

SHS of Ultrafine and Nanosized Si_3N_4 Powders: The Effect of Inorganic and Organic Additives on the Microstructures, Morphology, and Phase Compositions of Products

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Abstract—The relationship between the microstructure and phase composition of a product obtained by self-propagating high-temperature synthesis (SHS) and different reaction mechanisms is studied using the example of silicon nitride. The formation of nanosized silicon nitride particles upon the combustion of silicon in nitrogen and other phenomena typical of substances of this class, such as self-organization and self-assembly, are observed. The chemical condensation SHS of silicon nitride is studied in the presence of inorganic salts as modifying additives. The resulting Si_3N_4 powders have a structure of secondary spherical particles being composed of primary ultrafine and nanosized ones. The Si_3N_4 powders under study were fractionated depending on the particles size and microstructure by chemical dispersion. Ultrafine particles of the light fraction form as homogeneous rods by the conventional vapor–liquid–crystal mechanism. The fine-crystalline fractions are formed by hollow crystals assembled into globules. Microstructural analysis shows that the crystal walls consist of nanosized Si_3N_4 particles. The effects of organic additives introduced into the charge stock on the phase formation, microstructure formation, and particle size of SHS silicon nitride are studied. The combustion products are found to be composite powders whose phase compositions depend on the additive and the synthesis conditions. According to the data from X-ray powder diffraction and chemical analysis, the final products can contain up to 100% of $\beta\text{-Si}_3\text{N}_4$, up to 60% of $\alpha\text{-Si}_3\text{N}_4$, up to 80% of SiC, and up to 70% of $\text{Si}_2\text{N}_2\text{O}$. It is shown that silicon nitride-based composite powders containing silicon carbide and/or silicon oxynitride can be obtained in one step. The role of ferric chloride hexahydrate as the SHS catalyst is studied. An ultrafine structurally homogeneous powder of $\beta\text{-Si}_3\text{N}_4$ is obtained in the presence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

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INTRODUCTION

Silicon nitride (Si_3N_4) is one of the most intensively studied ceramic materials. Due to its superior high-temperature mechanical properties and high thermal-shock and chemical resistances, this material is suitable for many structural applications, such as parts of automobile engines, heat exchangers, ball bearings, cutting tools, and ceramic armor [1, 2]. Silicon nitride is an important semiconductor resistant to oxidation and corrosion [3]. Porous Si_3N_4 ceramics with elongated $\beta\text{-Si}_3\text{N}_4$ grains, which are applied as filtering materials, including gas filters, isolating diaphragms, bioreactors, and catalyst supports, are of great industrial importance [4, 5].

The properties of the final material depend considerably on the initial powders and their production method. Considerable changes can be obtained upon comparing thermal stability, strain properties, and oxidation behavior depending on the purity, phase composition, and microstructure of the starting Si_3N_4

powders. Therefore, a wide application of silicon nitride-based ceramic materials requires extreme purity and good characteristics of the starting powder. The type and amount of synthetic additives, mixing and grinding procedures, and synthesis parameters also define the properties of a Si_3N_4 ceramic material.

The most important procedures for the preparation of silicon nitride powder are the nitrogenation of Si, the carbothermal reduction of SiO_2 followed by nitrogenation, gas-phase reactions of silanes with NH_3 , and the pyrolysis of polysilanes. Si_3N_4 is known to exist as two main crystalline phases: α and β ones having hexagonal structure, but differing in phase sequence. The Si_3N_4 powders obtained synthetically differ in the crystallization processes and the $\alpha/\beta\text{-Si}_3\text{N}_4$ ratio.

The particle size and shape and the degree of particle agglomeration are important characteristics of ceramic powders, which define the sintering activities and packing densities of initial products. These pow-

Table 1. Analysis of the Si₃N₄ fractions isolated upon chemical dispersion

Isolated fraction	Milling method	Si ₃ N ₄ , wt %	Si _{free} , wt %	O, wt %	S _{sp} , m ² /g
Light	Trituration	95.2	0.30	0.95	2.9
	Milling	94.5	0.44	1.10	10.4
Dark	Trituration	80.0	19.5	0.74	1.7
	Milling	94.0	3.9	0.75	3.9

der always contain a typical amount of impurities, mainly, free silicon, carbon, and oxygen.

The properties of Si₃N₄-based ceramics can be improved by the grain microstructure and morphology, which includes grain diameter, size ratio, and grain-size distribution [6–8], as well as by the chemistry of secondary phase, its composition, content, and crystallization [9–13].

Self-propagating high-temperature synthesis (SHS) is a very efficient process for the production of various ceramic materials, including powders [14, 15]. The synthesis uses the heat released by the exothermic reaction proceeding directly in the combustion wave after external inflammation. SHS is widely applied in the production of Si₃N₄ powder [16–22]. The experimental and theoretical studies of silicon combustion in nitrogen allowed elaborating the process for the large-scale production of silicon nitride powder in the SHS mode [16, 19, 23].

Upon the SHS of silicon nitride, the obligatory technological procedure is to dilute the starting silicon with an inert refractory substance, since silicon in the fast-moving combustion wave front undergoes melting and forms a barrier to the penetration of nitrogen gas into the reaction zone. To prevent the coagulation of molten particles, the starting silicon powder is usually diluted by 30–70% with the final Si₃N₄ product. However, the target product can be obtained in an alternative way where the additives are inorganic (metal salts) or organic compounds added to the charge material in a much lower volume.

SHS products are typically sinters, which is why they should be treated further to obtain powders. This can be carried out by either mechanical grinding or chemical treatment. Mechanical grinding (conventional ball milling, trituration, and planetary milling) is a simple method for preparing a nanosized powder. The grinding procedure can provide fine powders (up to 10–20 nm), but the long process time, contamination of powder with the material of balls and vessel walls, and high power consumption pose a problem that needs to be solved.

Earlier we showed that carefully controlled milling followed by thermochemical treatment (chemical dispersion in various media) of the SHS products synthesized under the optimum conditions make it possible

to obtain a uniform distribution of ultrafine and nanosized particles [24–26].

The chemical dispersion of the finely divided sinter of the SHS product with corresponding solutions allow us to further increase the product dispersity and obtain powders with a perfect crystalline lattice due to the dissolution of its defects and isolation of “primary” ultrafine and nanosized particles formed in the combustion wave. Alongside the purification of the product and decomposition of agglomerates, there is also an even decrease in the particle size of the synthesized compound as a result of its partial dissolution.

The aims of the present work were

- to study the effects of SHS parameters on the phase composition and morphology of powders synthesized;
- study the effects of adjusters and the nature of liquid and gas phases on the crystallization of the products that formed;
- elaborate procedures for controlling the crystal grain size;
- study the effects of chemical dispersion conditions on the change in the morphology and particle size of SHS powders and their specific surface areas; and
- define optimum conditions of chemical dispersion provided that the chemical and phase compositions of “primary” ultrafine and nanosized particles remain unchanged.

EXPERIMENTAL

To study the mechanisms of transformations and formation of combustion products in the synthesis of silicon nitride, the so called “condensation” synthesis was used as one of the SHS variants. The process proceeded in severe temperature conditions favoring the evaporation of the solid reagent (silicon) and the nitrogenation of its vapors in nitrogen gas. The process was carried out under a low pressure (10–150 bar instead of 150–500 bar).

Technical-grade nitrogen with an oxygen content up to 2% (v/v) and high-purity nitrogen were used for the studies. We used silicon powders with a particle size from 20 to 40 μm.

The experiments were performed on cylindrical samples of bulk density. Charge materials were mixed in a porcelain mortar or ball mill. The weight portions of charge materials with a weight of 40–50 g were placed into a quartz tube with a diameter of 35 mm and burned in the nitrogen atmosphere in a constant-pressure vessel. To remove air, the internal part of the vessel was preblown with nitrogen prior to synthesis. The charge sample installed vertically inside the vessel was ignited from the upper end of glowing tungsten wire through the intermediate layer of titanium pow-

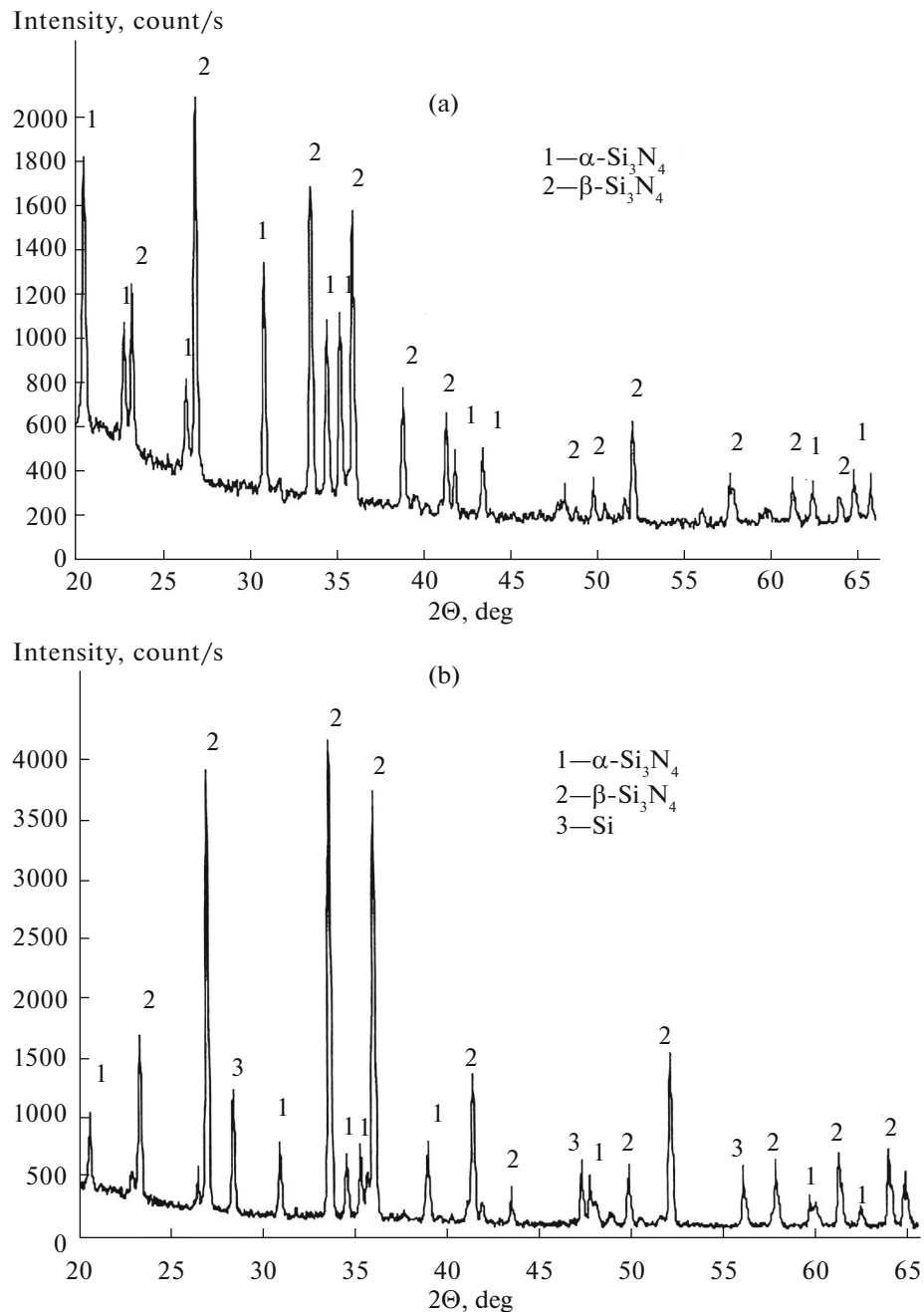


Fig. 1. X-ray diffraction patterns of the flocculent (a) and finely crystalline (b) Si_3N_4 phases isolated by the chemical dispersion of the sintered product.

der (the weight of titanium powder was 1 g). The burning point was determined by the thermoelectric technique [27] using tungsten-rhenium thermocouples (VR-5/20) with diameters of 100 and 200 μm . Thermocouples covered with a boron nitride daubing below the welded joint were placed into the center of the sample. The relative measurement error was 50 K. The resulting sinter was ground in a ball mill or agate mortar.

The X-ray powder diffraction (XRPD) study was performed on a DRON-3M diffractometer using the $\text{CuK}\alpha$ radiation. X-ray diffraction patterns were solved using the Powder Diffraction File (PDF-2) databank. The microstructures of combustion products were studied on a LEO-1450 electron microscope with an INCA ENERGY 350 (EDS) integrated X-ray analyzer. The chemical analysis for the content of main (Si, N) and impurity elements was performed accord-

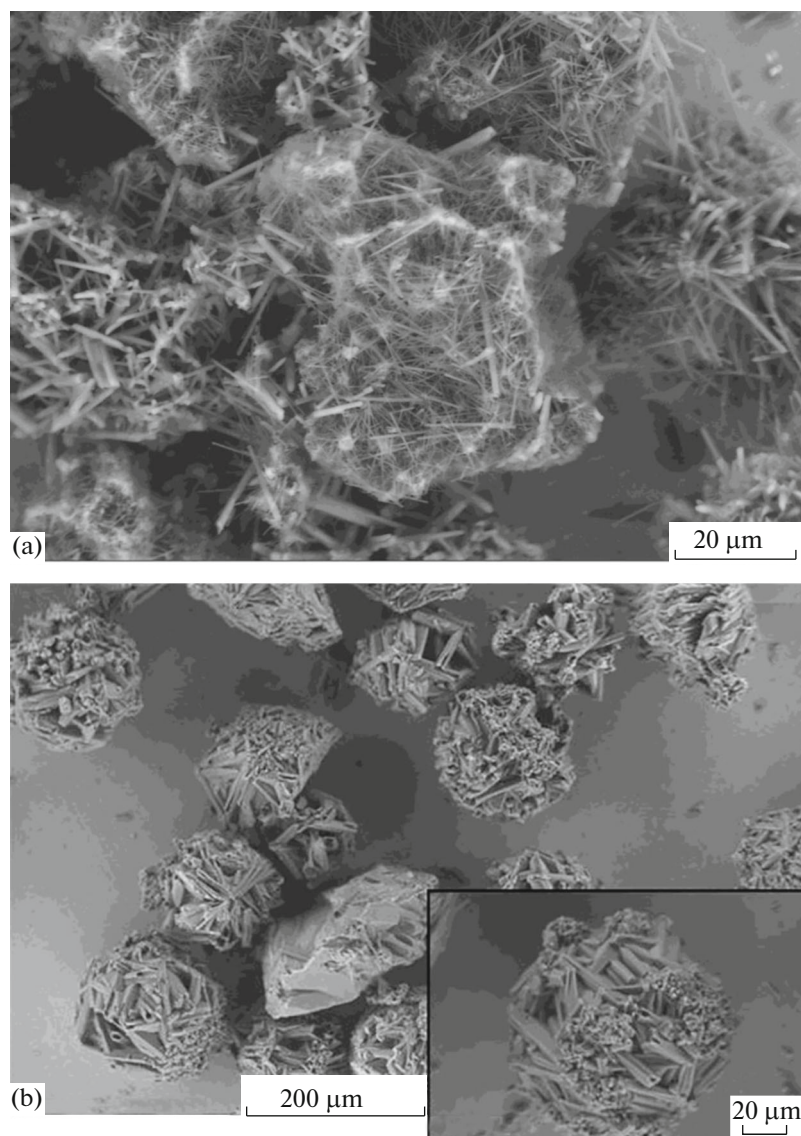


Fig. 2. Microstructures of the flocculent (a) and finely crystalline (b) fractions of the Si_3N_4 powder obtained in the presence of 5% NaCl.

ing to the procedures developed for an analysis of refractory compounds [28].

RESULTS AND DISCUSSION

Inorganic Additives

To prepare silicone nitride by SHS technology, special modifying agents favoring a decrease in the melting and boiling points of silicon (NaCl , CaCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), as well as gasifying additives NH_4Cl and NH_4F , were added.

The addition of 5% of NaCl into the charge stock allowed performing the synthesis under the pressure of 40–60 bar. The total contents of silicon, nitrogen, and

oxygen found by elemental analysis were 33.8–39.4 wt % of N, 61.2–66.0 wt % of Si, and 0.4–1.2 wt % of O.

The product obtained in the presence of 5 wt % NaCl and trituated in the agate mortar was found to decompose during chemical dispersion into individual fractions differing in color, particle size, and microstructure. Two fractions were isolated: light flocculent (bright) and coarse finely crystalline (dark) ones. The main difference in the chemical compositions of fractions consisted in the free silicon content after the alkaline treatment of the product (Table 1).

X-ray powder diffraction and chemical analyses showed that dispersion in 5% KOH completely purifies the light flocculent fraction from free silicon (Fig. 1a), viz., the contents of α - and β - Si_3N_4 phases

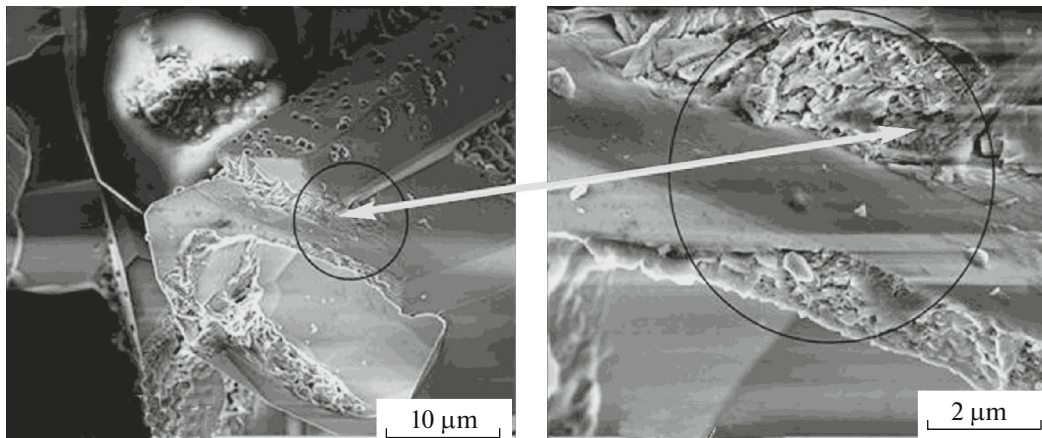


Fig. 3. Particle microstructure of the Si_3N_4 crystalline fraction.

in the light fraction were almost identical. The removal of free silicon from the dark fraction required long-term treatment of the powder with 40% KOH. Upon such treatment, the microstructure of the powder remained unchanged (Fig. 1b).

Microstructural analysis showed that the Si_3N_4 particles of the light fraction are loose agglomerates

composed of light (semitransparent) round rods with diameters of 200–300 nm and length of $\sim 2\text{--}3\ \mu\text{m}$ (Fig. 2a).

Coarse dark particles had a predominantly spherical shape, being either an ideal ball or sphere with a developed internal porosity, and consisted of ultrafine particles (rods) of hexagonal structure with diameters of 8–15 μm and lengths of 30–50 μm (Fig. 2b). The rods, being hollow inside, consisted of laminar plates. In turn, the internal parts of layers were filled with nanosized particles with a length less than 300 nm and thickness of 50–70 nm typical of $\beta\text{-Si}_3\text{N}_4$ (Fig. 3).

One can propose the following features of Si_3N_4 crystal formation during synthesis: the light fraction forms according to the conventional rod-formation scheme by the vapor–liquid–crystal mechanism. The process conditions are sufficient to provide the evaporation and reaction of a Si particle within typical combustion times. The reasons for the formation of “skeleton” rods (finely crystalline fraction) were likely the deficiency of material, nitrogen deficiency in this case, and the dramatic difference between the crystal growth rate and the growing rate of its projecting parts, the mass transfer to which had the maximum rate.

Taking into account the data from other researchers, one can conclude that Si_3N_4 nanosized particles are produced in the gas–vapor phase. The finely divided aggregates forming at high temperatures arise from coagulation processes and consist of nanosized primary particles. The resulting systems are characterized by energy instability, which results in a nonequilibrium structure for which the spherical shape is thermodynamically more favorable (Fig. 2b). Such particles constitute the main bulk of reaction product. The precise mechanism for the formation of a sphere has not been determined and requires further studies. However, the data can lead to a new and simple way

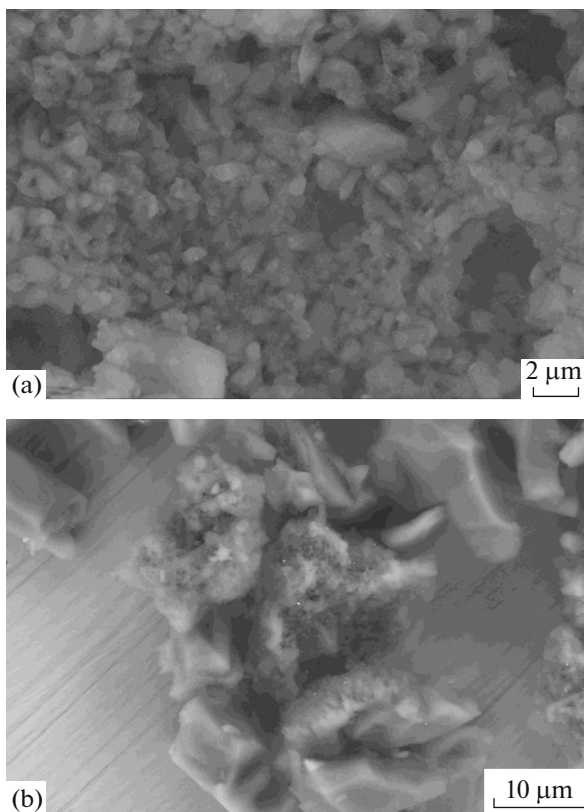


Fig. 4. Microstructures of the light (a) and dark (b) fractions of the silicon nitride sinter crushed in a planetary mill.

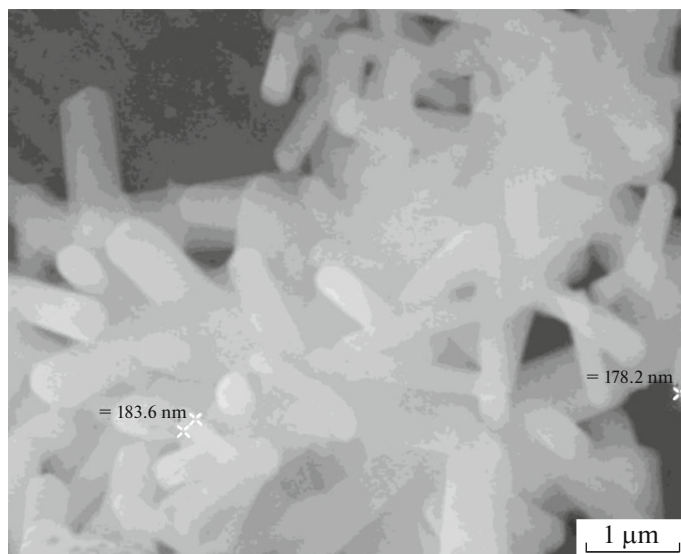
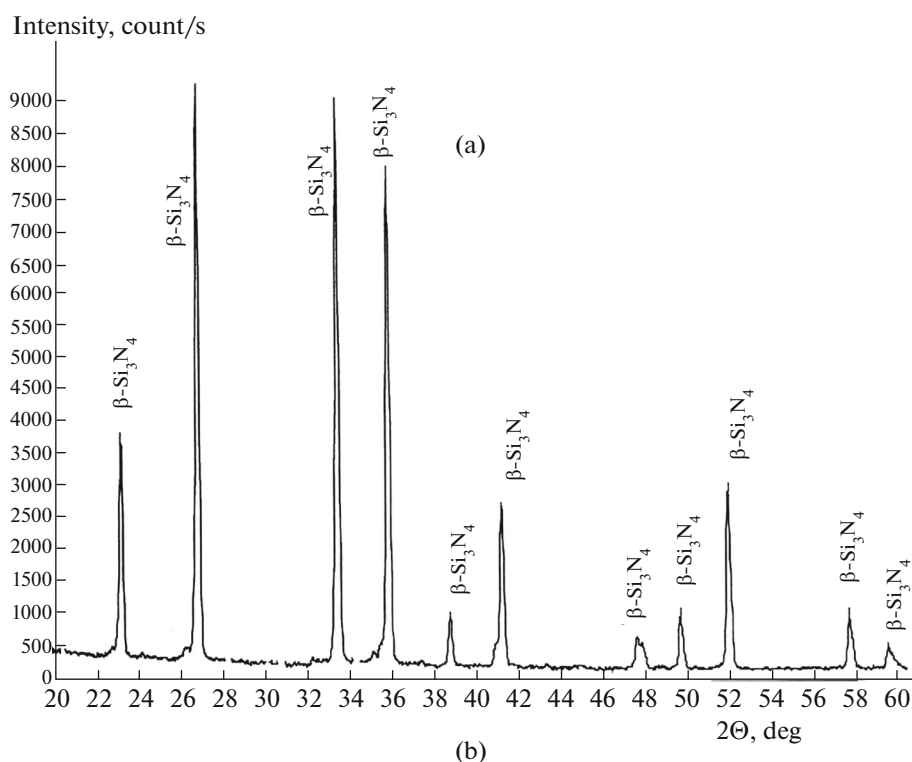


Fig. 5. X-ray diffraction pattern and microstructure of silicon nitride powder obtained in the presence of the combined $\text{NH}_4\text{Cl}+\text{FeCl}_3$ additive.

for the large-scale production of microcrystalline Si_3N_4 .

When the Si_3N_4 sinter obtained by SHS is milled for several minutes in a planetary mill, two fractions can also be isolated by chemical dispersion, which in contrast to powders isolated from the ground product are close in chemical compositions and almost free of free silicon. The light fraction powders were soft agglomerates consisting of ultrafine particles with an

irregular splinter shape whose sizes range from 1 to $0.01\ \mu\text{m}$ (Fig. 4a). The crystalline fraction consisted of fragments of decomposed hexagonal rods (Fig. 4b). For purified powders, the specific surface area increased noticeably and the free silicon content decreased due to chemical dispersion (Table 1).

Microstructures analogous to the above-described ones were also observed when the modifying agent was calcium chloride CaCl_2 .

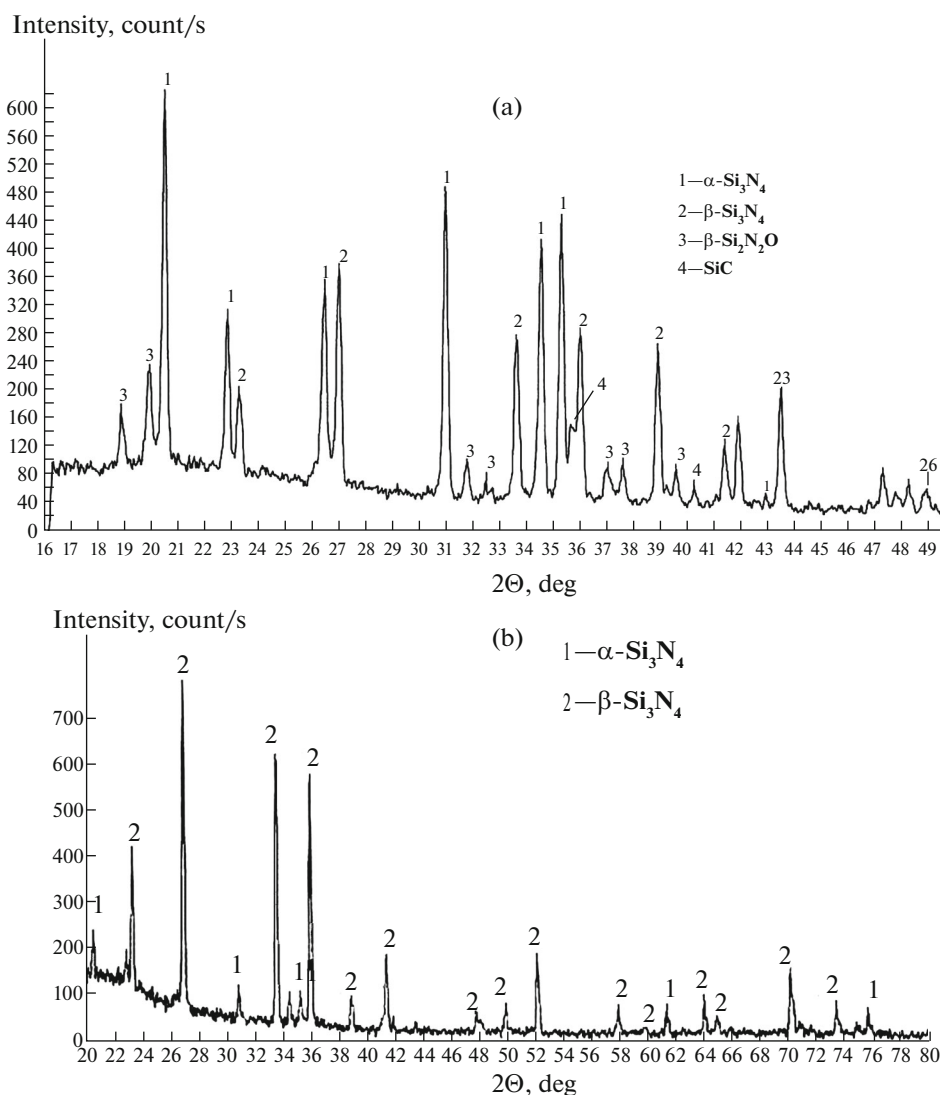


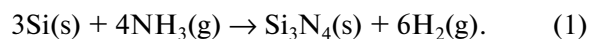
Fig. 6. X-ray diffraction patterns of the composites obtained in the presence of 7.5 (a) and 4.5 wt % (b) of urea.

In the presence of just ammonium halides (NH₄Cl, NH₄F) as the gasifying additive, fibrous Si₃N₄ particles having a thickness of 0.1–0.3 μm and a length of several tens of micrometers are obtained [29]. Such particles are typical for gas–transport reactions. However, the presence of metal impurities accelerates the α→β transition according to the literature data [30, 31]. For example, the addition of 2.5% of ferric chloride to the charge stock containing silicon and 5.0% of NH₄Cl results in the formation of a single-phase β-Si₃N₄ product of the following composition (in wt %): N, 39.9; Si(total), 58.4; Si(free), 0.2; O, 0.4; C, 0.2; and Fe, 0.04.

Chemical dispersion allows the isolation of a pure β-silicon nitride product consisting only of soft agglomerate-assembled ultrafine parti-

cles analogous to those of the light-fraction of Si₃N₄ powder obtained in the presence of NaCl (Fig. 5).

The β-Si₃N₄ nanorods can grow according to the following model. At the first step, at the reaction temperature, Fe(III) reacts with Si to form iron silicides as the liquid phase, which serve as the catalyst. At the second step, at a high temperature, the gas-forming agent NH₄Cl decomposes into NH₃ and HCl. In turn, ammonia decomposes stepwise into NH, NH₂, and N and then reacts with supersaturated Si atoms in iron silicides to form nucleation seeds of Si₃N₄ nanorods:



Iron is also the catalyst for reaction (2) supplying new portions of NH₃ [32]:

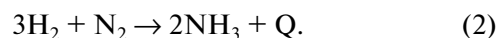
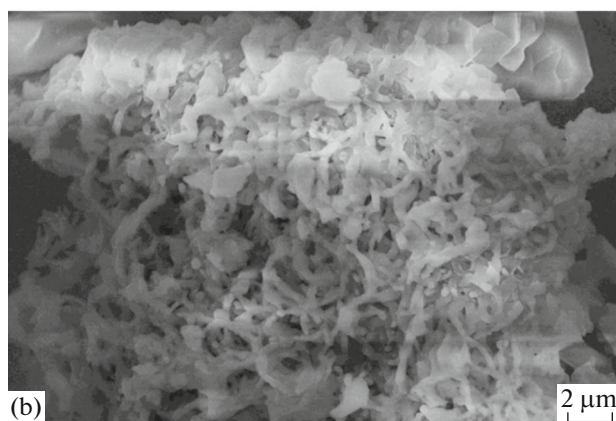
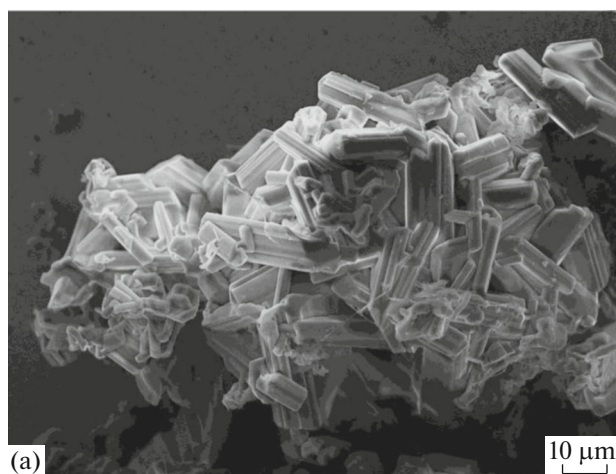


Table 2. Phase compositions of the SHS silicon nitride-based products as a function of the reacting nitrogen gas pressure and the nature and amount of organic additive

Sample	Additive	Nitrogen pressure	Phase composition		
			% Si ₃ N ₄	% Si ₂ N ₂ O	% SiC
A(1)	7.5% CO(NH ₂) ₂ + 2.5% FeCl ₃	70 bar	71.8	22.1	6.1
A(2)	4.5% CO(NH ₂) ₂ + 2.5% FeCl ₃	70 bar	93.0	5.5	1.5
A(3)	7.5% CO(NH ₂) ₂	70 bar	95.2	3.3	1.5
B(1)	4.0%(NH ₄) ₂ C ₂ O ₄ + 2.5% FeCl ₃	130 bar	82.0		5.3
B(2)	4.0%(NH ₄) ₂ C ₂ O ₄ + 2.5% FeCl ₃	90 bar	87.0	5.3	5.0
B(3)	4%(NH ₄) ₂ C ₂ O ₄ · H ₂ O	70 bar	90.4		2.3
C(1)	4% Ph ₄ Si + 2.4% FeCl ₃	90 bar	43.0	23.7	33.3
C(2)	4% Ph ₄ Si + 2.4% FeCl ₃	90 bar	61.5	22.5	16.0
C(3)	4% Ph ₄ Si	70 bar	42.0	38.7	19.3
D	4% C ₁₀ H ₈	90 bar	61.1	20.0	3.2

As soon as nucleating seeds (nuclei) form, the β -Si₃N₄ nanorods begin to grow in the axial direction.

The isolation of homogeneous purified β -Si₃N₄ particles by chemical dispersion must improve powder compaction when compared to fibrous structures.

**Fig. 7.** Microstructure of the composite obtained in the presence of urea (NH₂)₂CO.

Organic Additives

During the SHS of silicon nitride, organic additives are more interesting as gasifying additives than inorganic ones. The silicon–nitrogen–organic compound system contains nonmetals (oxygen, carbon, and nitrogen) with which silicon can form refractory compounds under SHS conditions. Organic additives added to the charge stock in the amount of 2.5–5 wt % make it possible to obtain complex composites containing silicon nitrides, oxynitrides, and carbides in different ratios.

We have performed preliminary studies of the combustion of various-dispersity silicon powders in nitrogen in the presence of organic compound additives and the effects of these additives on the main regularities of combustion [33, 34].

The decomposition of organic compounds at high temperatures results in the formation of reactive products, viz., radicals [35]. The reaction of silicon with hydrocarbon radicals affords organosilicon compounds which, while having low boiling points, undergo gasification and thereby transfer silicon into the gas phase. Since organosilicon compounds have low stability at high temperatures, they must decompose in the high-temperature zone by the reaction $\text{SiR}_g \rightarrow \text{Si}_g + \text{R}'$ to form silicon in the gas phase. The increase in the mass transfer of reagents using gas-transport radical carriers can be the main reason for the intensification of silicon combustion in nitrogen. The presence of carbon-containing radicals in the reaction system is evidenced by the presence of carbon black in the tempered combustion products, since the nucleation seed for carbon black can only be a hydrocarbon radical [36]. It is also important to note that the presence of carbon black in the system prevents the coagulation of molten silicon particles to improve the conditions of nitrogen filtration.

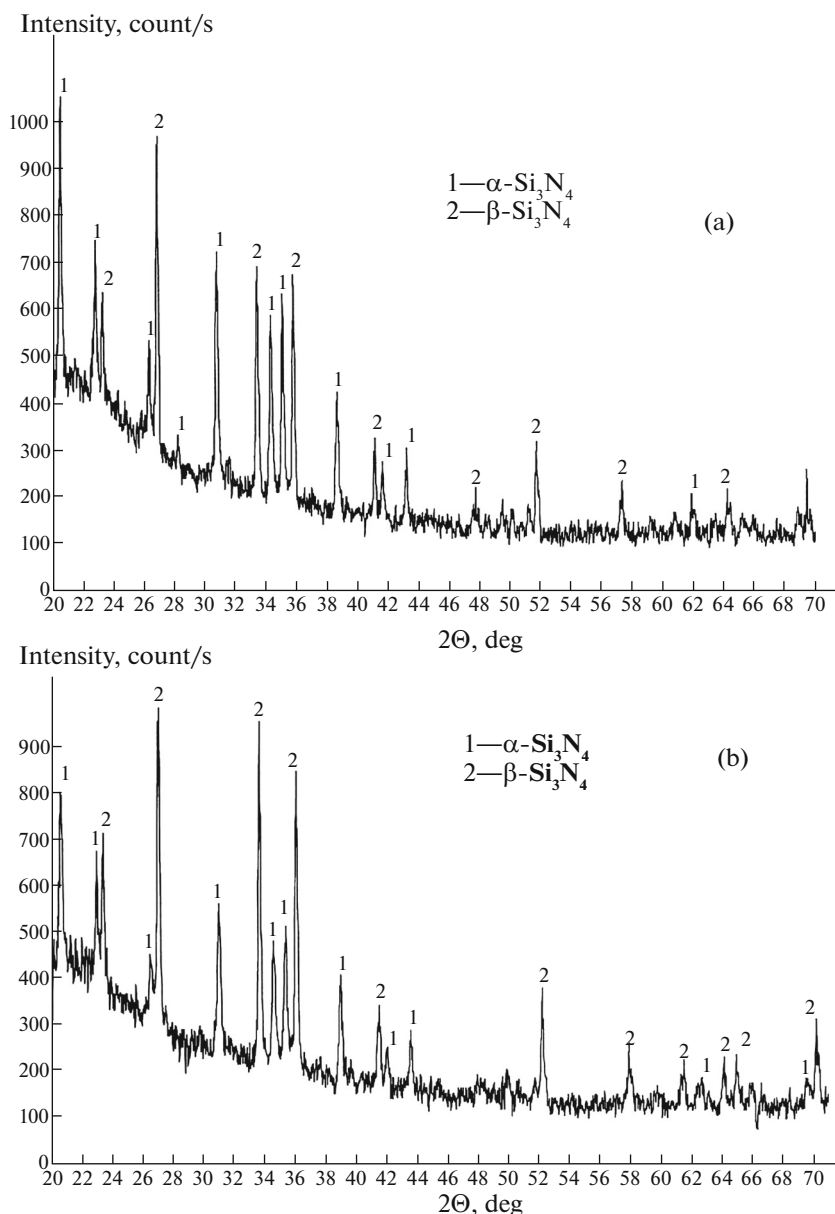


Fig. 8. X-ray diffraction patterns of the silicon nitride powders obtained in the presence of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ under the pressure of 130 bar (a) and 90 bar (b).

The experiments differed in the weight percentages of organic compounds added to the starting charge stock, their natures, the presence of catalyst (iron(III) chloride hexahydrate), and the pressure of reacting nitrogen gas.

Table 2 gives the SHS conditions and possible phase compositions of the resulted products calculated according to the data from a chemical analysis of milled and chemical dispersion-purified synthesis products.

In the presence of urea $(\text{NH}_2)_2\text{CO}$ as the additive, the synthesis was performed under the constant pressure of $P = 70$ bar varying only the urea content in the

starting charge stock and the presence or absence of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ catalyst. Upon the addition of 7.5% of urea and 2.5% of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, composite A(1) containing $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$ (with the content of the α form being higher than that of the β one according to the XRPD data) and a considerable amount of silicon oxynitride (up to 22%) was obtained (Fig. 6).

When the urea content was decreased to 4.5%, the practically single-phase product A(2) containing $\beta\text{-Si}_3\text{N}_4$ and a small amount of $\alpha\text{-Si}_3\text{N}_4$ (as an impurity) was isolated after chemical dispersion in a KOH solution.

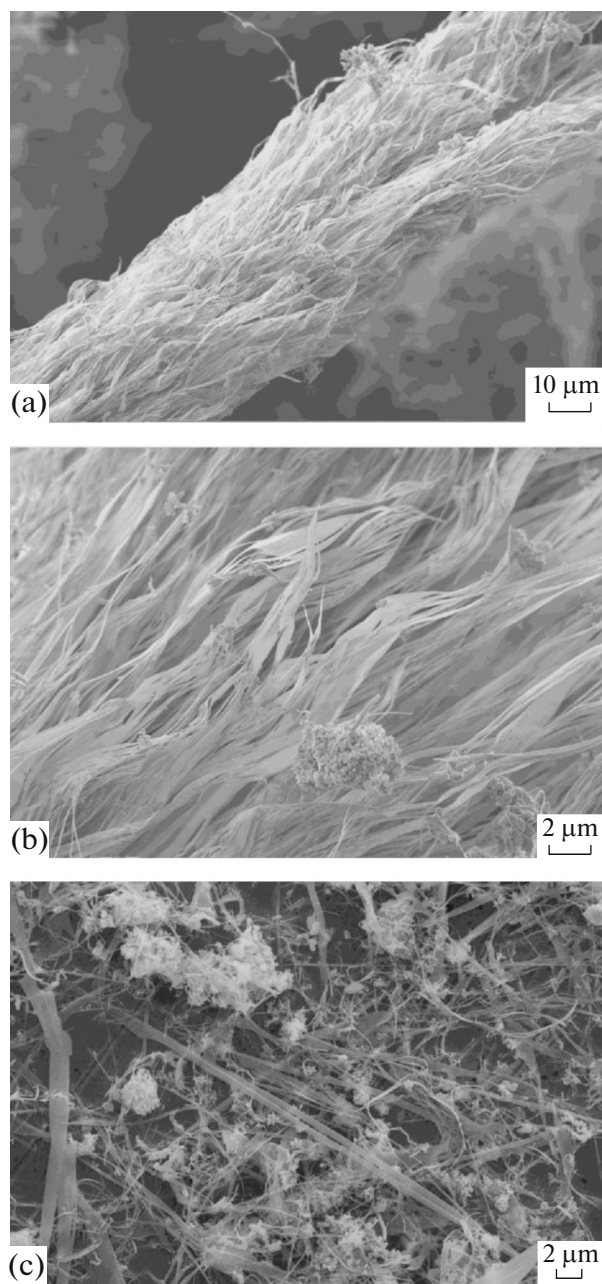


Fig. 9. Microstructures of the silicon nitride powders obtained in the presence of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ under the pressure of 130 bar (a, b), and 90 bar (c).

The single-phase product A(3), consisting of $\beta\text{-Si}_3\text{N}_4$ only, is also obtained if 7.5% of urea is added to silicon without the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (see Table 2).

Thus, at least 7.5% of urea needs to be added and the presence of FeCl_3 as a catalyst is obligatory to prepare a composite of the composition $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, $\text{Si}_2\text{N}_2\text{O}$.

The microstructure of formed and purified product is imperfect crystals of different shapes, including spherical nanoparticles, nanowires, and fragments of columnar crystals assembled into agglomerates (Fig. 7). This is likely explained by different reaction mechanisms in the combustion wave, which will be the subject of further studies.

The synthesis of silicon nitride in the presence of ammonium oxalate was performed under different pressures of nitrogen (reacting gas), but at an identical content of additive, as well as in the presence and in the absence of ferric chloride as the catalyst.

According to the XRPD data, the contents of $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ are almost identical (Fig. 8a) in product B(1) and the β phase predominates in product B(2) (Fig. 8b).

The main difference between the synthesis products is found upon a comparison of the microstructures of powders. Under a pressure of 130 bar, nanotapes assembled into bundles and oriented identically, as well as small soft agglomerates composed of nanosized rods typical of $\beta\text{-Si}_3\text{N}_4$, are obtained (Figs. 9a, 9b).

The powders obtained under a pressure of 90 bar are nanowires with thicknesses of several nanometers and lengths of tens of micrometers and agglomerates of nanoparticles (Fig. 9c). Comparing the data from the microstructural and XRPD analyses, one can assume that the nanotapes and agglomerates of columnar nanoparticles correspond to $\beta\text{-Si}_3\text{N}_4$ and the nanowires correspond to $\alpha\text{-Si}_3\text{N}_4$.

According to the data from XRPD and chemical analysis, upon a decrease in the pressure to 70 bar in the absence of FeCl_3 catalyst, product B(3) consisting mainly of $\beta\text{-Si}_3\text{N}_4$ and a small amount (up to 9 wt %) of silicon oxynitride $\text{Si}_2\text{N}_2\text{O}$ is obtained (see Table 2). Upon the dispersion of product B(3) in a KOH solution, spherical particles with a diameter less than $100 \mu\text{m}$ were segregated, which consisted of rods and were covered with agglomerates of nanoparticles.

The increase in the carbon content by the addition of the organosilicon compound as the gasifying agent, viz., tetraphenylsilane Ph_4Si , and the modifying agent, viz., $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, to the charge stock results in the formation of a product containing Si_3N_4 as the basis and some amounts of Si (free), SiC, and $\text{Si}_2\text{N}_2\text{O}$. The powder was separated into two fractions by chemical dispersion: light C(1) and dark C(2) ones. Table 2 gives approximate phase compositions for the purified products of synthesis. According to the XRPD data, the light fraction C(1) contains all four phases ($\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, $\text{Si}_2\text{N}_2\text{O}$, and SiC) almost in equal amounts (Fig. 10a). In the dark fraction C(2), the α - and $\beta\text{-Si}_3\text{N}_4$ phases are predominant (Fig. 10b).

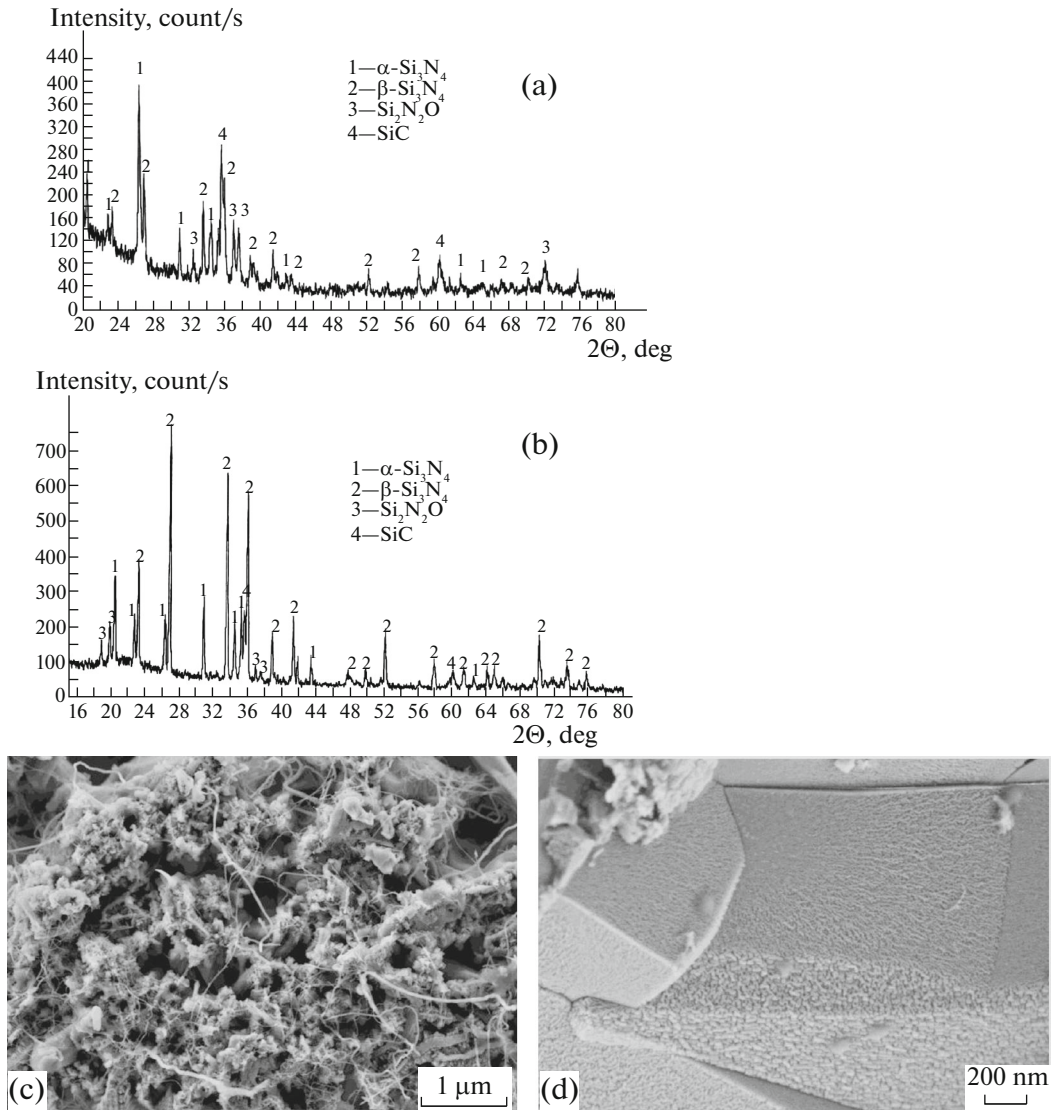


Fig. 10. X-ray diffraction patterns of the light (a) and dark (b) fractions of the chemical dispersion-purified product obtained in the presence of Ph_4Si additive and their microstructures (c, d).

The microstructures of powders C(1) and C(2) are semi-transparent light thin fibers with diameters of 50–200 nm and lengths of 4–6 μm , soft agglomerates of nanoparticles, and rods covered with nanoparticles (Fig. 10); i.e., ultrafine composite materials with different ratios of constituent phases are produced simultaneously.

If ferric chloride is not added to the charge stock containing silicon and tetraphenylsilane, the SHS reaction proceeds incompletely. The microstructural analysis of the purified product C(3) showed an intermediate structure formation. The rods forming the bulk was found at the intermediate step to be composed of nanosized particles whose growth resulted in the formation of columnar particles being hollow

inside (Fig. 11a). Simultaneously, the formation of nanofibers with an indefinite length and a diameter less than 10 nm was observed (Fig. 11b).

The complex composites containing $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, SiC, and $\text{Si}_2\text{N}_2\text{O}$ also form in the presence of 4.0 wt % of naphthalene C_{10}H_8 as the organic additive (Fig. 12a). The microstructure of the isolated product was nanosized spherical particles assembled into agglomerates (Fig. 12b).

Thus, the studies performed make it possible to conclude that the addition of oxygen-free organic compounds (tetraphenylsilane and naphthalene) results in the formation of silicon nitride-based composites with more complex compositions compared to the addition of oxygen-containing organic com-

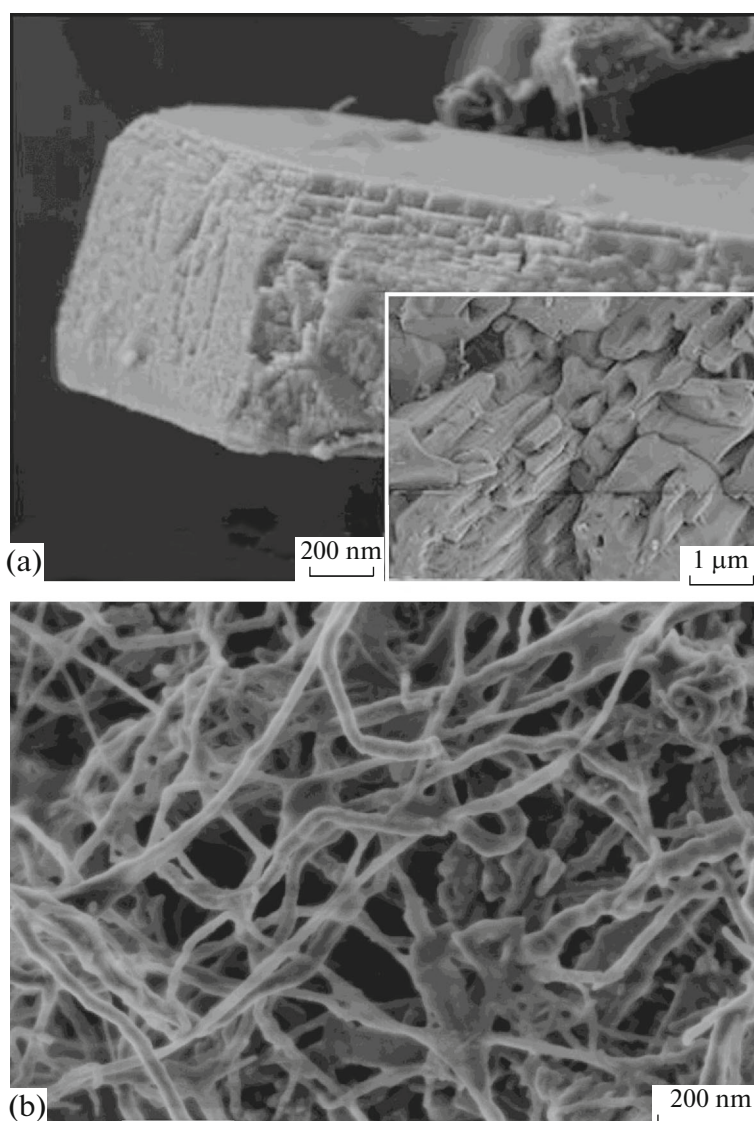


Fig. 11. Microstructure of the purified powder C(3).

pounds. The presence of catalyst, viz., $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, plays a key role in the SHS of composites.

The development of synthesis and isolation processes of silicon nitride-based composite materials with definite structures and phase and chemical compositions depending on the inorganic and organic compounds added is a subject for subsequent studies.

CONCLUSIONS

Using the example of silicon nitride, we attempted to establish the dependence between the morphologies of particles formed during SHS and different reaction mechanisms. Using different controlling additives, the regularities and mechanisms of Si_3N_4 powder synthesis were studied, which allowed us to determine the

optimum SHS parameters necessary for the formation of nanocrystalline structures.

Some powders of Si_3N_4 obtained by SHS with organic and inorganic additives were found to have the structure of secondary spherical particles composed of primary ultrafine and nanosized ones. By chemical dispersion, the synthesis products were separated into fractions differing in particle size and microstructure.

The effects of carbon-, oxygen-, and nitrogen-containing additives on the elemental and phase compositions of combustion products were studied. The composition of organic compounds added was found to affect not only the phase ratios of reaction products, but also the shapes and sizes of resulting particles. It was shown that the silicon nitride-based composite powders containing silicon carbide and/or silicon oxynitride can be prepared in one step. The phase ratio

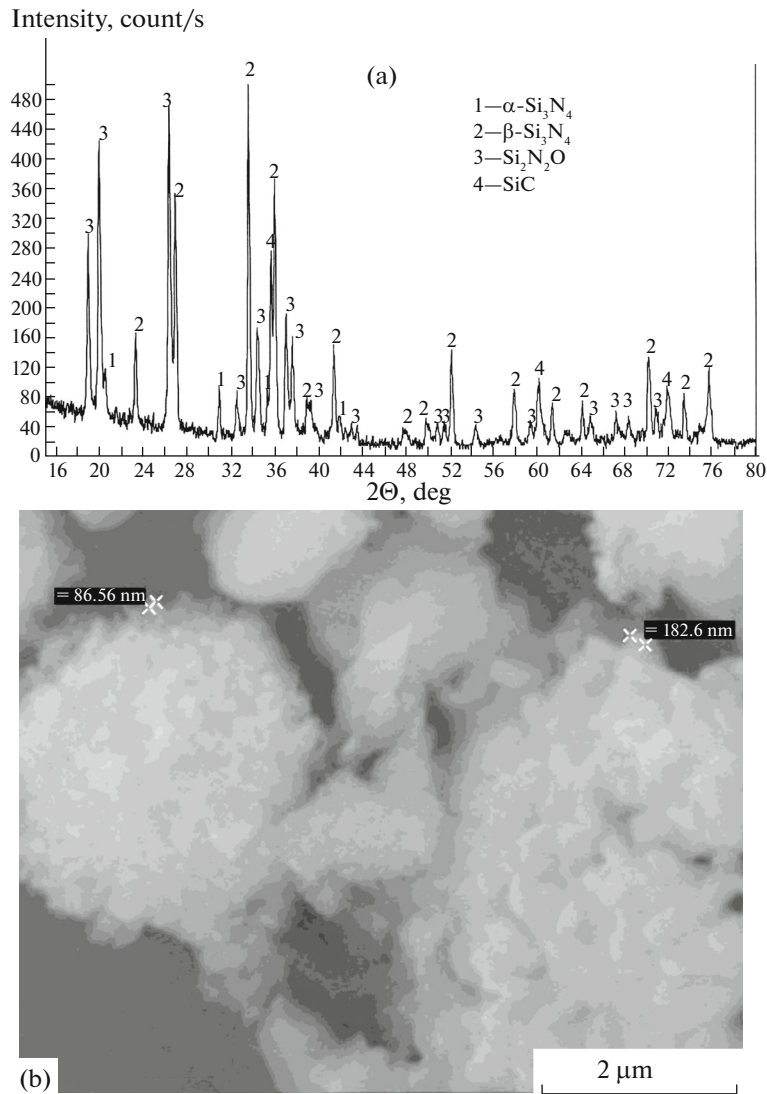


Fig. 12. X-ray diffraction pattern and microstructure of the composite obtained in the presence of 4 wt % of naphthalene C_{10}H_8 .

in the composite powders synthesized can be controlled through the amount of introduced additive and the change in its composition. The conditions for the preparation of composite powders with different phase compositions were determined.

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