

## SYNTHESIS AND CHARACTERIZATION OF CAST ALUMINUM MATRIX NANOCOMPOSITES

PRUSOV Evgeny, PANFILOV Alexey, KECHIN Vladimir

*Vladimir State University named after Alexander and Nikolay Stoletovs, Vladimir,  
Russian Federation*

### Abstract

Using nanoparticles as reinforcement for aluminum matrix composites allows significantly increase mechanical and operational properties of details. However, input of exogenous nanoparticles into the aluminum melts is associated with significant technological difficulties caused by their agglomeration and poor wettability with liquid aluminum. For these reasons, it is ineffective to use traditional liquid phase methods of composites production (stir casting, etc.) for synthesis of aluminum matrix nanocomposites. One of solutions is the input of exogenous nanoparticles in metal melts within mechanically activated and compacted mixture of reaction-active powder precursors. Within designated approach was developed liquid-phase technological process of production of aluminum matrix nanocomposites of the system Al-Al<sub>3</sub>Ti-TiB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, including mechanical activation of titanium and boron powders with alumina nanoparticles in planetary ball mill, compacting the mixture and entering the preforms into matrix melt, holding of composite melt for components interaction, stirring and pouring. Selection of reinforcing components based on thermodynamic analysis of interphase interaction processes in considered system. The effect of temperature and time parameters of technological process of aluminum matrix nanocomposites manufacturing and thermal conditions of composite melt crystallization on structure formation and phase composition of cast samples are studied. Adding of nanoparticles leads to decrease in the mean size of intermetallic compounds and changes their morphology to a more compact and also improves the uniformity of their distribution in the structure of cast material. X-ray phase analysis confirms the formation of target endogenous reinforcing phases and retention of exogenous nanoparticles in conditions of liquid-phase technology of nanocomposites production.

**Keywords:** Aluminum matrix nanocomposites, liquid-phase technology, structure, phase composition

### 1. INTRODUCTION

The possibilities for further improving the mechanical and operational properties of traditional materials are almost exhausted by now. In this context, great attention of researchers in many countries is paid to the development of new functional and constructional materials with designed properties. The emergence of nanomaterials science at the turn of the 20<sup>th</sup>/21<sup>st</sup> centuries is considered by scientists as one of the new alternatives to extensive ways of materials development [1]. With a wide implementation of nanomaterials in the industry attributed the possibility of achieving breakthrough results in improving the mechanical, tribological, thermal, electrical and other properties of the working parts.

Problems of practical implementation of the fundamental research results in the field of nanomaterials are caused by particularities of the matter properties change at the transition to nanoscales. Nanostructured metallic materials are strongly nonequilibrium and tend to grain growth, especially at elevated temperatures [2]. In this regard, more promising approach is the use of nanoparticles as reinforcing and modification components at producing of metal matrix composites. The combination of nanoparticles with chemically compatible matrix allows protect them from destabilizing external influences, which increases the efficiency of created materials practical application. It is shown [3], that immediately after the new phase nucleation the nanoparticles are able to rapid absorption at the interphase boundary and inhibition the further growth of this phase. It is assumed that the distribution of nanoparticles along the boundaries of growing phases is caused by the tendency to reduce the Gibbs free energy at the interphase boundary [4]. Sedimentation stability of

nanoparticles determines their presence in the melt in the suspended state [5] and also surfactant effect limiting the crystal growth [6].

The use of nanoparticles as a reinforcing phase in the aluminum matrix composites production allows to significantly improve their properties in comparison not only with traditional materials, but also with micro-sized particle-reinforced metal matrix composites [7]. However, entering of exogenous nanoparticles into aluminum melts is associated with significant technological difficulties arising from their agglomeration and poor wettability by liquid metals [8]. For these reasons, it is ineffective to use the traditional liquid phase methods suitable for producing the composites with micro-sized particles (stir casting, inert gas injection, etc. [9]) to manufacture the cast nanocomposites. One of the ways to solve this problem is input of exogenous nanoparticles into metal melts as part of mechanically activated and compacted mixture of reaction-active powder precursors (a method of liquid-phase reactionary synthesis).

The present research aims to study the influence of technological modes of melting and pouring on structure and phase composition of cast aluminum matrix nanocomposites.

## 2. MATERIALS AND METHODS

For realization designated approach, a liquid-phase technological process of the fabrication of the Al-Al<sub>3</sub>Ti-TiB<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nanocomposites was developed. To form the specified endogenous reinforcing phases (TiB<sub>2</sub>, Al<sub>3</sub>Ti) in the matrix alloy, titanium powder (99.5 wt.% purity; average size 150 μm) and amorphous boron powder (99.0 wt.% purity; average size 63 μm) were used as the initial components. Selection of reinforcing components based on thermodynamic analysis of interphase interaction processes in considered system. The initial components of the powder charge were proportioned for Ti:B = 5:1. Additionally, Al<sub>2</sub>O<sub>3</sub> nanoparticles (15 nm) were introduced into the composition of powder mixtures in the amount of 0.25 wt.% (to the total melt mass). All powders were dried at 110-120 °C for 1.5 h to remove the bounded moisture. Mechanical activation was performed in a planetary ball mill Fritsch Pulverisette 6 (Germany) for 30 min at 300 rpm and ball-to-powder mass ratio 20:1. Prepared powder mixtures were dosed in aluminum foil packages and compacted on laboratory hydraulic press Carver 3664 (USA) into cylindrical preforms with a diameter of 10 mm and a height of 8-10 mm to residual porosity 30-35 %.

The matrix melt (aluminum 99.99 wt.% purity) was prepared in alumina crucible in vertical chamber electrical resistance furnace and overheated to the specified temperature (from 700 to 950 °C in different series of experiments), after that powder preforms were introduced into aluminum melt. After holding for a specified time (from 5 to 60 min) the composite melt was stirred and poured into metal mould at 750 °C for obtaining ingots with a diameter of 20 mm and a height of 80-100 mm.

The microstructure of the composites was observed using digital metallographic microscope Raztek MRX9-D (Russia). Phase analysis was performed on a Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm) at a goniometer rotation speed of 4 grad/min in steps of 0.05° (2 $\theta$ ) by the method of Bragg-Brentano. Identification of phases was carried out in Diffrac.Suite software using database ICDD PDF-2.

## 3. RESULTS AND DISCUSSION

During elaboration of technological process of nanocomposites production by the method of liquid-phase reactionary synthesis, different ways for introducing into the matrix melt of exogenous ceramic nanoparticles as part of a mixture of powder precursors were tested: portion feeding in the free-flowing state on melt surface with constant manual stirring, melt infiltration of precursors and flux (sodium cryolite) mixture, introduction of the mixture into the melt in a briquetted form. According to experimental results, the method of introducing the powder briquettes consisting of reactive components (Ti, B) and exogenous nanoparticles (Al<sub>2</sub>O<sub>3</sub>) is recognized as the most acceptable variant for the technological realization of liquid-phase reactionary

synthesis. In this technology of composites production, metal particles of titanium are not only precursors of endogenous intermetallic reinforcing phases but also perform the transportation function to enter the particles of amorphous boron and alumina nanoparticles into the melt.

It is assumed that during exothermic reactions between the aluminum melt and the introduced components, the resulting endogenous phases are involved in the thermal motion of the liquid and the convective flows caused by the release of heat in the reaction zone, involving in these process exogenous  $\text{Al}_2\text{O}_3$  nanoparticles. As a result, endogenous phases and exogenous nanoscale components are uniformly distributed in the melt. In addition, exothermic reactions that create high temperature gradients at the interphase boundaries provide the wetting and assimilation in aluminum melt the exogenous nanoparticles, which are not wetted under usual isothermal conditions. The introduction of powder preforms [5 Ti + 1 B] was accompanied by an increase in the overall temperature of the aluminum melt at 80-100 °C, which is associated with high intensity of exothermic reactions of  $\text{Al}_3\text{Ti}$  and  $\text{TiB}_2$  formation in self-propagation mode. In compositions containing nanoparticles at introducing of preforms [5 Ti + 1 B + 0.25  $\text{Al}_2\text{O}_3(\text{nano})$ ] was observed a slight (by 10-15 °C) decreasing the exothermic effect and reduction of the reaction rate recorded by changing the thermographs appearance and exothermic peaks offset.

For determining the time-temperature parameters of liquid-phase reactionary synthesis a series of experiments was carried out to obtain aluminum matrix nanocomposites at temperatures from 700 to 950 °C with holding in the liquid state from 5 to 60 min and subsequent pouring into steel or copper molds. It was found that introduction of powder preforms at temperatures from 700 to 850 °C does not ensure the complete synthesis of targeted endogenous reinforcing phases with the required exothermic effect. The necessary wetting of exogenous nanoparticles is not achieved in this case; the resulting materials have a non-uniform structure with large  $\text{TiB}_2$  and  $\text{Al}_3\text{Ti}$  agglomerates. At the bottom of the crucible after melt pouring out the residues of unreacted powder charge are found. In this regard, 850 °C is the minimum temperature necessary for the assimilation of powder preforms and for the interfacial reactions proceeding with required intensity. Further increasing of the temperature up to 950 °C almost does not affect the nature of reactions between the components.

For materials of the Al- $\text{Al}_3\text{Ti}$ - $\text{TiB}_2$ - $\text{Al}_2\text{O}_3$  system the recommended holding time at 850 °C is 25-35 min. Pouring of the alloy before the indicated time is undesirable, because unreacted fragments of the powder preforms may be present in the material structure. Increasing of the duration of composite melt holding until pouring promotes a deeper interaction of the initial components but can lead to the growth of endogenous phases to large sizes and change their morphology to unfavorable, which ultimately will have a negative impact on the properties of the resulting nanocomposite.

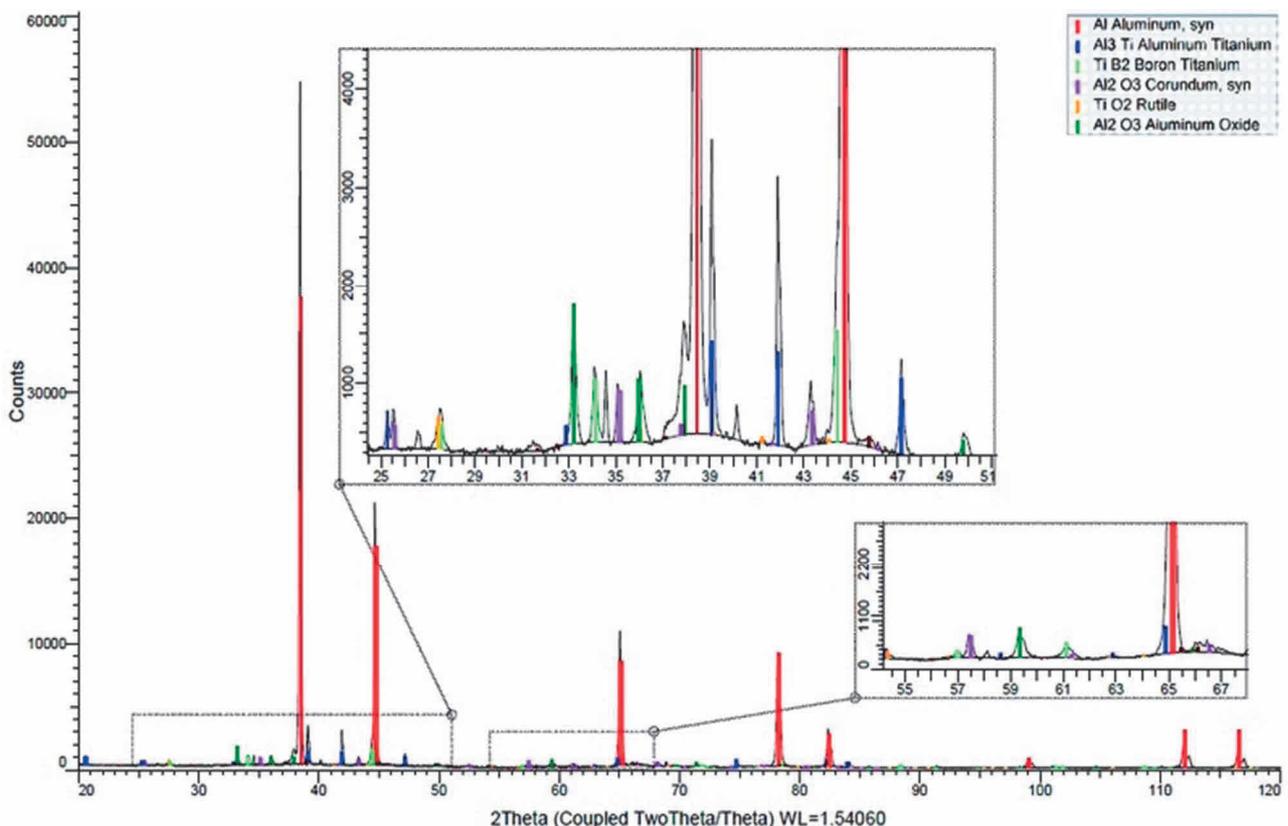
Comparative metallographic analysis of Al + 5 Ti + 1 B and Al + 5 Ti + 1 B + 0.25  $\text{Al}_2\text{O}_3$  cast composites samples indicates on reducing of average size of intermetallic compounds  $\text{Al}_3\text{Ti}$  at the addition of alumina nanoparticles from 20-30  $\mu\text{m}$  to 5-8  $\mu\text{m}$  and a change in their morphology to a more rounded and compact. In the samples of Al-Ti-B composites without exogenous nanoparticles most of  $\text{TiB}_2$  phase is observed along the grain boundaries of the solid solution in the form of small "chains" and is represented by holomorphic crystals with sizes of 2-5  $\mu\text{m}$  and individual agglomerates up to 30  $\mu\text{m}$  in size. Increasing of cooling speed (pouring into copper ingot) resulted in the grinding of the primary  $\text{Al}_3\text{Ti}$  crystals; at the same time, the increase of the cooling rate had practically no effect on the  $\text{TiB}_2$  particle size. In many sections of the structure, fused particles and clusters of titanium aluminides reaching 150-200  $\mu\text{m}$  were found, and in some cases needle-like precipitations of the  $\text{Al}_3\text{Ti}$  phase up to 250  $\mu\text{m}$  in size were observed. Adding of exogenous nanoparticles contributed to reduction of the average size of intermetallic compounds and changing their morphology to a more compact (the complete disappearance of needle inclusions was noted in the structure of the cast samples), as well as to a more uniform distribution of the reinforcing phases due to the destruction of agglomerates; the synthesized  $\text{TiB}_2$  particles were 1-3  $\mu\text{m}$  in size. Due to the high sedimentation stability, the nanoparticles are in a suspended state in a composite melt; accumulating along the boundaries of the primary

crystallizing intermetallics. They prevent the diffusion of aluminum into the aluminide phases, limiting their growth and slowing down the process of coalescence into agglomerates or larger inclusions.

Characterization of the phases detected in cast samples of composite materials is presented in **Table 1**. According to the results of X-ray diffraction studies, in the cast billets of Al + 5 Ti + 1 B composition are presented phases Al, Al<sub>3</sub>Ti and TiB<sub>2</sub>, which are formed in concordance with the generalized equation of chemical reaction:



In the samples obtained with addition of alumina nanoparticles complementarily to the above was observed phases  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, H-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (**Figure 1**). One of the discovered oxide phases (hexagonal H-phase) cannot be unambiguously assigned to the known polymorphous modifications of Al<sub>2</sub>O<sub>3</sub> ( $\beta$ ,  $\chi$ ,  $\epsilon$ , etc.), which also was noted by other researchers [10]. The presence of H-phase can be attributed to a change in the crystal lattice of Al<sub>2</sub>O<sub>3</sub> nanoscale particles under the influence of melt temperature and exothermic reactions taking place between the precursors. Formation of titanium oxide (in the rutile modification) is apparently caused by the possibility of chemical interaction of aluminum oxide nanoparticles with metallic titanium. Under considered conditions, TiO<sub>2</sub> formation cannot be explained from the point of view of classical thermodynamics, since Al<sub>2</sub>O<sub>3</sub> is a more stable compound in comparison with TiO<sub>2</sub> (standard enthalpies of formation are -1675.1 kJ/mol and -944.1 kJ/mol, correspondingly [11]). Presumably, the formation of TiO<sub>2</sub> in the studied system is caused by the influence of size effects, changing the regularities of thermodynamic behavior of the components upon transition to the nanolevel.



**Figure 1** Phase composition of Al + 5 Ti + 1 B + 0.25 Al<sub>2</sub>O<sub>3</sub> nanocomposite

**Table 1** Crystal-geometric parameters of phases in Al-Ti-B and Al-Ti-B-Al<sub>2</sub>O<sub>3(nano)</sub> aluminum matrix composites

Phase	Space group	Lattice parameters		
		Type	a, nm	c, nm
<b>Al-Ti-B</b>				
$\alpha$ -Al	Fm-3m	cub.	0.4049	-
Al <sub>3</sub> Ti	I4/mmm	tetr.	0.3854	0.8584
TiB <sub>2</sub>	P6/mmm	hex.	0.3030	0.3229
<b>Al-Ti-B-Al<sub>2</sub>O<sub>3(nano)</sub></b>				
$\alpha$ -Al	Fm-3m	cub.	0.4049	-
Al <sub>3</sub> Ti	I4/mmm	tetr.	0.3854	0.8584
TiB <sub>2</sub>	P6/mmm	hex.	0.3030	0.3229
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	R-3c	rhomb.	0.4759	1.2993
H-Al <sub>2</sub> O <sub>3</sub>	P63/mmc	hex.	0.3112	0.4988
TiO <sub>2</sub>	P42/mnm	tetr.	0.4594	0.2958

#### 4. CONCLUSION

A liquid-phase technology of aluminum matrix nanocomposites production using the method of self-propagating high-temperature synthesis of endogenous reinforcing phases in aluminum melt is developed. Particularities of technological process of cast aluminum matrix nanocomposites production are studied. The technique of powder precursors introducing into the matrix melts is elaborated. Time-temperature parameters of nanocomposites ingots production are defined. Formation of targeted endogenous reinforcing phases and persistence of exogenous nanoparticles in cast billets demonstrated the feasibility of the proposed technological solutions for aluminum matrix nanocomposites production.

#### ACKNOWLEDGEMENTS

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