

Role of Halide Salts Na_3AlF_6 and Na_2TiF_6 in Self-propagating High-temperature Synthesis of Al-10%TiC Nanocomposite Alloy in Aluminum Melt

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Abstract. The effect of additives of halide salts Na_3AlF_6 and Na_2TiF_6 to the initial mixture of powders of titanium and carbon on the process of Self-propagating High-temperature Synthesis (SHS) a reinforcing carbide phase TiC in the aluminum melt was investigated with the aim of obtaining nanocomposite alloy Al-10%TiC. The use of salt Na_3AlF_6 in amounts of 0.1% of the melt mass as a flux together with additive of aluminum powder enabled synthesized TiC particles to be reduced to a ultrafine level (0.17-0.35 micron), whereas the use of halide salt Na_2TiF_6 as a precursor of titanium in place of 20% of titanium powder in the SHS charge (without aluminum powder) - to a nanoscale level (not over 0.1 micron).

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Introduction

The process of Self-propagating High-temperature Synthesis (SHS) of refractory inorganic compounds (carbides, borides, nitrides, intermetallic compounds and others) was discovered in 1967 and based on exothermic chemical reactions between the initial reagents, most often, powders, in the combustion mode [1]. This process is also known as Combustion Synthesis (CS). To date over thousand of different substances and materials: powdered, porous, monolithic, composite and other have been produced using the SHS process [2].

The first results on the implementation of the SHS process in the aluminum melt to produce grain refiners were published in 1991 [3]. Stoichiometric mixtures of powders of aluminum and transition metals (3Al+Ti) or (3Al+Zr) were compacted into briquettes and dipped into the melt. Heating up in the melt led to the initiation of the SHS process in the briquettes with emission of flash and gas from the melt and formation of intermetallic compounds TiAl_3 or ZrAl_3 that were distributed by intensive mixing over the body of the melt in the form of intermetallic particles with size from 5 to 20 microns (*in-situ* particle formation of intermetallic compounds in the melt). The melt was poured into a mold with the formation of grain refiners for aluminum alloys. It should be noted that halide salts were not added to the original mixture of powder reagents in these first experiments.

In the subsequent works, the possibility of application of the SHS process to obtain *in-situ*

aluminum alloys with more complex structure, first of all, widely used grain refiner Al-5%Ti-1%B (the following are mass %) was studied. Powders of aluminum, titanium, and boron were mixed in the stoichiometric ratio and in bulk form in aluminum foil were introduced in the molten aluminum to implement the SHS reaction $3\text{Al} + 2\text{Ti} + 2\text{B} = \text{TiAl}_3 + \text{TiB}_2$ [4]. It turned out that the implementation of the SHS process in the aluminum melt largely depended on additions of halide salts Na_3AlF_6 and $\text{K}_{1-3}\text{AlF}_{4-6}$ to the original mixture of powders (SHS charge). It has been known that these halide salts are used as fluxes with names: cryolite and flux NOCOLOK, respectively, in casting and brazing of aluminum alloys [5, 6]. They have refinement impact on the aluminum melt, release it from attending non-metallic impurities, remove the oxide film on aluminum, improve its wettability and reactivity. Additives of these salts, first of all Na_3AlF_6 in the amount of 0.1% of the melt mass to the SHS charge, contributed to a more active and complete course of SHS reactions, released the final alloy from residues of unreacted charge, significantly reduced the size of intermetallic phases TiAl_3 and changed the shape of its particles with a needle on more favorable block. So it was proved the importance of the application of halide salts as fluxes during the SHS process in the molten aluminum.

In recent years an increased interest has been expressed in aluminum composite alloys containing particles of the dispersed ceramic phase of titanium carbide TiC. Such alloys with a small content of the

ceramic phase can be used as effective grain refiners or master alloys for aluminum alloys [7, 8], and with increased content as dispersion-strengthened aluminum-matrix composites with high physical and mechanical, first of all, tribological properties [9, 10].

The use of a stoichiometric mixture of powders of titanium and carbon with the addition of flux cryolite in the amount of 0.1% of the melt mass made it possible to realize the SHS process in the melt of aluminum with a temperature of 900 °C to obtain *in-situ* composite alloy Al-TiC with mass up to 20% of the reinforcing phase in the form of a large number of small inclusions TiC with the size of 2-4 microns [11, 12]. Alloy containing 10% TiC showed the best combination of mechanical properties. In the manufacture of Al-TiC composites, the positive role of halide salt Na₃AlF₆ has been intimated as a flux, contributing as a synthesis of particles of TiC in the aluminum melt, and the introduction of ready-made particles of TiC in the melt [10, 12].

Of particular interest is the development of methods of increasing the dispersion of ceramic phase TiC and bringing it to nanoscale level (not over 0.1 micron), which should lead to increase of a level of properties of composite alloy Al-TiC with a little content of the ceramic phase [13]. In technology of SHS powders, more than 20 specific methods have been developed to reduce the size of the synthesized particles to nanoscale level [14]. One of the most effective methods is to substitute the initial reagents from pure elements, in particular metals, for their chemical compounds (precursors), which are decomposed in the combustion wave and the element reacts in an atomic state. The use of halide salt K₂TiF₆ as a source of titanium together with graphite powder as a source of carbon made it possible to obtain particles of titanium carbide with the size of 0.5-1 micron in the aluminum melt [7]. On this basis it can be assumed that the use of low-melting titanium-containing halide salts as a source of atomic titanium in the SHS charge can result in the formation of nanosized carbide phase in the molten aluminum. Here halide salt is seen not as a flux, but as a precursor, that is a source of titanium.

This work is devoted to the investigation of the influence of additives of halide salt Na₃AlF₆ as a flux and titanium-containing salt Na₂TiF₆ as a precursor on the course of the SHS process, formation and dispersion of titanium carbide phase in the aluminum melt with the aim of obtaining nanocomposite alloy Al -10%TiC. The study suggested the holding as a theoretical analysis of the SHS process on the basis of thermodynamic calculations and experimental heats with determination of the composition, structure and

mechanical properties of obtained samples of the composite alloy.

Materials and methods

The thermodynamic research was performed by the computer program "THERMO", developed in the Institute of structural macrokinetics and materials science of Russian Academy of Sciences [15]. This program allowed us to calculate the adiabatic (in the absence of a heat loss) combustion temperature and the equilibrium composition of the products of combustion of the mixture of different elements or compounds on the basis of the method of minimization of thermodynamic potential.

The experimental heats were performed using the following materials: cast aluminum of brand A7 (the basic substance content of no less than 99,70%), titanium powder of brand TPP-7 (the basic substance content of no less than 97,9%, the size of particles ≤240 microns), carbon black of brand P-701 (the basic substance content of no less than 99,7%, the size of particles ≤ 0,15 micron), aluminum powder of brand PA-4 (the basic substance content of no less than 98,00%, the size of particles ≤140 microns), halide salts Na₃AlF₆ (the basic substance content of no less than 98,0%), and Na₂TiF₆ (the basic substance content of no less than 99,0%).

In the preparation of the SHS charge, the titanium powder was mixed with carbon black in the stoichiometric ratio in accordance with the equation $Ti + C = TiC$. Basic composition for making 200 grams of cast composite alloy Al-10%TiC included 20 g of a powder mixture of 16 g of titanium and 4 g of carbon black, as well as separately 180 g of aluminum ingot for creation of the melt in the crucible. For research of influence of addition of aluminum powder and salts, 5, 10, 15, or 30 % aluminum powder from weight of 20 g were added to the SHS charge. The flux cryolite Na₃AlF₆ was also added in this mixture in the amount of 0.1% of the melt mass 200 g. To examine the influence of addition of halide salt Na₂TiF₆, a part of elemental metal powder of Ti (10, 20 or 30%) was replaced with titanium-containing halide salt Na₂TiF₆. Halide salt was added in the amount, equivalent in content of Ti, so that the total amount of Ti content in metal powder and salt was 16 g. The flux cryolite was not added in such mixtures.

Powder components were subjected to preliminary drying at a temperature of 100-110 °C for 2 to 3 hours required to remove moisture, adsorbed on the surface of powders. Then initial powders were mixed and simultaneously ground in a ball mill with the number of revolutions of 105 rpm for 1 hour. Samples (portions) of the charge of about 6-8 grams were wrapped in aluminum foil with thickness of

0.05 - 0.1 mm and in turn were inserted in the aluminum melt at a temperature of 900 °C. Each sample was holding in the melt until beginning the active SHS reaction of formation of titanium carbide, accompanied by flash and gas emission. The melt was mechanically stirred during the reaction. Upon completion of the SHS reaction from entering the last sample, the melt temperature was measured using a thermocouple to determine the maximum temperature of the SHS reaction, the melt was kept for 5 min, stirred and poured into a steel mold to obtain cylindrical samples of the composite alloy of diameter 20 mm.

After cooling, a part of samples was notched on the side and failed in impact bending to determine a mode of fracture and a visual appearance of fracture surface. A brittle fracture with uniform and homogeneous structure of the fracture surface testified that the SHS process was fully completed and a desired structure of the composite alloy was formed. A ductile fracture and heterogeneous "dirty" structure, with inclusions of unreacted charge, testified that the SHS reaction was not fully and the desired structure of the composite alloy was not formed.

The samples with homogeneous structure of the fracture surface were used to make sections with the polishing machine POLILAB. To identify microstructure, these samples were etched with a solution of 50% HF+50% HNO₃ for 10 to 15 seconds. Metallographic analysis was performed by using scanning electron microscope (SEM) Jeol JSM-6390A, the elements distribution was tested with application of EDS analyzer Jeol JED-2200 associated with the same microscope. The concentration of elements was determined as the average of 4 to 5 local measurements at different sites. The phase composition of the samples was determined with X-ray diffractometer (XRD) ARL X'tra (Thermo Scientific) using Cu-radiation with continuous scanning in interval of angles 2[theta] from 20 to 80 degrees at a speed of 2 degrees per minute.

The tensile strength and yield strength, elongation and reduction in area were determined by diagrams of tension of samples of composite alloy Al-10%TiC (length of the test portion 35 mm, diameter 5 mm) made with using a tensile testing machine R-5. Brinell hardness tests were made with hardness tester TSH-2M under a load of 102,6 kg (a ball of diameter 2.5 mm, a time of loading 20 seconds).

Results

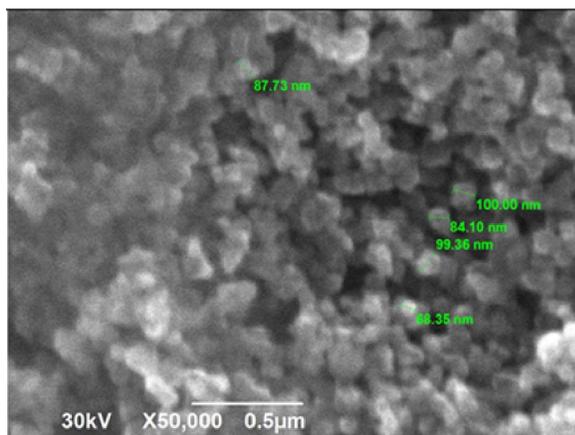
At first, an experimental study of the possibilities of synthesis of composite alloy Al-10%TiC without adding halide salts in the SHS

charge was conducted. However, the SHS reaction was not observed (no flash and gas emission) at the initial temperature of the aluminum melt of 900 °C. The increase of the initial melt temperature up to 1000 °C and addition of aluminum powder (5 and 10% of weight of the charge) to the SHS mixture did also not give positive results: there was a complete absence or minor emission of flash and gas, the fractures of samples were tough, with large inclusions of unreacted charge on the fracture surface. The obtained results were accepted as unsatisfactory.

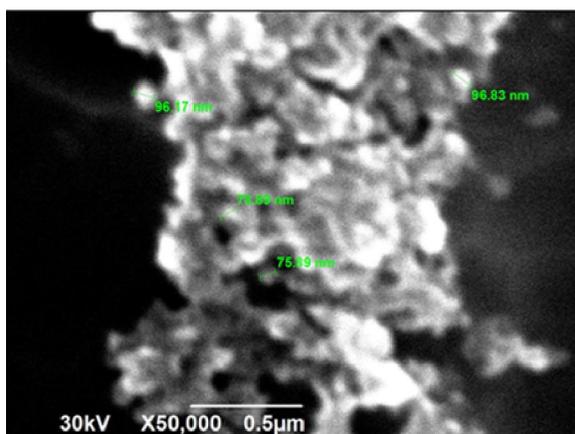
As noted above, the addition of flux cryolite in the amount of 0.1% of the melt mass to a stoichiometric mixture of powders of titanium and carbon leads to realization of the SHS process with formation of TiC particles with the size of about 2-4 microns [11, 12]. In the present work, 5, 10, 15 or 30 % of aluminum powder were added to the SHS charge with 0.1% Na₃AlF₆ to reduce the size of TiC particles. In this case, a full exothermic SHS process was observed with significant overheating of the melt (up 1200 °C). The final samples had clean homogeneous surface of fracture. Microscopic analysis confirmed that ultrafine particles of carbide phase of block shape are formed at all variants of this composition. The best result with the smallest size of particles (170-350 nm) was obtained for the alloy with addition of 5% of aluminum powder and, respectively, of 0.1% Na₃AlF₆. Introduction of more aluminum powder leads to the enlargement of the carbide phase and promotes the formation of agglomerates.

Further research was conducted with salt Na₂TiF₆ as a source of titanium. In this case, the general formula of the SHS charge was as follows: (100 - x) Ti + C + x Na₂TiF₆, where x was mass percentage of titanium in halide salt, replacing x% metallic titanium powder in the original charge (10, 20 or 30%). At carrying out of the heats, the intense SHS reaction was observed consistently with flash and gas emission, the increase of melt temperature in the course of the reaction up to 1250 °C. The fracture surface of the samples was distinguished for its smooth gray color. Pictures of microstructures of the samples are presented in Figure 1. With the increase in the salt content up to 20-30%, the size of carbide phase particles is reduced to nanoscale level (not over 100 nm). However, the sample obtained at 30% has agglomerates of carbide phase particles which are not distributed uniformly over the body of the melt (Fig. 1, b), therefore, the replacement of the metallic titanium by halide titanium-containing salt in the amount of 20% was recognized as the best (Figure 1, a) to produce nanocomposite alloy Al-10%TiC with reinforcing nanoparticles of TiC. X-ray phase

analysis of the sample with 20% of salt Na_2TiF_6 (Figure 2) showed the presence of the following components: pure aluminum – 81.7%, titanium carbide – 8.3%, chiolite $\text{Na}_3\text{Al}_3\text{F}_{14}$ – 10%. Mechanical properties of nanocomposite alloy Al-10%TiC obtained with 20% of salt Na_2TiF_6 are presented in Table 1.



a



b

Figure 1. SEM micrographs of cross-sections of Al-10%TiC samples made with (a) 20% and (b) 30% Na_2TiF_6

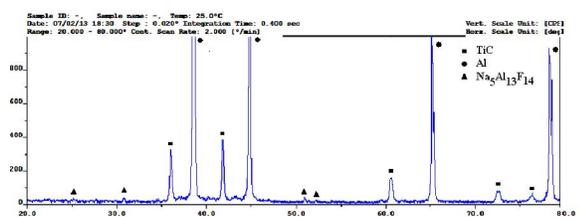


Figure 2. XRD plots of Al-10%TiC composite made with 20% Na_2TiF_6

Table 1. Mechanical properties of aluminum and Al-10%TiC composite made with 20% Na_2TiF_6

Sample composition	Hardness, Brinell	Tensile strength, MPa	Yield strength, MPa	Elongation, %	Reduction in area, %
Aluminum (A7)	250	81	67	9,4	20,0
Al-10%TiC	849	206	155	3,8	2,4

Discussion

The results show that the SHS method opens up great opportunities for regulation of the size and morphology of synthesized ceramic particles not only in the classical technology of SHS powders [14], but also at carrying out of the SHS in molten aluminum. The presence of halide salts in the SHS charge has a very positive impact on the SHS processes in the melt. These halide salts can play both previously known role of fluxes in the aluminum melt [4, 11, 12], and reagents, precursors, i.e. the sources of elements for the formation of refractory compounds in the SHS reactions. In the latter case, they replace all or part of the reagents which are pure elements, and that contributes to the reduction in size of SHS products. Previously, the use of halide salt K_2TiF_6 as the sole source of titanium allowed obtaining particles of titanium carbide of both micron and submicron sizes up to 0.5-1 micron in the aluminum melt [7, 9, 16]. In this work, the use of halide salt Na_2TiF_6 as an additional source of titanium along with metal powder of titanium allowed obtaining nanoparticles of titanium carbide with a size of not over 0.1 micron in the aluminum melt.

Results of Table 1 show how the presence of these nanoparticles in the aluminum matrix increases significantly the hardness and strength of composite alloy while reducing ductility. It should be noted that nanocomposite alloy Al-10%TiC has a significantly greater tensile strength 206 MPa and lower relative elongation of 3.8% compared to the same of microcomposite alloy Al-10%TiC with the TiC particle size of 3-5 micrometers, in which these characteristics are equal, respectively 132 MPa and 7% [9].

To understand the mechanism of action of a halide salt as a flux, thermodynamic calculations of the effect of the addition of halide salt Na_3AlF_6 (cryolite) in the amount of 0.1% of the melt mass to the composition of the SHS charge were performed. A part of the results of calculations are presented in Fig. 3 and 4. The calculations showed that the interaction of flux with oxides of aluminum and titanium begins at the same adiabatic temperature (1285 K), which approximates the melting point of cryolite (about 1050 °C). In addition, at temperatures

developing in local areas of exothermic reaction of titanium and carbon (up to the 1400 °C), the presence of a large number of products of interaction of cryolite with oxides of aluminum and titanium in the melt was noted (Fig. 3,4).

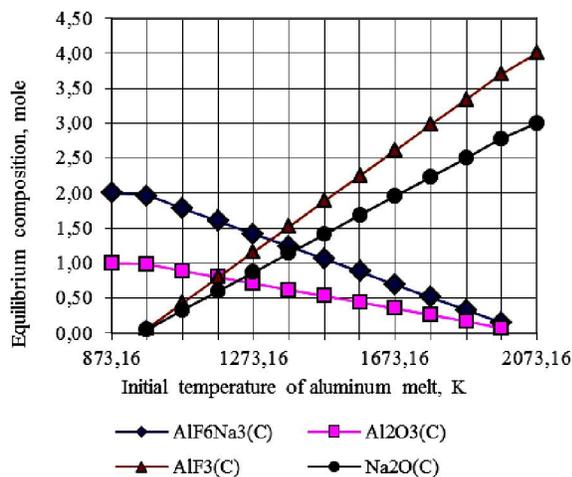
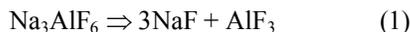


Figure 3. Equilibrium composition of products of reaction of cryolite Na_3AlF_6 with aluminum oxide Al_2O_3 as a function of temperature

On the basis of these results of thermodynamic calculations, the following phenomenological model of chemical stages of interaction of cryolite Na_3AlF_6 with oxides may be offered, explaining refining effect of this flux.

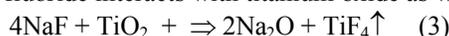
Originally, the salt is decomposed into two products:



Sodium fluoride is the main component providing refinement impact on alumina:



Thermodynamic calculations show that with the increase of the initial temperature, the amounts of salt and aluminum oxide are reduced and the number of the reaction products (AlF_3 and Na_2O) increases. Sodium fluoride interacts with titanium oxide as well:



But the main component of providing refinement impact on titanium oxide is aluminum fluoride:



At the same time, liquid aluminum reduces titanium oxide:



Formed in the previous two reactions aluminium oxide reacts with the second remaining part of the salt which is sodium fluoride:



In the end, the overall reaction of interaction of cryolite with titanium oxide will look as follows:

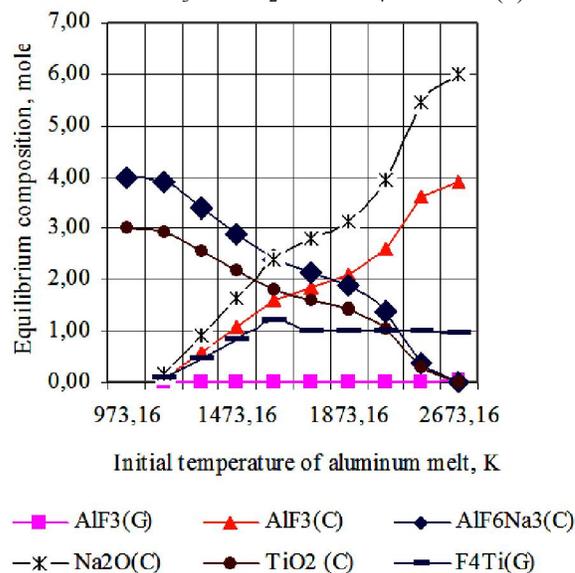
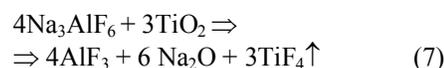
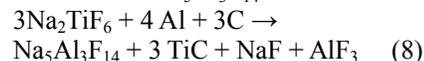


Figure 4. Equilibrium composition of products of reaction of cryolite Na_3AlF_6 with titanium oxide TiO_2 as a function of temperature

Gaseous titanium fluoride is produced in small quantities and rises immediately to the surface of the melt, carrying small impurities. The other two products (Na_2O , AlF_3) partially transform to gas, and partially rise to the surface and are removed in the crystalline state together with the slag.

In the case of the synthesis of nanocomposite alloy Al-10%TiC using titanium-containing halide salt Na_2TiF_6 , atomic titanium generated by decomposition of this salt has a great affinity for carbon and forms the target phase of titanium carbide. Sodium and fluorine interact with aluminum attending in excess and representing at given temperatures already melt and form a chemical compound of chiolite $\text{Na}_5\text{Al}_3\text{F}_{14}$:



The compound of chiolite decays in the further processing to yield salt Na_3AlF_6 , which can be useful and play a role of flux when using alloy Al-10%TiC as a grain refiner.

Conclusion

The results obtained during the investigation of the SHS process with the purpose of synthesis of nanocomposite alloy Al-10%TiC in the melt of aluminum show:

1) the addition of aluminum powder in the amount of 5% together with 0.1% Na_3AlF_6 to the SHS charge allows us to produce ultrafine particles of carbide phase TiC with the size of 170-350 nm;

2) the replacement of the metal titanium in the SHS charge in the amount of 20% by halide titanium-containing salt Na_2TiF_6 allows us to synthesize nanoparticles of titanium carbide with the size of less than 100 nm;

3) synthesized ceramic nanoscale phase TiC change mechanical properties of initial aluminum in much greater extent than microscale phase TiC for the same content.

Further research of the SHS process in the melt aluminum is suggested to perform with a view to a greater uniformity of distribution of nanoparticles TiC and improved mechanical properties of TiC nanocomposites obtained *in situ* with less content of TiC. It is expected to do that with the use of titanium-containing halide salts on the basis of fluoride and chloride of potassium, instead of sodium, in connection with a known fact that fluorides and chlorides of alkaline metals are in the following order: LiF (LiCl) \rightarrow NaF (NaCl) \rightarrow KF (KCl) in accordance with ascending degree of wetting solid surface [17].

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