing agent, and various activating halide salts are used alongside elemental reactants. This approach results in relatively low combustion temperatures, the formation of numerous intermediate vapor-gas reaction products, and final by-products consisting of condensed and gaseous phases. These by-products separate the target powder particles and prevent their agglomeration into larger particles.

The study summarizes the results of azide SHS synthesis of Si<sub>3</sub>N<sub>4</sub>–TiC ceramic compositions with various nitride-to-carbide phase ratios of Si<sub>3</sub>N<sub>4</sub>:TiC = 4:1, 2:1, 1:1, 1:2, and 1:4, according to the following stoichiometric equations, using halide salts such as Na<sub>2</sub>SiF<sub>6</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> [33; 34].

#### Si–Ti–NaN<sub>3</sub>–Na<sub>2</sub>SiF<sub>6</sub>–C system



#### Si–Ti–NaN<sub>3</sub>–(NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>–C system



In these stoichiometric reactions, the composition of the reaction products is expressed in moles. When

converted to weight percent (wt. %), the following ratios are obtained for the expected theoretical composition of the target  $\text{Si}_3\text{N}_4$ –TiC compositions after the removal of the water-soluble byproduct salt, NaF, from the condensed reaction products:

- (1), (6)  $4\text{Si}_3\text{N}_4 + \text{TiC} = 90.4 \% \text{Si}_3\text{N}_4 + 9.6 \% \text{TiC}$ ,  
 (2), (7)  $2\text{Si}_3\text{N}_4 + \text{TiC} = 82.4 \% \text{Si}_3\text{N}_4 + 17.6 \% \text{TiC}$ ,  
 (3), (8)  $\text{Si}_3\text{N}_4 + \text{TiC} = 70.1 \% \text{Si}_3\text{N}_4 + 29.9 \% \text{TiC}$ ,  
 (4), (9)  $\text{Si}_3\text{N}_4 + 2\text{TiC} = 53.9 \% \text{Si}_3\text{N}_4 + 46.1 \% \text{TiC}$ ,  
 (5), (10)  $\text{Si}_3\text{N}_4 + 4\text{TiC} = 36.9 \% \text{Si}_3\text{N}_4 + 63.1 \% \text{TiC}$ .

The results of the phase composition analysis of the washed solid combustion products from reactions (1)–(10), determined experimentally, are presented in Table 1. In most cases, the products consist of a highly dispersed powder with a complex composition, appearing as submicron equiaxed particles ranging in size from 100 nm to 1  $\mu\text{m}$  (Fig. 1).

From the data in Table 1, it is evident that the experimental phase composition of the products from azide SHS differs significantly from the expected theoretical composition of  $\text{Si}_3\text{N}_4$ –TiC powder compositions. The content of the target carbide phase TiC is significantly lower than its theoretical value (ranging from 2.7 to 19.9 %), the amount of  $\text{Si}_3\text{N}_4$  is excessive, and an undesirable secondary phase, titanium nitride, is present (ranging from 1.9 to 19.2 %). These results can be attributed to the fact that very fine and lightweight particles of technical carbon may be partially or completely removed from the burning, highly porous bulk charge

sample by gases released during the decomposition of sodium azide and halide salts, preventing their participation in the formation of titanium carbide. As a result, silicon nitride forms in larger quantities, and titanium nitride forms due to an excess of nitrogen (since combustion in a nitrogen atmosphere is essential for *in-situ* nitride formation in SHS compositions), while titanium carbide forms in smaller amounts than predicted by the initial stoichiometric reaction equations and thermodynamic calculations. Additionally, the synthesized compositions may contain impurities of unreacted free silicon (up to 1.9 %) or carbon (up to 1.5 %).

To address these shortcomings, several directions for further research on applying the SHS process to produce highly dispersed  $\text{Si}_3\text{N}_4$ –TiC compositions can be pursued. The simplest approach is to use polytetrafluoroethylene (PTFE ( $\text{C}_2\text{F}_4$ )<sub>n</sub>) as an activating and carbon-containing additive in the charge, promoting the formation of TiC, as successfully demonstrated in previous studies [35; 36].

In this context, the aim of the present study was to maximize the convergence of the theoretical and experimental compositions of the  $\text{Si}_3\text{N}_4$ –TiC powder composition by modifying the initial reactant composition with full or partial replacement of carbon with PTFE and optimizing the conditions of the azide SHS process.

## Research methodology

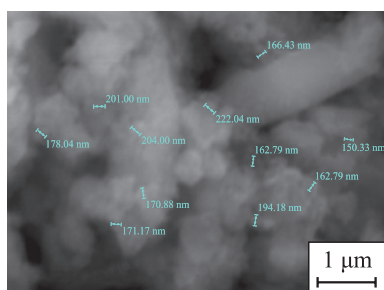
To synthesize the target  $\text{Si}_3\text{N}_4$ –TiC composition with phase molar ratios ranging from 2:1 to 1:4, chemical reaction equations involving full (11)–(14) and partial (15), (16) substitution of carbon with polytetrafluoroethylene (PTFE) were used:

Table 1. Experimental phase composition of washed solid products from azide SHS

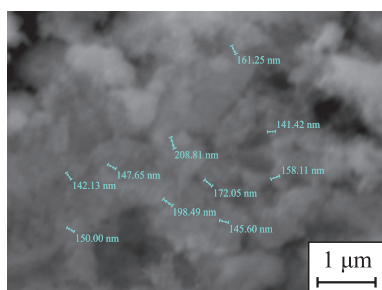
Таблица 1. Экспериментальный фазовый состав промытых твердых продуктов азидного СВС

| Equation                                                            | Si <sub>3</sub> N <sub>4</sub> :TiC<br>(mol) | Content, wt. %                   |                                  |      |      |     |     |
|---------------------------------------------------------------------|----------------------------------------------|----------------------------------|----------------------------------|------|------|-----|-----|
|                                                                     |                                              | α-Si <sub>3</sub> N <sub>4</sub> | β-Si <sub>3</sub> N <sub>4</sub> | TiN  | TiC  | C   | Si  |
| Si–Ti–NaN <sub>3</sub> –Na <sub>2</sub> SiF <sub>6</sub> – C system |                                              |                                  |                                  |      |      |     |     |
| (1)                                                                 | 4:1                                          | 51.2                             | 34.8                             | 7.9  | 6.1  | –   | –   |
| (2)                                                                 | 2:1                                          | 43.2                             | 29.8                             | 18.9 | 8.1  | –   | –   |
| (3)                                                                 | 1:1                                          | 55.7                             | 29.2                             | 1.9  | 11.3 | –   | 1.9 |
| (4)                                                                 | 1:2                                          | 51.6                             | 29.3                             | 2.3  | 15.3 | 1.5 | –   |
| (5)                                                                 | 1:4                                          | 48.6                             | 27.6                             | 4.0  | 19.9 | 0.8 | –   |
| (6)                                                                 | 4:1                                          | 65.5                             | 25.0                             | 5.0  | 2.7  | –   | 1.8 |
| (7)                                                                 | 2:1                                          | 60.8                             | 24.0                             | 5.1  | 9.3  | –   | 0.7 |
| (8)                                                                 | 1:1                                          | 48.6                             | 27.6                             | 19.2 | 4.7  | –   | –   |
| (9)                                                                 | 1:2                                          | 43.2                             | 29.8                             | 18.9 | 8.1  | –   | –   |
| (10)                                                                | 1:4                                          | 43.0                             | 21.1                             | 16.1 | 8.9  | –   | –   |

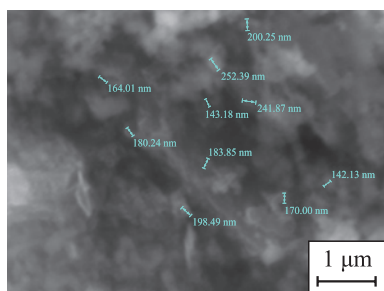




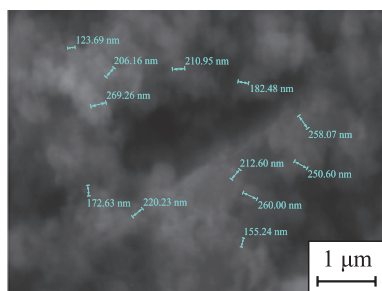
(1)  $11\text{Si} + \text{Ti} + 4\text{NaN}_3 + \text{Na}_2\text{SiF}_6 + \text{C}$



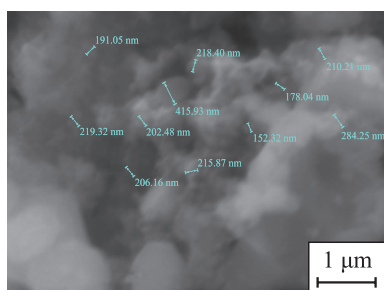
(2)  $5\text{Si} + \text{Ti} + 4\text{NaN}_3 + \text{Na}_2\text{SiF}_6 + \text{C}$



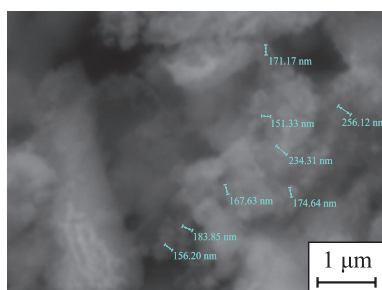
(3)  $2\text{Si} + \text{Ti} + 4\text{NaN}_3 + \text{Na}_2\text{SiF}_6 + \text{C}$



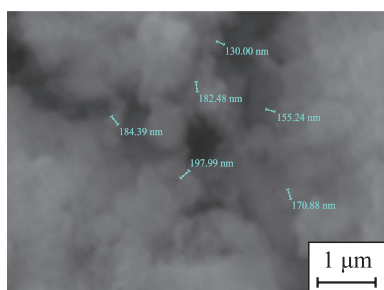
(4)  $2\text{Si} + 2\text{Ti} + 4\text{NaN}_3 + \text{Na}_2\text{SiF}_6 + 2\text{C}$



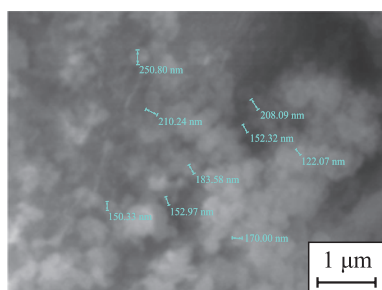
(5)  $2\text{Si} + 4\text{Ti} + 4\text{NaN}_3 + \text{Na}_2\text{SiF}_6 + 4\text{C}$



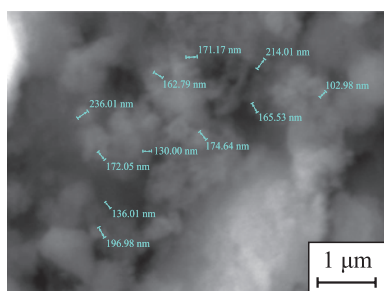
(6)  $11\text{Si} + \text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + \text{C}$



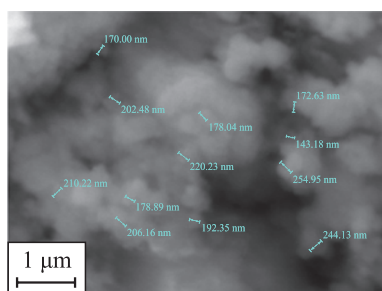
(7)  $5\text{Si} + \text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + \text{C}$



(8)  $2\text{Si} + \text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + \text{C}$



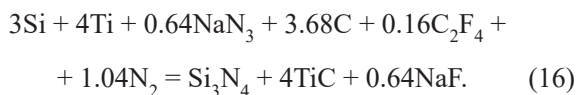
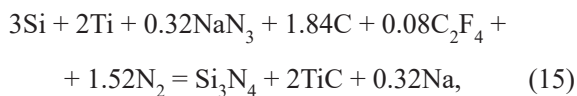
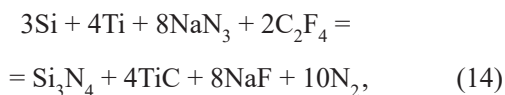
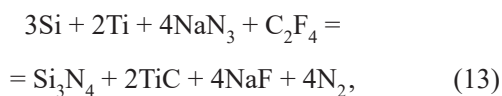
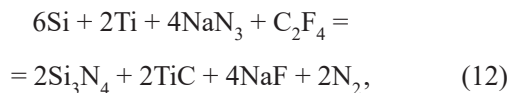
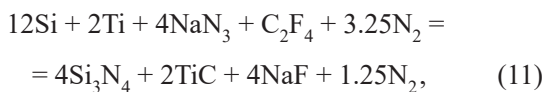
(9)  $2\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$



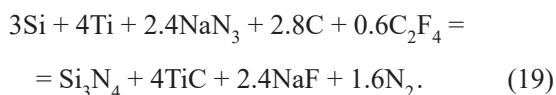
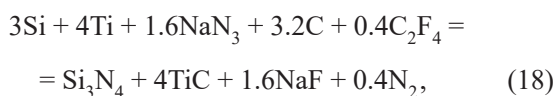
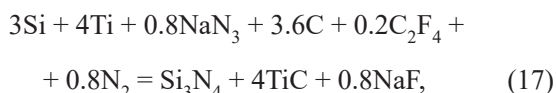
(10)  $2\text{Si} + 4\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 4\text{C}$

**Fig. 1.** Microstructure of combustion products from charges according to equations (1)–(10)

**Рис. 1.** Микроструктура продуктов горения шихт в соответствии с уравнениями (1)–(10)



To achieve the  $\text{Si}_3\text{N}_4$ –TiC composition with the maximum titanium carbide phase content ( $\text{Si}_3\text{N}_4$ :TiC = 1:4), carbiding mixtures with increased PTFE content were also used:



Thermodynamic calculations were conducted using the Thermo software [37] to predict the feasibility of combustion reactions by determining thermal effects (enthalpies), adiabatic temperatures, and the compositions of synthesis products.

The following raw materials were used in the experiments:

- silicon powder, grade Kr0 (main substance content  $\geq 98.8$  wt. %, average particle size  $d = 5 \mu\text{m}$ );
- titanium powder, grade PTOM-1 (98.0 wt. %,  $d = 30 \mu\text{m}$ );
- sodium azide powder, analytical grade ( $\geq 98.71$  wt. %,  $d = 100 \mu\text{m}$ );
- carbon black, grade P701 ( $\geq 99.7$  wt. %,  $d = 70 \text{ nm}$ , agglomerates up to  $1 \mu\text{m}$ );
- polytetrafluoroethylene, grade PN-40 ( $\geq 99.0$  %,  $d = 40 \mu\text{m}$ ).

Combustion of the starting reactant mixtures (charge) with a bulk relative density of 0.4 was conducted in a paper crucible with a diameter of 30 mm and a height of 45 mm. The experiments were performed in a laboratory SHS-Az reactor with a volume of 4.5 L, equipped with two thermocouples, under a nitrogen pressure of 4 MPa. The thermocouples were used to measure combustion temperatures and calculate the combustion rate. The pressure variation in the reactor during the combustion process was monitored with a pressure gauge.

The synthesized product was weighed and compared to the theoretical yield calculated from reactions (11)–(19). The combustion product was washed with water to remove water-soluble impurities, and the pH of the wash water was measured to assess the presence of free sodium in the combustion product and the completeness of the chemical reaction. The phase composition of the synthesized combustion products was determined using an automated ARL X'tra X-ray diffractometer (Thermo Scientific, Switzerland).  $\text{CuK}_\alpha$  radiation was employed with continuous scanning over the angular range of  $2\theta = 20\text{--}80^\circ$  at a scan rate of  $2^\circ/\text{min}$ . The resulting spectra were processed using the WinXRD software package. The surface topography and powder particle morphology were examined using a JSM-6390A scanning electron microscope (Jeol, Japan) equipped with a Jeol JED-2200 energy-dispersive spectroscopy attachment.

## Results and discussion

The results of thermodynamic calculations for reactions (11)–(19) performed using the Thermo software are presented in Tables 2–4.

From the presented data, it is evident that all reactions exhibit high adiabatic temperatures sufficient for the realization of the SHS process in a combustion mode. The reaction products contain all the phases corresponding to the right-hand sides of equations (11)–(19), including the target phases of silicon nitride ( $\text{Si}_3\text{N}_4$ ) and titanium carbide (TiC), the water-soluble byproduct salt NaF, and minor impurities of free silicon (Si) and titanium (Ti).

The results of the microstructural analysis of the combustion products of the initial powder mixtures (charges) from reactions (11)–(19) after washing with water to remove the byproduct salt NaF are shown in Fig. 2.

As shown in Fig. 2, the combustion products of charges from reactions (11)–(19) consist of highly dispersed equiaxed particles, comprising a mixture of nanosized (less than 100 nm) and submicron (100–500 nm) particles of titanium carbide and tita-

Table 2. Thermodynamic analysis results for reactions (11)–(14)

Таблица 2. Результаты термодинамического анализа реакций (11)–(14)

| Reaction equation | $T_{ad}$ , K | Combustion products composition, mol |        |        |                    |        |        |        |                                    | $\Delta H$ , kJ |
|-------------------|--------------|--------------------------------------|--------|--------|--------------------|--------|--------|--------|------------------------------------|-----------------|
|                   |              | F(g)                                 | Na(g)  | Si(g)  | N <sub>2</sub> (g) | NaF(g) | NaF(l) | TiC(s) | Si <sub>3</sub> N <sub>4</sub> (s) |                 |
| (11)              | 3033         | 0.0314                               | 0.0314 | 2.0400 | 2.6100             | 3.9686 | –      | 2.0000 | 3.3200                             | –5271           |
| (12)              | 2984         | 0.0253                               | 0.0253 | 1.0602 | 2.7068             | 3.9747 | –      | 2.0000 | 1.6466                             | –3695           |
| (13)              | 2893         | 0.0196                               | 0.0196 | 0.3998 | 4.2666             | 3.9804 | –      | 2.0000 | 0.8667                             | –2908           |
| (14)              | 2810         | 0.0284                               | 0.0284 | 0.3246 | 10.2164            | 7.3922 | 0.5794 | 4.0000 | 0.8918                             | –5027           |

Table 3. Thermodynamic analysis results for reactions (15), (16)

Таблица 3. Результаты термодинамического анализа реакций (15), (16)

| Reaction equation | $T_{ad}$ , K | Combustion products composition, mol |        |                    |        |        |        |        |                                    | $\Delta H$ , kJ |
|-------------------|--------------|--------------------------------------|--------|--------------------|--------|--------|--------|--------|------------------------------------|-----------------|
|                   |              | F(g)                                 | Na(g)  | N <sub>2</sub> (g) | Si(g)  | Ti(g)  | NaF(g) | TiC(s) | Si <sub>3</sub> N <sub>4</sub> (s) |                 |
| (15)              | 3702         | 0.0117                               | 0.0117 | 0.0074             | 0.0056 | 0.0002 | 0.3083 | 1.9998 | 0.9981                             | –1342           |
| (16)              | 3380         | 0.0108                               | 0.0108 | 0.0025             | 0.0019 | 0.0023 | 0.6292 | 3.9999 | 0.9994                             | –1896           |

Table 4. Results of thermodynamic analysis of reactions (17)–(19)

Таблица 4. Результаты термодинамического анализа реакций (17)–(19)

| Reaction equation | $T_{ad}$ , K | Combustion products composition, mol |        |                    |        |        |        |        |                                    | $\Delta H$ , kJ |
|-------------------|--------------|--------------------------------------|--------|--------------------|--------|--------|--------|--------|------------------------------------|-----------------|
|                   |              | F(g)                                 | Na(g)  | N <sub>2</sub> (g) | Si(g)  | NaF(g) | TiC(l) | TiC(s) | Si <sub>3</sub> N <sub>4</sub> (s) |                 |
| (17)              | 3426         | 0.0199                               | 0.0199 | –                  | 0.6002 | 0.7801 | 3.9999 | –      | 0.7999                             | –1964           |
| (18)              | 2271         | 0.0114                               | 0.0114 | 0.8959             | 0.7438 | 1.5886 | –      | 4.0000 | 0.7521                             | –2304           |
| (19)              | 2937         | 0.0157                               | 0.0157 | 2.0485             | 0.6728 | 2.3843 | –      | 4.0000 | 0.7757                             | –2645           |

niium nitride, as well as silicon nitride fibers with diameters of 50–200 nm and lengths of up to 5  $\mu$ m.

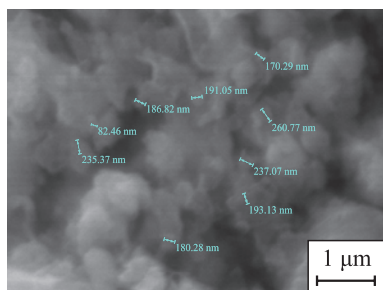
The results of X-ray phase analysis for the washed combustion products of systems with the maximum titanium carbide phase content (Si<sub>3</sub>N<sub>4</sub>:TiC = 1:4) are presented in Fig. 3.

The results of quantitative processing of the XRD spectra presented in Fig. 3 are summarized in Table 5. These results show the phase content in the washed combustion products of charges with the maximum titanium carbide phase fraction (Si<sub>3</sub>N<sub>4</sub>:TiC = 1:4) under various conditions: full replacement of carbon black with PTFE (reaction 14), carbiding mixtures with minimal PTFE content (reaction 16), and carbiding mixtures based on reactions (17)–(19) to synthesize the Si<sub>3</sub>N<sub>4</sub>–TiC composition. The experimental data are compared with theoretical phase compositions of target products Si<sub>3</sub>N<sub>4</sub> and TiC based on the stoichiometric equations (11)–(19).

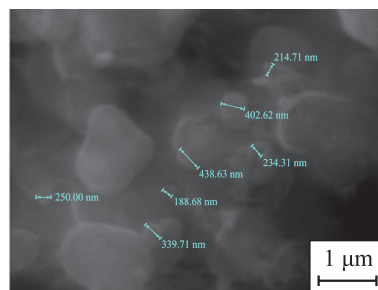
From the data in Table 5, it is evident that using PTFE as a carbon source for synthesizing nitride-carbide compositions via azide SHS is a promising research direction. A comparison of the experimental phase composi-

tions of combustion products from charges (11)–(14) with theoretical values indicates that full replacement of carbon black with PTFE is not advisable, although the titanium carbide phase content increases compared to azide SHS without PTFE. For example, the titanium carbide content in the combustion products of charge (5): 2Si + 4Ti + 4NaN<sub>3</sub> + Na<sub>2</sub>SiF<sub>6</sub> + 4C with the maximum TiC content (Si<sub>3</sub>N<sub>4</sub>:TiC = 1:4), is 19.9 wt. %. With full replacement of carbon black by PTFE in charge: 3Si + 4Ti + 8NaN<sub>3</sub> + 2C<sub>2</sub>F<sub>4</sub>) the titanium carbide content increases to 31.0 wt. %. However, partial replacement of carbon black and its combined use with PTFE as a carbon source allows the titanium carbide content to reach 52.3 wt. % in the combustion products of charge (16): 3Si + 4Ti + 0.64NaN<sub>3</sub> + 3.68C + 0.16C<sub>2</sub>F<sub>4</sub> + 1.04N<sub>2</sub>.

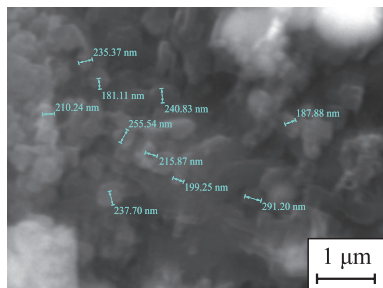
The best results were obtained using carbiding mixtures with increased PTFE content according to equations (17)–(19), where the TiC content in the experimental products ranged from 58.6 to 61.7 wt. %. Furthermore, the use of PTFE reduced the content of the secondary phase, titanium nitride, to 2.0–4.0 wt. % in the products of carbiding mixtures (17)–(19).



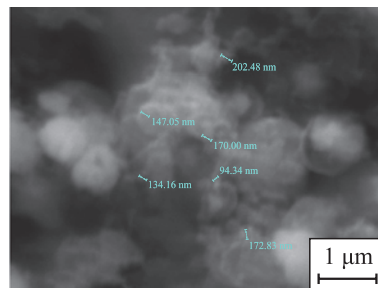
(11)  $12\text{Si} + 2\text{Ti} + 4\text{NaN}_3 + \text{C}_2\text{F}_4 + 3,25\text{N}_2$



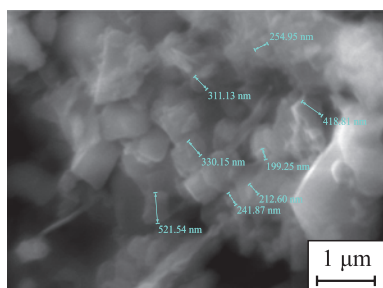
(12)  $6\text{Si} + 2\text{Ti} + 4\text{NaN}_3 + \text{C}_2\text{F}_4$



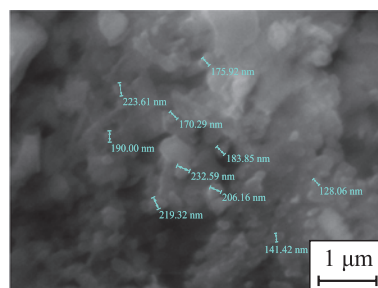
(13)  $3\text{Si} + 2\text{Ti} + 4\text{NaN}_3 + \text{C}_2\text{F}_4$



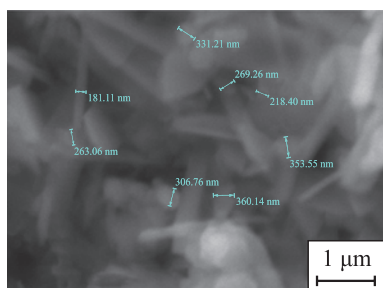
(14)  $3\text{Si} + 4\text{Ti} + 8\text{NaN}_3 + 2\text{C}_2\text{F}_4$



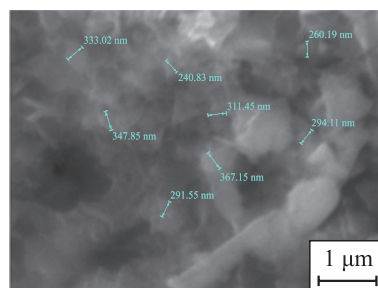
(15)  $3\text{Si} + 2\text{Ti} + 0.32\text{NaN}_3 + 1.84\text{C} + 0.08\text{C}_2\text{F}_4 + 1.52\text{N}_2$



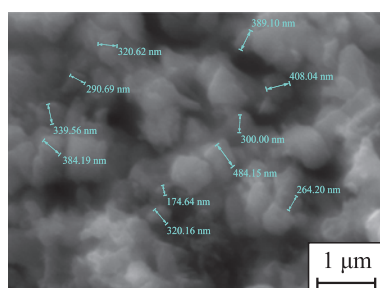
(16)  $3\text{Si} + 4\text{Ti} + 0.64\text{NaN}_3 + 3.68\text{C} + 0.16\text{C}_2\text{F}_4 + 1.04\text{N}_2$



(17)  $3\text{Si} + 4\text{Ti} + 0.8\text{NaN}_3 + 3.6\text{C} + 0.2\text{C}_2\text{F}_4 + 0.8\text{N}_2$



(18)  $3\text{Si} + 4\text{Ti} + 1.6\text{NaN}_3 + 3.2\text{C} + 0.4\text{C}_2\text{F}_4$



(19)  $3\text{Si} + 4\text{Ti} + 2.4\text{NaN}_3 + 2.8\text{C} + 0.6\text{C}_2\text{F}_4$

**Fig. 2.** Microstructure of combustion products from charges according to equations (11)–(19)

**Рис. 2.** Микроструктура продуктов горения шихт в соответствии с уравнениями (11)–(19)



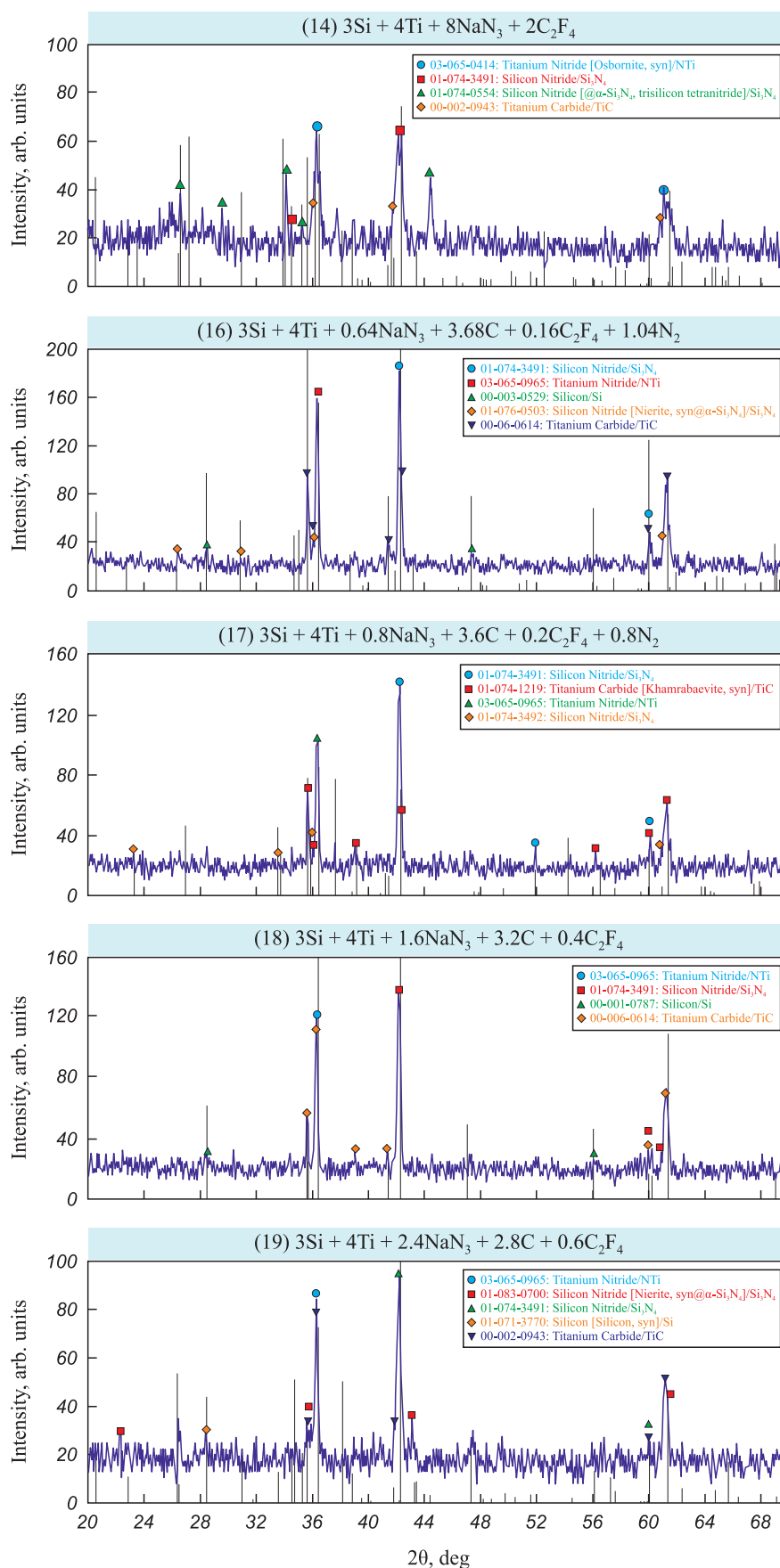


Fig. 3. X-ray diffraction patterns of combustion products from charges (14), (16)–(19)

Рис. 3. Рентгеновские дифрактограммы продуктов горения шихт (14), (16)–(19)

**Table 5. Theoretical and experimental phase compositions of washed products from azide SHS according to equations (11)–(19)****Таблица 5. Теоретический и экспериментальный фазовые составы промытых продуктов азидного CBC согласно уравнениям (11)–(19)**

| Reaction equation | Si <sub>3</sub> N <sub>4</sub> :TiC (mol) | Content, wt. %                 |      |                                  |                                  |      |      |     |
|-------------------|-------------------------------------------|--------------------------------|------|----------------------------------|----------------------------------|------|------|-----|
|                   |                                           | Theoretical                    |      | Experimental                     |                                  |      |      |     |
|                   |                                           | Si <sub>3</sub> N <sub>4</sub> | TiC  | α-Si <sub>3</sub> N <sub>4</sub> | β-Si <sub>3</sub> N <sub>4</sub> | TiC  | TiN  | Si  |
| (11)              | 2:1                                       | 82.4                           | 17.6 | 62.0                             | 17.0                             | 12.0 | 9.0  | –   |
| (12)              | 1:1                                       | 70.1                           | 29.9 | 52.0                             | 20.0                             | 23.0 | 5.0  | –   |
| (13)              | 1:2                                       | 53.9                           | 46.1 | 53.0                             | 14.0                             | 27.0 | 6.0  | –   |
| (14)              | 1:4                                       | 36.9                           | 63.1 | 42.0                             | 7.0                              | 31.0 | 10.0 | –   |
| (15)              | 1:2                                       | 53.9                           | 46.1 | 26.6                             | 14.1                             | 44.1 | 5.2  | –   |
| (16)              | 1:4                                       | 36.9                           | 63.1 | 27.8                             | 10.0                             | 52.3 | 9.9  | –   |
| (17)              | 1:4                                       | 36.9                           | 63.1 | 29.7                             | 7.7                              | 58.6 | 2.0  | 2.0 |
| (18)              | 1:4                                       | 36.9                           | 63.1 | 28.0                             | 9.0                              | 59.0 | 4.0  | –   |
| (19)              | 1:4                                       | 36.9                           | 63.1 | 28.7                             | 3.0                              | 61.7 | 3.6  | 3.0 |

## Conclusion

The presented results demonstrate that the SHS technology can make a significant contribution to the development of methods for producing highly dispersed Si<sub>3</sub>N<sub>4</sub>–TiC nitride-carbide compositions. The SHS process is attractive for its simplicity and cost-effectiveness and is one of the promising *in-situ* chemical methods for the direct synthesis of ceramic powders within the desired composition from a mixture of inexpensive starting reagents.

Traditional azide SHS using NaN<sub>3</sub> and gasifying halide fluorides, such as Na<sub>2</sub>SiF<sub>6</sub> and (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub>, is characterized by comparatively low combustion temperatures, the formation of large amounts of intermediate vapor and gaseous reaction products, as well as final byproduct condensed and gaseous products that separate the target powder particles. This enabled the synthesis of a highly dispersed (<1 μm) Si<sub>3</sub>N<sub>4</sub>–TiC powder composition, with Si<sub>3</sub>N<sub>4</sub> predominantly in the α-modification phase during the combustion of all studied mixtures.

However, in all cases of traditional azide SHS application, the amount of TiC phase synthesized in the experiments was significantly lower than expected. Additionally, all synthesized compositions contained the TiN phase, with its content exceeding that of titanium carbide in mixtures without PTFE additives. Furthermore, the synthesized compositions may include impurities of unreacted free silicon (up to 3.0 wt. %).

The use of PTFE as an activating and carburizing additive with partial replacement of carbon in the mixtures (15)–(19) in azide SHS eliminated, in most cases, the shortcomings of the traditional approach for various

ratios of target phases Si<sub>3</sub>N<sub>4</sub> and TiC. This allowed for the synthesis of highly dispersed Si<sub>3</sub>N<sub>4</sub>–TiC powder compositions with a phase composition significantly closer to the calculated theoretical composition.

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## Вклад авторов

**Yu. V. Titova** – defined the study's objective, summarized the results, and contributed to writing and editing the manuscript.

**A. F. Yakubova** – conducted the experiments, prepared and presented the experimental results, participated in the analysis and discussion, and contributed to the writing of the article.

**G. S. Belova** – formulated the research objectives, planned the experiments, analyzed and discussed the results, and contributed to the writing of the article.

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