Application of SHS auxiliary reaction of titanium carbide for introduction of AlN nanoparticles into aluminum melt

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Abstract. For ex-situ introduction of AlN nanopowder, obtained by azide technology of self-propagating high-temperature synthesis (SHS) or combustion synthesis in the mixture with the flux cryolite: (AlN-35%Na₃AlF₆), into the aluminum melt, an exothermic master powder composite (EMPC) of different composition (AlN-35%Na₃AlF₆) – (Ti+C) – Na₂TiF₆ was first used, leading to the realization of in-situ process of SHS of reinforcing phase TiC in the combustion mode in the aluminum melt. The conditions were found for reliable ignition of the EMPC and fabrication of cast hybrid nanocomposites Al-Al-TiC, including the calculated composition Al-7.7%AlN-19%TiC with an increased content of AlN reinforcing phase.

1. Introduction
Due to a low weight, excellent mechanical properties, thermodynamic and dimensional stability at high temperatures, aluminum matrix composites reinforced with AlN nanoparticles are promising for use in aerospace, automotive and defense technology [1]. However, due to a high cost of AlN nanopowder, as well as a high cost and other disadvantages of existing solid-phase and liquid-phase methods of manufacturing Al-AlN nanocomposites, there is currently no industrial production of these nanocomposites [1]. In this regard, the study of the possibility of using the achievements of a simple energy-saving powder technology, based on the process of self-propagating high-temperature synthesis (SHS) or combustion synthesis, is of great interest for manufacturing Al-AlN nanocomposites [2-4]. Firstly, the cost of nitride nanopowders, obtained by SHS azide technology (SHS-Az) for subsequent introduction into the matrix melt (ex-situ), is about 2-3 times lower than the cost of similar nanopowders obtained by plasma chemical synthesis. Secondly, the SHS process creates a high temperature and thus contributes to wetting of ceramic nanoparticles and their incorporation into the matrix (ex-situ). Thirdly, the synthesis of inexpensive reinforcing ceramic nanoparticles can be carried out directly in the matrix (in-situ), ensuring their good adhesion to the matrix. The papers [2, 5, 6] present the results of our previous studies on the ex-situ fabrication of Al-AlN nanocomposites using different methods of introduction into the melt of aluminum (or its alloys) a nanopowder of SHS-Az brand of composition (AlN-35wt.%Na₃AlF₆), where a by-product Na₃AlF₆ (kryolite) played the role of flux. Direct mixing of AlN nanopowder in a bulk form in the Al melt did not lead to success due to the poor wettability of AlN nanopowder with liquid Al and clumping AlN nanoparticles in the agglomerates. The use of pressed briquettes of nanopowdery pseudo-master alloy of Cu-4%(AlN-35%Na₃AlF₆) composition allowed us to obtain a cast composite of the calculated composition of Al-1.2%Cu-0.035%AlN. Composite master alloy, obtained by melting the flux
carnallite KCl·MgCl₂ with nanopowder (AlN-35%Na₃AlF₆), allowed us to introduce a maximum of 1%AlN into the matrix of alloy Al6%Mg. Nanocomposite with content up to 4%AlN was able to be obtained by mixing nanopowder (Al-35%Na₃AlF₆) in Al5%Cu alloy in the solid-liquid state (semi-solid process). In this paper, an attempt is made to increase the content of AlN reinforcing phase in an aluminum matrix nanocomposite by using an auxiliary SHS reaction of Ti+C=TiC in the mode of combustion in the aluminum melt, that is, by complex reinforcement using a combination of approaches: ex-situ (introduction of pre-synthesized AlN nanopowder into the matrix melt) and in-situ (synthesis of TiC particles in the matrix melt during composite fabrication). (It should be noted that the hybrid reinforcement of aluminum alloys with mixtures of ceramic particles of different types has been successfully used and allows using the advantages of different particles [4, 7].)

In connection with this, the aim of this work was to study for the first time the possibility of using exothermic master powder composite (AlN-35%Na₃AlF₆)-(Ti+C) of different composition for the realization of process of SHS of titanium carbide in the aluminum melt and the achievement of incorporation of AlN nanopowder into the melt to produce a hybrid nanocomposite Al-AlN-TiC.

2. Materials and methods of research

The following materials were used for the study (hereafter wt.%): pig aluminum of A7 brand of 99.7% purity; titanium powders of 97.95% purity: TPP-7 brand (average particle size 230 μm), PTS brand (100 μm) and PTM brand (45 μm); carbon black of P-701 brand (purity 99.7%, average particle size 70 nm, average agglomerate size 1 μm); halide salt Na₂TiF₆ (purity 99.0%, 15 μm). Aluminum nitride for carrying out the research was prepared by us with SHS azide method and represented a powder mixture of AlN (65%) and Na₃AlF₆ (35%) in phase composition [5]. This mixture consisted of equiaxed particles of micron size (up to several μm) and a large number of nanoparticles with a size from 50 to 100 nm.

First the SHS charge Ti+C was prepared. Powders of Ti and C were dried at 100–110°C for 2–3 h, and then mixed in a ball mill for 1 h. Then a predetermined amount of powder (AlN-35%Na₃AlF₆) was added to the SHS charge and mixed manually in a porcelain mortar for 5-10 minutes until a uniform distribution of the components. In most cases, Na₂TiF₆ salt was also added to the mixture to facilitate the initiation of SHS process. The resultant mixture of powders (Ti+C)-(AlN-35% Na₃AlF₆)-Na₂TiF₆ can be designated as Exothermic Master Powder Composite (EMPC) for subsequent introduction into the aluminum melt. (For example, the milled particulates of Al₂O₃ with Al and Mg powders intended for injection of reinforcing particles Al₂O₃ into molten Al was designated as Master Metal Matrix Composite (MMMC) [8]. In our opinion, this composite would be more correctly designated as Master Powder Composite (MPC), although we previously designated it as nanopowdery pseudo-master alloy or composite master alloy [2, 5, 6].) The introduction of our EMPC was carried out in two ways: either in the form of capsules made of aluminum foil with a thickness of 50-100 μm, into which a portion of the EMPC of about 6-10 g was wrapped, or in the form of compacted cylindrical briquettes with a relative density of 0.4 of the same weight with a diameter of 23 mm.

To fabricate samples of Al-Al-TiC composites with a mass of 200 g, the corresponding amount of aluminum A7 was melted in a graphite-fireclay crucible TG 3, which was installed in a melting electric resistance furnace of PP 20/12 brand. The melt was heated to a temperature of 900°C, at which portions of EMPC were introduced alternately in the form of capsules or briquettes. The portions of EMPC were dipped into molten metal with a steel spoon. Each portion was kept under the melt level until the beginning of the active SHS reaction in the combustion mode, accompanied by spark and gas evolution. During the reaction, the melt was thoroughly stirred. After introducing all the portions of EMPC and the completion of the SHS reaction, the melt was kept for 5 minutes, stirred and poured into a steel chill with a hole diameter of 20 mm to obtain a cast sample of the composite in the form of a rod with a diameter of 20 mm and a length of 110 mm.

After cooling, the cast sample was notched on the side and failed in impact bending to determine a visual appearance of fracture surface. A heterogeneous "dirty" structure, with inclusions of starting
EMPC, testified that the SHS reaction was not fully and the composite body contained both inclusions of the unreacted charge and agglomerates of AlN particles, that is, the body of the composite was not properly filled with particles of the reinforcing TiC and AlN phases and the desired structure of the composite was not formed.

Metallographic analysis was performed using Jeol JSM-6390A scanning electron microscope. The phase composition was determined by X-ray phase analysis on an automated diffractometer ARL X'tra ("Thermo Scientific") using CuKα radiation with continuous scanning in the range of angles 2θ = 20÷80 degrees at a speed of 2 degrees/min. The hardness of the sample was carried out by Brinell hardness tester TSH-2M using a load of 1226 N and a ball with diameter of 6.35 mm.

3. Results and discussion

It is known that the mixture of titanium and carbon powders in the production of nanoscale titanium carbide by SHS reaction Ti+C=TiC is permissible to dilute with up to 40% inert material [9]. With more dilution, the Ti+C mixture becomes not capable of burning. In carrying out these studies, taking into account the high dispersion of aluminum nitride powder of the SHS-Az brand, the amount of this material in the powder mixture (AlN-35% Na₃AlF₆)-(Ti+C) was limited to 25%.

First, the possibility was studied to use titanium powder of TPP-7 brand in the EMPC. TPP-7 powder is traditionally used in the fabrication of composite Al-10% TiC by SHS in Al melt with the introduction of charge (Ti+C) [3]. To do this, a mixture of powders 75%(Ti+C)+25%(AlN-35%Na₃AlF₆) with the addition of 2.5% and 6% Na₂TiF₆ by weight of the mixture was placed in Al foil capsules and injected into Al melt. However, after the introduction of EMPC of these compositions into the Al melt, the combustion process has not been initiated, there was no spark and gas evolution from the melt, although in similar conditions, with the addition of Na₂TiF₆, but without adding (AlN-35%Na₃AlF₆) to the mixture (Ti+C), the combustion process was steadily initiated, resulting in the formation of the composite Al-10% TiC. In that case, for reliable initiation of the SHS process, it was enough to add no more than 1% of the Na₃AlF₆ salt by mass (Ti+C). The results obtained here can be explained by the fact that the TPP-7 titanium powder consists of large particles with an average size of 230 μm and has a relatively small specific surface, which can easily be filled with a high-dispersed powder (AlN-35% Na₃AlF₆), preventing direct contact of particles of powders Ti and C and initiating the SHS reaction between them.

Next, we investigated the possibility of using more fine powder of titanium of PTS brand with an average particle size of 100 μm. 60 g of a mixture 75%(Ti+C)+25%(AlN-35%Na₃AlF₆) was prepared already on the basis of PTS titanium powder:

\[ 15 \text{ g (AlN-35%Na₃AlF₆)}+45 \text{ g (Ti+C)}=60 \text{ g}. \]

For a stable initiation of SHS reaction, 2 g (3%) salt Na₂TiF₆ was added to the mixture. The resultant mixture was divided into 10 equal portions, 7 portions of which in bulk form were placed in Al capsules, and 3 portions were compacted into briquettes. 135 g of pure aluminum was placed into the crucible and melted to produce the calculated composition of Al-5.1%AlN-23.7%TiC composite. The prepared portions of EMPC without preheating were introduced into Al melt. All portions were ignited in the melt with the evolution of gas and sparks. The briquettes were burning more intensely than the mixtures of the bulk density in capsules. After completion of combustion, a large amount of slag was formed on the melt surface, which indicated a low melt absorption of lightweight AlN nanopowder with a bulk density of about 2 g/cm³ at a density of Al melt 2.3 g/cm³. The reason for this could be a deficient temperature of the melt after completion of combustion, resulting in a deficient wettability of AlN nanopowder with liquid Al and the floating of the nanopowder in the slag.

In this regard, two powder mixtures were prepared, based on the reduced to 3.3% calculated content of the target AlN component in a composite sample weighing 200 g:

\[ 10 \text{ g (AlN-35%Na₃AlF₆)}+60 \text{ g (Ti+C)}. \]
PTS titanium powder was used in the first mixture, and PTM titanium powder was used in the second mixture. To assure the initiation of SHS reaction in the aluminum melt, 3 g (4%) Na$_2$TiF$_6$ was added to each of the above mixtures. The resultant mixture was distributed into portions of about 7 g, which were wrapped in Al foil. When introducing the capsules into Al melt weighing 130 g, all portions were ignited, the reaction significantly increased the melt temperature and was accompanied by flashes of yellow-green flame, more intense when using PTM titanium. In the case of the use of PTS titanium, after the pouring out of the melt, a part of the slag left at the bottom of the crucible and welded to it. It was the remains of EMPC with the heavier titanium carbide with a density of 4.9 g/cm$^3$. Cast composite sample had a good appearance, its surface was clean, shrinkage sink was absent, but the fracture surface was contaminated with inclusions of EPMC (figure 1).

![Figure 1. General view of Al-3.3%AlN-30.5%TiC sample by using PTS titanium powder:](a) sample surface; (b) fracture surface.](image)

When using PTM titanium, the melt was very viscous, and therefore there was no complete separation of the metal part with slag in the crucible, and the cast sample of the composite had numerous slag inclusions (figure 2).

![Figure 2. General view of Al-3.3%AlN-30.5%TiC sample by using PTM titanium powder.](image)

The fracture surface of this specimen was also contaminated. No sediment was found at the bottom of the crucible after pouring out the melt. According to the results of the use of PTS titanium, it was seen that the decrease in the amount of AlN from 5.1% to 3.3% in the target composite has resulted in a reduction of the amount of slag, including the sediment at the bottom of the crucible. A high melt viscosity by using PTM titanium, hindering the separation of slag and metal parts of the melt, indicated the completeness of the SHS reaction and a high degree of incorporation of the reinforcing phases of TiC and AlN into the melt.

Further research was conducted with PTM titanium with the increase in the AlN content up to 5% in the composite Al-5%AlN-28.2%TiC with the following initial components:

\[ 130 \text{ g Al} + 15 \text{ g (AlN-35%Na}_2\text{AlF}_6)+ 55 \text{ g (Ti+C)}=200 \text{ g.} \]
The amount of salt Na₂TiF₆ was reduced from 3 g to 1.6 g (from 4% to 2%) due to the fact that this initiating reaction substance was added only to the first two portions, combustion initiation of which occurs more difficult than subsequent. The introduction of portions of such EMPC in Al capsules occurred with the initiation of SHS process. The melt of the composite was thick, but with the separation of slag and metal parts, which allowed us to cast a sample of the composite with a much better appearance, which corresponded to figure 1a. The surface of the sample had fine-grained uniform dense structure, was free of shells, non-metallic inclusions, pores and cracks. The fracture surface was contaminated as in figure 1b.

A similar experiment was carried out with PTM titanium with an increase in the calculated AlN content from 5% to 6.7% in Al-6.7%AlN-25.9%TiC composite with the following content of the initial components:

\[130 \text{ g Al} + 20 \text{ g (AlN-35\%N}_3\text{AlF}_6) + 50 \text{ g (Ti+C)} = 200 \text{ g},\]

when Na₂TiF₆ salt was also added only to the first two portions. The SHS process was initiated by the introduction of portions in the form of capsules of such EMPC, but the resultant sample had large slag inclusions and a defective surface, and its appearance was similar to that shown in figure 2. This result can be explained by a too high content of TiC and AlN reinforcing phases and their good absorption by the melt.

To significantly reduce the amount of TiC in the EMPC, but retain the opportunity to initiate the SHS process, experiments were carried out to obtain Al-7.7\%-AlN-19\%TiC composite with a different content of (Ti+C) mixture in portions of compacted EMPC, depending on the order of introduction of briquettes into the melt (table 1) with the following content of the initial components:

\[130 \text{ g Al} + 21 \text{ g (AlN-35\%N}_3\text{AlF}_6) + 33.8 \text{ g (Ti+C)} = 184.8 \text{ g}\]

with addition of 0.7 g Na₂TiF₆ in each briquette (from 7 to 10.6%).

| The order of introduction into melt | Content of AlN-35\%Na₃AlF₆ in briquette, % | The number of briquettes | Content of components in the briquette, g |
|-----------------------------------|---------------------------------------------|--------------------------|------------------------------------------|
| 1                                 | 30                                          | 2                        | AlN-35\%Na₃AlF₆ | (Ti+C) | Na₂TiF₆ |
| 2                                 | 40                                          | 2                        | 3.0                                      | 7.0   | 0.7     |
| 3                                 | 45                                          | 3                        | 3.0                                      | 4.5   | 0.7     |

As can be seen from the table, the first EMPC briquettes contain the largest amount (70%) of SHS charge (Ti+C) and the smallest amount (30%) of inert additive (AlN-35\%Na₃AlF₆), since the SHS process is the most difficult to initiate when introducing the first portions of EMPC. Introduction of briquettes at indicated order led to initiation of combustion of each briquette. As a result, it was possible to fabricate a hybrid nanocomposite of the calculated composition Al-7.7\% AlN-19\%TiC. The resultant composite sample had a smooth clean surface and a fracture surface without slag inclusions. Its hardness was 41HB. According to results of the electron microscope study, the nanocomposite had a fine-grained uniform dense microstructure, without pores, cracks and non-metallic inclusions. Figure 3 shows the results of X-ray phase analysis of the sample material, which show the presence of Al (the basis of the composite), TiC and AlN, which indicate advantageous going the reaction of synthesis of TiC and the incorporation of AlN nanopowder of SHS-Az brand into Al matrix. In figure 3, there are no lines of halogen salt Na₃AlF₆, that is, this salt played the role of flux in Al melt, but was not included into the composition of the solidified composite. According to the results of quantitative X-ray phase analysis, the cast composite obtained had an actual composition of Al-3.5\% AlN-10.1\% TiC.
4. Conclusion
The conditions of reliable ignition of the EMPC (Ti+C) – 35%Na3AlF6 – Na2TiF6 in molten Al have been found to realize the in-situ process of SHS of reinforcing phase TiC and incorporate the nanoscale reinforcing phase AlN ex-situ introduced into the melt. To do this requires to use fine titanium powder of PTM brand, to add 3–10% Na2TiF6 salt, to introduce the EMPC by portions in the form of compacted briquettes, to introduce first the EMPC portions with a high content of SHS charge (Ti+C) and a lower content of inert additive (AlN-35%Na3AlF6). In this manner a cast Al matrix hybrid nanocomposite of calculated composition Al-7.7% AlN-19%TiC with a high content of reinforcing phase AlN was first fabricated. The mismatch between the calculated composition of the composite and the actual one Al-3.5% AlN-10.1% TiC can be explained by incomplete completion of SHS reaction and incomplete incorporation of the reinforcing phases of AlN and TiC into Al melt, by transition of part of these phases and initial reagents into slag. Research in this direction should be continued in order to increase the completeness of the SHS reaction of TiC in aluminum melt, the degree of incorporation of AlN and TiC reinforcing phases into aluminum melt, the uniformity of the distribution of reinforcing phases in the melt.

Acknowledgements
This work was executed at financial support of RFBR under the project No. 16-08-00826.

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