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OBTAINING INTERMETALLIC COMPOUNDS IN Al–Ti–Zn SYSTEM

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Binary intermetallic compounds – titanium aluminides (TiAl, Ti_3Al) – when added to the alloys, significantly increase their strength and special properties. The most promising direction to produce intermetallic compounds are mechanochemical technologies, including mechanical alloy building. Mechanical alloying makes it possible to introduce much smaller particles into the metal matrix than can be achieved using standard powder metallurgy technologies. In addition to mechanical synthesis, aluminum-based intermetallic compounds were produced by self-propagating high-temperature synthesis (SHS) of solid chemical compounds. The synthesis was carried out according to a multistage scheme: preparation of titanium and aluminum powder, mixing; synthesis of the Al_3Ti intermetallic compound by the SHS method in vacuum followed by mechanical activation of stoichiometric charges. The aim of the research was to study the dynamics of the development of nanodispersed phases in the process of synthesis during mechanical alloying. The power absorbed by the unit mass of the material for different processing times of the charge was calculated. When the level of the specific power (dose) of mechanical treatment was 3.5 kJ/g, the maximum content of intermetallic compound in the resulting material was achieved. Based on calculations and the data obtained during X-ray phase analysis, the dependence of the change in the content of ternary intermetallic compounds in the final product on the absorbed power was determined. As a result of the studies using raster electron microscopy and X-ray analysis, it was found that mechanical alloying of nanostructured intermetallic compounds Ti_4ZnAl_{11} and $Ti_{25}Zn_9Al_{66}$ with the size of nanodisperse phases less than 12 nm in the Al–Ti–Zn system, the weight ratio of proportion of the latter reaches 74 %.

Key words**:** mechanical chemistry; mechanical alloying; powder materials; self-propagating high-temperature synthesis; aluminum alloys; aluminum; titan; zinc

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Introduction. Metal compounds based on aluminum, being part of aluminum, magnesium and titanium alloys, have a great influence on strength and special properties of the material – wear, corrosion and heat resistance. The greatest effect is achieved with binary and ternary metallic compounds in the alloy in the form of intermetallic compounds. Intermetallic compounds can be present in a structurally free state, be a part of eutectics structure or in the form of scattered particles released during the dispersion decomposition of hardened alloys [1, 2, 4, 5, 10-15].

Binary intermetallic compounds – titanium aluminides (TiAl, Ti_3Al) – added to the alloys, significantly increase their strength and special properties. Alloys doped with titanium aluminides are used when it is necessary to obtain the lightest construction in combination with the required strength (aircraft technology, rocket production), and high heat and corrosion resistance (chemical industry and shipbuilding) [6].

Ternary metal compounds also have a significant impact on the mechanical properties of some aluminum alloys, more specifically, they can significantly change the modulus of elasticity [3].

The formation of intermetallic compounds, their concentration, size and morphology of grains significantly depend on the chemical composition of the alloy – the presence and content of the required metal components in a certain proportion – and the mode of crystallization of the alloy. There is only a limited opportunity to influence these parameters in the process of melting and crystallization of the melt.

Powder metallurgy opens wide possibilities for creating artificial («synthetic») alloys reinforced with double or triple intermetallic compounds, which can be realized by adding pure aluminum (as well as titanium or zinc) to powders or its dilute alloys of previously synthesized intermetallic powders of a given chemical composition. At the same time, the system may differ significantly from the equilibrium state and contain a significantly larger number of reinforcing phases than in the classical state. This content is determined only by the interests of the researcher and the complex of strength and service characteristics obtained after thermoplastic processing of the mixture.

In addition, the hardening of aluminum alloy with aluminum containing a hardening component (which major component is aluminum) allows to obtain a more homogeneous composite material as opposed to hardening with «unrelated» phases – carbides, nitrides, oxides, borides, etc. of silicon, chromium, tungsten and other metals.

Thermoplastic processing of aluminum powders with intermetallic compounds will undoubtedly lead to some changes in the quantity and phase composition of the latter, since they are partially dissolved in the alloy, but it needs to be tested experimentally.

To study the possibility of hardening various aluminum alloys containing titanium or zinc, there was an attempt to create ternary intermetallic compounds consisting of these three metals.

The most promising direction to produce intermetallic compounds is mechanochemical technology, including mechanical alloy building. Mechanical method allows to introduce much smaller particles into the metal matrix than can be achieved using standard powder metallurgy technologies. The process is implemented with high-speed processing of elemental powders or powders of simple alloys in grinding units with high specific power. The alternation of the destruction and welding of particles in combination with the diffusion-intensifying deformation makes the powder more homogeneous, ultimately leading to the formation of a new alloy. Processing of metal and ceramic powders in high-energy units allows to achieve four interrelated effects - dispersion, surface activation, mechanical formation of alloys, mechanochemical formation of compounds. The observed mechanochemical reactions lead to the appearance of new compounds, which is impossible in reactions stimulated, for example, only by the temperature factor [3, 7].

Research methods. In addition to mechanical synthesis, there is a method for producing intermetallic compounds based on aluminum – self-propagating high-temperature synthesis (SHS) of solid chemical compounds. This technological process is based on the exothermic reaction of interaction of initial reagents in the form of combustion. For SHS reagents are used in the form of powders. The question of the processes occurring in the Al–Ti and more complex systems that determine the phase composition and structure of the final product remains poorly understood [1, 7].

The research was aimed at studying the possibility of synthesizing ternary intermetallic compounds in the Al–Ti–Zn system, in particular $Al_{11}Ti_4Zn$ and $Al_{66}Ti_{25}Zn_9$, from powder materials using the methods of mechanochemistry and SHS and determining the conditions for their production.

The synthesis was carried out according to the original multistage scheme: preparation of powders of titanium and aluminum, mixing; synthesis of the Al_3Ti intermetallic compound by the SHS method in vacuum with subsequent mechanical activation of stoichiometric charges.

At the first stage, fine powder was obtained by grinding in water in an attritor of a standard design [3] from titanium powder of the TPP-8 brand with a fraction of 0-160 μm. The dehydration of the powder was carried out first by filtration on a vacuum filter, then drying at a temperature of 100-105 °C for several hours. The target fraction of 0-63 microns was selected from the dried fine powder.

After that aluminum powder PA-4 of 0-63 μm fraction was mixed with titanium powder in a ball mill (in the required proportion) and pressed into tablets under a pressure of 300 MPa.

Then the synthesis of Al_3Ti intermetallic compound from tablets was carried out using the SHS method in vacuum. The installation for conducting SHS consists of a steel hermetic retort with a water-cooled upper lid placed in a laboratory resistance furnace SSHOL-2.5, a vacuum pump, an oil trap, an expansion flask, vacuum hoses and valves. The vacuum level was controlled with an OBMB1-100 pressure sensor. The retort was filled with even layers of compressed tablets mixed with alumina.

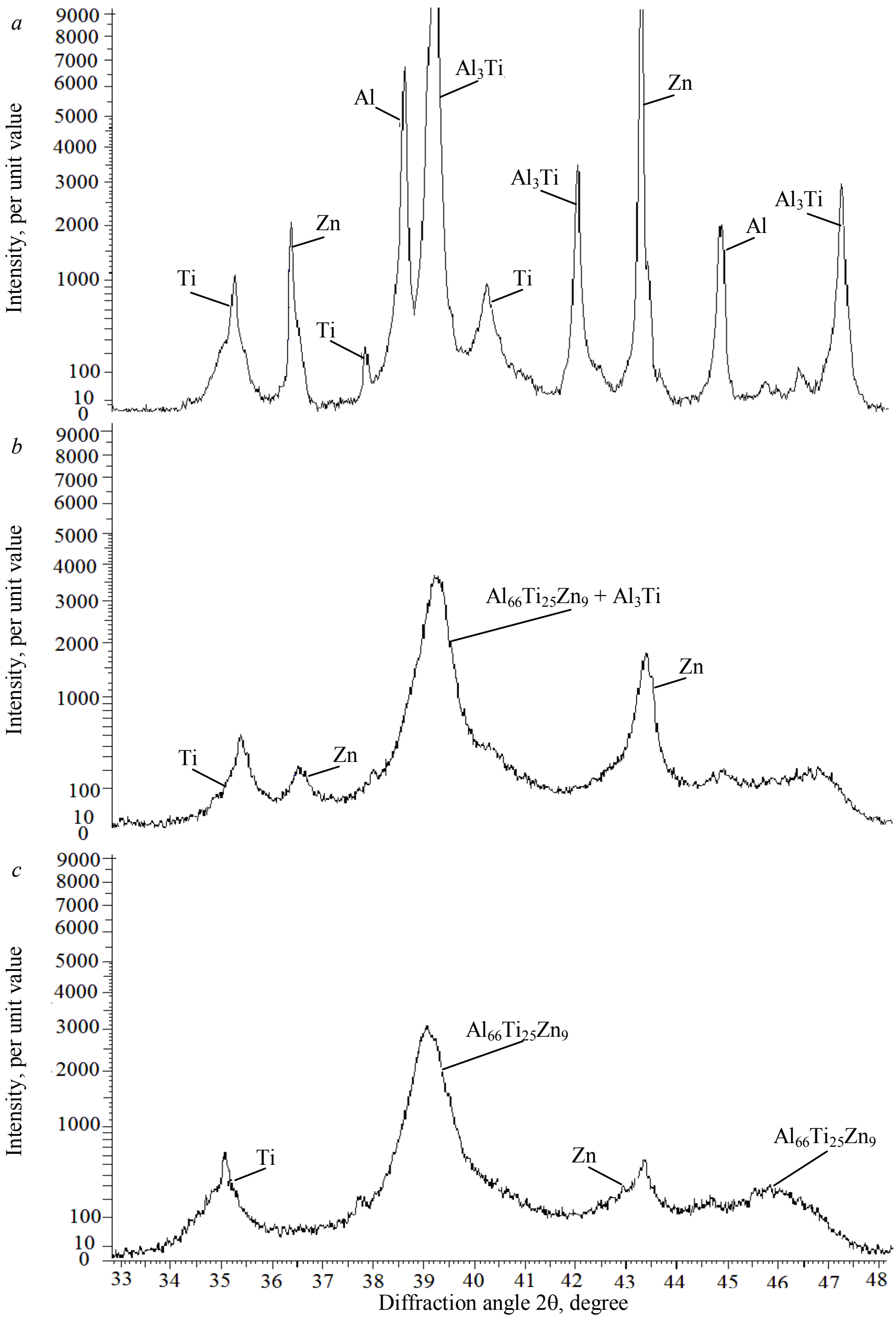

Fig. 1. Charge corresponding to the composition of intermetallic compound $Al_{66}Ti_{25}Zn_9$: *a* – initial mixture; *b* – after 4 cs treatment the weight content of $Al_{66}Ti_{25}Zn_9$ is 66 %; *c* – after 8 cs treatment the weight content of $Al_{66}Ti_{25}Zn_9$ was 74 %

The dynamics of the development of nanodispersed phases in synthesis during mechanical doping was studied by the X-ray phase method using a Bruker D8 Advance X-ray diffractometer with a vertical θ-θ-goniometer using a β-filtered $Cu_{K\alpha}$-radiation ($\lambda = 1.5418$ Å, Ni-filter), the diffraction pattern was recorded a high-speed LynxEye detector (pickup angle of 3.2°) from Bruker, a scanning step of 0.02° at 2θ and a signal accumulation time of 0.7 s/step. Modes of operation of the tube $U = 40$ kV, $I = 40$ mA. The survey was carried out with Bragg-Brentano focusing during sample rotation (30 rp/m). The processing of the obtained X-ray diffraction patterns was performed using the Bruker DiffracPlus software package.

The phase composition was determined by comparing the set of interplanar distances of the experimentally obtained radiographs with the radiometric data of the phases of the PDF-2 powder base (ICDD). Further processing of the diffraction data was carried out according to the Rietveld method using the DiffracPlus Topas program. The method is based on the construction of a model diffraction pattern, which considers all the structural features of the phase components of the target object and the instrumental parameters of the survey, and a comparative analysis with the experimental scattering pattern. By refining the profile (cell parameters, zero shift and preferential orientation parameter) and structural parameters of the model (coordinates and atomic populations) during a series of iterations, the best fit of the observed and calculated diffraction pattern was achieved. Goodness of Fit shows the $GOF = R_{wp}/R_{exp}$ criterion, which characterizes the inconsistency of the model with the experimental data. Refinement was carried out until the GOF value did not exceed 1.5-2.5 %. Based on the Rietveld calculation, the amounts of phases and the size of their crystallites were determined.

Changes in the particle size of the powder after activation were also recorded using a scanning electron microscope (SEM) – SUPRA 55VP-25-78.

As a result of the experiment, it was found that the implementation of SHS leads to the high-speed nature of the Al_3Ti formation reaction: after prolonged heating to 220 °C for 2 h, the temperature of the space inside the retort rose during 80 s to 870 °C.

After heating, the material acquired an uneven structure, which is a frim «core» and a fragile «shell». According to X-ray analysis, the «core» consisted of 90 % Al_3Ti, and the «shell» had 65 % of Al_3Ti. This intermetallic compound turned out to be nanostructured with crystallite sizes ≈ 40-90 nm.

The «cores» of the material were ground in a vibratory mill to a fraction of 0-63 μm. From powders of the

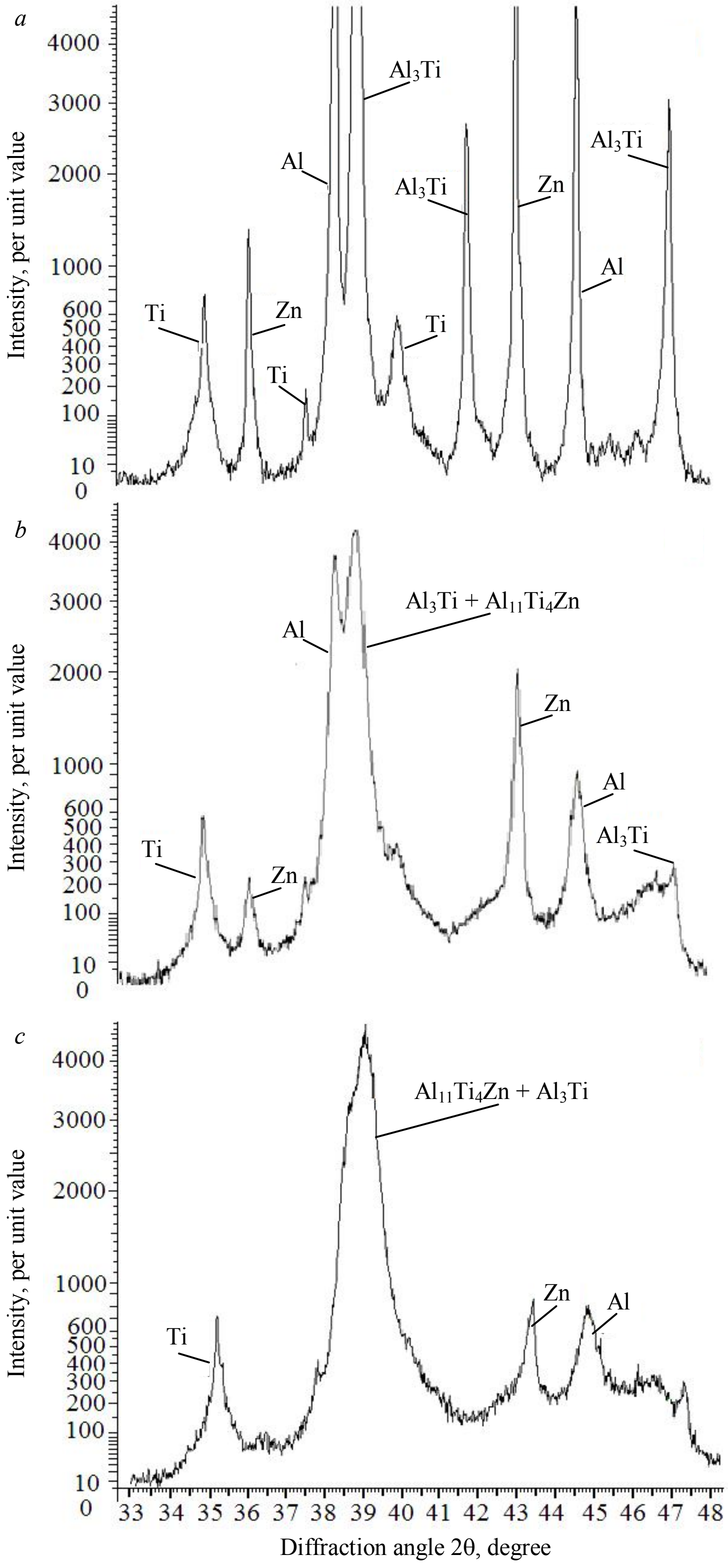

Fig.2. Charge corresponding to the composition of intermetallic compound $Al_{11}Ti_4Zn$: *a* – initial mixer; *b* – after 4 cs treatment the weight content of $Al_{11}Ti_4Zn$ was 26 %; *c* – after 8 cs treatment the weight content of $Al_{11}Ti_4Zn$ was 54 %

alloy 88.4 Al – 11.6 Zn (weight ratio), zinc PC1 and Al_3Ti, we prepared a charge for obtaining the intermetallic compounds $Al_{11}Ti_4Zn$ and $Al_{66}Ti_{25}Zn_9$. Mechanical alloying of the charge was carried out in an attritor according to the method [3] with steel balls with a diameter of 7-10 mm with a total weight of 20 kg per 1150 g of the powder mixture. Each powder mixture was processed at 8 cs.

Characteristic areas of diffractograms with different activation times are shown in Figs.1 and 2.

During high-energy mechanical processing, we found out the occurrence and increase of weight content to 74 % and more of the triple intermetallic $Al_{66}Ti_{25}Zn_9$ (see Fig.1), the particle size of which is 0-40 microns (Fig.3). These particles consisted of nanocrystalline clusters of no more than 3-4 nm at any stage of processing. In the second mixture, the weight content of the $Al_{11}Ti_4Zn$ intermetallic compound reached 54 % (after 8 cs treatment), the cluster size ranged from 5 to 12 nm.

Comparison of the morphology and dispersion of the initial charges and the products of their processing within 8 cs (Fig.3) showed a significant decrease in particle size with a slight change in their shape. This is characteristic of both studied intermetallic compounds.

The granulometric composition of $Al_{11}Ti_4Zn$ powders before and after machining was analyzed on a Microsizer 201A laser diffractometer in a 1 % solution of potassium tartrate in distilled water, an inhibitor of corrosion of aluminum-based powders in water. The results of determining the particle size distribution of $Al_{11}Ti_4Zn$ powders are shown in Fig.4.

The energy characteristics of mechanical doping are energy intensity - the ratio of the useful power of the grinding unit to the mass of the material being processed and the dose – the specific energy absorbed by a unit of mass of the material during mechanical processing. Figure 5 shows the dependence of the change in the content of $Al_{66}Ti_{25}Zn_9$ on the dose of high-energy mechanical processing. From the obtained data it follows that at the level of specific power (dose) of machining 3.5 kJ/g, the maximum content in the resulting material is reached.

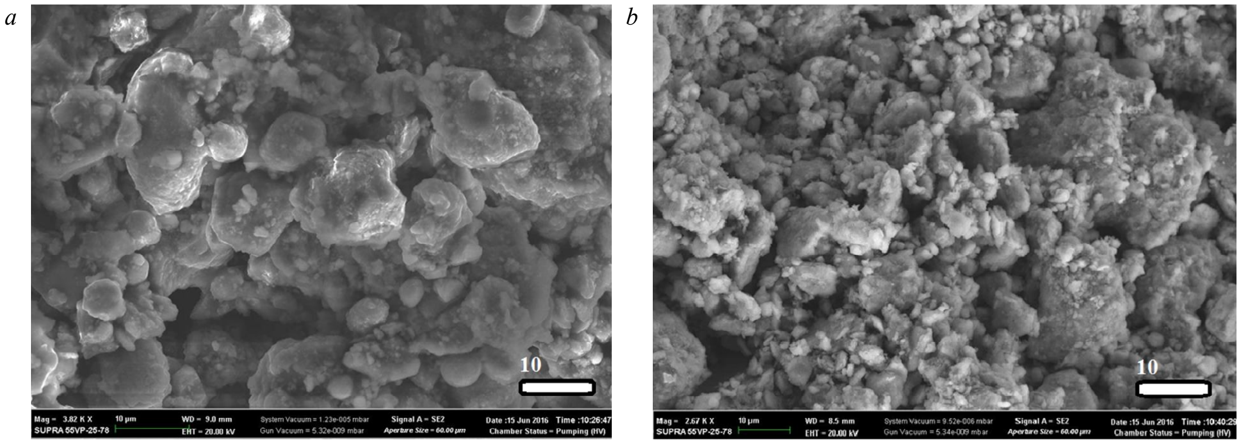

Fig.3. SEM image of powder charge corresponding to the composition of intermetallic compound $Al_{11}Ti_4Zn$ before (*a*) and after mechanical alloying for 8 cs (*b*)

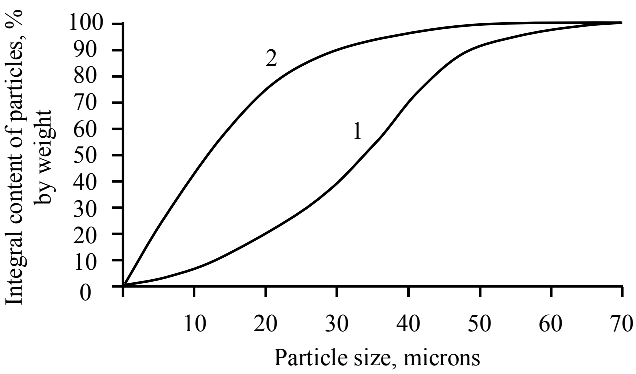

Fig.4. Integral curves of grain fineness of $Al_{11}Ti_4Zn$ powders before (1) and after (2) mechanical alloying

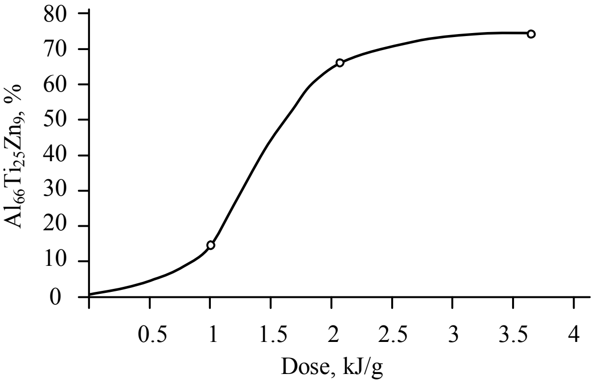

Fig.5. Dependency of $Al_{66}Ti_{25}Zn_9$ content from dose during high-energy mechanical treatment

The obtained intermetallic compounds were used as an alloying agent (at the level of 3-7 % by weight) to the D16 alloy powder (Al–Cu–Mg–Mn systems) for thermoplastic processing of the produced mixtures by hot extrusion with the production of hardened rod stocks [9].

Conclusions

1. The principal possibility of obtaining in the Al–Ti–Zn system by mechanical alloying of powders of nanostructured intermetallic compounds $Al_{66}Ti_{25}Zn_9$ and $Al_{11}Ti_4Zn$ has been established.

2. According to the proposed method, nanostructured intermetallic compound $Al_{66}Ti_{25}Zn_9$ was synthesized with the size of nanodispersed phases of 3-4 nm; moreover, at the level of specific power (dose) of mechanical treatment 3.5 kJ/g, its weight ratio can reach 74 % and more.

3. The synthesis of the $Al_{11}Ti_4Zn$ intermetallic compound by mechanical alloying proceeds less intensively using the same method: at the same level of the mechanical treatment dose, its weight ratio reaches only 54 %. The size of nanodispersed phases is 5-12 nm.

REFERENCES

1. Evstigneev V.V., Filimonov V.Yu., Vasilenko S.N. Two mechanisms of structure formation in a heterogeneous Ti–Al powder mixture during synthesis in the thermal explosion mode. 2004. N 1, p. 239-243 (in Russian).

2. Ermilov A.G., Bogatyreva E.V. Preliminary mechanic activation. Moscow: Izd. dom MISiS, 2012, p. 135 (in Russian).

3. Trotskii M.V., Petrovich S.Yu., Andreeva V.D., Lipin V.A. Patterns of the occurrence and changes of nanoscale hardening phases in mechanically alloyed powders of the Al–Mg–Mn–Ti system. Sbornik dokladov MNPK v ramkakh nedeli nauki SPbPU. Part 1. St. Petersburg: Izd-vo Politekhnicheskogo universiteta, 2014, p. 137-141 (in Russian).

4. Boronenko M.P., Lavrikov V.V., Seregin A.E., Yurukin P.A., Yukhimuk R.F. Control of grinding energy and mechanical activation of AGO-3 planetary mill. *Vestnik Yurginskogo gosudarstvennogo universiteta*. 2016. N 2 (41), p. 7-16 (in Russian).

5. Gopienko V.G., Petrovich S.Yu., Cherepanov V.P., Grishchenko I.B., Baranov V.A. Metal powders of aluminum, magnesium, titanium and silicon. Consumer properties and applications. Ed. by A.I.Rudskaya. St. Petersburg: Izd-vo Politekhnicheskogo universiteta, 2012, p. 356 (in Russian).

6. Kozlov E.A., Brodova I.G., Bashlykov D.V., Yablonskikh T.N., Abakshin E.V. Structure, phase composition and properties of promising Al alloys with Ti, Zr after their high-speed deformation in solid and liquid states. *Fizika metallov i metallovedenie*. 1999. Vol. 87. N 3, p. 34-45 (in Russian).

7. Surkov V.A. Analysis of methods for producing intermetallic compounds of *p*, *d*-metals. *Vestnik Kazanskogo tekhnologicheskogo universiteta*. 2014. Vol. 17. N 10, p. 27-33 (in Russian).

8. Tret'yakov K.V. Phase and structural transformations in aluminides of transition metals Fe, Co and Ni during mechanochemical synthesis and mechanic activation: Avtoref. dis. ... kand. khim. nauk. Moskovskii gosudarstvennyi universitet. Moscow, 2006, p. 139 (in Russian).

9. Khmelevskaya V.B., Moseiko E.S., Myakon'kov M.B. Production and use of nanomaterials and nanostructuring to enhance the work of mechanisms. St. Petersburg: Izd-vo Politekhnicheskogo universiteta, 2012, p. 140 (in Russian).

10. Bozic D., Dimcic B. Nanocomposites with unique properties and applications in medicine and industry. Rijeka: InTech, 2011, p. 360.

11. Shishkovsky I., Missemer F., Kakovkina N., Smurov I. Intermetallics Synthesis in the Fe–Al System via Layer by Layer 3D Laser Cladding. *Cristals*. 2013. N 3, p. 517-529.

12. Gnanapoongothai T., Murugan R., Palanivel B. First-principle study on lithium intercalated antimonides Ag_3Sb and Mg_3Sb_2. *Ionics*. 2014. Vol. 21. N 5, p. 1351-1361.

13. Lee C.H., Lee S.H., Chun S.Y., Lee S.J., Kwon Y.S. Nanocomposite Formation in the Fe_2O_3-M (M = Al, Ti, Zn, Cu). *Systems by Mechanical Alloying*: *Materials Science Forum*. 2004. Vol. 449-452, p. 253-256.

14. Baimakov A.Yu., Petrovich S.Yu., Lipin V.A., Shahmin A.L., Seytenov R.A. The influence of alloying additions on interaction of aluminum alloys with aqueous media. *Light Metals*. *The Minerals*, *Metals and Materials Society*. 2015, p. 387-391.

15. Zolotorevsky V.S., Belov N.A., Glazoff M.V. Casting Aluminium Alloys. Amsterdam: Elsevier, 2007, p. 530.

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