



## IMPROVING THE MANUFACTURING TECHNOLOGY OF ALTi MODIFIER FOR ALUMINUM ALLOYS

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### ABSTRACT

The paper presents the results of laboratory studies on the manufacture of AlTi grain refiner. The developed technology includes self-propagating high-temperature synthesis of Al<sub>3</sub>Ti from a titanium sponge and molten aluminum; mechanical grinding of Al<sub>3</sub>Ti; adding of ground Al<sub>3</sub>Ti particles into the aluminum melt. The modifying ability of the experimental AlTi modifier is not inferior in effectiveness of the AlTiB at the same titanium content in the modifiable metal.

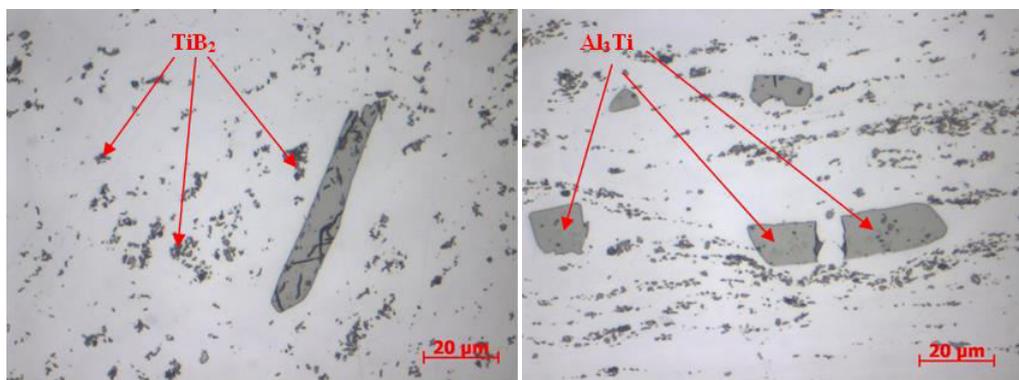
**Keywords:** alloying, master alloy, grain refinement, AlTi, AlTiB, self-propagating high-temperature synthesis, SHS, titanium sponge, titanium aluminide, intermetallic compound, microstructure.

### INTRODUCTION

The blank production of flat ingots for rolling and cylindrical ingots for pressing from aluminum wrought alloys is widely used in many fields of mechanical engineering, including aircraft industry and in space technology [1-6]. Therefore, the technological and operational properties of these ingots are subject to increased requirements, which largely depend on size of the grain and its uniform distribution in volume of ingot. This is achieved by modifying the aluminum melt with special master alloys - modifiers. The Al<sub>5</sub>Ti<sub>1</sub>B alloying bar [7, 8] of various manufacturers, such as KBM Affilips, LSM, KB Alloy, HOESH, Aleastur and others, obtained widespread application in the aluminum industry. The production of Al<sub>5</sub>Ti<sub>1</sub>B master alloy typically includes

aluminothermic reduction of potassium hexafluorotitanate (K<sub>2</sub>TiF<sub>6</sub>) and potassium tetra fluoroborate (KBF<sub>4</sub>) with subsequent separation of salt and metal phases. Further, a bar stock with a diameter of  $9.5 \pm 0.5$  mm is obtained from the melt of master alloy using continuous casting and rolling technology, usually with Continuis Properzzi equipment.

Al<sub>5</sub>Ti<sub>1</sub>B alloying composition contains two main types of intermetallic compounds: titanium aluminide (Al<sub>3</sub>Ti) with a particle size 30-100 μm and titanium diboride (TiB<sub>2</sub>) with a particle size 5-20 μm (Figure-1). These intermetallic compounds, after addition the master alloy into the aluminum melt, act as crystallizing nucleus and support to grain refinement of crystallized ingots. The average consumption of Al<sub>5</sub>Ti<sub>1</sub>B per ton of melt is 2 kg.



**Figure-1.** The macrostructure of Al<sub>5</sub>Ti<sub>1</sub>B alloying bar.

The main disadvantages of manufacturing and application of Al<sub>5</sub>Ti<sub>1</sub>B master alloy are listed below:

- the high cost of master alloy due to use of such expensive materials as complex fluorides of titanium and boron (K<sub>2</sub>TiF<sub>6</sub>, KBF<sub>4</sub>);
- the problem of uniform distribution of Al<sub>3</sub>Ti and TiB<sub>2</sub> in the bar stock, in the melt and in the ingot during crystallization;
- the presence of large Al<sub>3</sub>Ti clusters with a size up to 100 μm in master alloy does not provide a sufficient number of crystallizing nucleus, leads to the loss of intermetallic compounds in ceramic foam filters, and also due to liquation of Al<sub>3</sub>Ti;
- Emissions of gaseous fluorides (BF<sub>3</sub>, HF) during preparation of master alloy and formation of second hazard class toxic waste of potassium fluoroaluminates during aluminothermic



reduction of complex titanium and boron fluorides.

The most complete information about the composition, properties and technological features of manufacturing and application of aluminum master alloys in Russia and abroad is posted in publications of V.I. Napalkov [9, 10].

One of the way for improving the manufacturing technology of Al5Ti1B master alloy is dissolution of a titanium sponge impregnated with molten potassium tetra fluoroborate in liquid aluminum [11].

## MATERIAL AND RESEARCH METHODOLOGY

The purpose of this research is to develop a manufacturing technology of AlTi modifier with an average Al<sub>3</sub>Ti particle size from 5 to 15 μm, possessing the same modifying ability as AlTiB master alloy at the same titanium content in modifiable metal.

At present time, the AlTi alloying bar is practically not used for modification of aluminum and its alloys, due to the increased consumption to achieve effective grain refinement of crystallized metal. In practice, a tablet mixture of titanium and halide-containing fluxes with a weight ratio of 4 to 1 has become widespread [12], but this is difficult to use in the technology of continuous casting of ingots.

In the known Al5Ti1B master alloy the main function of grain refinement during metal crystallization is performed by TiB<sub>2</sub> particles with size of 5-10 μm. Therefore, to ensure the modifying ability of AlTi modifier at the level of AlTiB master alloy, it is necessary to find an effective solution to reduce Al<sub>3</sub>Ti particle size in the AlTi compound from 20-70 μm to a size of no more than 10 μm. As such a solution, AlTi modifier manufacturing technology was proposed and experimentally confirmed. This includes the following basic operations [13]:

- obtaining an AlTi alloy with a Ti content of 30-37 Wt% by the method of self-propagating high-temperature synthesis (SHS) at an initial aluminum temperature of 800-900 °C (Figure-2, where the region of the desired alloy concentration is highlighted in red). The basis of this alloy is Al<sub>3</sub>Ti, the titanium content of which is 37.2 Wt%;
- mechanical crushing and grinding of the obtained alloy to particle sizes less than 10 microns;
- obtaining AlTi modifier by adding the obtained Al<sub>3</sub>Ti particles into the aluminum melt;
- crystallization of the melt in bar form.

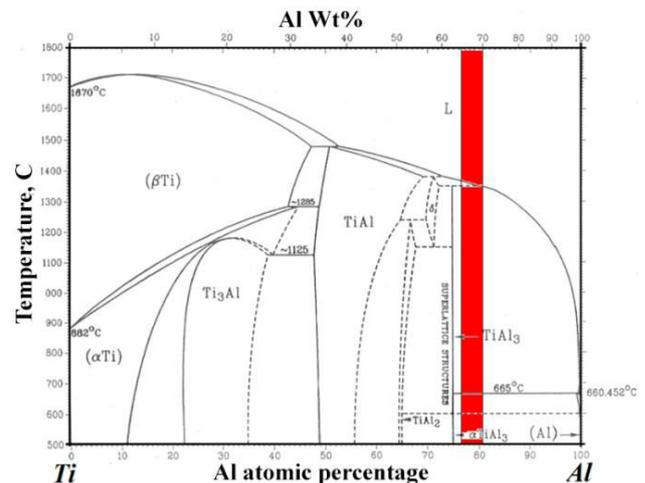


Figure-2. Phase diagram of Al-Ti system [14].

To obtain an AlTi alloy with a Ti content of 30-37 Wt% a titanium sponge was used as a feedstock. The estimated amount of titanium sponge was placed in a heated crucible and filled by molten aluminum. The temperature of the feedstock, at which SHS process begins ranges from 800 to 900 °C and then increases to 1350-1400 °C. The duration of this process is 1-2 min.

The X-ray phase analysis of the AlTi alloy was realized on a Shimadzu XRD-7000 automated X-ray diffractometer in Cu K $\alpha$ -radiation. Radiographs were taken on powders in the range of angles 2 $\theta$  from 5° to 70° in increments of 0.03 deg. The scanning speed was 1.5 deg/m. Then, the obtained results were processed using an information retrieval system for X-ray phase identification of materials combining qualitative and semi-quantitative analysis (using the "corundum numbers" method).

The results of X-ray phase analysis confirmed that the basis of SHS products is Al<sub>3</sub>Ti compound with a small admixture of aluminum.

Studies of the microstructure of alloy based on Al<sub>3</sub>Ti and AlTi master alloy was realized on micro analyzer Superprobe JXA-8200 (Jeol Ltd., Japan) staffed by a scanning electron microscope of high resolution and energy dispersive spectrometer (EX-84055 MU).

It should be noted that methods for producing Al<sub>3</sub>Ti using self-propagating high-temperature synthesis (SHS) are known [7, 15-17], but they are based on use of aluminum and titanium powders mixture and do not involve the use of a lump titanium sponge and aluminum melt.

## RESULTS AND DISCUSSIONS

The Figure-3 shows the microstructure of Al-33.8%Ti alloy obtained by high temperature synthesis. The microstructure of the alloy is represented by three main phases: the base is an Al<sub>3</sub>Ti intermetallic compound (1) with a particle size of 5 to 7 μm; yellow inclusions (2) are particles of an intermetallic compound of titanium and aluminum of an intermediate composition AlTi<sub>1.25</sub>. The third phase (3), highlighted in blue, is aluminum located mainly along the grain boundaries of Al<sub>3</sub>Ti.

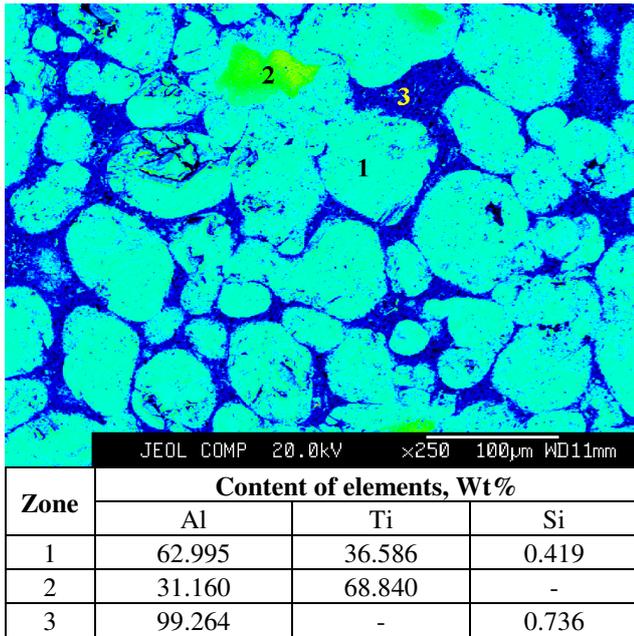


Figure-3. The results of X-ray spectral analysis of main phases of the Al-33.8%Ti alloy.

Further, ingots from the obtained AlTi alloy were grinded and milled in an AGO-2 planetary mill to a particle size of approximately 8 μm. Then powder was dissolved in a melt of aluminum and sodium fluoroaluminate (NaF×AlF<sub>3</sub>) at a temperature of 830-850 °C. During melting, the melt was mechanically mixed for 10 minutes. Then sequentially kept for 60 minutes and cast into bars.

The Figure-4 shows the microstructure of manufactured Al-5%Ti master alloy obtained by addition into the aluminum a powder of Al-33.8%Ti alloy with an average particle size of 8 μm. This alloying composition has a dendritic and fragmentation structure of Al<sub>3</sub>Ti particles several microns in size. Agglomerates of Al<sub>3</sub>Ti particles are also predominantly rounded form with a size of several tens of microns, which is the main factor that reduces the modifying ability of the Al-Ti master alloy.

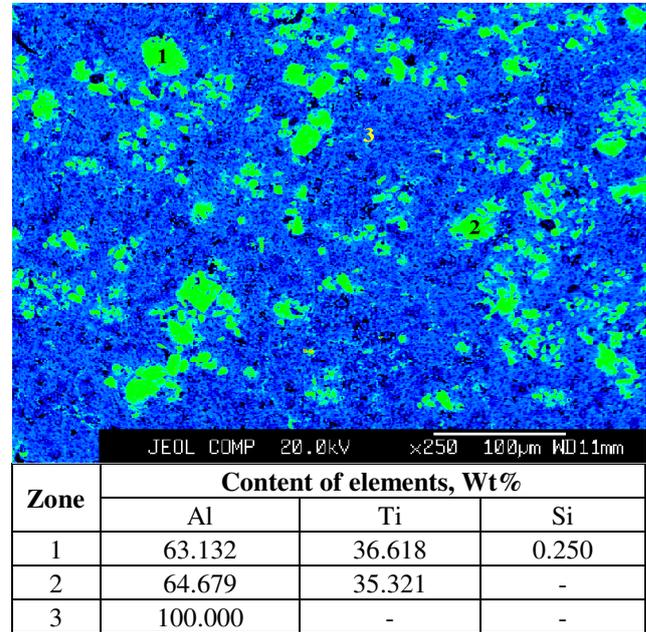
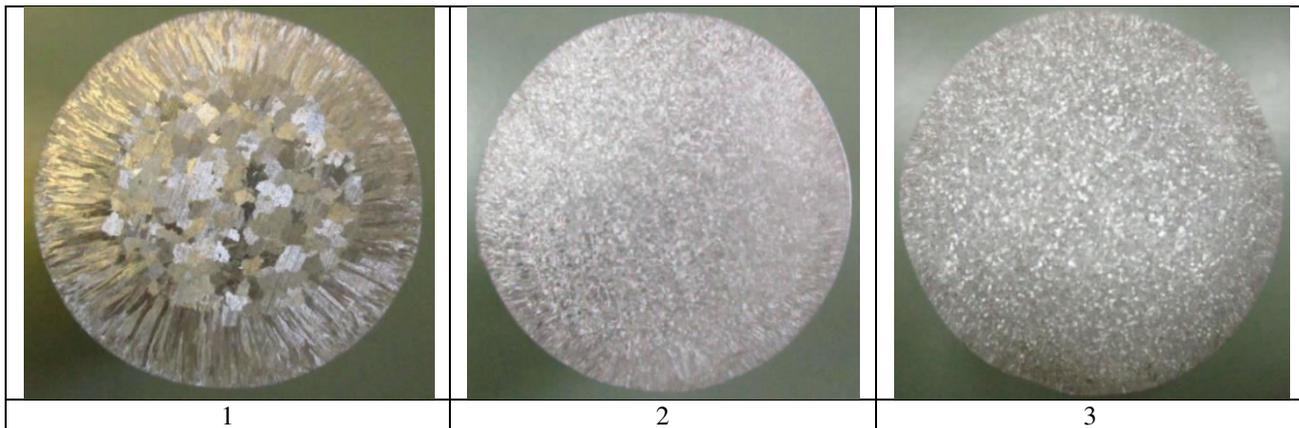


Figure-4.

Table-1. The results of modifying ability test for Al-5%Ti and Al-5%Ti-1%B master alloys.

Sample	Raw material weight, g	Modified Al weight, g	Master alloy quantity, g	Master alloy type	Temperature, °C	Ti content in modifiable metal, %	Grain amount per 1 cm <sup>2</sup> of macrosection
1	300	293		initial Al	740±10	-	32
2	300	295	0.295	Al-5%Ti	735±10	0.005	840
3	300	289	0.287	Al-5%Ti-1%B	740±10	0.005	812



**Figure-5.** The macrostructure of Al modified by Al-5%Ti and Al-5%Ti-1%B master alloys: 1 - initial Al; 2 - Al-5%Ti; 3 - Al-5%Ti-1%B

Amount of aluminum grains per 1 cm<sup>2</sup> of the microsection was calculated at a Ti content of 0.005% in modified metal. Table-1 and Figure-5 shows that the experimental Al-5%Ti master alloy is not inferior in effectiveness to Al-5%Ti-1%B.

## CONCLUSIONS

The result of laboratory studies is practice application of manufacturing technology of AlTi modifier using a titanium sponge [13-19], which allow to avoid the use of such expensive materials as complex titanium and boron fluorides (K<sub>2</sub>TiF<sub>6</sub>, KBF<sub>4</sub>). Manufactured AlTi modifier has Al<sub>3</sub>Ti intermetallic compound size up to 15 μm and a similar modifying ability as the well-known AlTiB master alloy with at the same titanium content in the modifiable metal.

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## REFERENCES

- [1] Zolotarevsky V. S., Belov N. A. 2005. Metallurgical science of aluminum casting alloy. Moscow.
- [2] Bazhin V. Yu., Sizyakov V. M., Vlasov A. A. 2013. Surface defects in foil direct chill strip from highly-alloyed aluminum alloys. Metallurgist. 56(11-12): 863-866.
- [3] Uskov I. V., Belyaev S. V., Uskov D. I., Gilmanshina T. R., Kirko V. I., Koptseva N. P. 2016. Next-Generation Technologies of Manufacturing of Waveguides from Aluminum Alloys. ARPJ Journal of Engineering and Applied Sciences. 11(21): 12367-12370.
- [4] Bazhin V. Yu. 2015. Structural modification of petroleum needle coke by adding lithium on calcining. Coke and Chemistry. 58(4): 138-142.
- [5] Illarionov I. E., Gilmanshina T. R., Bogdanova T. A., Kosovich A. A. 2019. Gas production ability of coatings used in low-pressure casting of car wheels. Tsvetnye Metally. 1: 72-77. DOI: 10.17580/tsm.2019.01.11
- [6] Kosovich A. A., Bogdanova T. A., Baranov V. N., Belyaev S. V., Partyko E. G. 2019. Preventing the rejection of light alloy wheels by «turning of oxide spot» defect during low-pressure die casting. ARPJ Journal of Engineering and Applied Sciences. 14(21): 3712-3717.
- [7] Kandalova E. G. 2000. Development of a technology for producing Al-Ti and Al-Ti-B modifying master alloys based on the SHS process: the candidate of tech. science dissertation. Samara.
- [8] Frolov V. F. 2016. Research and development of a new technology for the production of flat ingots from aluminum alloys 1XXX series for foil rolling production: the candidate of tech. science dissertation. Krasnoyarsk.



- [9] Napalkov V. I., Mahov S. V. 2002. Alloying and modifying of aluminum and magnesium. Moscow.
- [10] Napalkov V. I., Mahov S. V., Pozdnyakov A. V. 2017. Modifying of aluminum and magnesium alloys. Moscow.
- [11] Kulikov B. P., Nechaev V. A., Zheleznyak V. E. 1996. Improving the technology for preparation of titanium-containing aluminum alloys. *Tsvetnye Metally*. 9: 68-69.
- [12] Savchenkov S. A., Bazhin V. Yu. 2013. Tableted Titanium master alloys Ti80F20. Actual problems of modern science in the XXI century: 3rd International Scientific and Practical Conference. Makhachkala.
- [13] Kulikov B. P., Baranov V. N., Zheleznyak V. E. 2017. A method of obtaining a modifying master alloy Al-Ti. Patent RF no. 2637545, C22C 1/04.
- [14] Lyakisheva N. P. 1996. Diagrams of binary metallic systems: a handbook. Moscow.
- [15] Vershinnikov V. I., Borovinskaya I. P., Merzhanov A. G. 2009. A method of producing powder materials based on nickel aluminide and titanium aluminide. Patent RF no. 2354501, B22F 3/23.
- [16] Lazutova E. B., Chechushkin O. P. 2015. The method of obtaining master alloys for the production of aluminum alloys. Patent RF no. 2542191, C22C 35/00.
- [17] Talako T. L., Lecko A. I., Belyaev A. V. 2008. A method of obtaining a powder material based on titanium aluminides. Patent Belarus no. 10752, B22F 9/16.
- [18] Kirko V. I., Dobrosmyslov S. S., Nagibin G. E., and Koptseva N. P. 2016. Electrophysical-mechanical properties of the composite SnO<sub>2</sub>-Ag (Semiconductor-metal) ceramic material. *ARPJ Journal of Engineering and Applied Sciences*. 11(1): 646-651.
- [19] Yuriev P. O., Lesiv E. M., Bezrukikh A. I., Belyaev S. V., Gubanov I. Y., Kirko V. I., Koptseva N. P. 2016. Study of change in the scm's strength properties depending on the aqueous-clay suspension's concentration and muscovite's amount in its composition. *ARPJ Journal of Engineering and Applied Sciences*. 11(15): 9007-9012.