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Preparation of ceramic nitride-carbide composition AlN–SiC by SHS method using halide salt and sodium azide

Aleksandr Amosov, Yuliya Titova, Dmitriy Maidan,
Kirill Smetanin

Samara State Technical University, Samara, Russia
Vyksa Metallurgical Plant, Vyksa, Russia

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Properties and application AlN–SiC ceramics

Properties of composite ceramics of aluminum nitride with silicon carbide:

- ✓ good thermal conductivity;
- ✓ corrosion resistance;
- ✓ better mechanical characteristics [C. K. Unni and D. E. Gordon, “Mechanical properties of monolithic AlN and SiCw/AlN composites”, *J. Mater. Sci.*, vol. 30, pp. 1173–1179, 1995].

Silicon carbide has a crystal structure similar to aluminum nitride, and can form a single-phase homogeneous solid solution with it at $T > 1960\text{ }^{\circ}\text{C}$, which leads to an improvement in **bending strength** and **fracture toughness**, that is, to a **reduction in brittleness** [A. Zangvil, R. Ruh, “Phase relationship in the silicon carbide-aluminum nitride system”, *J. Am. Ceram. Soc.*, vol. 71, pp. 884–890, 1988].

But even without the formation of a solid solution, **in the two-phase state** of sintered spatially separated powdery components AlN and SiC, **AlN–SiC composites** have significantly **better toughness** and **thermal shock resistance**.

Composite ceramics AlN–SiC proved to be promising for use not only in metallurgy and mechanical engineering as a structural material working under mechanical load at high temperatures, but also in electronics as a new high-temperature ceramics that has a high absorption capacity of microwave radiation and can be used in high-power amplifiers and microwave components. [P. Gao, Ch. Jia, W. Cao, C. Wang, D. Liang, G. Xu, “Dielectric properties of spark plasma sintered AlN/SiC composite ceramics”, *Int. J. Miner. Metallur. Mater.*, vol. 21, no. 6, pp. 589, 2014].

Methods for producing AlN–SiC ceramics

Traditional energy-intensive methods for producing AlN–SiC ceramics:

- ✓ **carbothermic reduction of silica and alumina in a nitrogen atmosphere** [D. H. A. Besisa, E. M. M. Ewais, Ya. M. Z. Ahmed, F. I. Elhosiny, T. Fend, D. V. Kuznetsov, “Investigation of microstructure and mechanical strength of SiC/AlN composites processed under different sintering atmospheres”, *J. Alloy Compd.*, vol. 756, pp. 175-181, 2018];
- ✓ **pressureless sintering SiC and AlN ceramic powders** [D. H. A. Besisa, E. M. M. Ewais, Ya. M. Z. Ahmed, F. I. Elhosiny, T. Fend, D. V. Kuznetsov, “Thermal shock resistance of pressureless sintered SiC/AlN ceramic composites”, *Mater. Res. Express*, vol. 5, no. 1, paper 015506, 2018];
- ✓ **hot pressing SiC and AlN ceramic powders** [R. Ruh, A. Zangvil, “Composition and properties of hot-pressed SiC-AlN solid solution”, *J. Am. Ceram. Soc.*, vol. 65, pp. 260-265, 1982].

These methods for producing AlN–SiC ceramics require a high temperature of about 2000° C and a long exposure time of up to several hours.

Methods for producing AlN–SiC ceramics

More modern methods for producing AlN–SiC ceramics:

- **spark plasma sintering (SPS)** [P. Gao, Ch. Jia, W. Cao, C. Wang, D. Liang, G. Xu, “Dielectric properties of spark plasma sintered AlN/SiC composite ceramics”, *Int. J. Miner. Metallur. Mater.*, vol. 21, no. 6, pp. 589, 2014];
- **self-propagating high-temperature synthesis (SHS)** [C. Kexin, J. Haibo, H. P. Zhou, J. M. F. Ferreira, “Combustion synthesis of AlN-SiC solid solution particles”, *J. Eur. Ceram. Soc.*, vol. 20, pp. 2601–2606, 2000].
- In the case of the SPS method, the energy consumption is noticeably lower, since the SPS process is performed at a temperature of about 1600° C and takes about 10 minutes but requires expensive equipment. **The SHS method is much more economical, since the synthesis of the AlN–SiC composite occurs due to its own combustion heat generation in very simple equipment from cheap starting reagents, most often Al, Si, C (soot) powders and N₂ gas. Therefore, much attention is paid to the development of the SHS method.**

Application SHS method for preparation of AlN–SiC

The application of the energy-efficient SHS method for preparation of AlN–SiC was first investigated in [H. Xue and Z. A. Munir, “The synthesis of composites and solid solutions of SiC–AlN by field-activated combustion”, *Scripta Mater.*, vol. 35, no. 8, pp. 919–982, 1996]. Here, silicon nitride powder Si_3N_4 was used as a solid nitrogen source, and the reaction equation:



Reaction is strongly exothermic with an adiabatic temperature of 2502 K, which should ensure its self-propagation in the combustion mode, **but the combustion could not be carried out without the application of an electric field with an intensity E of at least 8 V/cm**. The temperature and velocity of combustion increased with increasing field strength, and in the interval of $8 < E < 25$ V/cm, the combustion products were composite 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 product of burning contained impurities of silicon and carbon.

Application SHS method for preparation of AlN–SiC

In [C. Kexin, J. Haibo, H.P. Zhou, and J.M.F. Ferreira, “Combustion synthesis of AlN-SiC solid solution particles”, *J. Eur. Ceram. Soc.*, vol. 20, pp. 2601–2606, 2000], the formation of ceramics was studied by reaction with gaseous nitrogen source:



where x varied from 0 to 0.85, and the nitrogen pressure was 3, 8, or 12 MPa. The combustion led to the formation of a solid solution of AlN–SiC without impurity of unreacted Al and Si only at sufficiently high nitrogen pressures: 12 MPa for $x = 0.3$ and 8 MPa for $x = 0.5$ or 0.6 carbon.

Even higher nitrogen pressures (50 and 70 MPa) were used for SHS of solid AlN–SiC solution from other components [I.P. Borovinskaya, T. G. Akopdzhanyan, E.A. Chemagina, and N.V. Sachkova, “Solid solution $(\text{AlN})_x(\text{SiC})_{1-x}$ ($x=0.7$) by SHS under high pressure of nitrogen gas”, *Int. J. Self-prop. High-Temp. Synth.*, vol. 27, no. 1, pp. 33-36, 2018]:



At a pressure of 50 MPa, the combustion temperature was 1400°C and the combustion product along with a solid solution of $\text{AlN}_{0.7}\text{SiC}_{0.3}$ contained a large amount of unreacted Al (up to 12wt.%) and Si. The pressure increase up to 70 MPa led to an increase in the combustion temperature up to 2050° C and a decrease in the Al impurity content up to 0.5wt.%.

SHS-Az method

Azide technology of SHS, which is abbreviated as **SHS–Az**, is based on the use of a solid powder of sodium azide (NaN_3) as a nitriding reagent in the SHS process instead of gaseous or liquid nitrogen for synthesis of nitrogen-containing compounds (nitrides or carbonitrides).

In this research, for the first time, the use of the azide SHS, in which the nitriding reagent is not nitrogen gas, but a powder of sodium azide NaN_3 , as well as halide salts [G.V. Bichurov, “Halides in SHS azide technology of nitrides obtaining”, in “Nitride Ceramics: Combustion synthesis, properties, and applications”, A.A. Gromov and L.N. Chukhlomina, Eds. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA, pp. 229-263, 2015], is investigated for the preparation of AlN–SiC ceramics.

The process of azide SHS provides great opportunities for regulating the dispersion and structure of synthesized ceramic powders and bringing them to the nanoscale level. Experience has been gained in using the azide SHS process to produce aluminum nitride and silicon carbide nanopowders separately from each other [Y. V. Titova, A. P. Amosov, A. A. Ermoshkin, Y. M. Markov, T. N. Khusainova, and A.V. Popova, “Preparation of silicon-carbide nanopowder and compositions based on it using SHS azide technology”, *Rus. J. Non-Ferr. Met.*, vol. 55, no. 6, pp. 620-626, 2014.].

Equations of chemical reactions for the AlN–SiC synthesis



On the base of our experience, equations of chemical reactions in the system " $y\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + (y + 1)\text{C}$ " are selected in this research for the synthesis of the AlN–SiC composition:

- $\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 2\text{C} = 2\text{SiC} + 20\text{AlN} + 6\text{NaF} + 4\text{H}_2$;
- $4\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 5\text{C} = 5\text{SiC} + 20\text{AlN} + 6\text{NaF} + 4\text{H}_2$;
- $6\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 7\text{C} = 7\text{SiC} + 20\text{AlN} + 6\text{NaF} + 4\text{H}_2$;
- $8\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 9\text{C} = 9\text{SiC} + 20\text{AlN} + 6\text{NaF} + 4\text{H}_2$;
- $10\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + 11\text{C} = 11\text{SiC} + 20\text{AlN} + 6\text{NaF} + 4\text{H}_2$.

The following raw materials were used: KrO silicon powder (the base substance content $\geq 99.1\text{wt.}\%$, the average particle size is $5\ \mu\text{m}$), PA-4 aluminum powder ($\geq 98.00\text{wt.}\%$, $40\ \mu\text{m}$), ammonium hexafluorosilicate powder $(\text{NH}_4)_2\text{SiF}_6$ ($\geq 98.97\text{wt.}\%$, $20\ \mu\text{m}$), sodium azide powder NaN_3 ($\geq 98.71\text{wt.}\%$, $100\ \mu\text{m}$), P701 carbon black (soot) ($\geq 99.7\text{wt.}\%$, the average particle size is $70\ \text{nm}$, the average size of agglomerates is $1\ \mu\text{m}$).

Thermodynamic analysis of AlN-SiC possibility synthesis



Results of thermodynamic calculations of adiabatic temperature and composition of reaction products of the system " $y\text{Si} + 20\text{Al} + 6\text{NaN}_3 + (\text{NH}_4)_2\text{SiF}_6 + (y + 1)\text{C}$ " are shown in Table:

Y, mole	Adiabatic temperatures, K	Quantity, mole									
		Al_g	F_g	H_g	Na_g	H_{2g}	N_{2g}	NaF_g	NaF_l	AlN_l	SiC_s
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

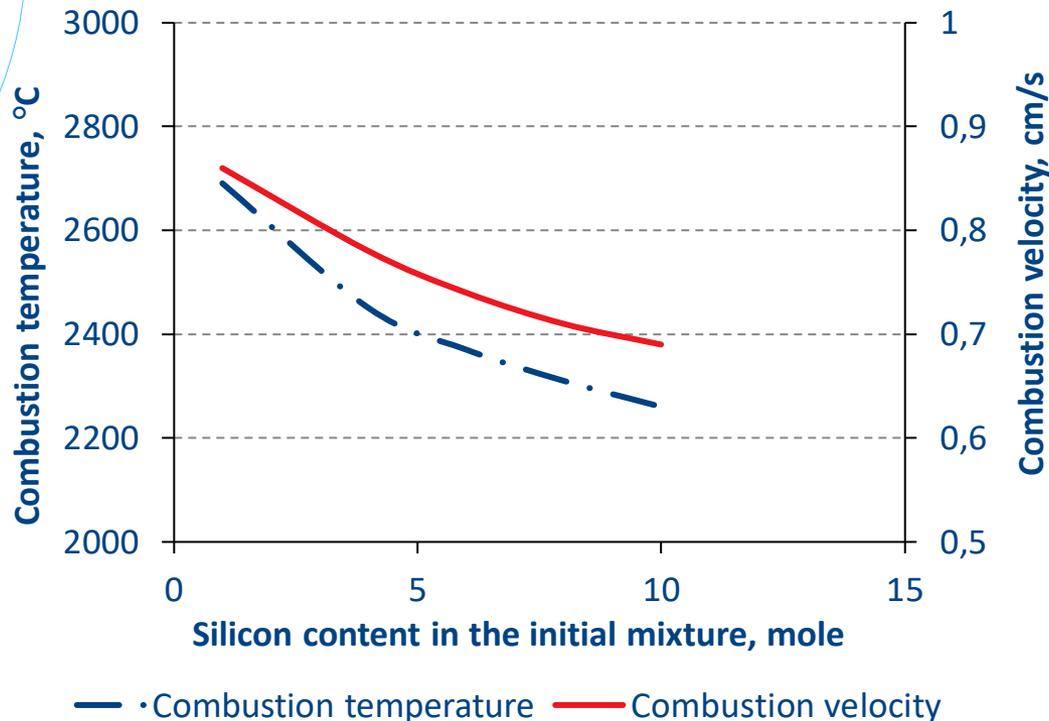
T_{ad} of reactions are high enough to realize the combustion mode, and the condensed reaction products are the target phases of AlN and SiC with impurity of a water-soluble side salt NaF, which is easily removed by water washing.

Results of experimental studies



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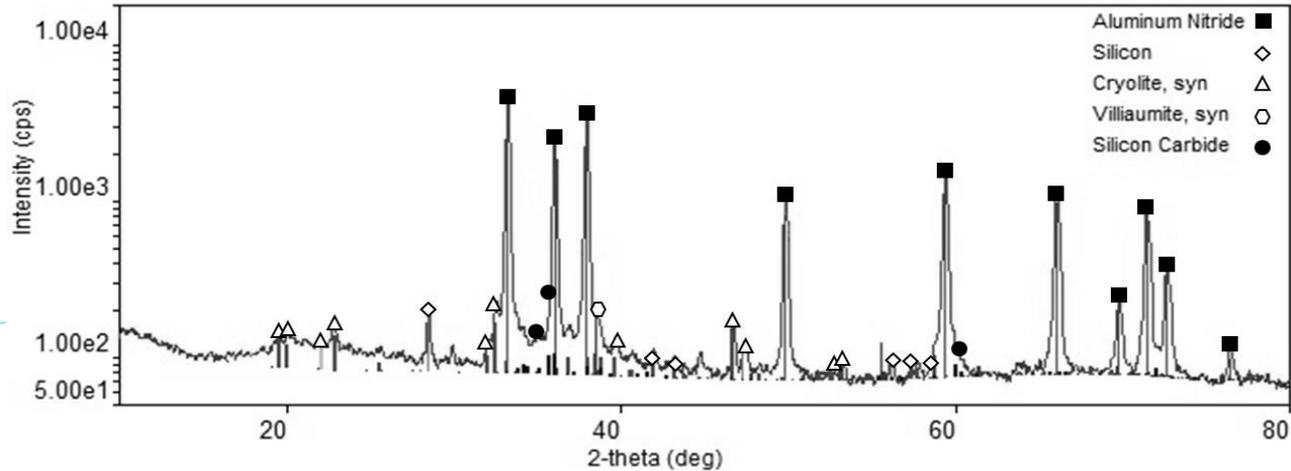
The results of experimental studies of the maximum temperature and linear velocity of combustion are shown in Figure:



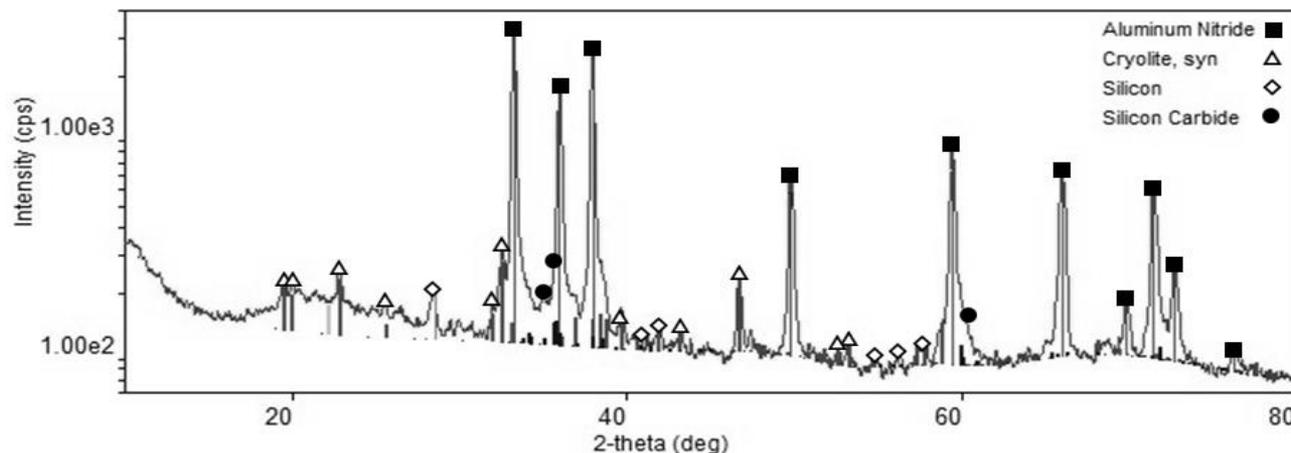
Experimental T_{\max} are significantly lower than the calculated T_{ad} due to heat loss, which is not taken into account in thermodynamic calculations. The temperature and velocity of combustion decrease with increasing content of silicon and carbon (parameter y), which corresponds to the results of calculations.

XRD pattern of washed combustion products

Of the mixture " $\text{Si}+20\text{Al}+6\text{NaN}_3+(\text{NH}_4)_2\text{SiF}_6+2\text{C}$ "

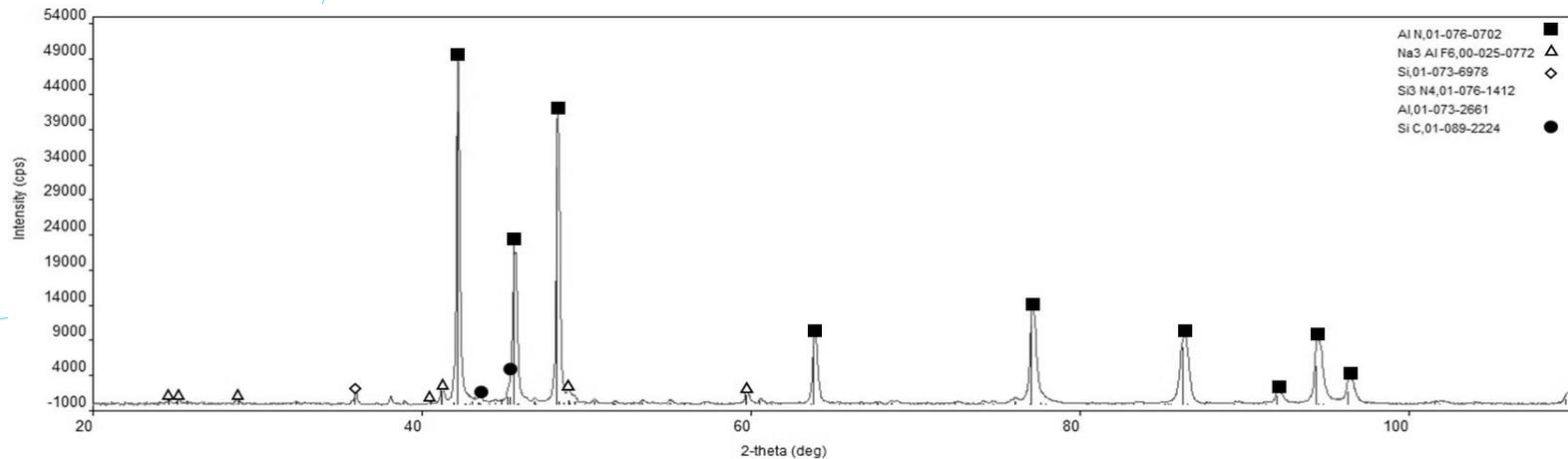


Of the mixture " $4\text{Si}+20\text{Al}+6\text{NaN}_3+(\text{NH}_4)_2\text{SiF}_6+5\text{C}$ "

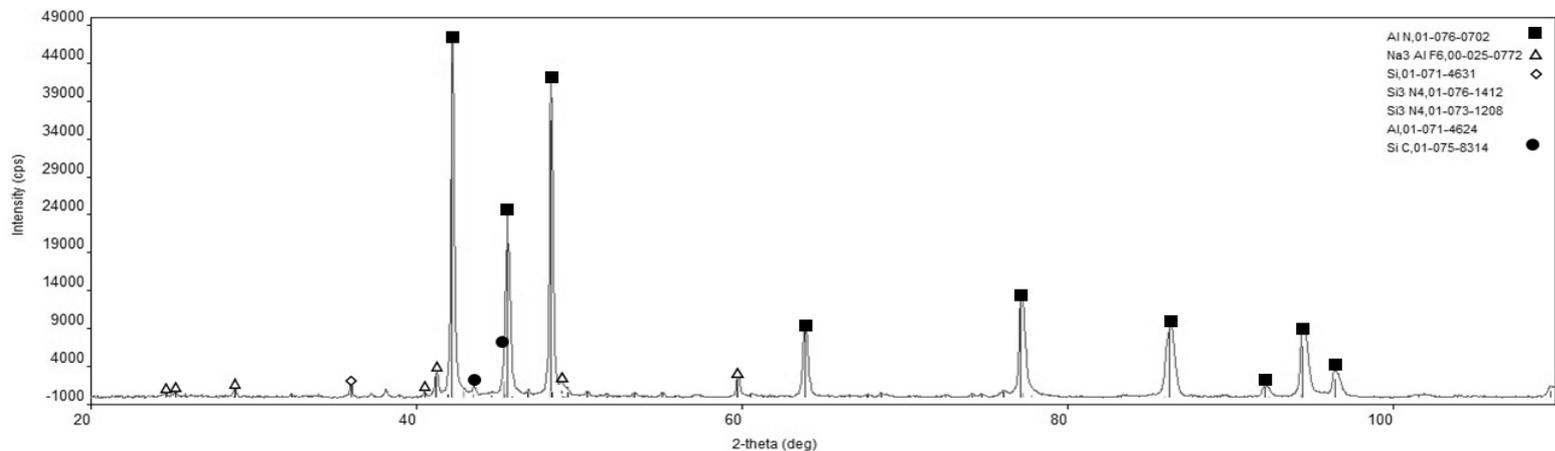


XRD pattern of washed combustion products

Of the mixture "6Si+20Al+6NaN₃+(NH₄)₂SiF₆+7C"



Of the mixture "8Si+20Al+6NaN₃+(NH₄)₂SiF₆+9C"



Phase composition in washed combustion products

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

Phase composition in washed combustion products



The Table and the XRD pattern show that the target composition of AlN-SiC can be synthesized during the combustion of all mixtures, but the reaction products also include a quite significant content of from 7.7 to 15.5 wt.% of a water-insoluble side phase of Na_3AlF_6 (cryolite) and an impurity of free silicon (0.7–0.9wt%).

These results of the experimental study show the composition of the cooled reaction products of SHS-Az and therefore differ significantly from the results of thermodynamic calculation of the product composition of AlN and SiC with impurity of about 6 wt.% of a water-soluble side salt NaF at the maximum possible adiabatic temperature of SHS-Az reactions. When cooling, the composition of products changes, which leads to the formation of cryolite Na_3AlF_6 , which can not exist at a temperature above 1000°C , since it melts and decomposes at this temperature.

Phase composition in washed combustion products



It should be emphasized that, despite the high combustion temperatures ($> 2200^{\circ}\text{C}$), which are over the critical value of 1960°C , the SHS reaction product is not a single-phase solid solution of AlN-SiC , but a composition of two phases: AlN and SiC .

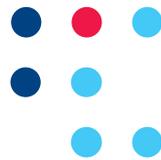
This can be explained by the presence of a significant amount of cryolite by-product, which separates the AlN and SiC phases and prevents the formation of their solid solution.

SEM magnification of combustion product particles



These results of the study of the surface topography and morphology of the powder particles of the synthesized product show that when burning mixtures with a silicon content of 1-4 mole, mainly equiaxed particles of aluminum nitride powder with a size from 150 nm to 1 μm are formed, which is consistent with the results of energy-dispersive analysis of the content of chemical elements in the combustion product.

The combustion products of mixtures containing 6 mole and more of silicon are equiaxed particles of aluminum nitride and silicon carbide of a smaller size from 100 to 600 nm.



Conclusion



Thus, it is shown that when using the azide SHS method, it is possible to synthesize the target **ceramic nitride-carbide powder composition AlN–SiC in the form of equiaxed particles with an ultrafine size from 100 nm to 1 μm**, but the washed condensed synthesis products, **along with the target phases AlN and SiC**, also include a water-insoluble admixture of cryolite Na_3AlF_6 in noticeable amounts from 7.7 to 15.5 wt.%.

The product of azide SHS of this composition can be used for liquid-phase hybrid reinforcement of aluminum-matrix composites with ultrafine powders **AlN and SiC**, in which **the cryolite plays a positive role of flux and is not included in the final composition of the composite, without contaminating it.**

[Y. V. Titova, A. V. Sholomova, A. A. Kuzina, D. A. Maidan, and A. P. Amosov, “Azide SHS of aluminum nitride nanopowder and its application for obtaining Al-Cu-AlN cast nanocomposite”, *IOP Conf. Series: Mater. Sci. Eng.*, vol. 156, article no. 012037, 2016].

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Amosov A. P., Titova Yu. V.,
Maidan D. A., Smetanin K.A.

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