Specificity of the titanium-powder alloying tablets usage in aluminium alloys

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An issue of improving the extruded titanium alloying elements with the purpose of the components dilution speed and completeness enhancing is discussed in the paper. Investigation of titanium alloying tablet obtained by cold extrusion has been fulfilled. Problems of the powdered titanium densing are listed and discussed. Determined were chemical compositions of titanium alloying elements from different suppliers, implemented was an estimation of mechanical strength subject to the density of tablets, obtained were the data on absorption and dilution in aluminium solutions, studied was the flux and titanium powder distribution in alloying tablet. Comparative analysis of the alloying tablet porosity has been carried out by means of the ImageJ image analysis and processing software. Molasses has been used in the produced alloying tablet as a binder, which guarantees the flux uniform distribution throughout tablet volume with homogeneous pores formation after annealing, as distinct from the tablets of other manufacturers. The flux uniform distribution throughout tablet volume assures forming the aluminium alloy structure with the given composition of intermetallic compounds.
The obtained alloying tablet possesses higher mechanical properties and demonstrates rate of dissolution in aluminium solution 15–20% higher than that of analogues. It was found that titanium powders should have improper (irregular) form and advanced surface of particles to allow pressing them at low pressures in rigid matrices and obtain products in tablets with the required porosity and strength. It was revealed that improvement of flux adhesion with titanium powder and powders compressibility is achieved by means of introducing a binder, molasses, which envelops particles and provide and additional strength of tablets on extrusion.

Key words: alloying tablets, titanium, titanium powder, cold extrusion, aluminium alloys, dissolution rate, molasses.

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Introduction

Titanium is one of alloying elements which is actively applied both in ferrous and non-ferrous metallurgy for modifying structure and properties of alloys [1, 2]. It is known that undersize-particles titanium powders are well moulded and sintered, while materials of coarse powders are used as pseudoligatures for alloyed steel production [3–6].

Modern technologies of aluminium alloys manufacturing are directed towards alloying by separate refractory element [7–10]. Alloying tablets (pseudoligatures) represent one of alternatives to chemical elements introduction to melt along with the cast pig or rod alloying elements and powders [11, 12]. The briquetted alloying materials with Ti80F20 flux are destined for aluminium alloys doping by titanium and are used for aluminium alloys of all groups (1xxx and 8xxx series).

The extruded titanium briquettes consist of uniformly distributed particles of powder, which are segregated by a layer of fusible matrix — combined flux. Density of a briquette depends on magnitude of compacting pressure in a punch. At that, the area of contact is growing and an influence of the pores presented in volume on the processes proceeding in the briquette during melting in liquid melt is lessening. Interaction of elements in a volume of briquette takes place in a solid phase (powder dissolution), and in a liquid one — in a melt of salts as well [13, 14].

Resting on the user's test data it is possible to choose the following advantages of the alloying tablets application:

– the tablet dissolution rate (25–30 min) at the melt operating temperatures of 730–750 °C because of high porosity and strength of the alloying element;

– the metal temperature change during tablets dissolution within the established interval (10–15 °C);

– capability of a furnace charge composition adjustment on alloying and simplicity of the extruded briquettes use without additional weighing;

– the cost of transport cutting down and the storage facilities reduction.

Generally, tablets are of a cylindrical form and are moulded of titanium powder with addition of a special nonhygroscopic fusible flux in various proportions (from 75% to 100%), for ensuring quick dissolution in a melt. Tablets are manufactures by extrusion in a metal matrix in especial unit. The powdered flux nonuniform distribution in a body of a titanium-powder tablet due to the difference of their densities is a main reason of a poor quality of alloying elements and leads to negative consequences during the aluminium alloys manufacturing. Difficulties with the powdered composite briquettes storing and transportation to furnace units are the applied problems.

Currently available titanium alloying tablets production techniques don't reflect a know-how of manufacturing the high-quality modifying tablets of titanium (homogeneous structure, uniform flux distribution, stable content of titanium, strength, porosity, and density). In this connection, elaboration and more accurate definition of process and technical arrangements for producing high-quality extruded powders in the context of existing technical specifications and instruction are of scientific and practical interest.

Materials and experimental technique

Specimens of alloying elements from three suppliers have been selected in order to reveal the main disadvantages of the producible titanium alloying.

Titanium powders of TPP-2 ("VSMPO-AVISMA") brand as a furnace charge material and an Aleastur flux composition (NaCl —45 % (wt.), KCl — 55 % (wt.)) have been used to produce the alloying tablets with molasses as a binder, which has been poured in amount of 7–9% for 100 mass parts of titanium powder and flux.

The powdered mixtures have been compacting at room temperature. The resultant briquettes have been annealed for 60 min at the temperature of 80–100 ^{o}C. Grinding of the powders has been carried out on a Retsch MM 301 vibratory mill. Particles of titanium powder have been distributed by size by means of a Horiba LA-950 laser diffraction/scattering particle size distribution analyzer. Macrostructures of the powders have been examined by an Axio Lab.A1 microscope with localized lighting system.

The powders have been blended for an hour on a laboratory mixer with gate-impeller mixer. A Buehler Simplimet fully automatic electro-hydraulic press has been used for powders extrusion. As a rule, on cold extrusion, the calculated by formula quantity of prepared powder is fed up to a mould and then pressed by punch. An automatic machine (a Bipel 200 complex with horizontal extrusion) in a hands-off mode is feeding the powder from press bin to matrix, fills up the matrix, compresses a briquette and then pushes it out to a conveyor. The blending and pressing results can be checked-up by physicotechnological properties of a furnace charge on determining granulometric composition, bulk weight, fluidity, density and chemical composition. In practice, only a part of manufacturing characteristics is registered and compared are the two parameters: mechanical strength test and density of briquettes.

Comparative assessment of the alloying materials dissolution rate has been implemented in laboratory environment on a laboratory-scale plant for triplex process. In a crucible furnace with capacity of 10 kg, aluminium of a A7E (1000 g) grade has been melted down, heated up to 730–740 ^{o}C, added with cut templates of the tablets according to the calculations and then samples have been chosen after 2, 4, 6...40 min to check the chemical state of aluminium. Dissolution kinetics of tablets and percentage of alloying components absorption have been estimated according to the results of chemical compositions of the samples.

Results of investigations and their discussion

As a result of implemented study on titanium powders, it has been found that metallics should have an irregular form with uniform flux distribution in the mould volume to guarantee solid cohesion and flux distribution over the tablet volume.

In case of titanium with various form of particles usage in an alloying tablet, the local formation of cracks take place (Fig. 1) and the flux slipping through the voids of titanium powder with particles of oblong form is observed. In case of a nonuniform flux distribution (Fig. 2), examination of chemical composition of a tablet (Table 1) by the laser surface scanning method reveals essential deviations (up to 15–20%) in titanium content already at a 1-cm^2 square.

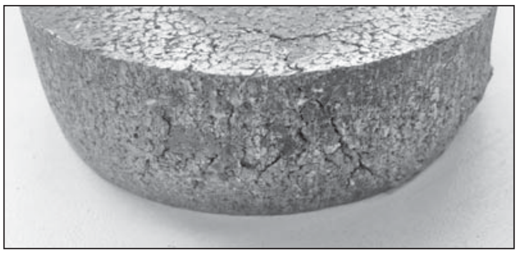

Fig. 1. Local cracks on a tablet surface

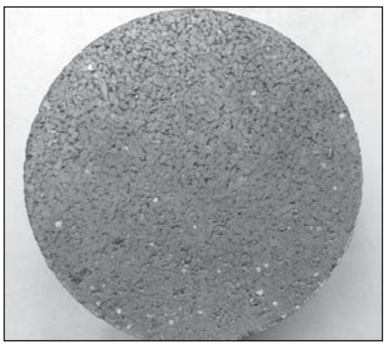

Fig. 2. Flux nonuniform distribution on a tablet surface

Table 1
Chemical composition of Ti80F20 tablets

Number of sample	Chemical composition, %								
	Fe	Si	Mn	Ti	Cr	Cu	Mg	Zn	Flux
1	0.30	0.11	0.009	78.2	0.01	0.001	<0.010	0.031	18.6
2	0.29	0.10	<0.010	68.5	0.01	0.007	0.004	0.069	22.0
3	0.18	0.09	0.002	84.6	0.02	0.020	0.003	0.042	19.3

In Fig. 3 it is evident that if particles of titanium powder have a spheroidal form, then additional voids appear on the particles compacting. That degrades mechanical strength and leads to the tablet destruction during carrying, charging and entry of the first portions of metal on melting.

According to the existing methods of titanium powders manufacturing [15, 16], the following demands are made. Powders of titanium should have an improper (irregular) form and advanced surface of particles to allow pressing them at relatively low pressures in rigid matrices and obtain products in tablets with the required porosity and strength.

In order to achieve the given parameters of briquette and its weight, density is calculated with the following formula:

$$\rho = M/(3.14 \cdot R^2 \cdot h) \quad (1)$$

where ρ — density, g/cm^3; M — tablet weight, g; R — tablet radius; h — tablet height.

To provide the tablet density (2.5–5.0 g/cm^3) required by the instruction of RUSAL UC, it has been previously found that the optimum compacting pressure for alloying elements manufacturing equals to 250–300 kg/cm^2 (25.5–29.8 MPa). It is necessary to mention that high compacting pressure (350–500 kg/cm^2) may lead to internal destruction of titanium powders particles and later on, during an aluminium alloy doping, to melt penetration into the appeared voids where interaction of the flux particles with molten aluminium takes place with resulting formation of oxides, which are converting to slag on complete tablet dissolution. Moreover, the overconsolidated briquette have worse values of dissolution rate (35–40 min), since moving aluminium melt doesn't infiltrate the alloying tablet completely for the latter doesn't posses the required porosity and make a barrier oxide layer, which impede the tablet absorption during alloying process.

Application of lower powder compacting pressures (100–200 kg/cm^2) doesn't guarantee the required density and strength of alloying tablets which leads to powder crumbling and unavoidable loss of alloying tablet geometrics for more than 5–15%.

In the presented paper, the improvement of flux adhesion with titanium powder and accurate powders compacting are achieved by introducing the binding additive — molasses, which envelops particles and provide and additional strength of tablets on extrusion by simplifying their friction between the mold walls and particles by themselves.

Process of the powder component interaction with molasses take place in two stages: the first is a transport one or molasses (an adhesive) transference towards the surface of titanium powder and flux (a substrate) and their determinate orientation in the interfacial layer, at which a mechanical cohesion is ensured; the second stage includes the adhesive and substrate interaction stipulated by diametrically opposed intermolecular bonding (van der Waals forces). The adhesion process comes to the end with intermolecular interaction of contacting phases, which correspond to the minimal surface energy [5]. Tablets annealing at 80–100 °C is resulted in a 50–60% burning out of a binder with residuary small microcavities and keeping the given porosity and strength level (Fig. 4). The molasses content in briquettes after annealing is insufficient since addition of alloying element to aluminium melt doesn't cause its burning out which is confirmed by boiling absence on the melt surface. Comparative analysis of porosity of the alloying tablet manufactured with molasses and without it has been carried out by means of the ImageJ image analysis and processing software (Fig. 5).

To check quality of briquetting the alloying elements standard mechanical strength test is usually carried out

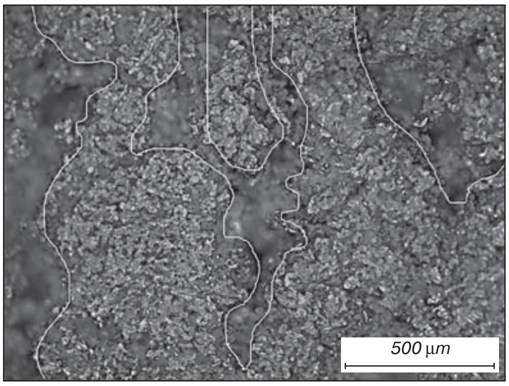

Fig. 3. Voids in an alloying tablet volume

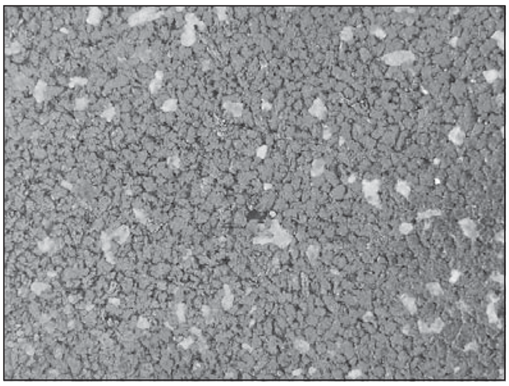

Fig. 4. Flux and pores uniform distribution on a tablet surface

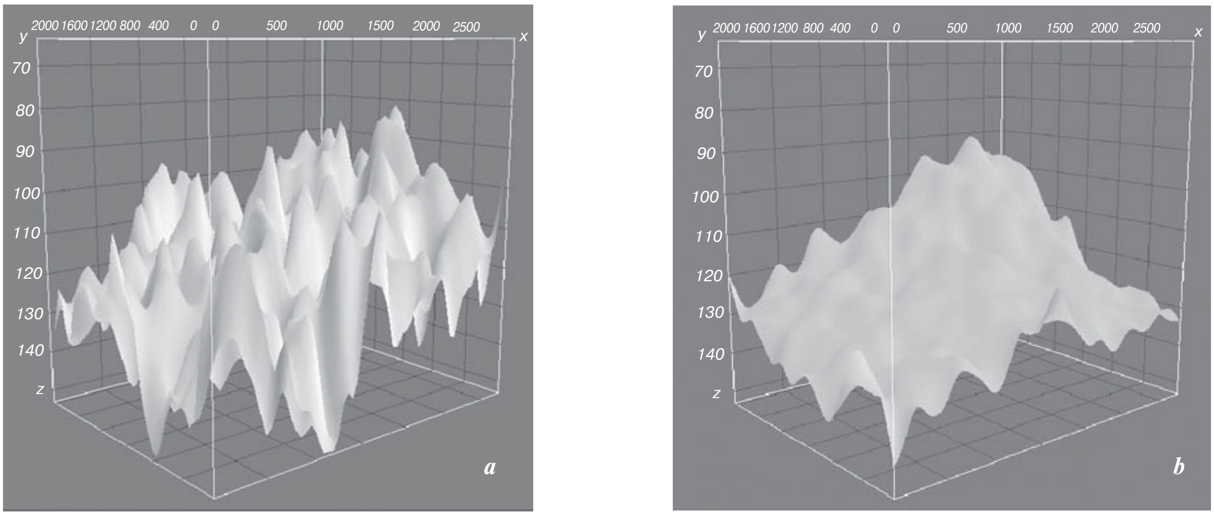

Fig. 5. Porosity background of an alloying composition:
a — with molasses; *b* — without molasses

in factory laboratories. Tablets of each sort of alloying element are thrown down from a height of 1m to a cast-iron area and then the strength is estimated at 5-point scale. In some cases an impact tool is used to break the tablet and visually estimate its porosity as well as the flux section distribution. The alloying tablets manufactured with molasses and without it have been estimated by the hereinabove procedure; the results are summarized in Table 2.

On the basis of the fulfilled investigations on comparative assessment of the alloying tablets dissolution rate, a kinetic dependence has been obtained (Fig. 6).

Table 2
The mechanical strength test at the measured density of tablets

Number of a sample	Sample 1	Sample 2	Sample 3	Average point	Average density, g/cm^3
1	4	4	3	3.66	3.95
2	3	4	3	3.33	3.28
3	4	4	5	4.33	4.12
With molasses	5	5	4	4.66	4.05

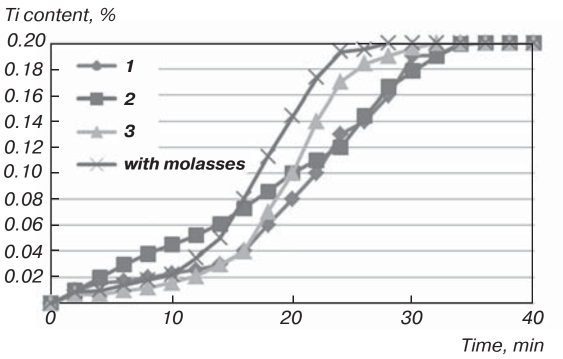

Fig. 6. Titanium content in aluminium melt

Time of alloying element assimilation up to Ti content of 0.20% for all specimens from different suppliers didn't exceed 40 min. But the least dissolution time of the alloying briquette with a binder — molasses — was 28 min.

Chemical analysis of the alloy specimens picked in the first time slot (5—7 min) shows insufficient increase of titanium content, which is explained by its slow transfer from the tablet surface. The diffusion processes with a solid solution formation actively take place in this time slot in a microvolume of an alloying element on a titanium powder — flux boundary and transition to Al_3Ti intermetallic compounds is beginning. After break-up of the alloying briquette, rapid discontinuous increase of alloying element content in alloy takes place in accordance with the chemical analysis results [17, 18]. In order to accelerate the melt saturation with an alloying element, it is necessary to either fulfill a melt stirring or apply the alloying element in a dispersed form, in case of using tablets [19, 20]. Thus, for faster assimilation of titanium-powder alloying elements, it is necessary that tablets would have the sufficient porosity that the melt could move through their pores and actively interacts with the particles until their complete dissolution. At the same time, it should be taken into account that the melt is under conditions of free or forced convection with increase in time of the melt isothermal holding at any selected temperature.

Conclusions

It was found that titanium powders should have an improper (irregular) form and advanced surface of particles to allow pressing them at low pressures in rigid matrices and obtain the pelletized products with the required porosity and strength.

It was revealed that improvement of flux adhesion with titanium powder and the molding formation of powders are achieved by means of introducing a binder, molasses, which *envelops particles and provide and additional strength of tablets on extrusion.*

It was established that alloying tablets of different manufacturers have high dissolubility in a flow of aluminium melt. Time of alloying element absorption up to Ti *content of 0.20% for all specimens from different suppliers didn't exceed 40 min. But the least dissolution time of the alloying briquette with a binder — molasses — was 28 min.*

References

1. Belov N. A. *Fazovyy sostav promyshlennykh i perspektivnykh alyuminievykh splavov* (Phase composition of industrial and prospective aluminium alloys). Moscow : Publishing House of "MISiS", 2010. 511 p.

2. Novikov I. I., Zolotorevskiy V. S., Portnoy V. K., Belov N. A., Livanov D. V., Medvedeva S. V., Aksenov A. A., Evseev Yu. V. *Metallovedenie. Uchebnik v 2 tomakh* (Physical metallurgy : textbook : in two volumes). Under the editorship of V. S. Zolotorevskiy. Vol. 1. Moscow : MISiS, 2009. 496 p.

3. Sizyakov V. M., Gopienko V. G., Aleksandrovskiy S. V. *Poluchenie poroshkov aluminiya, magniya i titana s ispolzovaniem metodov nanometallurgii* (Aluminium, magnesium and titanium powders obtaining by nanometallurgy methods). Saint-Petersburg : Saint-Petersburg State Mining Institute, 2008.

4. Vasiliev V. V., Kurilov P. G., Ligachev A. E., Mishin B. S. *Poroshkovaya metallurgiya i kompositsionnye materialy* (Powder metallurgy and composite materials). Moscow : MATI, 1983. 62 p.

5. Podrezov Yu. M. Vliyanie tekhnologicheskykh i strukturnykh parametrov poroshkovogo titana na zakonomernosty kontaktoobrazovaniya (The powdered titanium process variables and structural parameters influence on the contact formation mechanism). *Poroshkovaya metallurgiya = Powder Metallurgy.* 2009. No. 3/4. pp. 98—111.

6. Podrezov Yu. N., Laptev A. V., Nazarenko V. A. Strukturnaya chuvstvitelnost mekhanicheskykh svoystv poroshkovogo titana (Structural susceptibility of the powdered titanium mechanical properties). *Uchenye zametki : mezhuniversitetskiy sbornik ("Inzhenernaya mekhanika")* (Scientific notes : the interuniversity collection ("Engineering mechanics")). Vol. 25, Part II (June, 2009). Lutsk, 2009. pp. 198—203.

7. Cui X. et al. Fabrication of fully dense TiAl-based composite sheets with a novel microlaminated microstructure. Scripta Materialia. 2012. Vol. 66. No. 5. pp. 276—279.

8. Ding W., Xia T., Zhao W. Performance Comparison of Al—Ti Master Alloys with Different Microstructures in Grain Refinement of Commercial Purity Aluminum. Materials. 2014. Vol. 7, No. 5. pp. 3663—3676.

9. Makhov S. V., Kozlovskiy G. A., Moskvitin V. I. Osnovy protsessa aluminotermicheskogo polucheniya ligatury Al—Ti iz TiO_2, rastvorennogo v khlpridno-ftoridnom rasplave (The concepts of the process of aluminothermic obtaining of Al—Ti master alloy from TiO_2 dissolved in chloride-fluoride melt). *Tsvetnye metally = Non-ferrous Metals.* 2015. No. 11. pp. 34—38.

10. Moskvitin V. I., Nikolayev I. V., Fomin B. A. Metallurgiya legkikh metallov (Metallurgy of light metals). Moscow : Intermet Inzhiniring, 2005. 413 p.

11. Uliyanov D. S., Piskarev D. V., Shevtsov M. G. Kompleksnye tabletirovannye ligatury (Complexes tableted alloying elements). *Tsvetnye metally = Non-ferrous Metals.* 2011. No 7. pp. 65—67.

12. Gurevych L. M., Shmorgun V. G. Formirovanie intermetallidov pri vzaimodeystvii rasplava aluminiya s titanom (The intermetallic compounds formation on the aluminium melt interaction with titanium). *Metallurg = Metallurgist.* 2015. No. 12. pp. 68—74.

13. Napalkov V. I., Bondarev B. I., Tararyshkin V. I., Chukhrov M. V. *Ligatury dlya proizvodstva aluminievykh i magnievykh splavov* (Alloying compositions for aluminium and magnesium alloys production). Moscow : Metallurgiya, 1983. 159 p.

14. Napalkov V. I., Makhov S. V. *Legirovanie i modifitsirovanie aluminiya i magniya* (Aluminum and magnesium alloying and modifocation). Moscow : MISiS, 2002. 376 p.

15. Antsiferov V. N., Smetkin A. A., Yarmonov A. N., Peshcherenko S. N. *Sposob polucheniya titanovogo poroshka poroshka* (Method of titanium powder manufacturing). Patent RF, No. 2178341. Asserted 20.01.2002. Published Bulletin No. 2.

16. Gulyakin A. I., Mushkov S. V., Berdyannikova L. M., Semyannikov G. G. et al. *Sposob polucheniya titanovogo poroshka* (Method of titanium powder manufacturing). Patent RF, No. 2061585. Published 10.10.1994.

17. Sujata M., Bhargava S., Sandal S. Microstructural Features of $TiAl_3$ Base Compounds Formed by Reaction Synthesis. Materials and Design. 2011. Vol. 32, No. 1. pp. 207—216.

18. Lagosa M. A., Agotea I., Gutierreza M., Sargsyana A., Pambaguianb L. Synthesis of TiAl by Thermal Explosion + Compaction Route: Effect of Process Parameters and Post-Combustion Treatment on Product Microstructure. International Journal of Self-Propagating High-Temperature Synthesis. 2010. Vol. 19, No. 1. pp. 23—27.

19. Cheberyak O. I., Sivkov V. L., Bogdanov O. V., Geyko M. A. Formirovanie strukturnykh sostavlyayushchikh v psevdoligaturakh (Formation of structural components in pseudoligatures). *Zagotovitelnye proizvodstva v mashinostroyenii = Blanking Productions in Mechanical Engineering.* 2010. No. 11. pp. 8—10.

20. Cheberyak O. I., Sivkov V. L., Lyubimtsev A. A., Chuvagin N. F., Titov A. V. Osobennosti formirovaniya struktur v obieme psevdoligatur (Bulk Structure Formation in Quasi Preliminary Alloys). *Vestnik Yuzhno-Uralskogo gosudarstvennogo universiteta. Seriya: Metallurgiya = Bulletin of the South Ural State University. Series "Metallurgy".* 2012. No. 39. pp. 16—20. NFM