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Self-propagating high-temperature synthesis of AlN–TiC powder composition using sodium azide and C_2F_4 fluoroplastic

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Abstract: Producing powder compositions using conventional processing technology can lead to the formation of large agglomerates and, therefore, makes it difficult to obtain a uniform microstructure. The production of composites by self-propagating high-temperature synthesis can reduce costs and the number of technological stages, as well as lead to obtaining composites that are more homogeneous. Synthesis by the combustion of mixtures of powder reagents of sodium azide (NaN_3), fluoroplastic (C_2F_4), aluminum and titanium with different ratios of reagents in a nitrogen gas atmosphere at a pressure of 4 MPa was used for the production of a highly dispersed powder ceramic AlN–TiC composition. Thermodynamic calculations have confirmed the possibility of synthesis of AlN–TiC compositions of different formulations in combustion mode. The dependences of temperature and combustion rate on the composition of the initial mixtures of reagents were experimentally determined for all stoichiometric reaction equations. The study have shown that the experimentally found dependences of combustion parameters on the ratio of the initial components correspond to the theoretical results of thermodynamic calculations. The formulation of the synthesized composition differs from the theoretical composition by a lower content of target phases and the formation of Al_2O_3, Na_3AlF_6 and TiO_2 side phases. The powder composition consists of aluminum nitride fibers with a diameter of 100–250 nm and ultradisperse particles of predominantly equiaxed and lamellar shapes with a particle size of 200–600 nm. As the combustion temperature increases to produce the largest amount of titanium carbide phase, the particle size increases to the micron level.

Keywords: combustion; self-propagating high-temperature synthesis; ceramic powder; nitride-carbide composition; sodium azide; fluoroplastic (polytetrafluoroethylene); aluminum nitride; titanium carbide.

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INTRODUCTION

Currently, materials with low weight, high strength, corrosion resistance and wear resistance are top requested by the automotive and aerospace industries [1; 2]. Although aluminium alloys satisfy the requirements for light weight (low density), they have low strength and hardness. Aluminium alloys are characterised by excellent formability in addition to high thermal conductivity and good corrosion resistance [3].

Numerous studies on aluminium-based metal-matrix composites (MMCs) have found that Al-based MMCs reinforced with TiC particles, due to their excellent mechanical and physical properties, are especially attractive for use in the aerospace, automotive, defense and construction industries [4; 5]. In view of the above, TiC is attracting growing interest among researchers due to its high hardness, elastic modulus, low density, relatively high temperature stability, and good wettability with aluminium [5].

The compressive strength of the nanocomposite positively correlates to the content of the reinforcing component. The maximum compressive strength of the highly reinforced nanocomposite is 233 MPa, which is much higher than that of unreinforced aluminium alloy. Nanocomposite containing up to 0.5 wt. % of TiC has a lower relative density due to the predominance of hardening during processing. Using a finer powder will increase the relative density. The highly hardened nanocomposite exhibited a hardness of 1.18 GPa after sintering at a temperature of 873 K. This value is three times higher than that of the unreinforced microcrystalline sample, and two times higher than that of the unreinforced nanocrystalline sample [6].

When synthesizing the AlN–TiC composition, in addition to the target phases of aluminium nitride (AlN) and titanium carbide (TiC), a certain amount of ternary aluminium carbonitride, including Al_5C_3N and $Al_6C_3N_2$, is formed in the Al–C–N system. These materials are usually produced at a relatively high sintering temperature. In [7], it is indicated that Al_5C_3N is formed only when samples are subjected to hot pressing at ~2073 K.

Compared to other methods for producing ceramic compositions, combustion synthesis, or high-temperature sintering with self-propagation of a combustion wave, is of interest due to obvious advantages, such as short process duration, low energy consumption and high yield of pure products. Combustion synthesis has been used to synthesize many materials [8], including aluminium nitride (AlN) and carbide (TiC).

The possibility of producing a $Ti_2AlC_{0.5}N_{0.5}$ solid solution from powder mixtures consisting of Ti, Al_4C_3 and Al or AlN was studied by self-propagating, high-temperature synthesis (SHS) in gaseous nitrogen. The molar ratio of the three powder reagents was Ti : Al_4C_3 : Al (AlN) = = 2 : 1/6 : 1/3. For both types of samples, increasing the nitrogen pressure from 0.45 to 1.82 MPa increases the combustion temperature and thus accelerates the reaction front propagation. Compared to inert AlN, Al particles reacted vigorously with Ti and N_2 during the SHS process, resulting in higher reaction exothermicity for the Al-containing sample than for the AlN-containing sample. The $Ti_2AlC_{0.5}N_{0.5}$ solid solution was the main phase in the final products from Ti–Al_4C_3–Al powder compacts. However, increasing the nitrogen pressure had a negative effect on the release of $Ti_2AlC_{0.5}N_{0.5}$, since Ti was excessively nitride, and Al reacted with nitrogen. When AlN was used to replace Al, the formation of $Ti_2AlC_{0.5}N_{0.5}$ was deteriorated, due to weak exothermicity and TiAl deficiency. Moreover, Ti(C,N) titanium carbonitride predominated in the products synthesized from Ti–Al_4C_3–AlN samples at nitrogen pressures of 1.48 and 1.82 MPa. This means that the use of aluminium nitride instead of aluminium is undesirable for producing $Ti_2AlC_{0.5}N_{0.5}$ by synthesis using gaseous nitrogen [9; 10].

The SHS process is attractive, because of its simplicity and economic efficiency; it is one of the promising in situ methods for the direct synthesis of ceramic powders within the desired composition from a mixture of initial cheap reagents. SHS using sodium azide and gasifying halide salts has such distinctive features as relatively low combustion temperatures, the formation of a large amount of intermediate vapour and gaseous reaction products, as well as final condensed and gaseous by-products separating the particles of the target powders, which allows synthesizing highly dispersed (<1 μm) AlN–TiC powder composition [11; 12].

Synthesis of both target phases directly in the bulk of a composite powder (in situ) from inexpensive reagents, and not in advance with subsequent mechanical mixing (ex situ) of expensive nanopowders, makes it possible to achieve high homogeneity of the mixture of synthesized inexpensive highly dispersed nitride-carbide compositions.

The purpose of this study is to use a fluoroplastic activating additive (C_2F_4) to produce a highly dispersed composition of AlN–TiC powders with different phase ratios, using the method of azide self-propagating high-temperature synthesis.

METHODS

To synthesize target AlN–TiC compositions with a molar phase ratio from 1:4 to 4:1, the following chemical reaction equations were used:

$$2Al+2Ti+4NaN_3+C_2F_4=2AlN+2TiC+4NaF+5N_2; \quad (1)$$

$$Al+2Ti+4NaN_3+C_2F_4=AlN+2TiC+4NaF+5.5N_2; \quad (2)$$

$$Al+4Ti+8NaN_3+2C_2F_4=AlN+4TiC+8NaF+11.5N_2; \quad (3)$$

$$4Al+2Ti+4NaN_3+C_2F_4=4AlN+2TiC+4NaF+4N_2; \quad (4)$$

$$8Al+2Ti+4NaN_3+C_2F_4=8AlN+2TiC+4NaF+0.5N_2. \quad (5)$$

If we move from the formulation of AlN–TiC compositions expected, according to these stoichiometric equations in moles to the formulation in wt. %, taking into account the molar weights of the phases, the following ratios of the expected theoretical formulation of the synthesized AlN–TiC compositions after removal of the NaF water-soluble by-salt are obtained:

(1): AlN+TiC=40.6 % AlN+59.4 % TiC;

(2): AlN+2TiC=25.5 % AlN+74.5 % TiC;

(3): AlN+4TiC=14.6 % AlN+85.4 % TiC;

(4): 2AlN+TiC=57.8 % AlN+42.2 % TiC;

(5): 4AlN+TiC=73.3 % AlN+26.7 % TiC.

To predict the possibility of reactions occurring in the combustion mode by determining thermal effects (enthalpy), adiabatic temperatures and compositions of synthesis products, corresponding thermodynamic calculations were carried out using the Thermo computer program.

In the experimental study, the following raw materials were used: ASD-4 grade aluminium powder (main substance content is ≥98.8 wt. %, average particle size is 5 μm), PTM grade titanium (≥99.7 wt. %, 5 μm), classification "Ch" fluoroplastic powder (≥99.1 wt. %, 20 μm), classification "Ch" sodium azide powder (≥98.71 wt. %, 100 μm). The combustion of a mixture of initial reagents (charge) with a bulk relative density of 0.4 was carried out in a tracing paper cup with a diameter of 30 mm, and a height of 45 mm wrapped in carbon fabric using a SHS-Az laboratory reactor with a volume of 4.5 l, with two thermocouples at a nitrogen pressure of 4 MPa.

Using thermocouples (thermocouple wire of VR5-20 type, TU 48-1941-73, Moscow Electric Lamp Plant OJSC, Moscow, Russia), combustion temperatures were measured, and combustion rates were calculated. Using a pressure gauge (MP4-U, 1.5 kgf/cm^2, JSC Manotom, included in the general installation of a constant pressure SHS reactor with a fume hood (armored cabin)), the change in pressure in the reactor during the combustion process was determined.

The resulting synthesis product was weighed and compared with the theoretical yield from reactions (1)–(5). The combustion product was washed with distilled water to remove water-soluble impurities, and the acid-base balance of the washing water was determined, to identify the presence of free sodium in the combustion product, and the completeness of the chemical reaction. Washing consisted of diluting the powders with distilled water in a ratio of 1:10 at room temperature, stirring the resulting suspension, and then filtering the target products in a vacuum funnel for 5–10 min. The pH=7 value indicates the absence of free fluorine/sodium, which indirectly confirms the completeness of the conversion of the starting components into reaction products.

An experimental study of the combustion process was carried out using thermocouple measurements of temperatures and combustion rates. The study of combustion products using scanning electron microscopy and X-ray phase analysis showed that the application of azide self-propagating high-temperature synthesis with the addition of C_2F_4 to the initial charge as a carbon source, allows synthesizing AlN–TiC powder composition of various formulations.

The phase composition of the synthesized combustion products was determined using an ARL X'tra automated X-ray diffractometer (Thermo Scientific). Cu radiation was used with continuous scanning in the 2θ angle range from 20 to 80° at a speed of 2 degrees/min. The obtained spectra were processed using the WinXRD application package. Quantitative phase analysis was carried out using the full-profile analysis method (Rietveld method) with the help of the PDXL 1.8.1.0 program using the PDF-2009 and COD-2019 crystallographic databases. The essence of the method is to use profile intensities instead of integral ones, which allows extracting the maximum amount of information contained in step-by-step experiments of scanning powder diffraction patterns. The study of the morphology of powder particles was carried out on a Jeol JSM-6390A scanning electron microscope with a JeolJED-2200 attachment.

RESULTS

Thermodynamic analysis of the possibility of forming compositions

Table 1 presents the results of thermodynamic calculations of combustion reactions (1)–(5) using the Thermo program.

From the presented data, it is clear that all reactions have high adiabatic temperatures, sufficient both for the implementation of the SHS process in the combustion mode, and for the formation of the target phases of aluminium nitride and titanium carbide. The reaction enthalpy increases and strongly depends on the ratio of the nitride and carbide phases in the reaction products. The minimum enthalpy value corresponds to equation (1), the maximum reaction enthalpy value is calculated for equation (5). The equilibrium concentrations of reaction products correspond to the right-hand sides of equations (1)–(5), i.e., the target phases of aluminium nitride (AlN) and titanium carbide (TiC).

Experiment results

The results of the experimental determination of the temperature (T_C) and rate (U_C) of combustion of SHS-Az charges for the synthesis of AlN–TiC ceramic nitride-carbide compositions are presented in Table 2.

Table 1. *Results of thermodynamic analysis of reactions (1)–(5)*
Таблица 1. *Результаты термодинамического анализа реакций (1)–(5)*

Composition of the initial mixture of powders in reactions	Enthalpy, kJ	Adiabatic temperature, K	Quantity, mole			
			AlN	TiC	NaF	N_2
$2Al+2Ti+4NaN_3+C_2F_4$	−2139	2768	1.00	4.00	4.00	5.50
$Al+2Ti+4NaN_3+C_2F_4$	−2298	2798	1.00	2.00	4.00	5.50
$Al+4Ti+8NaN_3+2C_2F_4$	−2616	2920	2.00	2.00	4.00	5.00
$4Al+2Ti+4NaN_3+C_2F_4$	−3252	3120	4.00	2.00	4.00	4.00
$8Al+2Ti+4NaN_3+C_2F_4$	−4524	3278	8.00	2.00	4.00	2.00

From the data presented in Table 2, it can be seen that the experimental maximum combustion temperatures correspond to the calculated values of adiabatic temperatures in Table 1, but are slightly lower than the latter due to heat loss in the combustion zone. The minimum values of temperature and rate of combustion are observed in equation (1), which corresponds to the phase ratio AlN : TiC = 1 : 1.

Fig. 1 presents the results of microstructural analysis of the combustion products of the initial mixtures of powders (charges), represented by reaction equations (1)–(5), after water washing from the by-product water-soluble NaF salt. Fig. 1 a shows that the combustion products of the reaction charge (1), consist predominantly of aluminium nitride fibres with a diameter of 100–250 nm, and ultrafine plate-shaped particles of titanium carbide with a size of 200–600 nm. When the aluminium content in the initial mixture is reduced by 2 times (equation 2, Fig. 1 b), the combustion product is represented mainly by plate-shaped titanium carbide particles, with a size of 200–600 nm, and a small amount of aluminium nitride fibres with a diameter of 100–200 nm. When the aluminium content is reduced by half with a simultaneous increase in the titanium content by two times, compared to the initial mixture (equation (3), Fig. 1 c), the combustion products are titanium carbide particles of equiaxial and plate shapes with a size of 200–600 nm. In Fig. 1 d and 1 e, aluminium nitride fibres with diameters of 100–300 and 100–400 nm, respectively, are clearly visible.

The results of qualitative and quantitative X-ray phase analysis of the combustion products of the initial mixtures of powders (charges), represented by reaction equations (1)–(5), after the water washing operation are summarised in Table 3.

The results of X-ray phase analysis (Table 3) show the formation of five phases: target phases of aluminium nitride (AlN) and titanium carbide (TiC), side phases of sodium aluminium hexafluoride (Na_3AlF_6), as well as titanium and aluminium oxides (TiO_2, Al_2O_3). Thus, the reaction products (1) consist of 32.5 % of AlN, 47.4 % of TiC, 6.5 % of Na_3AlF_6, 12.8 % of TiO_2, and 0.8 % of Al_2O_3. Therefore, the synthesized composition differs from the expected theoretical 40.6 % AlN – 59.4 % TiC composition (1) in the lower content of target phases, while their ratio is maintained, and the presence of reaction by-products, the total amount of which is 20.1 %.

When the aluminium content is reduced by half compared to the charge (1), the combustion products of the charge (2) also consist of five phases: AlN – 20.6 %, TiC – 61.2 %, TiO_2 – 13.1 %, Al_2O_3 – 0.3 %, and Na_3AlF_6 – 4.8 %. In general, the formulation of the synthesized composition differs from the expected theoretical 25.5 % AlN – 74.5 % TiC composition (2) by an insufficient content of target phases, while their ratio is maintained, and the total amount of reaction by-products is slightly less than for the charge (1) – 18.2 %.

When the aluminium content is reduced by half, with a simultaneous increase in the titanium content by two times compared to the charge (1), the combustion products of the charge (3) contain only three phases: AlN – 14.4 %, TiC – 71.5 %, TiO_2 – 14 .5 %, with the largest amount of titanium carbide. This composition differs from the expected 14.6 % AlN – 85.4 % TiC composition (3) by the presence of titanium oxide.

As a result of combustion of the charge (4) with the addition of four moles of aluminium compared to the charge (1) and the same titanium content, four phases are formed: AlN – 53.2 %, TiC – 31.4 %, TiO_2 – 11.6 %, and Al_2O_3 – 3.8 %. The formulation of the synthesized composition differs from the theoretical 57.8 % AlN – 42.2 % TiC composition (4) by the presence of titanium and aluminium oxides in an amount of 15.4 %.

With an increase in aluminium content four times compared to the charge (1), and the same titanium content, the combustion products are phases similar to the charge (4): AlN – 66.4 %, TiC – 15.6 %, TiO_2 – 11.9 %, and Al_2O_3 – 6.1 %. This composition also differs from the theoretical 73.3 % AlN – 26.7 % TiC composition (5) by the presence of by-product titanium and aluminium oxides in an amount of 18 %.

DISCUSSION

The presented experimental results of the synthesis of a composition of highly dispersed AlN–TiC ceramic powders were obtained using fluoroplastic (C_2F_4), with specified

Table 2. *Combustion parameters of initial powder mixtures of reactions (1)–(5)*
Таблица 2. *Параметры горения исходных порошковых смесей реакций (1)–(5)*

Composition of the initial mixture of powders in reactions	Combustion temperature, T_C, °C	Combustion rate, U_C, cm/s	Maximum pressure, MPa	pH	Practical yield of combustion products, g
$2Al+2Ti+4NaN_3+C_2F_4$	2420	0.72	7.2	8	20.3
$Al+2Ti+4NaN_3+C_2F_4$	2520	0.77	7.8	8	17.0
$Al+4Ti+8NaN_3+2C_2F_4$	2670	0.81	7.0	8	16.2
$4Al+2Ti+4NaN_3+C_2F_4$	2700	0.75	7.3	8	18.3
$8Al+2Ti+4NaN_3+C_2F_4$	2940	0.87	6.5	8	20.5

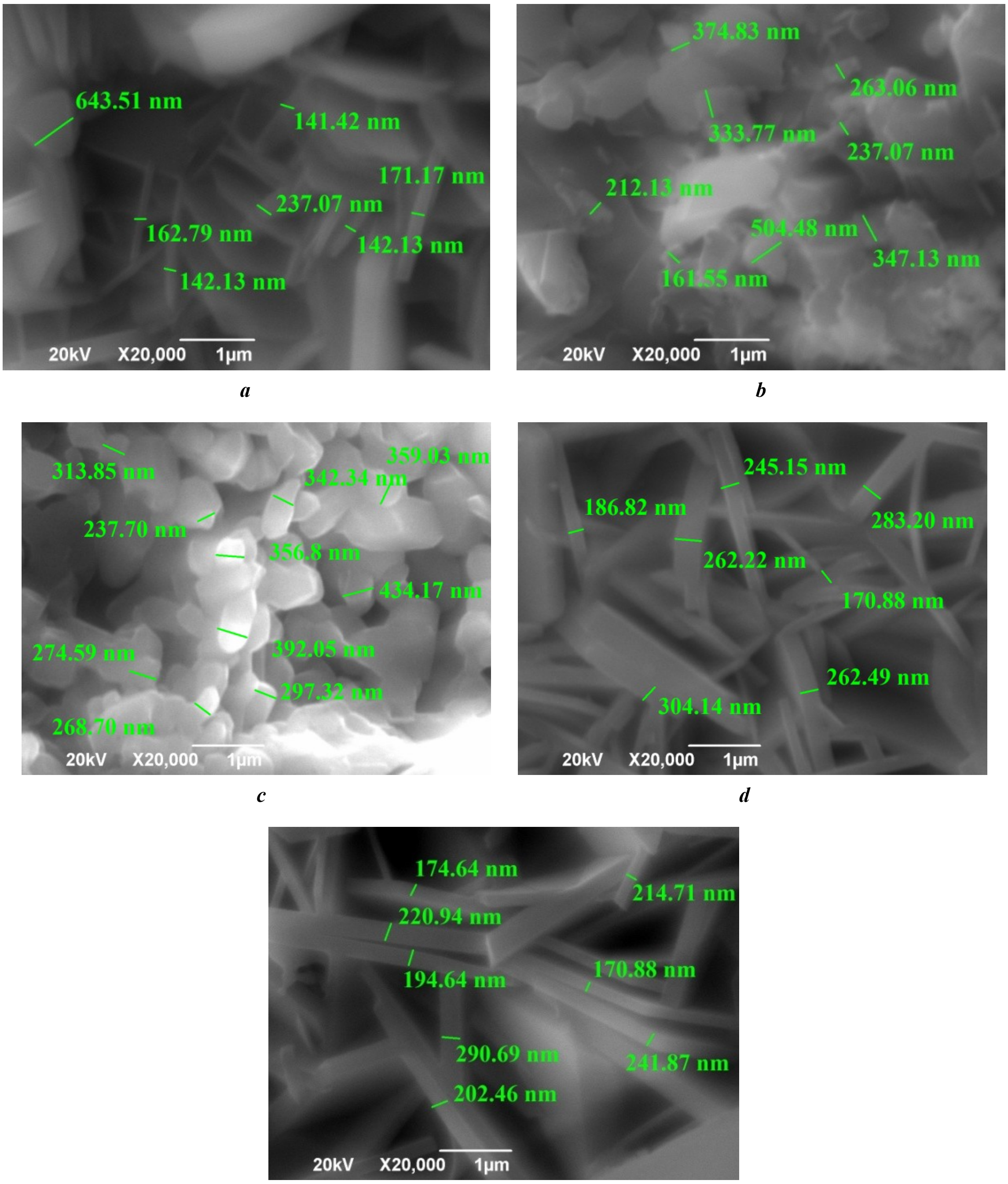

Fig. 1. *Morphology of particles of combustion products of the Al–Ti–NaN_3–C_2F_4 system:*
a *– 2Al+2Ti+4NaN_3+C_2F_4;* ***b*** *– Al+2Ti+4NaN_3+C_2F_4;* ***c*** *– Al+4Ti+8NaN_3+2C_2F_4;*
d *– 4Al+2Ti+4NaN_3+C_2F_4;* ***e*** *– 8Al+2Ti+4NaN_3+C_2F_4*
Рис. 1. *Морфология частиц продуктов горения системы Al–Ti–NaN_3–C_2F_4:*
a *– 2Al+2Ti+4NaN_3+C_2F_4;* ***b*** *– Al+2Ti+4NaN_3+C_2F_4;* ***c*** *– Al+4Ti+8NaN_3+2C_2F_4;*
d *– 4Al+2Ti+4NaN_3+C_2F_4;* ***e*** *– 8Al+2Ti+4NaN_3+C_2F_4*

molar ratios of nitride and carbide phases: 1:1, 1:2, 1:4, 2:1, 4:1. The experimental compositions of synthesis products, upon combustion of the initial powder mixtures of reagents with fluoroplastic, were found according to the stoichiometric equations of azide self-propagating high-temperature synthesis (1)–(5). It is shown that experimental compositions can differ significantly from theoretical phase compositions according to the original stoichiometric equations and the results of thermodynamic calculations. These differences are the lower actual content of the target phases of aluminium nitride, and titanium carbide in the composition of all combustion products synthesized experimentally, as well as the presence of side phases of titanium and aluminium oxides, and sodium aluminium hexafluoride (TiO_2, Al_2O_3, Na_3AlF_6), which should not exist according to theoretical calculations. It should be noted that our previous studies showed that aluminium nitride produced by the azide SHS method always contains a sparingly soluble

Table 3. *Results of qualitative and quantitative X-ray phase analysis of reactions (1)–(5)*
Таблица 3. *Результаты качественного и количественного рентгенофазового анализа реакций (1)–(5)*

Theoretical composition, %		Ratio AlN:TiC	Experimental composition, %				
AlN	TiC		AlN	TiC	Na_3AlF_6	TiO_2	Al_2O_3
40.6	59.4	1:1	32.5	47.4	6.5	12.8	0.8
25.5	74.5	1:2	20.6	61.2	4.8	13.1	0.3
14.6	85.4	1:4	14.4	71.5	–	14.5	–
57.8	42.2	2:1	53.2	31.4	–	11.6	3.8
73.3	26.7	4:1	66.4	15.6	–	11.9	6.1

impurity – sodium aluminium hexafluoride [12; 13]. However, in this work, sodium aluminium hexafluoride was formed only during the combustion of charges (1) and (2).

Despite the fact that the reaction products contain significant amounts of side oxide phases, the use of fluoroplastic as a carbon source allowed, increasing the yield of the target carbide, which could not be achieved when using soot (carbon black) in earlier studies [14–17].

Thus, in the case of practical application of the SHS-Az process (azide self-propagating high-temperature synthesis) to obtain a highly dispersed nitride-carbide composition AlN–TiC, it is recommended to use fluoroplastic for synthesis, while further research is required to prevent the formation and/or removal of oxides from the synthesized powder compositions.

CONCLUSIONS

The compositions of the initial mixtures of reagents were substantiated and the corresponding stoichiometric equations for the reactions of azide SHS of AlN–TiC powder compositions, with given molar nitride, and carbide phases were compiled: 1:1, 1:2, 1:4, 2:1, 4:1.

It is shown that in the case of all the reaction equations compiled, thermal effects and adiabatic temperatures are high enough for reactions to occur in the combustion mode, and the formation of target products in full accordance with the stoichiometric equations, and the given molar ratios of the nitride and carbide phases.

Studying the morphology of combustion products showed that in most cases, the use of the azide self-propagating high-temperature synthesis with selected compositions of the initial mixtures of reagents, leads to the production of highly dispersed compositions of powders in the form of fibres with a diameter of 100–250 nm, and particles of equiaxial and plate shapes with a size of 200–600 nm.

It has been found, that the experimental phase composition differs significantly from the theoretical phase composition, by the presence in the compositions of side phases of titanium and aluminium oxides, and in some cases, of sodium aluminium hexafluoride. When the combustion temperature is increased to obtain the largest amount of titanium carbide phase, an enlargement of the particle size to the micron level is observed.

Thus, by burning powder mixtures of sodium azide, fluoroplastic (C_2F_4), aluminium and titanium in a nitrogen atmosphere, it is possible to synthesize a highly dispersed composition of AlN–TiC ceramic powders of various compositions. However, the formulation of the synthesized compositions, along with the target phases, includes side oxides (TiO_2, Al_2O_3) and sodium aluminium hexafluoride (Na_3AlF_6). Further research will be aimed at preventing the formation and/or removal of oxides and sub-fluorides from the synthesized powder compositions.

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Самораспространяющийся высокотемпературный синтез порошковой композиции AlN–TiC с применением азида натрия и фторопласта C_2F_4

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Аннотация: Получение порошковых композиций с помощью обычной технологии обработки может привести к образованию крупных агломератов и, следовательно, осложняет получение однородной микроструктуры. Производство композитов методом самораспространяющегося высокотемпературного синтеза может снизить затраты и количество технологических стадий, а также привести к получению более однородных композитов. Для получения высокодисперсной порошковой керамической композиции AlN–TiC применен синтез методом горения смесей порошковых реагентов азида натрия (NaN_3), фторопласта (C_2F_4), алюминия и титана при разном соотношении реагентов в атмосфере газообразного азота при давлении 4 МПа. Термодинамические расчеты подтвердили возможность синтеза композиции AlN–TiC разного состава в режиме горения. Экспериментально определены зависимости температуры и скорости горения от состава исходных смесей реагентов по всем стехиометрическим уравнениям реакций. Показано, что экспериментально найденные зависимости параметров горения от соотношения исходных компонентов соответствуют теоретическим результатам термодинамических расчетов. Состав синтезированной композиции отличается от теоретического состава меньшим содержанием целевых фаз и образованием побочных фаз Al_2O_3, Na_3AlF_6 и TiO_2. Порошковая композиция представляет собой волокна нитрида алюминия диаметром 100–250 нм и ультрадисперсные частицы преимущественно равноосной и пластинчатой форм с размером частиц 200–600 нм. При увеличении температуры горения для получения наибольшего количества фазы карбида титана наблюдается укрупнение размера частиц до микронного уровня.

Ключевые слова: горение; самораспространяющийся высокотемпературный синтез; керамический порошок; нитридно-карбидная композиция; азид натрия; фторопласт (политетрафторэтилен); нитрид алюминия; карбид титана.

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