Investigation of possibility to fabricate Si₃N₄-TiN ceramic nanocomposite powder by azide SHS method

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Abstract. The process of self-propagating high-temperature synthesis with use of a powder of sodium azide NaN₃ as a nitriding agent (the SHS-Az method) was applied to fabricate a nanocomposite powder Si₃N₄-TiN. Combustion of the initial mixtures of NaN₃ only with precursors that are halides of silicon and titanium: Na₂SiF₆, (NH₄)₂TiF₆, Na₂TiF₆, (NH₄)₂TiF₆ did not allow us to synthesize the composite powder of Si₃N₄-TiN, as the phases of silicon nitride Si₃N₄ were not formed. After water washing, the ultrafine powdered product of combustion consisted of one target phase of titanium nitride only and a large amount of impurity of side phases. Replacement of the halide salt of one of the elements (Si or Ti) by the powder of this element in the initial mixture of SHS-Az system resulted in formation of silicon nitride together with the titanium nitride and impurities. The least amount of impurities was obtained by burning the initial mixtures of xSi + y(NH₄)₂TiF₆ + zNaN₃ system. Only the initial mixture of 9Si + (NH₄)₂TiF₆ + 6NaN₃ allowed us to obtain as a result of the SHS-Az process the nanostructured composite powder of Si₃N₄-TiN without impurities.

1. Introduction
Among nonoxide ceramics, the ceramics made of silicon nitride Si₃N₄ stands out because of its good combination of properties that, along with small weight, high values of hardness, stiffness, heat resistance, high-temperature strength, and corrosion resistance, has a high fracture toughness and is used for the manufacture of high-speed ball bearings of gas turbine engines, parts of automotive engines, and cutting tools [1]. However, the production of components made of very hard ceramic Si₃N₄ is only possible using diamond tools, which greatly complicates and increases the cost of manufacturing of components, especially of complex shape. A simple and cheap method of electrical discharge machining is not applicable here due to a very low conductivity of Si₃N₄ ceramics, so much attention is paid to obtaining a conductive composite ceramics based on Si₃N₄, primarily, the Si₃N₄-TiN ceramics [2, 3]. Titanium nitride TiN has not only high electrical conductivity but a high melting temperature, hardness, wear resistance, and corrosion resistance, it is compatible with Si₃N₄, improves the sintering and properties of Si₃N₄ ceramics [4]. In this case the structure of Si₃N₄-TiN composite ceramics is of great importance. Ceramics of Si₃N₄ - 30 vol. % TiN, obtained by spark plasma sintering of Si₃N₄ and TiN nanoparticles, has the wear resistance which is 3 times higher than that of composite ceramics of this composition, sintered by hot pressing of commercially available powders of micron size [5]. The composite ceramics with hard TiN nanoparticles damages a counterpart by friction much less than ceramics with TiN particles of micron size, that is important e.g. for hybrid bearings in which the balls are made of ceramics, and races are made of metal [6].
High quality composite nanostructured ceramics can be obtained by sintering only a homogeneous mixture of nanopowders, which is hard to achieve because of the great tendency of nanopowders to agglomerate [1,7]. The nanoparticles stick together, forming a porous, fairly strong aggregates, poorly distributed among the nanoparticles of the other phase, making it difficult to compact. Nanopowder mixture of Si₃N₄-TiN can be obtained as ex-situ by mechanical mixing of Si₃N₄ and TiN nanopowders, prepared in advance, and in-situ by formation of nanoparticles of Si₃N₄ and/or TiN by chemical reactions from precursors in the powder mixture [7]. However, it is not always possible to achieve uniform distribution of nanoparticles through simple mechanical mixing, and after sintering, the material can be anisotropic, porous, with low strength. More uniform distribution is achieved in the case of in-situ methods for forming nanoparticles through chemical reactions from precursors inside the body of the composite. Another important advantage of in-situ methods is the significantly lower cost of powders of the precursors in comparison with the high cost of nanopowders prepared in advance and used in ex-situ methods [8].

One of the most promising in-situ methods is the method of self-propagating high-temperature synthesis (SHS), also known as combustion synthesis, which is attractive for its simplicity and efficiency and is used for producing various ceramic powders including Si₃N₄-TiN composite [9-11]. Composite powder of Si₃N₄-TiN was synthesized by burning the mixture of elemental powders of Si (6 µm) and Ti (74 µm), diluted with submicron Si₃N₄ powder (40-50 wt. %), in the atmosphere of nitrogen at 5 MPa [9]. In another work, various titanium silicides (TiSi, Ti₂Si₃, TiSi₃) were used as the source of raw materials (precursors of Si and Ti), which also were burned in a nitrogen atmosphere at a pressure of 5 MPa [10]. The use of Ti₃Si was optimal which had generated a two-phase composite powder of Si₃N₄-TiN with a particle size of 5-10 microns without impurity of free silicon. Research of regularities of combustion of samples, pressed from a mixture of powders of Si₃N₄/Ti = 1/3, in the gaseous nitrogen at the pressure in the range from 0.45 to 1.82 MPa showed that the increase in pressure contributes to the degree of nitriding of Ti: complete nitriding of titanium was achieved at 1.48 MPa in the absence of its reaction with Si₃N₄ and Si₃N₄-TiN composite formed which was free from impurities [11].

However, the above composite powders of Si₃N₄-TiN obtained in-situ by SHS are not nanoscale. Of great interest is to apply the SHS method for synthesis of nanopowder composition of Si₃N₄-TiN. This possibility can be provided by the SHS method using a powder of sodium azide NaN₃ as a nitriding reagent (the SHS-Az method) whereby nanostructural composite powders of TiN-BN and AlN-BN were synthesized on the base of using powders of halide salts of Ti, B, and Al elements to be nitrided as precursors instead of powders of the pure elements of Ti, B, and Al in the composition of the reagents [12, 13]. The aim of this work was to investigate the possibility of obtaining the composite nanopowder of Si₃N₄-TiN by the SHS-Az method using halide salts of the elements of Ti and Si as precursors of these elements.

2. Materials and methods

In the present work, powders of silicon, titanium, sodium azide and halide salts of silicon and titanium, which are produced by industry in Russia, were used as initial reagents: silicon of Kr1 brand (purity 98.0 wt. %; particle size less than 10 µm); titanium of PTM brand (99.0 %; less than 45 µm); NaN₃ (98.71 %); Na₂SiF₆ (99.1 %); (NH₄)₂SiF₆ (99.1 %); Na₂TiF₆ (98.0 %); (NH₄)₂TiF₆ (99.0 %).

All initial powders were sifted on the vibrating screen of LE-203/1 type through a set of standard sieves. If necessary, the powders were dried in a vacuum drying box at a temperature of 80 °C within 1-2 hours. A mixture of the initial powders, taken in a predetermined ratio, was prepared manually in a porcelain mortar for 5-10 minutes until a uniform distribution of components. The prepared mixture of powders (the charge) was filled in a tracing paper cup with a diameter of 30 mm and a height of 45 mm and was placed in the filter assembly made from carbonic cloth. The relative density of the powder mixture was 0.34. The assembled structure was mounted on the subject shelf of a azide SHS laboratory reactor of a constant pressure with a volume of 4.5 liters. The pressure of 4 MPa of gaseous nitrogen was created in the reactor. The arrangement of this reactor and methods of work with the
measurements of the linear velocity and the maximum combustion temperature by thermocouple method using tungsten-rhenium thermocouples TR 5/20 was described in detail in [14]. Recording the temperature and rate of combustion was carried out using an analog-to-digital converter connected to a computer.

The cooled sample was removed from the reactor and was destroyed by hand in a porcelain mortar to obtain a free-flowing powder. Then water washing the powder product of combustion was carried out to remove by-product residue, which, as a rule, was soluble in water sodium halide (its main mass escaped from the sample at high combustion temperatures). The powder was diluted with distilled water to ratio of 1:10, the resulting suspension was shaken and filtrated on a vacuum funnel. Rinsing was monitored by measuring the acid-base balance of the wash water (pH).

Shooting X-ray spectra was carried out on an automated diffractometer ARL X trA-138 using Cu-radiation with continuous scanning in the range of angles 20 from 20 to 80 degrees with a speed of 2 deg/min. A quantitative estimate of the content of different phases was carried out by measuring the ratio of intensities of analytical lines. Morphology and particle size of the powder compositions was carried out using a scanning electron microscope (SEM) Jeol JSM-6390A.

3. Results and discussion

The masses of the components of the charge in the SHS-Az systems were calculated taking into account the stoichiometric ratio of the components, wherein the amount of halogen in the halide salts was bound to fix the sodium released by the decomposition of sodium azide NaN₃ in a neutral compound: chloride or fluoride of sodium. The calculation was carried out at the following ratio of Si₃N₄ and TiN in the composite powder: Si₃N₄+TiN, 3Si₃N₄+TiN, Si₃N₄+3TiN. For example, for the system 1: “xNa₂SiF₆ + yNa₂TiF₆ + zNaN₃”, where x, y, z are numbers of moles:

\[ 3Na_2SiF_6 + Na_2TiF_6 + 16NaNaI = Si_3N_i+TiN + 24NaF + 21.5N_2; (x=3, y=1, z=16); \]

the increase of silicon halide salt Na₂SiF₆ in the initial mixture:

\[ 9Na_2SiF_6 + Na_2TiF_6 + 40NaNaI = 3Si_3N_i+TiN + 60NaF + 53.5N_2; (x=9, y=1, z=40); \]

the increase of titanium halide salt Na₂TiF₆ in the initial mixture:

\[ 3Na_2SiF_6 + 3Na_2TiF_6 + 24NaNaI = Si_3N_i+3TiN + 36NaF + 32.5N_2; (x=3, y=3, z=24). \]

The reactions for the other investigated SHS-Az systems were similarly recorded, in which only the charge compositions are given for the sake of brevity:

System 2: “x(NH₄)₂SiF₆ + y(NH₄)₂TiF₆ + zNaN₃”, (3, 1; 24; 9, 1; 60; 3, 3, 36).

System 3: “xNa₂SiF₆ + y(NH₄)₂TiF₆ + zNaN₃”, (3, 1; 18; 9, 1; 42; 3, 3, 30).

System 4: “x(NH₄)₂SiF₆ + yNa₂TiF₆ + zNaN₃”, (3; 1; 22; 9; 1; 58; 3; 3, 30).

System 5: “xTi + yNa₂SiF₆ + zNaN₃”, (1; 3; 12; 3, 3, 12; 1, 9, 36).

System 6: “xTi + y(NH₄)₂SiF₆ + zNaN₃”, (1, 3; 12; 3, 3, 18; 1, 9, 54).

System 7: “xSi + yNa₂TiF₆ + zNaN₃”, (3, 1; 4; 9, 1; 4; 3, 3, 12).

System 8: “xSi + y(NH₄)₂TiF₆ + zNaN₃”, (3, 1; 6; 9, 1; 6; 3, 3, 18).

All 24 of the SHS-Az investigated charges were capable of self-combustion, but their temperature and speed of combustion could be very different: from 600 to 1800°C and from 0.15 to 1.7 cm/s, respectively. The phase composition of the combustion products also varies greatly in different systems.

The combustion products of system 1 include a large amount of the NaF salt (from 24 to 80 wt. %) as the combustion products of this system were not subjected to water washing. This salt was not detected in the products of combustion of other systems, because NaF is highly soluble in water and was removed by washing. Titanium nitride TiN (5-18%) is produced in combustion of powder mixtures of system 1, but silicon nitride Si₃N₄ is not formed, titanium silicide TiSi₂ (12-18%) and free silicon Si (0-46%) are also formed in this case. Such powdery product is agglomerates of particles of equiaxed or spherical shape with an average particle size of 200-300 nm.

In systems 2 and 3, only TiN and Si are formed, and the more titanium nitride (from 47 to 80%), the greater halide salt of titanium (NH₄)₂TiF₆, and the more free silicon (from 20 to 53%), the greater silicon-containing halide salt. In the system 4, free titanium Ti (10-39%) is added to the phases of TiN.
and Si in the combustion products; and in the case of charge composition $x=3$; $y=3$; $z=30$, a bit of silicon nitride of $\alpha$-Si3N4 (7%) and sufficient amount of water-insoluble salt Na2TiF6 (22%) are added. This case is the only charge composition among the 12 formulas for systems 1-4, whose products of combustion contain Si3N4 along with TiN. Thus, in the SHS-Az systems 1-4 consisting of sodium azide and only precursors which are reviewed halide salts of both elements Si and Ti, the composite powder of Si3N4-TiN is not synthesized, with the exception of formula “9(NH4)2SiF6 + Na2TiF6 + 58NaN3”, whose combustion products contain only 25% TiN and 7% $\alpha$-Si3N4, and much more (68%) by-products of Si, Ti, Na2TiF6. The size of particles of different shape of the powdered product of combustion of systems 1-4 is in the range of 100-500 nm, that is, this product is ultrafine powder consisting of titanium nitride TiN, free silicon Si, and titanium silicide TiSi2 (in the case of system 1) or free titanium Ti (in the case of system 4).

To continue the study of possibility of synthesis of nanostructured composite powder of Si3N4-TiN in the SHS-Az systems, the precursor that is a halide salt of one of the elements to be nitrided was replaced by powder of this pure element: it was the titanium powder Ti in systems 5 and 6, and it was the powder of silicon Si in systems 7 and 8. Such changes led to the fact that during the combustion of the almost all charge compositions of systems 5-8, the silicon nitride was formed along with the titanium nitride (with the exception of initial mixture “Ti + 9Na2SiF6 + 36NaN3” of system 5 and mixture “3Si + 3Na2TiF6 + 12NaN3” of system 7, whose combustion did not cause the synthesis of silicon nitride). For systems 5 and 6 with the titanium powder, the content of silicon nitride in the product of combustion was small: from 13 to 19%, and in this case it was a mixture of $\alpha$-Si3N4 and $\beta$-Si3N4 for system 5, but only $\alpha$-Si3N4 for system 6. For systems 7 and 8 with the powder of silicon, the content of silicon nitride in the product of combustion could be much more: up to 41-72% of a mixture of $\alpha$-Si3N4 and $\beta$-Si3N4. It is interesting to note that the combustion products of system 6: “$xTi + y(NH4)2SiF6 + zNaN3” contain a great quantity of TiN0.30 phase (38 to 65%) along with the TiN phase (16-21%). It should also be noted that for almost all charge compositions of system 5-8, the washed combustion products contained side phases of impurities (along with the target phases of TiN and Si3N4): Ti (0-15%), Si (13-72%), and Ti5Si3 (0-9%) for system 5; a water-insoluble salt Na2SiF6 (0-10%) or Si (0-23%) for system 6; Si (6-17%) for system 7; also Si (0-10%) for system 8. And the only initial mixture “9Si + (NH4)2TiF6 + 6NaN3” of the system 8 made it possible to obtain a pure mixture of target phases: 28% TiN, 11% $\alpha$-Si3N4, 61% $\beta$-Si3N4 without any impurities which corresponds approximately to the Si3N4-TiN composition of the composite powder. The diffraction pattern of the phase composition and the morphology of particles of this composite powder are shown in figures 1 (b) and 2 (b). Figure 2 (b) demonstrates the typical relatively large columnar crystals of $\beta$-Si3N4 with a transverse size of 200-600 nm and more thin fibers and small equiaxed particles of $\alpha$-Si3N4 and TiN with a size of 100-120 nm. This mixture of ultrafine and nanosized particles can be named as nanostructured composite powder of Si3N4-TiN. The great content of $\beta$-Si3N4 in the form of large columnar crystals without impurities of free silicon can be explained by the relatively high temperature of the combustion 1800oC [15]. Much lower combustion temperature (900oC) of neighbouring formula “3Si + (NH4)2TiF6 + 6NaN3” of the same system 8 leads to the formation of significantly smaller particles TiN and Si3N4 (70-100 nm), but it is accompanied by partial nitriding the silicon (10% free silicon remains in the product of combustion), as can be seen from figures 1 (a) and 2 (a). A similar explanation can be given to results of performing the SHS-Az method with another adjacent initial mixture “3Si + 3(NH4)2TiF6 + 18NaN3” with the combustion temperature 700oC and 5% free silicon in the final product with a particle size of 80-130 nm. The combustion products of these two neighboring initial mixtures can be assigned to the nanopowders, but they contain impurities of free silicon (5-10%) and much more TiN (57-81%) compared to Si3N4 (14-33%), which corresponds in moles approximately to the composition of (4-13)TiN-Si3N4-(1,5-1,8)Si.
Figure 1. XRD patterns of the washed products of combustion for system 8:
\( \alpha xSi + y(NH_4)_2TiF_6 + zNaN_3 \): (a) \( x=3; y=1; z=6 \); (b) \( x=9; y=1; z=6 \).

Figure 2. SEM image of particles of washed products of combustion for system 8:
“\( xSi + y(NH_4)_2TiF_6 + zNaN_3 \)” : (a) \( x=3; y=1; z=6 \); (b) \( x=9; y=1; z=6 \).
4. Conclusion
The obtained results show that the combustion of powder mixtures of sodium azide NaN$_3$ only with precursors, which are halide salts of silicon and titanium: Na$_2$SiF$_6$, (NH$_4$)$_2$SiF$_6$, Na$_2$TiF$_6$, (NH$_4$)$_2$TiF$_6$, does not allow producing a composite powder of Si$_3$N$_4$-TiN, because the phase of silicon nitride Si$_3$N$_4$ is not formed, and after water washing, ultrafine powdered product of combustion consists of only one target phase of titanium nitride TiN and a large amount of impurities of side phases. Replacement of the halide salt of one of the elements (Si or Ti) on the powder of this element in the initial mixture of SHS-Az system leads to the formation of silicon nitride together with titanium nitride. In this case with Ti powder, the content of silicon nitride in the product of combustion is small: from 13 to 19%, but with Si powder, the content of silicon nitride is much larger: can go up to 41-72% of a mixture of α-Si$_3$N$_4$ and β-Si$_3$N$_4$. The least amount of impurities (from 0 to 10% of free silicon) was obtained in combustion of initial mixtures of system 8: “xSi + y(NH$_4$)$_2$TiF$_6$ + zNaN$_3$”. Burning two mixtures of this system (x=3; y=6 and x=3; y=3; z=18) occurred at a high temperature of 700-900°C and led to the formation of nanopowder composites: (57-81%)TiN-(14-33%)Si$_3$N$_4$-(5-10%)Si. And the only initial mixture “9Si + (NH$_4$)$_2$TiF$_6$ + 6NaN$_3$”, that burned at a high temperature 1800°C, allowed us to obtain a pure mixture of target phases: 28% TiN, 11% α-Si$_3$N$_4$, and 61% β-Si$_3$N$_4$ without impurities, which can be described as a nanostructured composite powder of Si$_3$N$_4$-TiN consisting of ultrafine columnar crystals of β-Si$_3$N$_4$ with a transverse size of 200-600 nm and nano-sized fibers and equiaxial particles of α-Si$_3$N$_4$ and TiN with a size of 100-120 nm.

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