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## SHS of highly dispersed powder compositions of nitrides with silicon carbide. Review

© 2022 г. **A.P. Amosov, Yu.V. Titova, G.S. Belova, D.A. Maidan, A.F. Minekhanova**

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**Abstract:** The application of the process of self-propagating high-temperature synthesis (SHS) to prepare highly dispersed powder nitride-carbide compositions from the most common refractory nitride ( $\text{Si}_3\text{N}_4$ , AlN, TiN) and carbide (SiC) compounds with a particle size of less than 1  $\mu\text{m}$  is considered. The advantages of composite ceramics over single-phase ceramic materials and such trends of its development as the transition to nanostructured ceramics and the application of in situ processes of direct chemical synthesis of nanoparticles of components in the composite body are described. The attractiveness of the SHS process as one of the promising in situ processes characterized by simplicity and cost-effectiveness, the possibility of obtaining highly dispersed ceramic powders by burning mixtures of inexpensive reagents is shown. Considerable attention is paid to the consideration of the results of the application of azide SHS, based on the use of sodium azide and gasified halide salts as part of mixtures of initial powders of nitrided and carbidized elements during their combustion in nitrogen gas. The review of publications devoted to the application of SHS to obtain highly dispersed composite powders  $\text{Si}_3\text{N}_4\text{—SiC}$ , AlN—SiC and TiN—SiC, promising for use in sintering of the corresponding composite ceramic materials of submicron and nano-sized structure with improved properties, lower brittleness, good machinability, lower sintering temperatures compared with single-phase ceramic materials made of nitrides or carbides as well as for other applications, is presented. The results of the application of azide SHS are presented in detail both in the form of the results of thermodynamic calculations and the results of experimental research of combustion parameters, combustion product structure and composition. The advantages and disadvantages of using the combustion process for the synthesis of nitride compositions with silicon carbide, the causes of the disadvantages and the directions of further research to eliminate them are discussed.

**Keywords:** composite ceramics, nitrides, silicon carbide, powder compositions, self-propagating high-temperature synthesis (SHS), combustion products, composition, structure.

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## СВС высокодисперсных порошковых композиций нитридов с карбидом кремния Обзор

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**Аннотация:** Рассмотрено применение процесса самораспространяющегося высокотемпературного синтеза (СВС) для получения высокодисперсных порошковых нитридно-карбидных композиций из наиболее распространенных тугоплавких

нитридных ( $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ,  $\text{TiN}$ ) и карбидного ( $\text{SiC}$ ) соединений с размером частиц менее 1 мкм. Изложены преимущества композиционной керамики перед однофазными керамическими материалами и такие тенденции ее развития, как переход к наноструктурной керамике и использование *in situ* процессов прямого химического синтеза наночастиц компонентов в объеме композита. Показана привлекательность процесса СВС как одного из перспективных *in situ* процессов, характеризующегося простотой и экономичностью, возможностью получения высокодисперсных керамических порошков при сжигании смесей недорогих реагентов. Значительное внимание уделено рассмотрению результатов применения азидного СВС, основанного на использовании азиды натрия и газифицирующихся галоидных солей в составе смесей исходных порошков азотируемых и карбидизируемых элементов при их сжигании в газообразном азоте. Представлен обзор публикаций, посвященных применению СВС для получения высокодисперсных композиционных порошков  $\text{Si}_3\text{N}_4$ — $\text{SiC}$ ,  $\text{AlN}$ — $\text{SiC}$  и  $\text{TiN}$ — $\text{SiC}$ , перспективных для использования при спекании соответствующих композиционных керамических материалов субмикронной и наноразмерной структуры с повышенными свойствами, меньшей хрупкостью, хорошей обрабатываемостью, меньшими температурами спекания по сравнению с однофазными керамическими материалами из нитридов или карбидов, а также для использования в других приложениях. Подробно представлены результаты применения азидного СВС как в виде показателей термодинамических расчетов, так и данных экспериментального исследования параметров горения, структуры и состава продуктов горения. Обсуждены достоинства и недостатки использования процесса горения для синтеза композиций нитридов с карбидом кремния, причины возникновения сдерживающих факторов и направления проведения дальнейших исследований по их устранению.

**Ключевые слова:** композиционная керамика, нитриды, карбид кремния, композиции порошков, самораспространяющийся высокотемпературный синтез (СВС), продукты горения, состав, структура.

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## Introduction

Refractory nitride ( $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ,  $\text{TiN}$ ) and carbide ( $\text{SiC}$ ) compounds are widely used to produce the corresponding non-oxide ceramic materials, both structural, due to their high melting point, hardness, wear resistance, heat resistance, chemical stability, and functional, due to their electrical and catalytic properties [1—5]. Such ceramic materials are conventionally produced of the corresponding ceramic powders by reactive sintering or hot pressing. Lately, they have been added by spark plasma sintering (SPS) and microwave sintering methods. However, single-phase ceramic materials made of individual refractory compounds may exhibit poor sinterability and machinability, high brittleness, high coefficient of friction (COF), etc. Several approaches are used to address these problems.

Firstly, multiphase (multi-component) composite ceramics are used. For example, conductive titanium nitride is added to non-conductive silicon nitride,

making it possible to use a significantly less expensive electrical discharge machining process when making ceramic products compared to machining with expensive diamond tools [6]. Titanium nitride  $\text{TiN}$  not only exhibits high electrical conductivity but also high melting point, hardness, wear resistance and corrosion resistance, it is compatible with  $\text{Si}_3\text{N}_4$ , improves sintering and the properties of  $\text{Si}_3\text{N}_4$  ceramics [7].

Secondly, the transition to nanostructured ceramics is used, since it has been extensively shown that powder size reduction, the transition to nanopowders and the production of nanostructured ceramics can significantly improve the properties of ceramics [5, 8—10]. Taking  $\text{Si}_3\text{N}_4$ — $\text{TiN}$  composite ceramics as an example, the ceramics of  $\text{Si}_3\text{N}_4$ —30vol.% $\text{TiN}$  composition obtained by spark plasma sintering of  $\text{Si}_3\text{N}_4$  and  $\text{TiN}$  nanoparticles show the wear resistance being 3 times higher than the wear resistance of composite cera-

mics of the same composition obtained by hot pressing of commercially produced micron-sized powders [11]. Such composite ceramics with solid TiN nanoparticles cause significantly less frictional damage to the counterbody than ceramics containing micron-sized TiN particles, which is particularly important, for instance, for hybrid bearings having the balls made of ceramics and the rings made of metal [12].

Thirdly, *in situ* processes of obtaining composite ceramics by performing chemical synthesis of component nanoparticles in the composite body are applied. By far the simplest and most common approach to the production of composite nanoceramics involves mixing ready-made nanopowders, compacting and sintering them (*ex situ* processes). However, two problems are encountered at this point: the first one is the high cost of nanopowders (for example, the price of nitride and carbide nanopowders obtained by plasma-chemical synthesis, which are available on the market, is on average of 3 thous. euro per 1 kg [13]); the second one is that it is practically impossible to mix nanopowders homogeneously due to high tendency of nanoparticles to form quite solid agglomerates, which are extremely difficult to destroy when mixed [5, 9]. The presence of agglomerates impedes the homogeneous distribution of components and the compaction of the powder mixture, it requires higher temperatures for sintering, and results in the porosity of the sintered composite, it is the point of defects from which cracks can develop. In this context, in the case of highly dispersed powders, *in situ* chemical methods of direct synthesis of ceramic powders inside the desired composite body from a mixture of much cheaper initial reagents are preferable to *ex situ* mechanical methods of mixing the desired compositions of premixed ceramic powders [4, 8].

One of the advanced *in situ* processes is the process of self-propagating high-temperature synthesis (SHS) of the most diverse refractory compounds, including nitrides and carbides, which proceeds due to heat release during combustion in a simple, small-sized equipment and takes a little time [14–17]. Other known methods for obtaining Si, Al, Ti nitrides and Si carbide (the furnace method, plasma-chemical synthesis, carbothermal synthesis, gas-phase deposition, etc.) are characterized by high power consumption, complex equipment, and they do not always ensure the nanosize of  $\text{Si}_3\text{N}_4$ , AlN, TiN, SiC powders, and even more so of nanopowder compositions. SHS process is attractive not only for its simplicity and cost-effectiveness, but it also provides considerable opportunities for controlling the disper-

sion and the structure of synthesized ceramic powders, as well as bringing them to the nanosized level [18, 19]. Various techniques are used for this purpose: the reduction of combustion temperature; the use of gasified halide salt additives, condensed and gaseous by-products of SHS reactions separating synthesized particles and preventing their growth; the application of chemical compounds of elements (precursors) rather than the powders of pure elements, e.g. the ones of metals, as initial reagents, etc.

In particular, during the synthesis of nitrides, such opportunities are realized in the azide SHS process, designated as SHS-Az, where not nitrogen gas but sodium azide powder ( $\text{NaN}_3$ ) is used as a nitrating reagent, which decomposes in a combustion wave, releasing active nitrogen [20, 21]. Pure elemental powders of silicon, titanium, aluminum, etc. are used as reagents to be nitrated. A certain halide salt is added to these basic reagents as an auxiliary additive, during the decomposition of which a large amount of vaporous and gaseous reaction products are formed during combustion. These products dilute the reaction body and thus preventing it from sintering, and as a result, the end product is synthesized in the form of a powder, which does not require additional reduction in size after the synthesis. Low combustion temperatures, the formation of condensed by-products and gases separating the desired nitride particles are the distinctive features of azide SHS, leading to the synthesis of nitride micropowders. Upon replacing the pure powders of the nitrated elements (Si, Ti, Al) with their halide salts, being the precursors that decompose in a combustion wave with entering of a nitrated element into reaction in the form of single atoms rather than the micron-sized particles of the condensed substance, the size of nitrides synthesized by azide SHS can be significantly reduced and brought to the nanosized level. Besides, in the case of the synthesis of nitride compositions, the gaseous and vaporous condition of reaction products allows for their prompt and homogeneous mixing, which is unobtainable by mechanical mixing of premix nanopowders. By this means, it is possible to solve the problem of the high cost of nitride nanopowders, obtain significantly (almost by one order of magnitude) cheaper nanopowders (since the most expensive component in the azide SHS is sodium azide, with a cost of up to 300 euros/kg) with minimum power consumption and simple, small-sized equipment if compared to plasma-chemical synthesis. Moreover, the nitride synthesis performed directly in composite powder body (*in situ*) rather than the one

performed in advance with subsequent mechanical mixing (*ex situ*), allows to achieve a high homogeneity of the nitride mixture, i.e. to solve the second problem, namely obtaining a homogeneous mixture of nitride nanopowders. The practical experience of using azide SHS for the production of TiN—BN, AlN—BN, Si<sub>3</sub>N<sub>4</sub>—TiN nitride composite powders with the use of precursors, the halide salts of both nitrated composite elements, has been accumulated [22, 23]. However, obtaining these results was not that easy though. It has been found that the replacement of elemental powders of nitrated elements with their precursors (halide salts) impedes the production of the desired nitrides, most often it results in the formation of undesired hard-to-remove by-products and incomplete reaction, for example, as in the case of compositions containing the by-product cryolite Na<sub>3</sub>AlF<sub>6</sub> and free silicon impurity: AlN—BN—Na<sub>3</sub>AlF<sub>6</sub>, AlN—TiN—Na<sub>3</sub>AlF<sub>6</sub>, Si<sub>3</sub>N<sub>4</sub>—AlN—Na<sub>3</sub>AlF<sub>6</sub>—Si [23].

The positive results of studies on the application of SHS process for obtaining silicon carbide (SiC) nanopowders are known as well [24–26]. In the case of SiC synthesis from the elements, the reaction can be written as follows:



This reaction has a relatively small thermal effect of product formation compared, for example, with the reaction of titanium carbide formation from elements widely used in SHS:



and therefore has a relatively low adiabatic combustion temperature of 1860 K compared with 3290 K for the reaction of TiC formation. In this context, it is practically impossible to perform reaction (1) in combustion mode, i.e. to implement a self-sustaining SHS process in this system.

Several approaches have been developed to increase the reactivity of Si—C system: preheating of the reaction medium, electric field imposition, mechanical activation of the initial mixture of reagents, chemical activation of the reaction (1), for instance, using fluoroplastic powders, conducting the reaction (1) in a nitrogen gas or air medium. Almost all of these approaches can result in obtaining submicron SiC powders and some of them can result in obtaining nanosized SiC powders under the combustion mode. [24]. But it should be taken into account that when combusting Si + C mixture in nitrogen atmosphere, the combustion products can contain up to 3–7 wt.%

of silicon nitride impurities (Si<sub>3</sub>N<sub>4</sub>) along with silicon carbide.

This article presents the results of a review of publications devoted to the application of self-propagating high-temperature synthesis (SHS) to obtain highly dispersed (submicron and nanosized) powder nitride-carbide compositions from the most common refractory nitride (Si<sub>3</sub>N<sub>4</sub>, AlN, TiN) and carbide (SiC) compounds with a particle size of less than 1 μm. Considerable attention is paid to azide SHS method developed by the authors of the review. Synthesized highly dispersed composite powders Si<sub>3</sub>N<sub>4</sub>—SiC, AlN—SiC and TiN—SiC are promising for use in sintering of the corresponding composite ceramic materials of submicron and nanosized structure with improved properties, lower brittleness, good machinability, lower sintering temperatures compared to single-phase ceramic materials made of nitrides or carbides, as well as for other applications.

### Si<sub>3</sub>N<sub>4</sub>—SiC composition

As it has already been mentioned, silicon nitride Si<sub>3</sub>N<sub>4</sub> and silicon carbide SiC are known as high-temperature structural ceramics [1–3, 5]. Along with this, dielectric Si<sub>3</sub>N<sub>4</sub> is applied as an insulator in microelectronics, as well as a storage medium in flash memory devices, and semiconductor SiC is used in high-power and high-temperature transistor devices and LEDs, as well as in electric heaters. Besides, silicon carbide is used as a catalyst in the oxidation of hydrocarbons, and silicon nitride is used as a catalyst carrier.

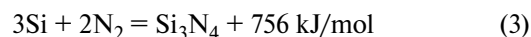
However, these ceramic materials differ markedly in certain characteristics (their specific values are highly dependent on the methods of ceramics production, therefore we will assume average values determined primarily at room temperature). For example, Si<sub>3</sub>N<sub>4</sub> ceramics is not as brittle as SiC, and it exhibits high fracture toughness (5.3 MPa·m<sup>1/2</sup> on average) and good flexural strength (at a level of 750 MPa), but it is characterized by low oxidation resistance at high temperatures (1.2 mg/cm<sup>3</sup> weight increase at *T* = 1573 K per 100 h) [1, 27]. SiC ceramics, to the contrary, have high wear, creep and oxidation resistance at high temperatures (0.02 mg/cm<sup>3</sup> weight increase under the same conditions), but it shows low values of flexural strength (450 MPa) and fracture toughness (2.8 MPa·m<sup>1/2</sup>). Silicon carbide is the most important component of ultra-high-temperature ceramic materials (5–65 vol.%) for the achievement of their maximum oxidation resistance [28, 29].

The results of many of studies show that the combination of nitride and silicon carbide in composite material  $\text{Si}_3\text{N}_4$ — $\text{SiC}$  allows to use the advantages of each of these single-phase ceramics and obtain composite ceramics with significantly improved properties, primarily for high-temperature applications [5, 27, 30–32]. The introduction of minimum of 5 vol.% of  $\text{SiC}$  into  $\text{Si}_3\text{N}_4$  matrix provides an opportunity of obtaining a composite with high fracture toughness ( $6.5 \text{ MPa} \cdot \text{m}^{1/2}$ ) by spark plasma sintering [32].  $\text{Si}_3\text{N}_4$ —20vol.% $\text{SiC}$  composite produced by hot isostatic pressing has fracture toughness of  $9.5 \text{ MPa} \cdot \text{m}^{1/2}$  at  $T = 1673 \text{ K}$  (compared with  $5.3 \text{ MPa} \cdot \text{m}^{1/2}$  of  $\text{Si}_3\text{N}_4$  single-phase ceramics), and it is considered as a promising material for gas turbine engines [31]. This conclusion is confirmed by the results of later studies, according to which hot-pressed nanocomposites  $\text{Si}_3\text{N}_4$ —(20÷30 vol.%) $\text{SiC}$  have flexural strength up to 1500 MPa (compared with 850 MPa of common  $\text{Si}_3\text{N}_4$  ceramics) and retain high strength up to  $T = 1673 \text{ K}$  (compared with 1473 K of  $\text{Si}_3\text{N}_4$  ceramics) [5]. The increase of  $\text{SiC}$  content up to 40 wt.% in hot-pressed composite  $\text{Si}_3\text{N}_4$ — $\text{SiC}$  results in binding strength improvement up to the level of 10.5–12.5  $\text{MPa} \cdot \text{m}^{1/2}$  [30]. Composite ceramics  $\text{Si}_3\text{N}_4$ — $\text{SiC}$  are highly perspective for their development and application due to the improvement of their composition, structure and properties, as well as the development of new methods of production and the reduction of manufacturing costs [9, 10].

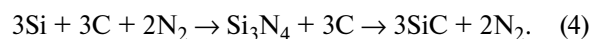
It has been noted before, that in the production of ceramic composites from highly dispersed powders, *in situ* chemical methods of direct synthesis of ceramic powder compositions from a mixture of initial reagents are more preferable than *ex situ* mechanical methods of mixing premixed powder components [5, 16]. Submicron and nanosized powder compositions  $\text{Si}_3\text{N}_4$ — $\text{SiC}$  can be synthesized by various chemical methods, including the coating of  $\text{Si}_3\text{N}_4$  particles with highly dispersed carbon through methane pyrolysis [33], the pyrolysis of an organic silicon-containing precursor [34], carbothermal reduction of silicon dioxide under nitrogen gas [35], gas-phase reactions [36], plasma-chemical synthesis [37]. The listed chemical methods are characterized by high power consumption due to the high temperature heating required and the long exposures used, they also require the use of expensive equipment. In this regard, a simple energy-saving SHS method which is based on combustion of inexpensive initial components is promising.

The first studies on the use of combustion for the synthesis of powder compositions  $\text{Si}_3\text{N}_4$ — $\text{SiC}$  were

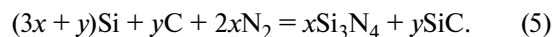
based on the combustion of mixtures of silicon and carbon black (soot) powders in nitrogen gas at a pressure ranging from 1 to 10 MPa [38–41]. The reaction (1) of synthesis of silicon carbide from elemental powders has a relatively low thermal effect and adiabatic temperature, which does not ensure a self-propagating combustion mode. However, the reaction of synthesis of silicon nitride from silicon powder in nitrogen gas



is highly exothermic with an adiabatic temperature of 2430 K, and it can proceed in self-propagating combustion mode. Therefore, the combustion of silicon and carbon powders mixture in nitrogen is initiated. Firstly, the silicon nitride is synthesized with a rise in temperature to high values exceeding 2273 K, at which the synthesized  $\text{Si}_3\text{N}_4$  dissociates and then the resulting silicon reacts with carbon forming  $\text{SiC}$ , more stable at high temperatures. Thus, when reaction (1) is performed in nitrogen gas, silicon carbide can be obtained in the combustion mode as follows [38]:



In this system of reagents, the intermediate product is synthesized first in the combustion mode  $\text{Si}_3\text{N}_4$  (the 1<sup>st</sup> reaction) with a rise in temperature to high values, upon which the subsequent transformation of silicon nitride into silicon carbide becomes thermodynamically favorable due to interaction with carbon (the 2<sup>nd</sup> reaction). If in the initial system of reagents silicon powder is taken in excess (4), i.e. in a larger amount than it is required for the complete conversion of  $\text{Si}_3\text{N}_4$  into  $\text{SiC}$ , it is possible to perform the reaction in the combustion mode at a nitrogen pressure of 3 MPa, with the formation of a composition of nitride and silicon carbide powders [40]:



In this reaction,  $x$  and  $y$  coefficient values were used to obtain from 36.8 to 100 vol.%  $\text{SiC}$  in the composition, the combustion temperature values were from 1440 to 1880 °C. The results of the experiments were explained by the presence of an intermediate stage between the 1<sup>st</sup> and 2<sup>nd</sup> reactions, at which molten silicon appears (the melting temperature of 1414 °C) reacting simultaneously in nitridation and carbidization and ensuring the formation of  $\text{SiC}$  particles, being finer than the ones appearing upon further transformation of  $\text{Si}_3\text{N}_4$  into  $\text{SiC}$ . A more detailed study of  $\text{Si}$ — $n\text{C}$ — $\text{N}_2$  system using silicon powders of Kr1 grade (particle size  $d < 15 \mu\text{m}$ )

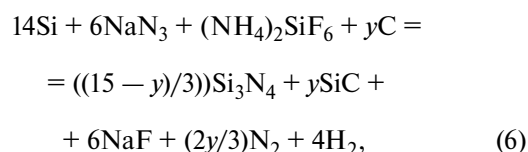
and carbon black of P803 grade ( $d < 1 \mu\text{m}$ ) showed that at nitrogen gas pressure of 1–7 MPa, combustion can be initiated with the carbon black content of  $n = 0.8$  maximum [41]. Upon that, the combustion temperatures are 1500–2000 °C, and the combustion product constitutes the composition of powders  $\text{Si}_3\text{N}_4$ –SiC with SiC content of 5–60 wt.%, and  $\text{Si}_3\text{N}_4$  constituting the rest, with a dominant content of  $\beta$ -modification, and a small amount of unreacted Si. The main part of the combustion product is comprised of particles with a size of 2–3  $\mu\text{m}$ , although there are also larger ones with a size of up to 15  $\mu\text{m}$  in the form of columnar crystals or agglomerates of fine particles. The application of polytetrafluoroethylene (PTFE) powder activator  $(\text{C}_2\text{F}_4)_n$  in the amount of 5–15 wt.% expands the limits of combustion of Si–C– $\text{N}_2$  system and ensures obtaining the composites with any ratio of  $\text{Si}_3\text{N}_4$  and SiC components from 0 to 100 %. Let us emphasize that these are the components of  $\text{Si}_3\text{N}_4$  and SiC powders with micron particle sizes and a small amount of  $\alpha$ -modification in silicon nitride  $\text{Si}_3\text{N}_4$ .

Upon the combustion of a mixture of ferrosilicon Fe–Si and carbon black powders in nitrogen atmosphere at a pressure of 4–6 MPa and subsequent acid enrichment of the combustion product in dilute hydrochloric acid, composite submicron and nanosized  $\text{Si}_3\text{N}_4$ –SiC powders with the content of 20 % SiC can be obtained [42]. At first, iron contained in ferrosilicon plays the role of a diluent that reduces the combustion temperature and separates the synthesized particles, as well as a catalyst for nitridation reaction, and then it is removed from the composite powder by being dissolved in acid. But the required acid treatment significantly complicates the process of obtaining  $\text{Si}_3\text{N}_4$ –SiC powder composition and does not ensure the complete removal of iron (Fe) from the composition.

It has long been known that the higher is  $\text{Si}_3\text{N}_4$  content of  $\alpha$ -modification compared to  $\beta$ -modification in  $\text{Si}_3\text{N}_4$ -based ceramics, the higher are the strength properties. However, not all production methods allow achieving high content of  $\alpha$ - $\text{Si}_3\text{N}_4$  [1]. It has been shown that during the combustion of silicon powder in nitrogen gas, it is possible to significantly increase the amount of synthesized phase  $\alpha$ - $\text{Si}_3\text{N}_4$  by diluting the charge with final product  $\alpha$ - $\text{Si}_3\text{N}_4$  and using additives of gasified halide salts  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{F}$  [43, 44]. In the combustion wave, the decomposition products of these salts react with silicon particles and ensure the transition of silicon to the gas phase that allows conducting the low-temperature mode for the formation of a fine fiber  $\alpha$ -modification of  $\text{Si}_3\text{N}_4$ , which is stable

at temperatures below 1450 °C. In particular, to obtain  $\alpha$ - $\text{Si}_3\text{N}_4$  content exceeding 95 wt.% it is necessary to carry out burning with minimum values of temperature and burning rate close to the limit of burning. For this purpose, it is necessary to use a charge with 28–40 % silicon content, with a high dilution with the desired product  $\alpha$ - $\text{Si}_3\text{N}_4$  up to 65 % and with 6–8 % mixture of gasifying halide salts  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{F}$  at the ratio 1 : 1. In this case, the combustion product contains from 0.1 to 1.5 % of free silicon. The dispersity of synthesized  $\alpha$ - $\text{Si}_3\text{N}_4$  depends on the dispersity of initial silicon powder: with micron Si powder of less than 30  $\mu\text{m}$  in size, more than 96 % of  $\alpha$ - $\text{Si}_3\text{N}_4$  is synthesized with 80 % of particles of a fibrous structure with fiber lengths over 10  $\mu\text{m}$ , and diameter of 1  $\mu\text{m}$ ; with submicron Si powder of less than 1  $\mu\text{m}$  in size, up to 96.6 % of fibrous  $\alpha$ - $\text{Si}_3\text{N}_4$  is synthesized with fiber lengths over 10  $\mu\text{m}$ , and diameter of 0.1–0.2  $\mu\text{m}$  and a small amount of elongated particles being 1–2  $\mu\text{m}$  thick and up to 5  $\mu\text{m}$  long. The carbon additive influences the mechanism of structure formation and allows synthesizing silicon nitride with an equiaxed shape of particles. Composite powders based on  $\alpha$ - $\text{Si}_3\text{N}_4$ , containing up to 10 % SiC, with an average particle diameter of 300–400 nm and an equiaxed shape were obtained with the complex addition of carbon up to 3.5 % in the form of carbon black and gasifying salts [44].

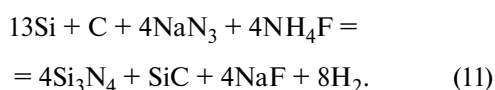
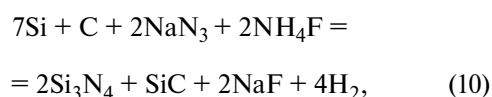
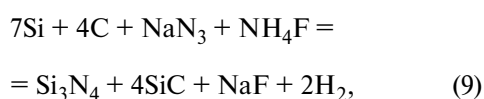
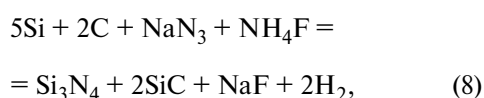
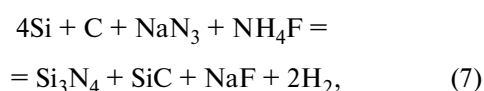
The marked increase of  $\alpha$ - $\text{Si}_3\text{N}_4$  amount and particle size reduction in the powders of  $\text{Si}_3\text{N}_4$ –SiC composition has been also ensured by azide SHS upon the combustion of the mixture of sodium azide ( $\text{NaN}_3$ ) with silicon (Si) and carbon black (C) elemental powders and activating halide salt additive  $(\text{NH}_4)_2\text{SiF}_6$  in nitrogen atmosphere [45]. The major reaction for obtaining  $\text{Si}_3\text{N}_4$ –SiC was as follows:



where carbon black content made up 5 or 15 mol. The reagent combustion temperature of the system (6) reached 1850 °C for  $y = 5$  and 1650 °C for  $y = 15$ . In case of  $y = 5$  the cooled combustion product consisted of  $\beta$ - $\text{Si}_3\text{N}_4$ ,  $\alpha$ - $\text{Si}_3\text{N}_4$ , NaF and Si, and in case of  $y = 15$  the combustion products included  $\alpha$ - $\text{Si}_3\text{N}_4$ , SiC, NaF and Si. The X-ray diffraction (XRD) phase analysis showed that at  $y = 5$  the content of  $\beta$ - $\text{Si}_3\text{N}_4$  superseded the content of  $\alpha$ - $\text{Si}_3\text{N}_4$ , silicon carbide was not detected, and at  $y = 15$ , to the contrary, silicon

carbide SiC was present, while there was no  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, i.e. silicon nitride consisted only of  $\alpha$ -modification. A noticeable amount of unreacted silicon remains in the washed combustion product. (Unfortunately, the content of phases in the combustion product of the reagent system (6) was not quantified.) Silicon carbide was synthesized in the form of equiaxed particles with an average size of 100 nm, and silicon nitride was synthesized in the form of whiskers with a diameter of 100–200 nm.

The application of another halide salt, ammonium fluoride NH<sub>4</sub>F, has been recently studied in order to obtain nitride-carbide powder composition Si<sub>3</sub>N<sub>4</sub>—SiC by azide SHS method over a wide range of phase ratios from 1 : 4 to 4 : 1 using the following chemical equations [46]:



In these equations, the composition of reaction products is expressed in moles; when passing to mass percent, the following ratios are obtained for the theoretical composition of the desired Si<sub>3</sub>N<sub>4</sub>—SiC composition, provided that water-soluble by-product salt NaF is removed from the reaction products:

$$(7): \text{Si}_3\text{N}_4 + \text{SiC} = 77.8\%\text{Si}_3\text{N}_4 + 22.2\%\text{SiC},$$

$$(8): \text{Si}_3\text{N}_4 + 2\text{SiC} = 63.6\%\text{Si}_3\text{N}_4 + 36.4\%\text{SiC},$$

$$(9): \text{Si}_3\text{N}_4 + 4\text{SiC} = 46.7\%\text{Si}_3\text{N}_4 + 53.3\%\text{SiC},$$

$$(10): 2\text{Si}_3\text{N}_4 + \text{SiC} = 87.5\%\text{Si}_3\text{N}_4 + 12.5\%\text{SiC},$$

$$(11): 4\text{Si}_3\text{N}_4 + \text{SiC} = 93.3\%\text{Si}_3\text{N}_4 + 6.7\%\text{SiC}.$$

The results of quantitative XRD phase analysis of the composition of synthesis products (after water washing and removal of NaF), which were obtained experimentally by combustion of the initial mixtures of powders (charges) in bulk form in a reactor at nitrogen gas pressure of 4 MPa, according to reactions (7)—(11), are presented in Table 1.

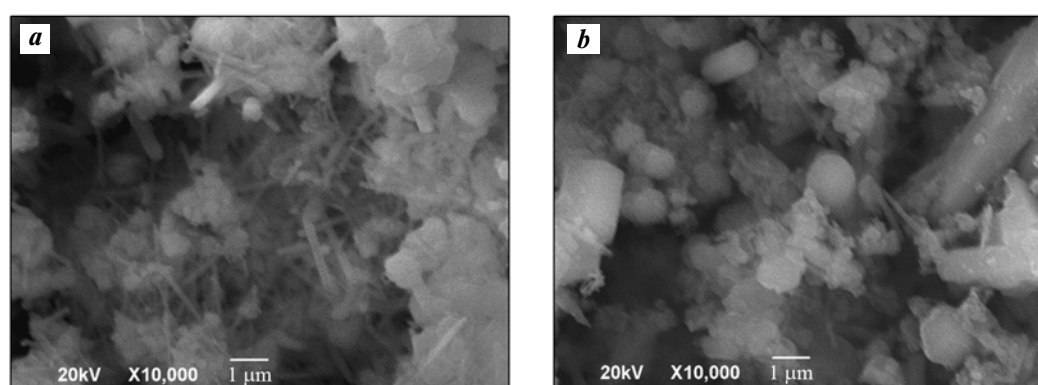
As Table 1 shows, the washed combustion products of all examined charge compositions consist of 4 phases: silicon nitride of two modifications ( $\alpha$ -Si<sub>3</sub>N<sub>4</sub> and  $\beta$ -Si<sub>3</sub>N<sub>4</sub>), silicon carbide ( $\beta$ -SiC) as well as silicon impurities (Si<sub>free</sub>). It is obvious that experimental composition of Si<sub>3</sub>N<sub>4</sub>—SiC differs markedly from the calculated theoretical composition, first of all, by a significantly lower content of silicon carbide, particularly in the cases of mole ratios of nitride and carbide phases of 2 : 1 and 4 : 1 (by factor of 4). Besides, more silicon nitride and less silicon carbide are formed compared to reaction equations (7)—(11), but free carbon is not found in combustion products. Such a difference observed between the experimental and theoretical results can be explained by the peculiarities of silicon carbide formation according to the sequence of reactions (4) upon the combustion of silicon and carbon powders in a nitrogen atmosphere. A part of very fine light particles of carbon black (soot) can be removed (blown out) from a burning highly porous bulk charge sample by gases released during the synthesis of intermediate product Si<sub>3</sub>N<sub>4</sub> (the 1<sup>st</sup> reaction), with the said particles not involved in further transformation of silicon nitride into silicon carbide through the interaction of Si<sub>3</sub>N<sub>4</sub> with carbon (with the 2<sup>nd</sup> reaction). As a result, more silicon nitride and less silicon carbide are left in combustion products compared to reaction equations (7)—(11). The lower is the carbon content in the charge with respect to silicon content in these equations, the higher is the combustion temperature and the more considerable is the gas release, the greater is the relative loss of carbon due to the removal of gases, and the more differs the experimental composition of Si<sub>3</sub>N<sub>4</sub>—SiC from the theoretical one.

The results obtained in the work [46] confirmed the effectiveness of using halide salt NH<sub>4</sub>F activating additive for obtaining the highly dispersed composition of Si<sub>3</sub>N<sub>4</sub>—SiC powders by azide SHS with different phase ratios in a wide range of silicon carbide content (from 1.6 to 41.8 %) without diluting the mixture with final product  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>. Synthesized compositions are characterized by a high content of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> (2.17—3.61 times more than of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>). Upon high carbon content in the charge, leading to the synthesis of 23.9

Table 1. Combustion product compositions of charges of reactions (7)–(11), wt. %

Таблица 1. Составы продуктов горения шихт реакций (7)–(11), мас. %

The composition of charges of reactions (7)–(11)	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	$\alpha$ -Si <sub>3</sub> N <sub>4</sub> + $\beta$ -Si <sub>3</sub> N <sub>4</sub>	$\beta$ -SiC	Si <sub>free</sub>
4Si + C + NaN <sub>3</sub> + NH <sub>4</sub> F (7)	70.2	19.4	89.6	9.7	0.7
5Si + 2C + NaN <sub>3</sub> + NH <sub>4</sub> F (8)	50.9	19.5	70.4	23.9	5.7
7Si + 4C + NaN <sub>3</sub> + NH <sub>4</sub> F (9)	38.2	17.6	55.8	41.8	2.4
7Si + C + 2NaN <sub>3</sub> + 2NH <sub>4</sub> F (10)	68.4	27.4	95.8	3.6	0.6
13Si + C + 4NaN <sub>3</sub> + 4NH <sub>4</sub> F (11)	69.3	28.1	97.4	1.6	1.0

Fig. 1. Microstructure of combustion products of charges 7Si + C + 2NaN<sub>3</sub> + 2NH<sub>4</sub>F (a) and 7Si + 4C + NaN<sub>3</sub> + NH<sub>4</sub>F (b)Рис. 1. Микроструктура продуктов горения шихт 7Si + C + 2NaN<sub>3</sub> + 2NH<sub>4</sub>F (a) и 7Si + 4C + NaN<sub>3</sub> + NH<sub>4</sub>F (b)

and 41.8 % silicon carbide in the composition,  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> is mainly formed in the form of equiaxed particles rather than the fibrous ones. The impurities of free silicon do not exceed 1.0 % for the compositions with SiC proportion of up to 10 %, but they reach 2.4–5.7 % for SiC content of 23.9 and 41.8 %, which is obviously associated with a large amount of silicon in the initial charge and incomplete reaction of SiC formation. Upon SiC content from 1.6 to 23.9 %, Si<sub>3</sub>N<sub>4</sub>–SiC compositions are submicron, and they consist of fibers with a diameter of 100–500 nm and a length of up to 5  $\mu$ m, as well as equiaxed particles with a size of 100–500 nm in the form of individual particles and their agglomerates (Fig. 1, a). Upon SiC content of 41.8 %, Si<sub>3</sub>N<sub>4</sub>–SiC composition is a mixture of submicron particles being 150–500 nm in size, with much larger particles up to 2  $\mu$ m in size (Fig. 1, b).

The obtained composite powders Si<sub>3</sub>N<sub>4</sub>–SiC distinguish from those synthesized earlier using the combustion process both by their higher dispersibility and higher  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> content, and therefore they are pro-

mising for use in the production of composite ceramic materials with improved properties at lower sintering temperatures.

### AlN–SiC composition

Aluminium nitride (AlN) is distinguished in technical ceramics for its unique combination of physical, electrical and chemical properties at a relatively low cost: light weight, high thermal conductivity, good electrical insulation properties, moderate coefficient of thermal expansion, stability at high temperatures in an inert atmosphere, non-toxicity [1]. At present, aluminum nitride is mainly used in electronics, where heat dissipation from electronic devices is important with a high electrical resistance and a coefficient of thermal expansion (CTE) close to that of silicon [47]. In this respect, when it comes to the production of electronic components, aluminum nitride is being used in almost all areas where the highly toxic beryllium oxide was previously applied. Aluminum nitride is most intensively



used for the production of integrated circuit packages and substrates, high-power transistors, power absorbers, and LEDs. However, both in this regard and in the case of its application as a structural material at high temperatures, the application of aluminum nitride is limited by its brittleness, low fracture toughness, and heat resistance [48]. Therefore, much attention is being paid to the development of composite ceramics of aluminum nitride with silicon carbide (SiC), which in addition to good thermal conductivity and corrosion resistance possesses significantly better mechanical properties (hardness, fracture toughness, creep resistance) [49]. Silicon carbide is also attractive since it has a crystal structure similar to the one of aluminum nitride and it can form a single-phase homogeneous solid solution with it, thus resulting in improved flexural strength and fracture toughness, i.e. reduced brittleness [50, 51]. But AlN—SiC composites have significantly better toughness and heat resistance even without the formation of a solid solution, in a two-phase condition of sintered, spatially separated powder components AlN and SiC [52, 53]. AlN—SiC composites with high thermal conductivity can be obtained by adjusting the grain size of AlN and SiC [54]. AlN—SiC composite ceramics appeared to be promising for application not only in metallurgy and mechanical engineering as a structural material functioning under mechanical load at high temperatures, but also in electronics as a new high-temperature ceramic, which has a high capacity of microwave radiation absorption and can be used in high-power amplifiers and microwave components, sensors, thermoelectric elements, solar power receivers, RF resonators and filters, etc. [51, 55].

The following conventional energy-intensive methods for producing AlN—SiC ceramics are known: the carbothermal reduction of silica and alumina in nitrogen atmosphere; the pressureless sintering of SiC and AlN ceramic powders or the hot pressing of the ones, which require a high temperature of 2000 °C and a long holding time of up to several hours [51, 53, 56—58]. More advanced methods include spark plasma sintering (SPS), as well as self-propagating high-temperature synthesis (SHS), which is also called combustion synthesis [48, 55]. In the case of SPS method, the energy consumption is considerably lower since SPS process is conducted at a temperature of about 1600 °C and lasts about 10 minutes but requires expensive equipment. SHS method is much more cost-effective since the synthesis of AlN—SiC composite proceeds due to its own heat release during combustion in very simple equipment, and it is performed from cheap initial reagents, most of-

ten the powders of Al, Si, C (carbon black) and N<sub>2</sub> gas. Therefore, much attention is paid to the development of SHS method, various options for the combustion of mixtures of various powders are being studied to obtain AlN—SiC composition.

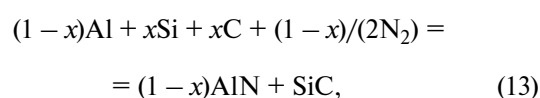
The application of the energy-efficient SHS method to obtain AlN—SiC was first studied in work [59]. Silicon nitride powder Si<sub>3</sub>N<sub>4</sub> was used as a solid source of nitrogen, and the reaction equation was as follows:



Reaction (12) is highly exothermic with an adiabatic temperature of 2502 K, which was supposed to ensure its self-propagation in the combustion mode, still the combustion could not be conducted without the imposition of an electric field with an intensity ( $E$ ) of at least 8 V/cm. As  $E$  increased, the combustion temperature and rate grew, and in the interval of  $8 < E < 25$  V/cm the combustion products were the composition of two phases AlN and SiC with a gradual increase in their mutual solubility, and at  $E = 25$  V/cm the combustion product was a stable single-phase solid solution AlN—SiC. The combustion process took several seconds, but the combustion product contained silicon and carbon impurities.

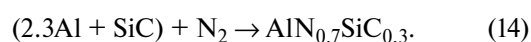
The application of microwave heating of reagent mixture specified in equation (12) allowed this mixture to be ignited and the SHS process to be implemented without the imposition of an electric field [60]. Depending on the weight of the mixture (from 0.5 to 16 g) and maximum combustion temperature (from 1027 to 1889 °C), the composition of the combustion products was different. At minimum combustion temperatures, it contained impurities of initial components Si<sub>3</sub>N<sub>4</sub>, Al, and C along with AlN and SiC phases, and at maximum temperatures, it included only Al and C impurities. As the combustion temperature increased, the grain size of combustion products grew. AlN—SiC solid solution could not be obtained since the combustion temperatures were below the critical value of 1960 °C, separating the areas of two-phase composite and single-phase solid solution.

In other studies, nitrogen gas N<sub>2</sub> was used as a source of nitrogen. In work [48], the formation of ceramics by the following reaction was studied:



where  $x$  varied from 0 to 0.85, and nitrogen pressure was 3, 8 or 12 MPa. The combustion led to the forma-

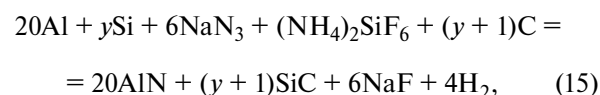
tion of AlN—SiC solid solution without unreacted Al and Si impurities only at considerably high nitrogen pressures: 12 MPa for  $x = 0.3$  and 8 MPa for  $x = 0.5$  and 0.6. Even higher nitrogen pressures (50 and 70 MPa) were used for SHS of AlN—SiC solid solution of other components [61]:



At the pressure of 50 MPa, the combustion temperature was 1400 °C, and the combustion product contained a large amount of unreacted Al (up to 12 %) and Si along with AlN<sub>0.7</sub>SiC<sub>0.3</sub> solid solution. An increase in pressure to 70 MPa resulted in the combustion temperature being increased up to 2050 °C and the Al impurity content being reduced to 0.5 %.

The possibility of implementing the SHS mode to obtain AlN—SiC solid solution at a low pressure of nitrogen gas (0.3–0.5 MPa) according to reaction (13) was studied in work [62]. The combustion temperature at a pressure of 0.3 MPa was ranging from 1972–2287 K, depending on the molar ratio of Al/Si components in the initial mixture from 0.5 to 2.5, which corresponded to  $x$  values from 0.665 to 0.286 in equation (13), and was low dependent on pressure. The maximum temperatures ranging from 2142 to 2287 K were obtained at Al/Si component ratios from 1 to 2 and allowed to synthesize AlN—SiC solid solution with residual Si. An almost pure and more homogeneous AlN—SiC solid solution was obtained by adding an additional amount of carbon black (20 %) to the initial powders. At the lower combustion temperatures, the SHS product was a composite of AlN and SiC phases being more contaminated with impurities of unreacted initial powders. In all cases, the synthesized AlN—SiC ceramics were powders with micron-sized particles.

In works [63, 64], the other SHS option, namely azide SHS using halide salt (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> and the following common chemical reaction equation, was applied to obtain AlN—SiC powder composite:



where coefficient value  $y$  took the values from 1 to 10. The results of thermodynamic calculations of the adiabatic temperature perform by using the THERMO software ( $T_{\text{ad}}$ ) and composition of reaction products (15) for different values of  $y$  are presented in Table 2.

As Table 2 shows, the adiabatic temperatures of reactions (15) are high enough for the combustion mode implementation, and the condensed reaction products are the desired phases of AlN and SiC with admixed water-soluble by-product salt NaF, which is easily removed by washing with water. According to the data of Table 2, after water washing, the synthesized AlN—SiC composition should contain from 2.8 to 24.0 wt.% of SiC.

The experimental studies of azide SHS process were conducted in laboratory reactor SHS-Az with a volume of 4.5 L at different contents of silicon and carbon powders in the initial charge, nitrogen pressure of 4 MPa, the relative bulk density of the charge of 0.4, and the diameter of the sample of 30 mm. Table 3 lists the results of quantitative XRD phase analysis of the composition of the synthesis products after water washing and removal of NaF.

Table 3 shows that the desired composition AlN—SiC can be synthesized during the combustion of mixtures of equation (15), however, the content of silicon carbide in the composition of the reaction products is much lower (from 1.3 to 5.9 wt.%) compared with

Таблица 2. Адиабатические температуры и состав продуктов реакций уравнения (15)

Table 2. Adiabatic temperatures and composition of reaction products of equation (15)

$y$	$T_{\text{ad}}, \text{K}$	Amount, mol.									
		Al <sub>g</sub>	F <sub>g</sub>	H <sub>g</sub>	Na <sub>g</sub>	H <sub>2g</sub>	N <sub>2g</sub>	NaF <sub>g</sub>	NaF <sub>l</sub>	AlN <sub>g</sub>	SiC <sub>s</sub>
1	2913	0.21	0.03	0.14	0.03	3.93	3.78	5.97	—	19.79	2.00
4	2858	0.13	0.03	0.12	0.03	3.94	3.78	5.97	—	19.87	5.00
6	2824	0.10	0.02	0.10	0.02	3.95	3.78	5.92	0.06	19.90	7.00
8	2812	0.09	0.02	0.10	0.02	3.95	3.78	5.56	0.42	19.91	9.00
10	2799	0.07	0.02	0.10	0.02	3.95	3.78	5.22	0.76	19.93	11.00

Table 3. The ratio of phases in washed combustion products of charges of equation (15)

Таблица 3. Соотношение фаз в промытых продуктах горения шихт уравнения (15)

Composition of charge	Composition of combustion products, wt. %					
	AlN	SiC	Na <sub>3</sub> AlF <sub>6</sub>	Si	α-Si <sub>3</sub> N <sub>4</sub>	β-Si <sub>3</sub> N <sub>4</sub>
Si + 20Al + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 2C	90.3	1.3	7.7	0.7	—	—
4Si + 20Al + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 5C	86.0	2.6	10.5	0.9	—	—
6Si + 20Al + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 7C	81.5	4.2	12.3	0.7	1.3	—
8Si + 20Al + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 9C	78.8	4.5	13.8	0.7	1.2	1.0
10Si + 20Al + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 11C	76.0	5.9	15.5	0.8	1.1	0.5

the results of thermodynamic calculations, and water-insoluble by-product phase Na<sub>3</sub>AlF<sub>6</sub> (cryolite) as well as free silicon impurity (0.7–0.9 wt.%) appear in the products. Upon that, the proportion of by-product cryolite Na<sub>3</sub>AlF<sub>6</sub> is quite considerable and increases from 7.7 to 15.5 wt.% with an increase in carbon content from 2 to 11 mol in the initial mixture. The appearance of cryolite Na<sub>3</sub>AlF<sub>6</sub> in SHS-Az products results in a decrease of AlN phase content in comparison with the results of thermodynamic calculations. Upon the proportion of silicon being  $\geq 6$  mol, the combustion products also contain a small amount of silicon nitride (less than 1.5 wt.%). Such a difference between the experimental and theoretical data can be explained by the fact that the results of the experimental study (Table 3) show the composition of the cooled products of SHS-Az reactions and thus differ markedly from the results of thermodynamic calculation (see Table 2) of the composition of the products at the maximum possible adiabatic temperature of SHS-Az reactions, in which there is no cryolite, and silicon carbide content is much higher (from 2.8 to 24.0 wt.%). When cooled, the composition of the products changes that leads to the formation of cryolite, which cannot exist at temperatures above 1000 °C as it melts and decomposes at this temperature [65]. It is worth emphasizing that despite high combustion temperatures ( $> 2200$  °C), the product of SHS reaction is not a single-phase AlN—SiC solid solution, but a composition of two phases: AlN and SiC. This can be explained by considerable content of cryolite by-product, which separates AlN and SiC phases and prevents the formation of solid solution of the ones.

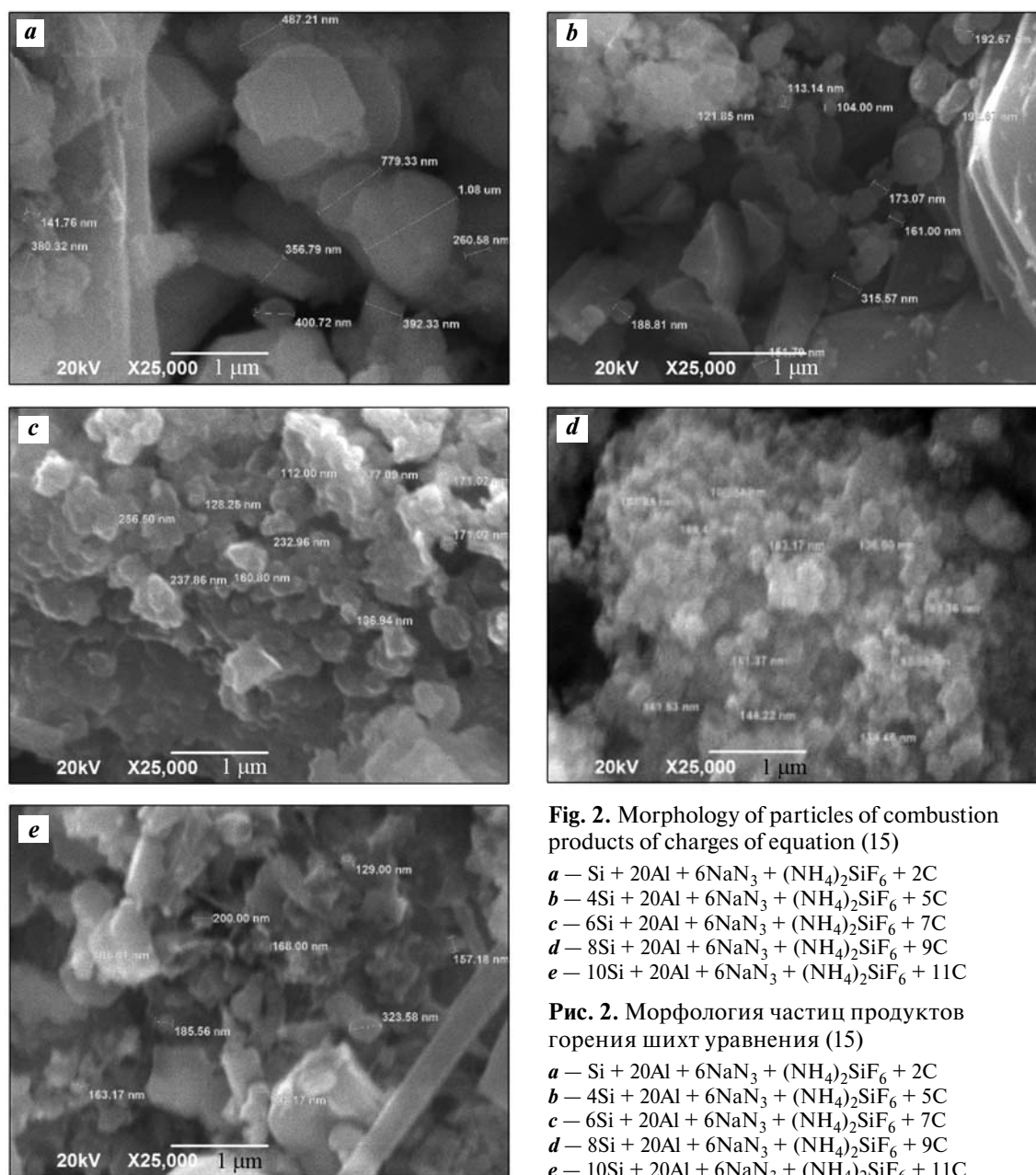
It is also worth noting that no free carbon is found in the experimental products although the content of SiC is much lower in the experimental combustion pro-

ducts compared with the one in the theoretical products, according to stoichiometric equation (15) and the results of thermodynamic calculations. As in the previous case of azide SHS of Si<sub>3</sub>N<sub>4</sub>—SiC composition, such a difference between experimental and theoretical results can also be explained by the peculiarities of silicon carbide formation according to the sequence of reactions (4) upon the combustion of silicon powder in nitrogen atmosphere. A considerable part of ultra-fine light carbon black particles can be removed from the burning highly porous bulk charge sample by gases released during the synthesis of intermediate product Si<sub>3</sub>N<sub>4</sub> (the 1<sup>st</sup> reaction) and thus not involved in subsequent transformation of silicon nitride into silicon carbide due to the interaction of Si<sub>3</sub>N<sub>4</sub> with carbon (the 2<sup>nd</sup> reaction). As a result, a part of intermediate product Si<sub>3</sub>N<sub>4</sub> may remain in the final experimental combustion products, and less amount of silicon carbide is formed compared to the results of theoretical calculations, but free carbon may not be detected in the combustion products.

The results of the morphology and particle size study of the powder product synthesized are shown in Fig. 2.

As we can see in Fig. 2, *a* and *b*, predominantly equiaxed particles of aluminum nitride powder with a size from 150 nm to 1 μm are formed during the combustion of mixtures with a silicon content of 1–4 mol. The combustion products of mixtures with silicon content ranging from 6 mol (Fig. 2, *c–e*) are equiaxed particles of aluminum nitride and silicon carbide of a smaller size being from 100 to 600 nm.

Thus, using the azide SHS method allows synthesizing the desired ceramic nitride-carbide powder composition AlN—SiC in the form of equiaxed particles ranging in size from 100 nm to 1 μm with SiC



**Fig. 2.** Morphology of particles of combustion products of charges of equation (15)

- a* —  $\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
*b* —  $4\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 5\text{C}$   
*c* —  $6\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 7\text{C}$   
*d* —  $8\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 9\text{C}$   
*e* —  $10\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 11\text{C}$

**Рис. 2.** Морфология частиц продуктов горения шихт уравнения (15)

- a* —  $\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
*b* —  $4\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 5\text{C}$   
*c* —  $6\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 7\text{C}$   
*d* —  $8\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 9\text{C}$   
*e* —  $10\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 11\text{C}$

content of up to 5.9 wt.%, but the washed synthesis products, being condensed, include water insoluble cryolite impurity  $\text{Na}_3\text{AlF}_6$ , upon that ranging in the amount from 7.7 to 15.5 wt.%, along the desired phases of AlN and SiC. An azide SHS product of such content can be applied for liquid-phase hybrid reinforcement of aluminum matrix composites with submicron AlN and SiC powders, upon which cryolite plays a positive role of flux and is not included in the final composition of the composite, without contaminating it [66].

### TiN—SiC composition

It bears repeating that silicon carbide (SiC) based ceramics is widely used as a wear-resistant and high-temperature structural material due to its high hardness and rigidity, phase stability and heat resistance, low density and thermal expansion coefficient. Since SiC is a semiconductor, it has also found application in diodes and LEDs. But due to its semiconductor properties, SiC exhibits high electrical resistance ( $2.0 \cdot 10^5 \text{ Ohm} \cdot \text{cm}$ ), which makes it impossible to use efficient electrical dis-

charge machining for the production of complex silicon carbide parts [67]. SiC based polycrystalline ceramics could find a wider application if they could be more easily machined to make them more electrically conductive. And the strengthening of SiC based ceramics would allow them to compete as a structural material with silicon nitride ( $\text{Si}_3\text{N}_4$ ) based ceramics. [67].

In this context, the addition of electrically conductive titanium nitride particles (TiN) with low electrical resistivity ( $22 \cdot 10^{-6} \text{ Ohm} \cdot \text{cm}$ ) is of considerable interest for the improvement of the properties of SiC based ceramics. Upon that, titanium nitride has high values of melting temperature (3223 K) and hardness (20 GPa), good corrosion resistance [68]. It is used to create wear-resistant coatings for metal-cutting tools and protective and decorative coatings to imitate golden color, and it is also applied as a heat-resistant material, in particular, it is used to make crucibles for melting of metals in an oxygen-free atmosphere. Submicron and nanosized titanium nitride powders are used in ceramics based on silicon nitride and sialons to increase the hardness and strength of these materials [69].

A rich variety of methods for obtaining titanium nitride is known. The main industrial methods for obtaining titanium nitride powders with a particle size of up to 50 microns are the carbothermal reduction of titanium oxide in nitrogen atmosphere and direct nitridation of titanium powder. [70]. Submicron powders and nanopowders are obtained by plasma-chemical synthesis or by precipitation from the gas phase during the reduction of titanium tetrachloride vapor with ammonia at a temperature of 900–1000 °C [71, 72]. These methods are characterized by high energy consumption and the application of complex equipment. For the first time, titanium nitride was obtained by a simple energy-saving method of SHS by burning titanium powders in nitrogen atmosphere [14]. Due to high temperature of synthesis (2200–2500 °C), titanium nitride was formed in the form of porous cakes of sintered crystallites up to 100  $\mu\text{m}$  in size. Nanostructured titanium nitride powders with particles of nanofibrous structure (the fiber diameter of 50–100 nm) and nanocrystalline structure (the average crystallite size of 100–200 nm) were obtained by azide SHS method [73]. To synthesize the ones, not titanium powder, but halide salt of ammonium hexafluorotitanate  $(\text{NH}_4)_2\text{TiF}_6$  was used as the nitrated agent. In this case, the formation of titanium nitride proceeded in gas phase, from atomic titanium formed during the decomposition of halide salt at temperatures of 710–1080 °C. According to literature data analysis, in

order to synthesize titanium nitride nanopowders, it is necessary to create low-temperature conditions for synthesis (500–900 °C) and to conduct the reduction and nitridation of titanium source at the atomic level, i.e. in the gas phase [74].

A method for obtaining silicon carbide ceramics with the admixtures of titanium nitride nanoparticles by sintering under pressureless conditions is known [75]. The initial materials were  $\alpha$ -SiC powder (particle size of 0.5–1.0  $\mu\text{m}$ ) in the form of matrix,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  as sintering additives and TiN nanoparticles (0–15 wt.%, average particle size of 20 nm) as a strengthening phase. The initial powders were pressed until rectangular samples were formed, afterwards they were compacted by cold isostatic pressing at a pressure of 250 MPa. Further, the samples were subjected to liquid-phase sintering in a vacuum furnace at a temperature of 1950 °C for 15 min, and then at 1850 °C for 1 h. The study of the microstructure showed that TiN nanoparticles inhibited the compaction of silicon carbide ceramics and suppressed the growth of grains of silicon carbide ceramics. TiN reacted with SiC and  $\text{Al}_2\text{O}_3$  to form new phases of TiC, AlN and some others. The formation of a new phase of titanium carbide (TiC), having higher hardness than the one of TiN, resulted in the fact that the hardness of sintered ceramics with 10 wt.% and 15 wt.% of TiN nanoparticles was higher than the hardness of the ones with 5 wt.% of TiN nanoparticles. However, the best combination of properties was obtained in silicon carbide ceramics with 5 wt.% of TiN nanoparticles, with a relative density of 92.8 %, flexural strength of 686 MPa, hardness of 92 HRA and fracture toughness of  $7.04 \text{ MPa} \cdot \text{m}^{1/2}$ . Adding up to 5 wt.% of SiC whiskers being 0.5–2.5  $\mu\text{m}$  in diameter and 10–50  $\mu\text{m}$  in length to such a ceramic composition resulted in flexural strength increase up to 1122 MPa together with some decrease in other mechanical characteristics [76]. Thus, the addition of TiN nanoparticles is an efficient technique for improving the mechanical characteristics of silicon carbide ceramics. The disadvantage of this method for manufacturing TiN–SiC ceramics is that it is multi-stage and quite complex, and expensive TiN nanopowder and silicon carbide fibers are used to obtain the composite.

SiC based composites with different content of coarser TiN powder (0–50 vol.%) were made of the mixture of  $\alpha$ -SiC (0.7  $\mu\text{m}$ ) and TiN (0.8–1.2  $\mu\text{m}$ ) powders by hot pressing at  $t = 1900$  °C with holding time of 60 min in flowing argon atmosphere under pressure 30 MPa, using

$\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  sintering additives (0.7 and 0.9  $\mu\text{m}$ ; 6.0 and 4.0 wt.%, correspondingly) [67]. Electrical measurements showed that increase in TiN additions reduces the resistivity from  $2.0 \cdot 10^5 \text{ Ohm} \cdot \text{cm}$  (0 % of TiN) to the plateau of  $2.0 \cdot 10^{-4} \text{ Ohm} \cdot \text{cm}$  (40–50 vol.% of TiN). Flexural strength gradually increased with increase in TiN content. The maximum strength of 921 MPa was observed at the content of 40 vol.% of TiN compared to 616 MPa for initial SiC.

A method has been recently proposed for obtaining SiC–TiN composite material based on hot pressing of a powder mixture containing 53–83 wt.% of silicon carbide powder (< 25  $\mu\text{m}$ ), 5–40 wt.% of titanium powder (< 25  $\mu\text{m}$ ) and 7 wt.% of sintering additive powder in the form of  $\text{Y}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$  at the ratio of 3 : 5 [77]. In the process of hot pressing, the combination of sintering and nitridation of the powder mixture was ensured at  $t = 1600^\circ\text{C}$  in nitrogen atmosphere within 30 minutes at a pressure of 30 MPa, then the temperature was increased to  $1850^\circ\text{C}$  and held for 30 minutes to obtain a composite material with main phases SiC and TiN. As a result, the ceramic composite gained considerably high flexural strength, hardness, and density: 340–400 MPa, 22.8–34.4 GPa, and 91–97 %, correspondingly. The advantages of this method include less stages and duration, the use of inexpensive titanium powder with a particle size of 25  $\mu\text{m}$  instead of expensive titanium nitride nanopowder.

The SHS process was applied to obtain more complex composition  $\text{Si}_3\text{N}_4$ –TiN–SiC from  $\text{TiSi}_2$  and SiC mixtures by combustion reaction at high nitrogen pressure of 10–130 MPa [78]. The analysis of mechanism of nitridation of  $\text{TiSi}_2$  showed that upon the nitridation of  $\text{TiSi}_2$ , TiN and Si are formed first, and upon further nitridation of Si,  $\text{Si}_3\text{N}_4$  phase is formed. At a higher nitrogen pressure, the nitridation reaction is completed, and thus relatively dense composites  $\text{Si}_3\text{N}_4$ –TiN–SiC are obtained.

The authors of this review studied the application of azide SHS method by using three halide salts  $(\text{NH}_4)_2\text{TiF}_6$  (1),  $(\text{NH}_4)_2\text{SiF}_6$  (2) and  $\text{Na}_2\text{SiF}_6$  (3) to obtain highly dispersed powder composition TiN–SiC with five the following molar phase ratios given: 1 : 1, 1 : 2, 1 : 4, 2 : 1 and 4 : 1 [79]. Silicon powder of Kr0 grade (average particle size of 5  $\mu\text{m}$ ); fine titanium powder of PTM-3 grade (15  $\mu\text{m}$ ); halide salts (50  $\mu\text{m}$ ); sodium azide powder of «Pure» classification (100  $\mu\text{m}$ ); carbon black of P701 grade (70 nm, average size of agglomerates of 1  $\mu\text{m}$ ) were used in experiments as starting reagents. The combustion of mixtures of powders was conducted in laboratory reactor

SHS-Az with an operating volume of 4.5 l at nitrogen gas pressure of 4 MPa. THERMO software was applied to calculate the equilibrium compositions of products, adiabatic temperatures ( $t_{\text{ad}}$ ) and the enthalpies of reactions of interaction of initial reagents ( $\Delta H^0$ ) for the synthesis of TiN–SiC composition with the above molar phase ratios and the use of the specified halide salts (Table 4–6).

As Table 4 shows, if salt 1 is used, the thermodynamic composition of the reaction products fully complies with all specified 5 mole ratios of phases TiN : SiC. If salts 2 and 3 (Table 5 and 6) are used, the thermodynamic composition of the reaction products complies with only two molar phase ratios: 2 : 1 and 4 : 1, i.e. TiN–SiC compositions with a high content of TiN phase, which are synthesized from mixtures with a high content of titanium powder. In the case of charges with a high content of silicon and carbon, which should have resulted in the formation of TiN–SiC with a mole ratio of phases 1 : 1, 1 : 2, and 1 : 4, i.e. with a high content of SiC phase, this phase is either not formed at all or is formed partially, with silicon nitride phase  $\text{Si}_3\text{N}_4$  being formed instead. Such results can be explained by the sequence of reactions (4) of formation of silicon nitride and silicon carbide upon the combustion of a mixture of silicon and carbon powders in nitrogen gas. As Tables 4–6 show, the adiabatic temperature of reactions is high for the charges with high titanium content, it is close to the temperature of dissociation of  $\text{Si}_3\text{N}_4$  (about  $2000^\circ\text{C}$ ), therefore, silicon nitride is completely transformed into silicon carbide, and there is no free carbon in the final product of the synthesis. While in the case of mixtures with high silicon and carbon contents, the adiabatic temperature is markedly lower (particularly, in the case of salts 2 и 3), therefore, silicon nitride is not transformed into silicon carbide or is partially transformed, and silicon nitride (in whole or in part) and free carbon remain in the final product.

If we convert from mole ratios of phases to weight percentages with respect to the composition of TiN–SiC, we obtain the following expected compositional contents according to stoichiometric reaction equations after removal of the water-soluble impurity NaF from the reaction products, wt.%:

$$\text{TiN} : \text{SiC} = 60.7 : 39.3; \text{TiN} : 2\text{SiC} = 43.6 : 56.4;$$

$$\text{TiN} : 4\text{SiC} = 27.9 : 72.1; 2\text{TiN} : \text{SiC} = 75.6 : 24.4; \quad (16)$$

$$4\text{TiN} : \text{SiC} = 86.1 : 13.9.$$

Table 4. Results of thermodynamic calculations using  $(\text{NH}_4)_2\text{TiF}_6$ Таблица 4. Результаты термодинамических расчетов при использовании  $(\text{NH}_4)_2\text{TiF}_6$ 

Initial mixture of powders	Composition of products, mol.					$t_{\text{ad}}, ^\circ\text{C}$	$\Delta H^0, \text{kJ}$
	SiC	TiN	NaF	H <sub>2</sub>	N <sub>2</sub>		
2Si + Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{TiF}_6$ + 2C	2.00	2.00	6.00	4.00	16.00	1691	–2308
4Si + Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{TiF}_6$ + 4C	4.00	2.00	6.00	4.00	16.00	1704	–2440
8Si + Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{TiF}_6$ + 8C	8.00	2.00	6.00	4.00	16.00	1712	–2704
2Si + 3Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{TiF}_6$ + 2C	2.00	4.00	6.00	4.00	15.00	1974	–2984
2Si + 7Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{TiF}_6$ + 2C	2.00	8.00	6.00	4.00	13.00	2277	–4336

Table 5. Results of thermodynamic calculations using  $(\text{NH}_4)_2\text{SiF}_6$ Таблица 5. Результаты термодинамических расчетов при использовании  $(\text{NH}_4)_2\text{SiF}_6$ 

Initial mixture of powders	Composition of products, mol.							$t_{\text{ad}}, ^\circ\text{C}$	$\Delta H^0, \text{kJ}$
	SiC	Si <sub>3</sub> N <sub>4</sub>	TiN	NaF	H <sub>2</sub>	N <sub>2</sub>	C		
Si + 2Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{SiF}_6$ + 2C	—	0.67	2.00	6.00	4.00	14.67	2.00	1557	–2057
3Si + 2Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{SiF}_6$ + 4C	1.00	1.00	2.00	6.00	4.00	14.00	3.00	1666	–2373
7Si + 2Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{SiF}_6$ + 8C	5.00	1.00	2.00	6.00	4.00	14.00	3.00	1667	–2638
Si + 4Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{SiF}_6$ + 2C	2.00	—	4.00	6.00	4.00	15.00	—	1676	–2365
Si + 8Ti + 6NaN <sub>3</sub> + $(\text{NH}_4)_2\text{SiF}_6$ + 2C	2.00	—	8.00	6.00	4.00	13.00	—	2127	–3718

Table 6. Results of thermodynamic calculations using  $\text{Na}_2\text{SiF}_6$ Таблица 6. Результаты термодинамических расчетов при использовании  $\text{Na}_2\text{SiF}_6$ 

Initial mixture of powders	Composition of products, mol.						$t_{\text{ad}}, ^\circ\text{C}$	$\Delta H^0, \text{kJ}$
	SiC	Si <sub>3</sub> N <sub>4</sub>	TiN	NaF	N <sub>2</sub>	C		
Si + 2Ti + 4NaN <sub>3</sub> + $\text{Na}_2\text{SiF}_6$ + 2C	—	0.67	2.00	6.00	10.67	2.00	1665	–1790
3Si + 2Ti + 4NaN <sub>3</sub> + $\text{Na}_2\text{SiF}_6$ + 4C	1.75	0.75	2.00	6.00	10.50	2.25	1694	–1968
7Si + 2Ti + 4NaN <sub>3</sub> + $\text{Na}_2\text{SiF}_6$ + 8C	5.60	0.80	2.00	6.00	10.40	2.40	1695	–2260
Si + 4Ti + 4NaN <sub>3</sub> + $\text{Na}_2\text{SiF}_6$ + 2C	2.00	—	4.00	6.00	11.00	—	1799	–2098
Si + 8Ti + 4NaN <sub>3</sub> + $\text{Na}_2\text{SiF}_6$ + 2C	2.00	—	8.00	6.00	9.00	—	2302	–3451

The experimentally found compositions of the washed combustion products of all initial mixtures of powders (charges) with three halide salts being used are presented in Table 7.

If we compare the experimental compositions of combustion products provided in Table 7 with the theoretical compositions given in Table 4–6 and ratios (16), it can be observed that the experimental

results differ significantly from the theoretical ones by the stable presence of silicon nitride (of  $\alpha$ - and  $\beta$ -modifications) in the combustion products of all initial mixtures and the complete absence or a much smaller amount of silicon carbide phase in these products, along with the absence of free carbon in them. A noticeable amount of silicon carbide is formed only during the combustion of charge with a high car-

Table 7. Phase ratio in washed combustion products of charges

Таблица 7. Соотношение фаз в промытых продуктах горения шихт

Composition of charge	Composition of combustion products, wt. %					
	TiN	SiC	$\alpha$ -Si <sub>3</sub> N <sub>4</sub>	$\beta$ -Si <sub>3</sub> N <sub>4</sub>	Si	C
2Si + Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> + 2C	45.8	—	49.8	4.4	—	—
4Si + Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> + 4C	41.2	6.4	43.9	7.6	0.9	—
8Si + Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> + 8C	28.8	19.9	42.5	7.4	1.4	—
2Si + 3Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> + 2C	80.0	—	14.0	6.0	—	—
2Si + 7Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> + 2C	87.7	—	5.6	6.7	—	—
Si + 2Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 2C	54.7	16.0	17.4	11.9	—	—
3Si + 2Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 4C	40.0	31.0	19.0	9.0	1.0	—
7Si + 2Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 8C	24.2	49.4	21.1	5.0	0.3	—
Si + 4Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 2C	71.0	—	18.0	9.0	1.2	0.8
Si + 8Ti + 6NaN <sub>3</sub> + (NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub> + 2C	61.0	4.0	27.0	7.0	1.0	—
Si + 2Ti + 4NaN <sub>3</sub> + Na <sub>2</sub> SiF <sub>6</sub> + 2C	54.0	20.0	15.0	11.0	—	—
3Si + 2Ti + 4NaN <sub>3</sub> + Na <sub>2</sub> SiF <sub>6</sub> + 4C	42.0	34.0	16.0	8.0	—	—
7Si + 2Ti + 4NaN <sub>3</sub> + Na <sub>2</sub> SiF <sub>6</sub> + 8C	23.0	49.0	21.0	6.0	1.0	—
Si + 4Ti + 4NaN <sub>3</sub> + Na <sub>2</sub> SiF <sub>6</sub> + 2C	64.0	10.0	17.0	9.0	—	—
Si + 8Ti + 4NaN <sub>3</sub> + Na <sub>2</sub> SiF <sub>6</sub> + 2C	76.0	—	19.0	5.0	—	—

bon content (4 and 8 mol), however, it is much less than the possible theoretical amount of SiC. In cases of combustion of charge with a low carbon content (2 mol), silicon carbide is either not formed at all, or it is formed in a small amount compared to the theoretically possible one. Upon that, in both cases (with large and small amounts of carbon in the charge), free carbon is practically undetectable in the composition of the final combustion product, although it is to remain entirely if SiC is not formed, or to be present partially if Si<sub>3</sub>N<sub>4</sub> is partially transformed into SiC by reactions (4). As it has already been mentioned in two previous cases of using azide SHS to obtain compositions Si<sub>3</sub>N<sub>4</sub>—SiC and AlN—SiC, the absence of free carbon in the combustion products can be explained by the peculiarities of silicon carbide formation according to the sequence of reactions (4) during the combustion of silicon powder in nitrogen atmosphere. Ultrafine light particles of carbon black can be partially or even completely removed from a burning highly porous charge sample of bulk density by gases released during the formation of Si<sub>3</sub>N<sub>4</sub> at the first stage of combustion, and

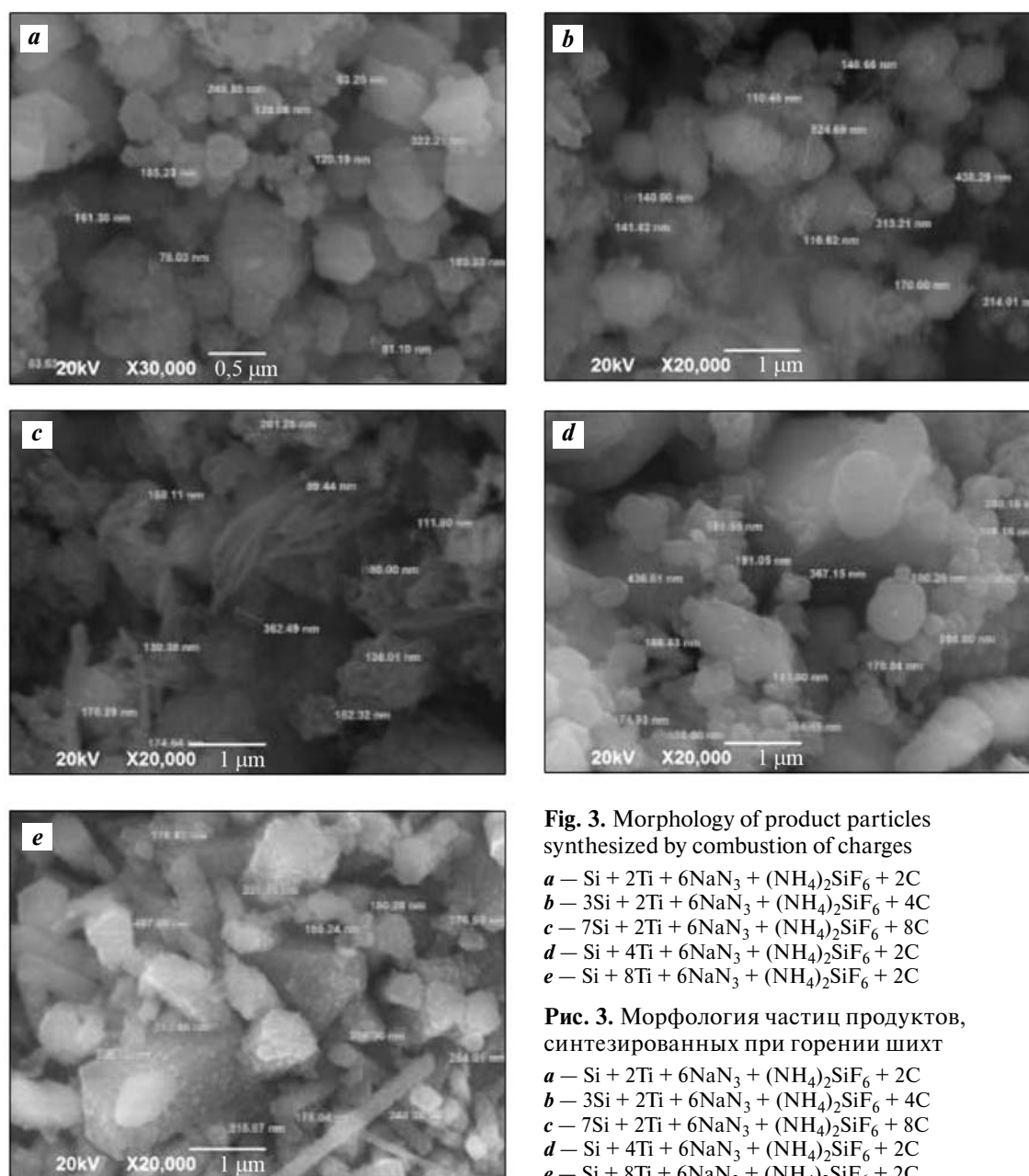
not involved in the transformation of Si<sub>3</sub>N<sub>4</sub> into SiC. As a result, silicon nitride remains in the combustion products entirely or partially, and silicon carbide is not formed at all, or it is formed in a much smaller amount than it is to be according to the stoichiometric reaction equations for the initial mixtures of powders. The lower the amount of carbon in the charge in relation to the titanium content in these equations, the higher is the combustion temperature, the more is the gas release (and consequently also more significant is the relative loss of carbon due to its removal by the gases), as well as the lower is the formation of SiC (or it is not formed at all).

The microstructure of typical combustion products of charges with halide salt 2 is shown in Fig. 3.

As Fig. 3 shows, the synthesized ceramic compositions are a highly dispersed mixture of nanosized and submicron particles of equiaxed and fibrous forms.

Thus, despite the positive results of the theoretical thermodynamic analysis, the considered experimental application of the azide SHS method did not allow to synthesize the desired composition of TiN—





**Fig. 3.** Morphology of product particles synthesized by combustion of charges

- a** —  $\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
**b** —  $3\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 4\text{C}$   
**c** —  $7\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 8\text{C}$   
**d** —  $\text{Si} + 4\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
**e** —  $\text{Si} + 8\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$

**Рис. 3.** Морфология частиц продуктов, синтезированных при горении шихт

- a** —  $\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
**b** —  $3\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 4\text{C}$   
**c** —  $7\text{Si} + 2\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 8\text{C}$   
**d** —  $\text{Si} + 4\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$   
**e** —  $\text{Si} + 8\text{Ti} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C}$

SiC powders in pure form, without the by-product silicon nitride phase of two modifications ( $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ ) in the composition. Moreover, at a high relative content of Ti in the charge, compared to the content of Si, only  $\text{Si}_3\text{N}_4$  can be synthesized, and silicon carbide may not be synthesized at all. Upon that, the possibility of using combustion for the synthesis of compositions of highly dispersed nanosized and submicron ceramic powders  $\text{TiN-Si}_3\text{N}_4$  and  $\text{TiN-Si}_3\text{N}_4\text{-SiC}$  with a relatively low content of free silicon impurity (up to 1.4 %) was experimentally shown for the first time, and that is a remarkable achievement,

since earlier application of SHS method allowed to obtain these compositions only of much coarser powders with a particle size of 5–10  $\mu\text{m}$  by combustion of titanium silicides and silicon carbide in nitrogen gas at high pressure [78, 80].

It is also worth noting that earlier an attempt was made to use the SHS-Az method to obtain a nanopowder composition  $\text{TiN-Si}_3\text{N}_4$  by burning the charges of the following systems:  $\text{Na}_2\text{SiF}_6\text{-NaN}_3\text{-Na}_2\text{TiF}_6$ ,  $(\text{NH}_4)_2\text{SiF}_6\text{-NaN}_3\text{-(NH}_4)_2\text{TiF}_6$ ,  $\text{Na}_2\text{SiF}_6\text{-NaN}_3\text{-(NH}_4)_2\text{TiF}_6$  and  $(\text{NH}_4)_2\text{SiF}_6\text{-NaN}_3\text{-Na}_2\text{TiF}_6$  with different ratio of components [23]. The combustion

product was a mixture of highly dispersed powders, but a pure nitride composition consisting only of silicon nitride and titanium nitride could not be obtained since the final product contained a large amount (from 10 to 40 wt.%) of non-nitrided Ti and Si by-products, as well as  $\text{TiSi}_2$  and  $\text{Na}_2\text{TiF}_6$  by-products of the reaction.

## Conclusion

The presented results of the review show that the application of the SHS process can significantly contribute to the development of methods for obtaining nitride-carbide powder compositions from the most common refractory nitride ( $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ,  $\text{TiN}$ ) and carbide ( $\text{SiC}$ ) compounds. The SHS process is attractive by its simplicity and cost-effectiveness, it is one of the promising *in situ* chemical methods for direct synthesis of ceramic powders in the desired composite body from the mixture of initial inexpensive reagents. Azide SHS using sodium azide  $\text{NaN}_3$  and gasified fluoride halide salts  $\text{NH}_4\text{F}$ ,  $\text{Na}_2\text{SiF}_6$ ,  $(\text{NH}_4)_2\text{SiF}_6$  and  $(\text{NH}_4)_2\text{TiF}_6$  has such distinctive features as relatively low combustion temperatures, the formation of a large amount of intermediate vapor and gas products of reaction, as well as final condensed and gas by-products that separate particles of the desired powders, making it possible to synthesize highly dispersed ( $< 1 \mu\text{m}$ ) powder compositions  $\text{Si}_3\text{N}_4\text{—SiC}$ ,  $\text{AlN—SiC}$  and  $\text{TiN—SiC}$ , where  $\text{Si}_3\text{N}_4$  has a large ratio of  $\alpha$ -modification.

However, in most cases, the amount of  $\text{SiC}$  phase synthesized in experiments appears to be considerably lower than the expected theoretical amount, and even no  $\text{SiC}$  at all may be present in the desired nitride-carbide composition. Upon that, almost all synthesized compositions contain  $\text{Si}_3\text{N}_4$  phase as an undesirable by-product phase in  $\text{AlN—SiC}$  and  $\text{TiN—SiC}$  compositions and in excessive amount in  $\text{Si}_3\text{N}_4\text{—SiC}$  compositions. Besides, the synthesized compositions may contain the impurities of unreacted free silicon. These disadvantages can be explained by the peculiarities of the formation of silicon carbide through the intermediate formation of silicon nitride during the combustion of a mixture of silicon and carbon powders in nitrogen atmosphere. (Combustion in nitrogen atmosphere is mandatory for *in situ* production of nitrides in composite body by SHS methods.) A considerable part of ultrafine light carbon black particles can be partially or entirely removed from the burning highly porous bulk charge sample by gases released during the

synthesis of intermediate product  $\text{Si}_3\text{N}_4$ , and thus not involved in subsequent decomposition of  $\text{Si}_3\text{N}_4$  and transformation into silicon carbide due to interaction with carbon. As a result, silicon nitride remains in the combustion products partially or entirely, and silicon carbide is formed in a smaller amount than it is to be according to the initial stoichiometric reaction equations and the results of thermodynamic calculations, or it is not formed at all. Upon that, an impurity of free silicon appears as well.

Several directions of further research of SHS process application to obtain highly dispersed compositions of nitrides with silicon carbide can be used for eliminating the specified disadvantages. Firstly, to charge an excessive amount of carbon black (soot) compared to the one required by the composition stoichiometry. As it has already been mentioned, almost pure (without  $\text{Si}_3\text{N}_4$  and Si impurities) and more homogeneous  $\text{AlN—SiC}$  solid solution was obtained by adding an additional amount of carbon black (20 %) to the mixture of initial powders of  $\text{Al—Si—C}$  [62].

Secondly, to use polytetrafluoroethylene  $\text{C}_2\text{F}_4$  (powder fluoroplast-4) as an activating and carbon-containing additive in the charge, which promotes the formation of  $\text{SiC}$  that was successfully done in work [41] by combustion synthesis of  $\text{Si}_3\text{N}_4\text{—SiC}$  compositions with a high content of  $\text{SiC}$  phase, but with micron-sized particles and a small proportion of  $\alpha$ -modification in silicon nitride ( $\text{Si}_3\text{N}_4$ ). It was shown in works [26, 81] that upon the combustion of mixtures of silicon powder with carbon or polyethylene (in argon atmosphere) at a high content of  $\text{C}_2\text{F}_4$ , silicon carbide is synthesized in the form of nanofibers and nanoparticles.

Thirdly, to burn charges in pressed rather than bulk form, in order to reduce the loss of carbon black from the charge due to its being blown out by gases released during the combustion. The pressed condition of the charge can hinder the filtration of nitrogen gas into it and the formation of nitrides, but when using sodium azide powder as a nitriding agent in the composition of the charge, a high degree of nitridation can be obtained even upon difficult filtration of nitrogen gas [20].

Fourthly, it is possible that when burning a pressed charge with sodium azide and polytetrafluoroethylene in an argon atmosphere rather than nitrogen,  $\text{AlN—SiC}$  and  $\text{TiN—SiC}$  compositions with a high content of  $\text{SiC}$  and without silicon nitride impurities will be synthesized.

Fifthly, to charge finely dispersed silicon carbide powder instead of carbon black in the amount required to obtain the desired nitride-carbide com-

position. In this case, the synthesis of SiC is not required as it is already present in the required amount, and all that is left to do is to synthesize nitride of the desired composition by combustion. For example, it was shown in work [42] that the introduction of SiC significantly expands the limits of stable combustion of ferrosilicon in nitrogen (50 % SiC instead of 10 % C) and increases the degree of nitridation of the synthesis products.

And sixthly the last, when synthesizing AlN—SiC composition, not to use sodium azide, but to use only ammonium halide salts and polytetrafluoroethylene in order to exclude the formation of by-product salt — cryolite  $\text{Na}_3\text{AlF}_6$  during the combustion in nitrogen.

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