

# Combustion Synthesis of TiN-BN Nanostructured Composite Powder with the Use of Sodium Azide and Precursors of Titanium and Boron

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## Abstract

The composite powder of TiN-BN is of interest from the point of view of the use for sintering the TiN-BN composite ceramics, which compared with TiN ceramics would have less brittleness, better machinability and good tribological properties. Possibility of obtaining a composite powder of TiN-BN with the application of process of combustion synthesis (CS) or self-propagating high-temperature synthesis (SHS) from powder mixtures of sodium azide and halide salts  $KBF_4$ ,  $NH_4BF_4$ ,  $(NH_4)_2TiF_6$  and  $Na_2TiF_6$  as precursors of titanium and boron was investigated. It was shown that these mixtures are capable of burning and obtaining agglomerated composite powders. TiN-BN powder with an admixture of KF is formed only in combustion of "KBF<sub>4</sub>-NaN<sub>3</sub>-Na<sub>2</sub>TiF<sub>6</sub>" system with the increased content of halide salt of boron KBF<sub>4</sub>. In all other cases, the synthesized product has other composition: TiN-BN-TiB, TiN-TiB, TiN, often with an admixture of salts KF, NaF, Na<sub>3</sub>TiF<sub>6</sub> as by-products. Agglomerated composite powders as TiN-BN and others consist of nano-sized (less than 100 nm) and ultra-dispersed (100-500 nm) particles. The size of the agglomerates is in the range from 10-30 microns to 100-200 microns.

**Keywords:** composite ceramic powder, TiN-BN, combustion synthesis, sodium azide, precursors, halides

## 1. Introduction

The titanium nitride (TiN) relates to refractory compounds, has high hardness, wear resistance, heat resistance, corrosion resistance (Pierson, 1996). The titanium nitride is most widespread as wear-resistant and corrosion-resistant coatings with thickness up to 10  $\mu m$  obtained by methods of physical and chemical vapor deposition (PVD and CVD). Much less common is the use of bulk ceramics sintered from a powder of TiN, because of a high brittleness and poor machinability of such ceramics. The TiN powders are used, for example, for the production of refractory ceramic products as crucibles for oxygen-free metal melting. Little is known of the works on the regularities of sintering of TiN and the study of mechanical properties of the bulk sintered ceramics of TiN (Kuwahara et al., 2001; Russias et al., 2005; Russias et al., 2007; Xue et al., 2013). The results of these works show that the main property of such ceramics is a high hardness, and therefore the ceramics is recommended for tribological applications. Problems of brittleness, poor machinability, the need for high temperatures during sintering, in which decomposition of TiN begins, are not yet decided.

To solve these problems, several approaches can be used. First, adding to the composition of this very hard ceramics TiN a relatively soft hexagonal boron nitride (h-BN), which has a layered graphite-like crystalline structure, and is used as a high temperature solid lubricant, has a low coefficient of thermal expansion, high thermal conductivity, thermal stability, chemical inertness (Pierson, 1996). Similar non-oxide ceramic composites containing h-BN, especially  $Si_3N_4$ -BN, Sialon-BN, MgAlON-BN, Al-BN demonstrate excellent corrosion and heat resistance, low coefficient of friction and wear in dry friction, good crack resistance, bending strength, mechanical machinability (G.-J. Zhang et al., 2002; Carrapichano et al., 2002; Z. Zhang et al., 2007).

However, the type and particle size of the additive of hexagonal BN play a big role (G.-J. Zhang et al., 2002). If h-BN is introduced in the form of large flakes or agglomerates of such flakes, then the densification of the composite and its strength after sintering become worse. To obtain a high strength of the composite it is necessary that the BN particles were very fine and uniformly distributed over the bulk of the composite. The study of the properties of composite coatings of TiN-BN shows when the size of the crystals of TiN and

interlayers of BN is brought to the nano-level and the coating becomes nanocomposite, it acquires the unique properties and becomes ultra-hard (Prilliman et al., 2006). From this it follows the second approach to solve problems of the TiN ceramics - not just the addition of h-BN but formation of very fine structure of the TiN-BN composite due to the very small TiN crystals and BN particles.

As noted in the work (G.-J. Zhang et al., 2002), very small particles of hexagonal BN can be obtained and uniformly distributed in the bulk of the composite not by mechanical mixing of powders of TiN and BN but by conducting chemical synthesis of these particles in the bulk of the composite in the realization of processes in-situ. So we come to the third approach in solving problems of the TiN ceramics - to use in-situ processes to obtain the TiN-BN ceramics, including highly dispersed TiN-BN composite powders of which the ceramics can be sintered.

One of the most promising in-situ processes is the process of combustion synthesis (CS), also known as self-propagating high temperature synthesis (SHS), which allows you to get a variety of refractory compounds (carbides, borides, nitrides and other compounds (Merzhanov & Borovinskaya, 2008). The combustion synthesis process is attractive because of its simplicity and efficiency and is used to obtain both the original ceramic powders including composite and immediately sintered ceramic materials (Russias et al., 2005; Russias et al., 2007; Yu. Zhang et al., 2001; Wanbao et al., 2004; Yeh & Teng, 2006; Zhan et al., 2009; Shen et al., 2009; Li et al., 2011). In this case, the boron nitride synthesized has a phase h-BN. There is information about how to obtain by the CS method composite powders of TiN-BN with a particle size of not more than 2-3  $\mu\text{m}$  and the content of 35-60 wt. % BN in the combustion of mixtures of powders  $x\text{B} + \text{TiN}$  in nitrogen atmosphere, where  $1 \leq x \leq 3$  (Bilyan et al., 2005). The CS process also provides a great opportunity for the regulation of the size and structure of the synthesized ceramic powders, bringing them to nanoscale level (Amosov et al., 2005). For this purpose, various techniques are applied: reducing the temperature of combustion, the use of condensed and gaseous by-products separating the synthesized particles and preventing their growth, using as initial reagents not powders of pure elements such as metals but their chemical compounds (precursors), etc. In particular, such opportunities in the synthesis of nitrides are realized in the azide combustion synthesis process, referred to as azide CS, where the powder of sodium azide  $\text{NaN}_3$  is used as nitriding reagent instead of nitrogen gas, and halide salts are used. The azide CS process was applied to obtain powders of nitride compositions  $\text{Si}_3\text{N}_4\text{-AlN}$ ,  $\text{Si}_3\text{N}_4\text{-BN}$ ,  $\text{AlN}\text{-BN}$  when powders of the first element (Si or Al) and the precursor - a halide salt of the second element (Al or B) to be nitrided in these compositions were used as initial reagents, which led to obtaining micro-sized composite powders with submicron structure (Bichurov et al., 2012). The BN particles in the azide CS process get turbostratic type with different degree of structure disordering and are positioned in the range of phases between highly ordered hexagonal h-BN and amorphous BN. The use of the precursor of element to be nitrided only with the exception of the powder of the pure element in the azide CS process allowed us to obtain nanostructured TiN powder by burning a powder mixture of sodium azide with the precursor - a halide salt of titanium  $(\text{NH}_4)_2\text{TiF}_6$  in nitrogen atmosphere and in a similar way to obtain a mixture of nano - and micro-sized BN particles by burning a mixture of sodium azide with a halide salt of boron  $\text{NH}_4\text{BF}_4$  (Shiganova et al., 2011).

Of great interest is to apply the same azide CS process for synthesis of nanostructured composite powder of TiN-BN using precursors of both elements to be nitrided (Ti and B). This powder can be used for sintering the corresponding composite ceramics with good machinability, less brittleness and lower temperatures during sintering in comparison with ceramics from the TiN. The synthesis of the composite powder in one stage, the application of simple cost-effective in-situ process is important both from a technical point of view of obtaining a uniform mixture of nanoscale components that is virtually unattainable by mechanical mixing of nanopowder components, and from an economic point of view due to the high cost of the nanopowder components (Nanomaterials and related products: Catalog & price-list, 2014).

The aim of this work was to develop a azide combustion synthesis method for obtaining nanostructured composite powder of titanium and boron nitrides TiN-BN using halide salts of titanium and boron as precursors.

## 2. Materials and Methods

In the present work, powders of sodium azide and halide salts of boron and titanium, which are produced by industry:  $\text{NaN}_3$  (purity 98,71 wt. %);  $\text{KBF}_4$  (purity 99,0 wt. %);  $\text{NH}_4\text{BF}_4$  (purity 99.00 wt. %);  $\text{Na}_2\text{TiF}_6$  (purity 98.00 wt. %);  $(\text{NH}_4)_2\text{TiF}_6$  (purity 99.00 wt. %) were used as the initial reagents in the azide combustion synthesis process.

All initial powders were sifted on the vibrating screen of LE-203/I 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 of sodium azide and halide salts, taken in a predetermined ratio, were prepared

manually in a porcelain mortar for 5-10 minutes until a uniform distribution of components. The prepared mixture of powders 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 CS 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 [19, 20]. Recording the temperature and rate of combustion was carried out using an analog-to-digital converter connected to a computer.

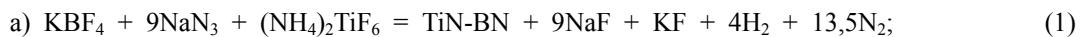
Upon completion of the combustion process, soaking was given for 15-20 minutes to cool synthesized sample. The sample was removed from the reactor and was destroyed by hand in a porcelain mortar to obtain a free-flowing powder. Then water washing the powder product of combustion was carried out to remove 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). The dried product, if necessary, was scattered by the vibrating screen through a sieve of 80  $\mu\text{m}$  and subjected to appropriate methods of analysis.

Qualitative X-ray diffraction (XRD) of the final product was carried out using a diffractometer ARL X'tra-138. Morphology and particle size of the nitride powder compositions was carried out using a scanning electron microscope (SEM) Jeol JSM-6390A. Particle size analysis of the synthesized products was carried out using a laser particle size analyzer ANALYSETTE 22 Compact.

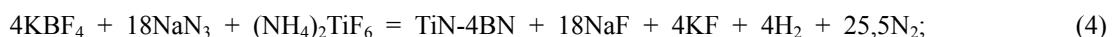
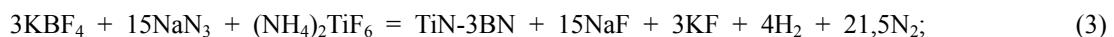
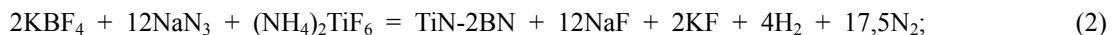
### 3. Results

Calculation of the mass of the components of the initial mixture for azide combustion synthesis process was made taking into account the stoichiometric ratio of the components in the "boron halide salt - sodium azide - titanium halide salt" systems. The number of halogen in halide salts was required to fully bind sodium released during the decomposition of sodium azide  $\text{NaN}_3$  to a neutral compound - sodium chloride or fluoride. Calculation was made for various ratios of TiN and BN in the composite powder:  $x\text{BN}-y\text{TiN}$ , where  $x$  and  $y$  - the number of moles, which may take the values  $x = 1; 2; 3; 4$  when  $y = 1$  and  $y = 1; 2; 3; 4$  when  $x = 1$ .

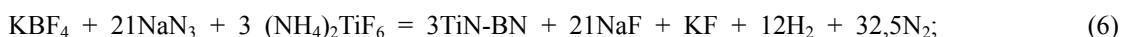
For example, for halide salts  $\text{KBF}_4$  and  $(\text{NH}_4)_2\text{TiF}_6$  with equimolar ratio  $x = y = 1$ :



for increased content of component  $\text{KBF}_4$  ( $x = 2, 3, 4$ ):



for increased content of component  $(\text{NH}_4)_2\text{TiF}_6$  ( $y = 2, 3, 4$ ):



The equations can be written for other halide salts similarly:

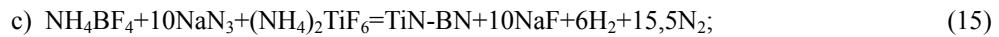


for increased content of component  $\text{KBF}_4$  ( $x = 2, 3, 4$ ):



for increased content of component  $\text{Na}_2\text{TiF}_6$  ( $y = 2, 3, 4$ ):





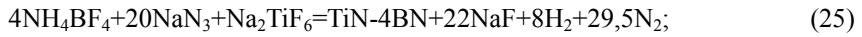
for increased content of component  $\text{NH}_4\text{BF}_4$  ( $x = 2, 3, 4$ ):



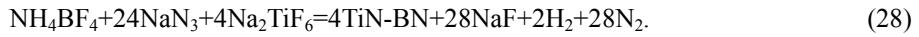
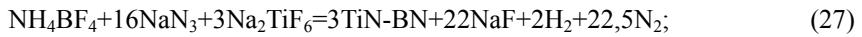
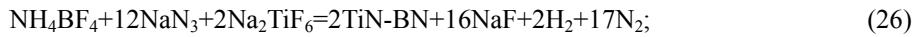
for increased content of component  $(\text{NH}_4)_2\text{TiF}_6$  ( $y = 2, 3, 4$ ):



for increased content of component  $\text{NH}_4\text{BF}_4$  ( $x = 2, 3, 4$ ):



for increased content of component  $\text{Na}_2\text{TiF}_6$  ( $y = 2, 3, 4$ ):

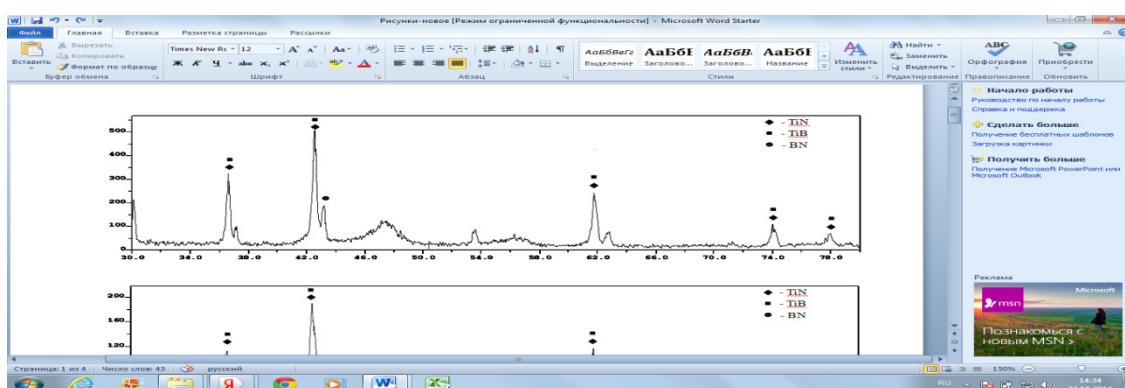


The results of experiments investigating the dependence of the combustion velocity  $U$  and temperature  $T_c$ , acid-base balance of the wash water pH, color and phase composition of the washed powder product from the ratio of the components in the formulations of the azide CS systems examined are shown in Table 1. X-ray diffraction patterns of some washed end products of the synthesis are shown in Figures 1 and 2. Figure 3 shows the particle morphology of the end product (the composite powder), and Figure 4 - particle size distribution of the composite powder.

Table 1. Effect of formulation of the initial mixture of different azide combustion synthesis systems on the characteristics of the combustion process and synthesis product

$x$ and $y$ , mole Color	$T_c, ^\circ\text{C}$ Phases	$U, \text{ cm/s}$	pH
« $x\text{KBF}_4\text{-NaN}_3\text{-}y(\text{NH}_4)_2\text{TiF}_6$ »			
$x = 1, y = 1$ Black	1200 TiN, TiB	0.50	7
$x = 2, y = 1$ Black	1400 TiN, TiB, BN	0.60	7
$x = 3, y = 1$ Black	1600 TiN, TiB, BN	0.70	8
$x = 4, y = 1$ Black	1750 TiN, TiB, BN	0.75	8
$x = 1, y = 2$ Black	900 TiN, TiB, BN	0.45	8
$x = 1, y = 3$ Black	750 TiN, TiB, BN	0.40	8
$x = 1, y = 4$ Black	600 TiN, TiB, BN	0.30	9
« $x\text{KBF}_4\text{-NaN}_3\text{-}y\text{Na}_2\text{TiF}_6$ »			
$x = 1, y = 1$ Black	1450 TiN, BN, KF	1.50	8
$x = 2, y = 1$ Black	1400 TiN, BN, KF	1.20	8
$x = 3, y = 1$	1350	1.00	8

Black and dark blue $x = 4, y = 1$	TiN, BN, KF 1300	0.70	8
Black and dark blue $x = 1, y = 2$	TiN, BN, KF 1400	1.20	7
Black $x = 1, y = 3$	TiN, KF 1350	1.00	6
Black and gold $x = 1, y = 4$	TiN, KF 1300	0.70	6
Black and gold $x = 1, y = 1$	TiN, KF « $\alpha$ NH <sub>4</sub> BF <sub>4</sub> -NaN <sub>3-y</sub> (NH <sub>4</sub> ) <sub>2</sub> TiF <sub>6</sub> » 1300	2.00	12
Dark gray $x = 2, y = 1$	TiN, BN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1400	2.00	12
Dark gray $x = 3, y = 1$	TiN, BN, Na <sub>3</sub> TiF <sub>6</sub> 1500	2.00	12
Dark gray $x = 4, y = 1$	TiN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1600	2.00	12
Dark gray $x = 1, y = 2$	TiN, BN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1200	1.50	12
Dark gray $x = 1, y = 3$	TiN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1100	1.20	12
Dark gray $x = 1, y = 4$	TiN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1000	1.00	12
Dark gray $x = 1, y = 1$	TiN, Na <sub>3</sub> TiF <sub>6</sub> , NaF 1300	1.00	8
Black $x = 2, y = 1$	TiN, TiB, Na <sub>3</sub> TiF <sub>6</sub> 1400	1.50	8
Black $x = 3, y = 1$	TiN, TiB, Na <sub>3</sub> TiF <sub>6</sub> 1450	1.70	9
Dark gray $x = 4, y = 1$	TiN, TiB, NaF 1550	2.00	9
Dark gray $x = 1, y = 2$	TiN, TiB, BN 1150	0.70	10
Black $x = 1, y = 3$	TiN, TiB, Na <sub>3</sub> TiF <sub>6</sub> 1000	0.40	11
Black $x = 1, y = 4$	TiN, TiB, BN 900	0.30	11
Black	TiN, TiB		



a)

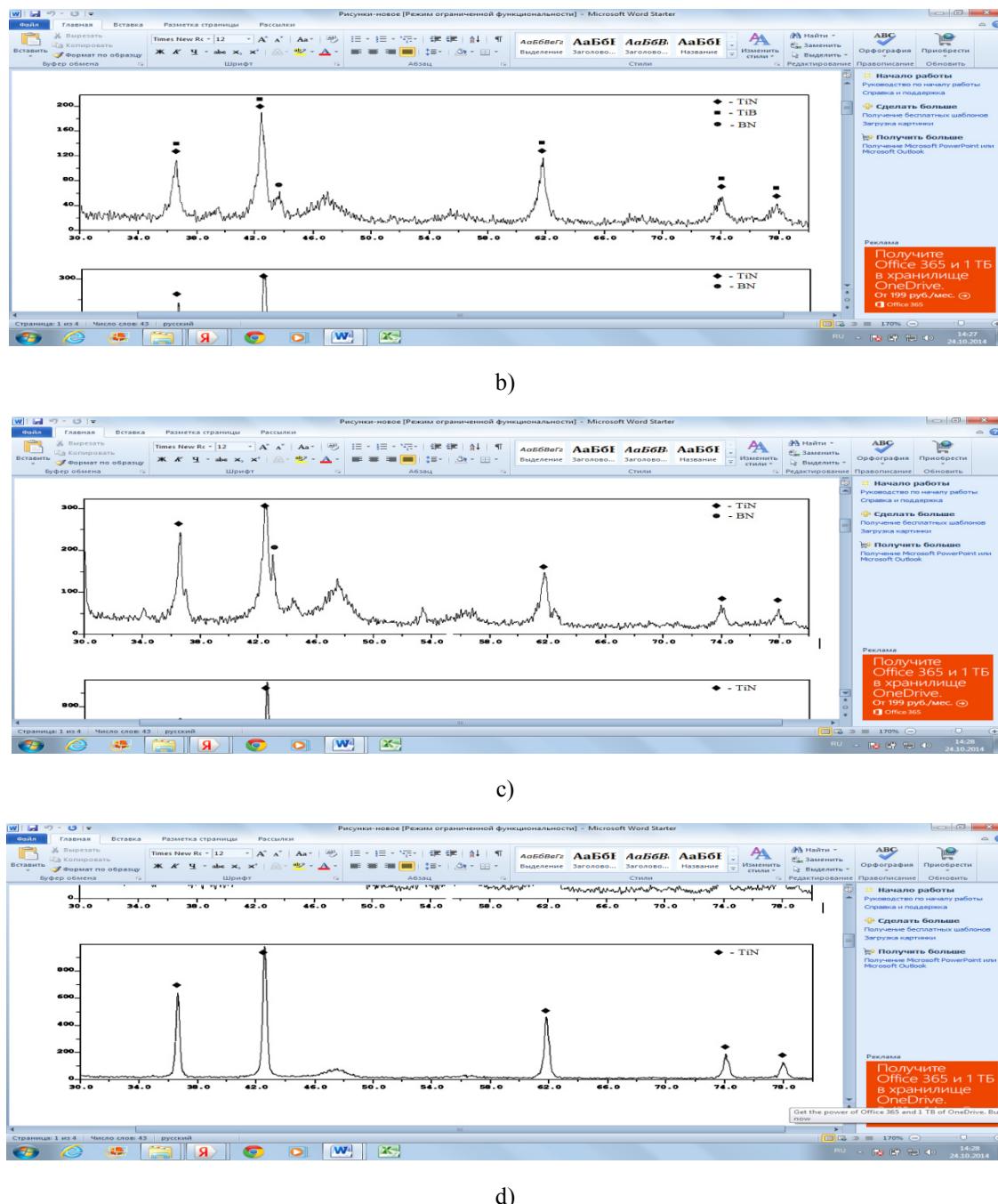


Figure 1. XRD patterns of final washed products obtained from the systems: (a) «3KBF<sub>4</sub>-15NaN<sub>3</sub>-(NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub>»; (b) «KBF<sub>4</sub>-21NaN<sub>3</sub>-3(NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub>»; (c) «3KBF<sub>4</sub>-13NaN<sub>3</sub>-Na<sub>2</sub>TiF<sub>6</sub>»; (d) «KBF<sub>4</sub>-15NaN<sub>3</sub>-3Na<sub>2</sub>TiF<sub>6</sub>»

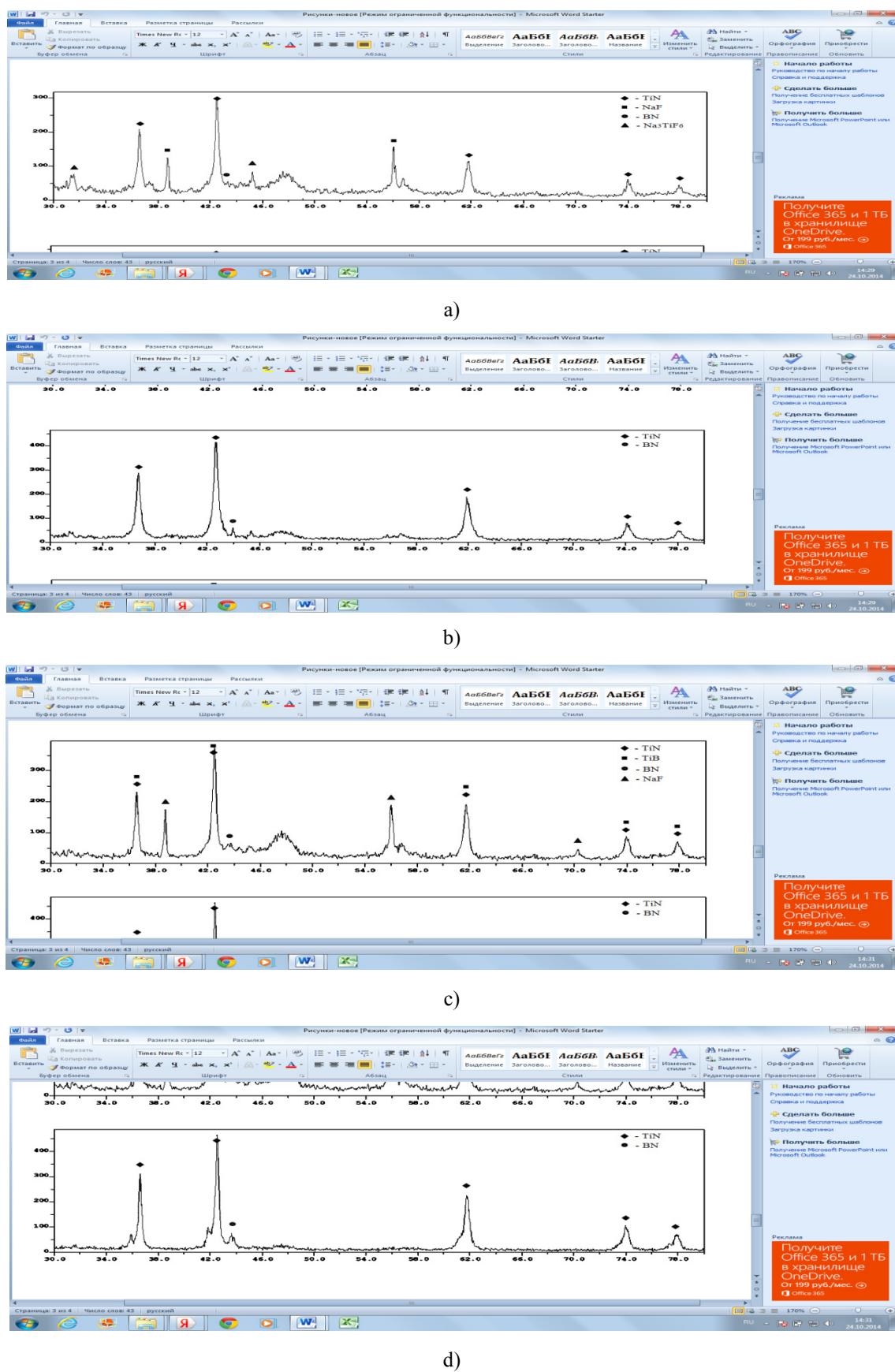


Figure 2. XRD patterns of final washed products obtained from the systems: (a) « $3\text{NH}_4\text{BF}_4\text{-}18\text{NaN}_3\text{-}(\text{NH}_4)_2\text{TiF}_6$ »; (b) « $\text{NH}_4\text{BF}_4\text{-}22\text{NaN}_3\text{-}3(\text{NH}_4)_2\text{TiF}_6$ »; (c) « $3\text{NH}_4\text{BF}_4\text{-}16\text{NaN}_3\text{-}\text{Na}_2\text{TiF}_6$ »; (d) « $\text{NH}_4\text{BF}_4\text{-}16\text{NaN}_3\text{-}3\text{Na}_2\text{TiF}_6$ »

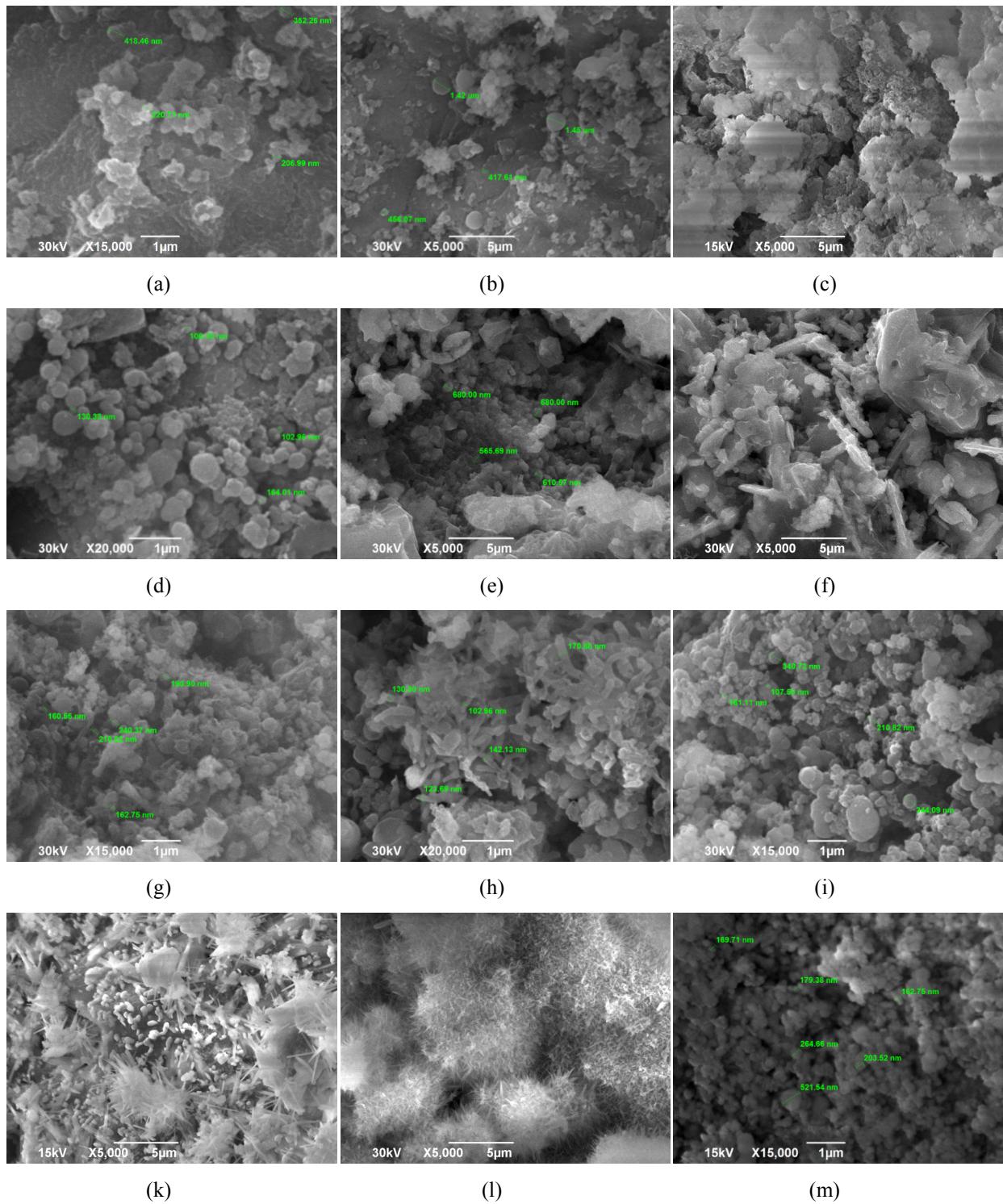


Figure 3. SEM images of the end product (composite powder) synthesized in the systems: (a) «KBF4-9NaN3-(NH4)2TiF6»; (b) «3KBF4-15NaN3-(NH4)2TiF6»; (c) «KBF4-21NaN3-3(NH4)2TiF6»; (d) «KBF4-7NaN3-Na2TiF6»; (e) «3KBF4-13NaN3-yNa2TiF6»; (f) «KBF4-15NaN3-3Na2TiF6»; (g) «NH4BF4-10NaN3-(NH4)2TiF6»; (h) «3NH4BF4-18NaN3-(NH4)2TiF6»; (i) «NH4BF4-22NaN3-3(NH4)2TiF6»; (k) «NH4BF4-8NaN3-Na2TiF6»; (l) «3NH4BF4-16NaN3-Na2TiF6»; (m) «NH4BF4-16NaN3-3Na2TiF6»

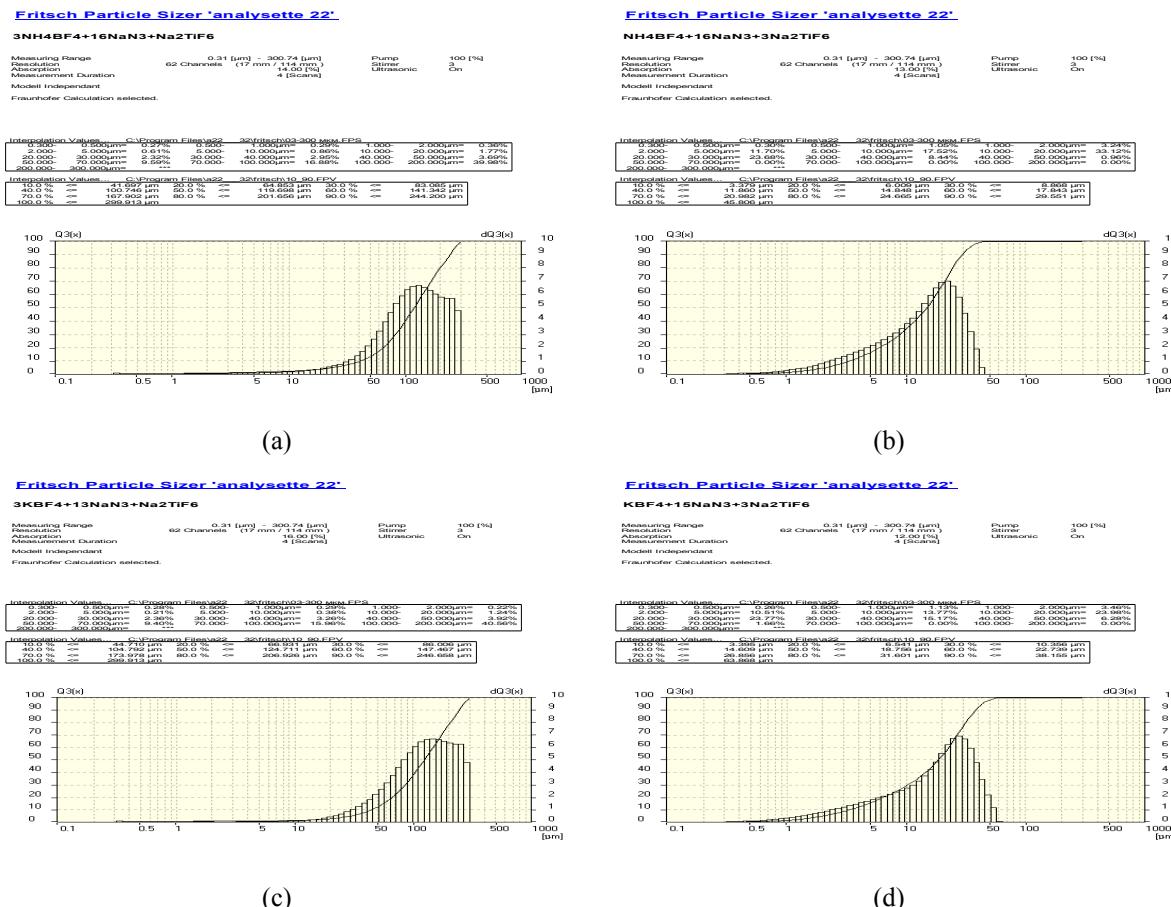


Figure 4. Particle size distribution in the powder of the final products, synthesized in the systems: (a) « $3\text{NH}_4\text{BF}_4\text{-}16\text{NaN}_3\text{-}\text{Na}_2\text{TiF}_6$ »; (b) « $\text{NH}_4\text{BF}_4\text{-}16\text{NaN}_3\text{-}3\text{Na}_2\text{TiF}_6$ »; (c) « $3\text{KBF}_4\text{-}13\text{NaN}_3\text{-}\text{Na}_2\text{TiF}_6$ »; (d) « $\text{KBF}_4\text{-}15\text{NaN}_3\text{-}3\text{Na}_2\text{TiF}_6$ »

#### 4. Discussion

The results obtained lead to the conclusion that all these azide combustion synthesis systems are capable of self-combustion and the formation of a powdery product. The phase composition of the product can be very different.

In all systems at all formulations of the initial mixture, TiN is synthesized, but BN is synthesized not at all formulations of the initial mixture. This fact can be explained by the fact that temperatures required for synthesis of TiN are 250-500 °C lower than that for synthesis of BN. For example, in the furnace synthesis from the element, 1100-1250 °C are required for TiN and up to 1500 °C for BN, and in the presence of ammonium halide salts and elements to be nitride, 1200 -1500 °C for TiN and 1600-2000 °C for BN (Samsonov et al., 1987; Kosolapova et al., 1985). As seen from Table 1, the measured temperature of combustion does not exceed 1750 °C. Such temperature is sufficient to form TiN, but not always sufficient for the formation of BN.

Equimolar formulations of the starting powder mixtures  $x = y = 1$  have average values of the temperature of combustion. By increasing the content of boron halide salt (increasing  $x$ ), the combustion temperature increases while increasing the content of titanium halide salt (increasing  $y$ ) decreases the combustion temperature. In this connection, the likelihood of formation of BN should increase with increasing content of boron halide salt and decrease with increasing content of the titanium halide salt. Approximately the same pattern is observed in the analysis of the results of Table 1 and Figures 1 and 2, but its concrete manifestations are also dependent on the chemical nature of the starting reactants.

In the " $x\text{KBF}_4\text{-}\text{NaN}_3\text{-}y(\text{NH}_4)_2\text{TiF}_6$ " system, the formation of BN is observed in all the formulations of the initial mixture, except equimolar  $x = y = 1$  (Table 1, Figure 1). Unfortunately, we used only qualitative X-ray analysis of the synthesis products, so we can not say how the content of BN varies quantitatively under change of the composition of the azide CS charge. Furthermore, XRD peaks of BN appear only at a content of not less than 5-7

wt.%. Therefore absence of BN peaks in the diffraction pattern may indicate that the BN content in the product synthesis is less than 5-7%. Besides TiN and BN, the presence of phase TiB is observed in the combustion products of all formulations of the system " $x\text{KBF}_4\text{-NaN}_3\text{-}y(\text{NH}_4)_2\text{TiF}_6$ ", that is, the composite powder TiN-BN-TiB is obtained as a result of the azide CS process in this system. As can be seen from Figures 3 (a, b, c), the particles of the powder have a rounded or irregular form, the average size of 200-400 nm and can be partially combined into agglomerates with size from several microns to tens of microns.

In the " $x\text{KBF}_4\text{-NaN}_3\text{-}y\text{Na}_2\text{TiF}_6$ " system, the TiB phase is not formed (Table 1, Figure 1). In fact, only in this system by increasing the content of boron halide salts  $\text{KBF}_4$  ( $x \geq 1$ ,  $y = 1$ ), the target composite powder TiN-BN (with impurity of unwashed KF) is formed. With increasing content of titanium halide salt  $\text{Na}_2\text{TiF}_6$  ( $y \geq 1$ ), the BN phase is not detected, only the TiN phase with small peaks of the KF impurity is detected. The average particle size of rounded particles of the TiN-BN powder of 70-130 nm in Figure 3 (d) increases to 600 nm in Figure 3 (e) and is converted into TiN particles of debris shape of a few micrometers in Figure 3 (f). In all these figures, the particles are combined together into agglomerates of different sizes. These results are roughly consistent with the results obtained at azide CS of powders TiN and BN separately from similar precursors of titanium and boron (Shiganova et al., 2011). The synthesized powder is preferentially black, but there are some gold-yellow particles that are observed in the samples obtained from initial mixtures with increasing content of titanium halide salt  $\text{Na}_2\text{TiF}_6$  ( $y \geq 1$ ). The black color indicates that the particle size is less than 1 micron, while gold-yellow hue points to the presence of some larger particles TiN.

In the " $x\text{NH}_4\text{BF}_4\text{-NaN}_3\text{-}y(\text{NH}_4)_2\text{TiF}_6$ " system, the TiB phase is also not formed (Table 1, Figure 2). Here, the main phases are the target phase TiN and side phases  $\text{Na}_3\text{TiF}_6$  and NaF. Peaks of the other target phase BN are visible only for formulations with increasing content of boron salt  $\text{NH}_4\text{BF}_4$  (very weak peak at  $x = 1$ , and more conspicuous peak at  $x = 4$ ). The peaks of the NaF salt can be explained by the fact that the particles of this salt are contained within the agglomerates and are not removed to completion with a water wash. The  $\text{Na}_3\text{TiF}_6$  salt is sparingly soluble in water and requires special cleaning for its removal from the desired product. The great value of pH = 12 of water after washing powder products of combustion of this system indicates that not all Na is linked to salts  $\text{Na}_3\text{TiF}_6$  and NaF and therefore is hydrolyzed and gives an alkaline pH. The TiN- $\text{Na}_3\text{TiF}_6$  powder consists in agglomerates of particles of a rounded shape with an average size of 200 nm (Figures 3 (g, h, i)).

In the " $x\text{NH}_4\text{BF}_4\text{-NaN}_3\text{-}y\text{Na}_2\text{TiF}_6$ " system, the target phase BN is also almost not formed (only weak peaks at  $x = 4$  and  $y = 3$ ), but the TiB phase appears in the product of burning all formulations (Table 1, Figure 2). The main phases are TiN, TiB and  $\text{Na}_3\text{TiF}_6$  or NaF. There is also great value of pH = 8-11 of water after washing the product of the combustion of this system. This powder is a mixture of TiN-TiB particles of rounded shape of 70-90 nm size and the needle-shaped particles of  $\text{Na}_3\text{TiF}_6$  or NaF similar to urchins of size of about 5 microns (Figures 3 (k, l)), which are absent in the TiN-TiB-BN powder of 170 -200 nm size in Figure 3 (m).

As follows from Figure 3, virtually all synthesized powders are agglomerates of smaller particles of different sizes and shapes. This is quite typical of CS powders, when incomplete grinding the combustion product gives agglomerated CS powders consisting of particles formed by the individual crystallites, i.e. single crystals with irregular outer facet, between which there is a significant splicing (Amosov et al., 2005). The size of agglomerates in the powders typically varies in the range 10-200 microns; these agglomerated particles may be porous. In the agglomerated particles, by-products and unreacted atoms Na can be encapsulated, which are difficult to remove with water washing and which provide spikes of by-products by X-ray diffraction, and alkaline pH.

Size of the agglomerates are identified in the study of particle size distribution of the agglomerated powders. The results of this study of the azide CS powdery product with laser particle size analyzer ANALISSETTE 22 Compact are presented in Figure 4. It follows from them that the agglomerates are strong enough and do not disintegrated with ultrasonic dispersion in the bath of the laser analyzer. With increasing content of boron halide salt  $\text{NH}_4\text{BF}_4$  or  $\text{KBF}_4$  in the starting material, the size of the bulk of the synthesized powder agglomerates is 100-200 microns, and with increasing content of titanium halide salt  $\text{Na}_2\text{TiF}_6$ , the size of the bulk powder agglomerates is significantly lower and is 10-30 microns. For a complete disintegration of the agglomerated powder, intensive grinding is required, for example, in planetary ball mill, when we can expect the collapse of the agglomerates into individual crystallites.

## 5. Conclusions

These results show that the use of mixtures of sodium azide with precursors - halide salts of boron and titanium  $\text{KBF}_4$ ,  $\text{NH}_4\text{BF}_4$ ,  $(\text{NH}_4)_2\text{TiF}_6$  and  $\text{Na}_2\text{TiF}_6$  - allow you to realize the azide combustion synthesis process and obtain the composite powder product of the agglomerated structure in the combustion mode. This product is a

target composite powder TiN-BN (with water-soluble impurity KF) only in the case of use of the system " $x\text{KBF}_4\text{-Na}_3\text{-}y\text{Na}_2\text{TiF}_6$ " with an increased content of boron halide salt  $\text{KBF}_4$  ( $x \geq 1$ ,  $y = 1$ ). In all other cases, the synthesized product is of a different composition: TiN-BN-TiB, TiN-TiB, TiN, often mixed with impurity side salts KF, NaF,  $\text{Na}_3\text{TiF}_6$ . These side salts are not always removed when the water wash because of agglomerate structure of the resulting powder of azide CS and finding these impurities within the agglomerates. The agglomerated composite powders as TiN-BN and the others are composed of nanoscale (less than 100 nm) and ultra-dispersed (100-500 nm) particles. The size of the agglomerates is in the range from 10-30 microns to 100-200 microns. Thus, the application of the azide combustion synthesis process made it possible to obtain the TiN-BN agglomerated composite powder with nano-sized and ultra-dispersed structure.

On further examination, it is advisable: (a) to carry out a quantitative X-ray analysis of the azide CS composite products, (b) to identify the phases of the particles that make up the composite by scanning electron microscope with attachment of energy dispersive analysis, (c) to apply methods of more complete grinding the powder agglomerates and the removal of impurities, (d) to use the obtained pure composite powders with nano-sized and ultra-dispersed structure for sintering composite ceramics with high properties.

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