Azide SHS of aluminium nitride nanopowder and its application for obtaining Al-Cu-AlN cast nanocomposite

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Abstract. Method of azide self-propagating high-temperature synthesis (SHS-Az), using sodium azide (NaN₃) as a nitriding reagent, was used for obtaining the nanopowder of aluminum nitride (AlN) from precursor that was sodium hexafluoroaluminate (Na₃AlF₆). The product of burning the mixture of Na₃AlF₆ + 3NaN₃ after water rinsing consisted of micro - and nanoparticles of AlN (65%) and the residue of salt Na₃AlF₆ (35%). This product of SHS-Az was mixed with copper powder and pressed into a briquette of nanopowder master alloy Cu-4%(65%AlN+35%Na₃AlF₆), which was successfully introduced into aluminium melt at a temperature of 850°C. The salt Na₃AlF₆ in the product of combustion played a role of flux during introducing into the aluminum melt and was not included in the final composition of the composite alloy. The microstructure of the obtained cast composite aluminium alloy with the calculated composition of Al-1.2%Cu-0.035%AlN showed that the reinforcing particles of AlN of different sizes, including nanoparticles, were distributed mainly along the grain boundaries of the aluminum alloy.

Keywords: SHS, sodium azide, Na₃AlF₆ precursor, aluminum nitride, nanopowder, Cu-AlN master alloy, Al-Cu-AlN cast nanocomposite.

1. Introduction
Currently, the nanopowder of aluminum nitride is attracting much attention because of the possibility of using it for obtaining new advanced materials: as the basis for the sintering of AlN ceramics with a unique combination of properties (excellent thermal conductivity with low electrical conductivity, high resistance to the action of molten metals and salts, high corrosion resistance and mechanical strength), and also as a reinforcing material in the light-weight aluminum matrix composites Al-AlN having a high heat resistance [1, 2].

Nanoparticles of aluminum nitride are difficult to obtain by mechanical comminution of conventional commercially available AlN powders, so a large number of chemical and physicochemical processes have been developed to produce AlN nanopowders, such as a direct nitriding, plasma-chemical synthesis, carbothermic synthesis, chemical deposition from the gas phase, electrical explosion of aluminum wire and etc. [3-7]. However, these technologies of producing AlN powders are characterized by a large power consumption, complicated equipment, and do not always ensure the nanosize of AlN powder.
The method of self-propagating high-temperature synthesis (SHS) is attractive in this respect because it proceeds at the cost of its own heat of combustion in a small-sized equipment and takes a little time [8]. However, the performing the SHS in the classic version, using gaseous nitrogen as a nitriding reagent, does not allow obtaining nanosized powder of aluminum nitride [9]. To solve the problem of obtaining nanopowder AlN by resource-saving technology of SHS, it is promising to use such version as azide SHS technology, which is denoted as SHS-Az and is being developed in Samara State Technical University since 1970 [10]. The SHS-Az technology is based on the use of sodium azide NaN$_3$ as a solid nitriding reagent and halide salts. The SHS-Az technology is characterized by low combustion temperature and the formation of large amounts of gaseous products, which hinder the coalescence of the initial nanoparticles of the synthesized product and make it possible to retain them in nanosized state. The use in the SHS-Az starting powder mixture of the powder of a precursor, that is aluminum fluoride AlF$_3$, as a starting reagent instead of the powder of metallic aluminum Al can reduce the temperature of combustion and makes it possible to carry out the reaction in the decomposition of the precursor at the atomic level, which ultimately allows synthesizing AlN powder with a particle size of from 70 to 100 nm [10, 11]. But when burning this mixture, along with the traditional by-product of SHS-Az reactions, that is sodium fluoride NaF, easily removable by water washing, a large quantity of other by-product is generated, that is sodium hexafluoroaluminate Na$_3$AlF$_6$, which is difficult to remove and complicates the process of obtaining nanopowder AlN of high purity.

However, these side salts NaF and Na$_3$AlF$_6$ represent typical fluxes for refining and modification of melts of aluminum alloys and are used to improve the wetting of the reinforcing ceramic particles during liquid-phase production of aluminum matrix composites (AMCs) [12, 13]. Therefore, when in use of the SHS-Az product for liquid-phase reinforcement of aluminum alloys, it is not necessary to wash this product from the side salts that was shown in the example of modification of aluminum alloys using nanopowdery composition of SiC - Si$_3$N$_4$ [13]. Because of the simplicity of technology and equipment, the nanopowders of SHS-Az brand can be 2-3 times less in cost than the similar nanopowders of plasma chemical synthesis.

The aim of this work is to study the possibility of synthesis of AlN nanopowder by SHS-Az method using an alternative precursor, that is sodium hexafluoroaluminate Na$_3$AlF$_6$, for subsequent use of the AlN nanopowder as a reinforcing phase in liquid-phase producing the cast aluminum matrix nanocomposite Al-AlN.

### 2. Materials and methods of investigations

As initial reagents in obtaining aluminum nitride, the powders of aluminum, sodium azide and sodium hexafluoroaluminate were used which are produced by the Russian industry: aluminum of ASD-1 brand (basic substance content not less than 99.7 wt. %; particle size less than 50 µm); NaN$_3$ (98.71 %); Na$_3$AlF$_6$ (99.1 %). The mixtures of powder reagents were prepared in accordance with the stoichiometric equation of a chemical reaction for producing aluminum nitride in a mode of SHS-Az:

$$\text{Na}_3\text{AlF}_6 + 3\text{NaN}_3 = \text{AlN} + 6\text{NaF} + 4\text{N}_2.$$  \hspace{1cm} (1)

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, 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 assembled structure was mounted on the subject shelf of anazide SHS laboratory reactor of a constant pressure with a volume of 4.5 litres. 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 [10, 11]. 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 was soluble in water. 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 at 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.

For a preliminary analysis of the burning temperature of the starting components and the composition of the synthesis products, the thermodynamic calculations was performed using the computer program "Thermo", developed at the Institute of Structural Macrokinetics and Materials Science Problems of RAS (Chernogolovka, Moscow region) [8].

Direct introduction of nanopowders in bulk form by mixing into the melt of aluminum alloys is practically impossible [13]. To estimate the potential application of the synthesized ceramic nanopowder AlN of SHS-Az brand for reinforcing and modifying of aluminum alloys, a nanopowdery master alloy was prepared that was a mechanical mixture of AlN nanopowder with plastic powder carrier, which was subjected to mechanical activation and was pressed into briquettes [13]. As a carrier material for lightweight nanopowder AlN, the powder of electrolytic copper of PMS-1 grade was chosen with an average particle size of 15-45 µm having regard to its high density (8900 kg/m³) relative to the aluminum melt (2400 kg/m³) and good solubility of copper in the melt. Mechanical mixing of the initial components of the master alloy was carried out in planetary mill "Pulverisette-5" for 90 minutes at a speed of 150 rpm. Cemented carbide balls with a diameter of 10 mm were used as grinding bodies. The weight ratio of balls to powder mixture was 10:1, the fill factor of the drums was 0.5. The homogeneity of mixing was evaluated by randomly selected samples. The charge was considered uniform if at least 95% of randomly selected samples had the specified chemical and granulometric compositions. To obtain the briquettes of nanopowdery master alloy, cold pressing the powder mixture was used. Uniaxial compaction of the powder mixture was carried out with a pressing pressure of 35 MPa in a cylindrical die with an internal diameter of 18.1 mm. The briquettes were introduced into the melt of primary aluminium of technical purity of A7 brand (99.70%).

### 3. Results and discussion

Table 1 presents the results of thermodynamic calculations showing the dependence of the adiabatic temperature $T_{ad}$ of the formation of aluminum nitride according to reaction (1) from the pressure of nitrogen pumped into the reactor ($P_{N_2}$). It can be seen from the presented data, that $T_{ad}$ is changed only at normal pressure of $P_{N_2} = 0.1$ MPa. $T_{ad}$ does not change at increasing pressures $P_{N_2} = 1\div6$ MPa and is equal to 1269 K. The yield of the products of the reaction corresponds to the stoichiometric one.

| Pressure of nitrogen pumped into reactor, $P_{N_2}$ MPa | Adiabatic temperature of combustion, $T_{ad}$,K | Enthalpy of reaction products, $\Delta H$, kJ | Composition of combustion products, moles |
|-----------------------------------------------------|-----------------------------------------------|---------------------------------------------|------------------------------------------|
| 0.1                                                 | 969                                          | $-3259$                                     | $\text{AlN}_3$                        |
| 1                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
| 2                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
| 3                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
| 4                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
| 5                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
| 6                                                   | 1269                                         | $-3259$                                     | $\text{NaF}_3$                         |
The results of an experimental study of the dependence of temperature and velocity of combustion of the mixture "Na₃AlF₆ + 3NaN₃" from the pressure of nitrogen in the reactor are shown in table 2.

Table 2. Results of experimental investigation of combustion parameters.

| Pressure of nitrogen in reactor, P_N₂, MPa | Temperature of combustion, T_c, °C | Velocity of combustion, U_c, cm/s |
|------------------------------------------|----------------------------------|---------------------------------|
| 0.1                                      | 720                              | 0.40                            |
| 1                                        | 850                              | 0.50                            |
| 2                                        | 910                              | 0.56                            |
| 3                                        | 930                              | 0.60                            |
| 4                                        | 950                              | 0.62                            |
| 5                                        | 950                              | 0.62                            |
| 6                                        | 950                              | 0.62                            |

Five experiments were carried out for each point of these dependencies. From the presented data, it is visible, that the temperature and velocity of combustion increase as the pressure increases up to 4 MPa, and then their values no longer depend on pressure. The maximum values of T_c and U_c are 950°C and 0.62 cm/s, respectively.

Figure 1 shows the results of X-ray phase analysis of the products of combustion of mixture "Na₃AlF₆ + 3NaN₃" at a pressure P_N₂ = 4 MPa.

![Figure 1](image-url)

**Figure 1.** XRD patterns of combustion products of mixture "Na₃AlF₆ + 3NaN₃": (a) until washing; (b) after washing.
The phase composition of unwashed combustion products is a mixture of aluminum nitride, sodium hexafluoroaluminate and sodium fluoride (figure 1 (a)). Due to its good solubility in water, the sodium fluoride is completely removed from the combustion products by rinsing in distilled water (figure 1 (b)). On the contrary, sodium hexafluoroaluminate can also be observed in the washed reaction products due to poor solubility in water, and its content is 35%.

Figure 2 shows the micrograph of the powder synthesized from the mixture of "Na₃AlF₆ + 3NaN₃".

Comparing the pictures presented in figures 2 (a) and 2 (b), and having regard to the results of the X-ray phase analysis, it can be concluded that during combustion of the mixture "Na₃AlF₆ + 3NaN₃", the equiaxed particles of irregular shape of aluminum nitride and sodium hexafluoroaluminate are formed, as well as fibers of sodium fluoride, which are present until washing in figure 2 (a) and are not present after washing in figure 2 (b). The aluminum nitride is represented by a mixture of micron-sized particles (several microns) and a large number of nanoparticles with size from 50 to 100 nm.

The washed product was used for mixing and pressing nanopowder master alloy of Cu-4%(65%AlN+35%Na₃AlF₆) composition in the form of disk-shaped briquette of 2.5 g mass and 18.1 mm diameter. At a compression pressure of 35 MPa, the briquette had a height of 1.5 mm, which corresponded to the density of 8290 kg/m³ and a porosity of 28%. The microstructure of compacted nanopowder master alloy is presented in figure 3.

The average size of powder particles formed after intense grinding-mixing in the master alloy is 6-15 μm. Pores are also observed in the structure of the briquette, the presence of which may facilitate its dissolution during subsequent introducing into the melt.
Such briquette of nanopowder master alloy of Cu-4%(65%AlN+35%Na₃AlF₆) composition dissolved in the melt of A7 aluminum of 197.5 g mass at a temperature of 850°C and allowed introducing the reinforcing particles of AlN into the aluminum alloy. This can be confirmed by X-ray diffraction of the sample of cast composite after crystallization, represented in figure 4.

![Figure 4. XRD pattern of cast aluminum composite.](image)

XRD analysis of the cast sample shows the presence of aluminum (base alloy), copper, copper aluminide Al₄Cu₉ and aluminum nitride AlN, which indicates an absorption of the nanopowder of aluminum nitride of SHS-Az brand in composition of nanopowder master alloy of Cu-4%(65%AlN+35%Na₃AlF₆) by aluminum melt. Figure 4 also shows the lack of lines of Na₃AlF₆ halide salt, i.e. the salt played the role of a flux in the aluminum melt, but was not included into the composition of the solidified alloy. The produced cast composite alloy has a calculated composition of Al-1.2%Cu-0.035%AlN. The microstructure of the sample of solidified alloy is presented in figure 5.

![Figure 5. Microstructure of cast aluminum composite alloy:](image)

(a) magnification ×1000; (b) magnification ×5000.

The SEM images demonstrate AlN particles of different size (of micron size, ultrafine and nanoscale), which are distributed over the body of composite alloy not uniformly, but mainly along the grain boundaries of aluminum alloy. This distribution is typical for highly dispersed reinforcing ceramic particles in cast aluminum composite alloys [14].

### 4. Conclusion

The use of halide salt Na₃AlF₆ as a precursor in the method of azide SHS allowed us to obtain a product of combustion, consisting after water rinsing of micro- and nanopowder of aluminum nitride (65%) and
residues of salt Na₃AlF₆ (35%). This product of combustion in the composition of compacted powder master alloy of Cu-4%(65%AlN+35%Na₃AlF₆) was introduced into the aluminum melt. This made it possible to produce the cast composite aluminum alloy with calculated composition of Al-1.2%Cu-0.035%AlN, in which the reinforcing particles of AlN of different sizes, including nanoparticles, are distributed mainly along the grain boundaries of the composite alloy. The salt Na₃AlF₆ in the product of combustion played a role of flux during introducing into the aluminum melt and was not included in the final composition of the aluminum matrix nanocomposite.

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