

Yanko T. B.<sup>1</sup>, Ovchinnikov A. V.<sup>1</sup>, Lyutyk N. P.<sup>2</sup>, Korzhyk V. N.<sup>2</sup>

<sup>1</sup> Titanium institute, JSC. Ukraine, Zaporizhya

<sup>2</sup> Research-Production Center "Plazer", Ltd. Ukraine, Kyiv

## TECHNOLOGY FOR OBTAINING OF PLASMA SPHEROIDISED HDH TITANIUM ALLOY POWDERS USED IN 3D PRINTING

*The features of additive technologies are considered and key characteristics of methods for producing titanium powders are presented. Typical sizes of titanium alloy powders used in additive processes are given. It is shown that the most effective way to obtain fine titanium powders is hydrogenation-dehydrogenation technology (HDH). However, to obtain the required flow parameters and sphericity, plasma spheroidisation (PS) technology should be used. The process flowsheet producing spherical powders of titanium alloys for aviation applications by complex HDH and PS method is proposed. [dx.doi.org/10.29010/085.7]*

*Keywords:* additive manufacturing; titanium alloys; powders; spheroidisation.

### Introduction

Modern solutions for technical assignments including their economics require the following: minimisation of raw material and energy consumption, concentration on the most important production directions with obtaining of maximum profit.

Resource and energy spending is based on the definite technological process and related equipment.

The above fully applies to metallurgical industry where the most important target is significant decrease in energy consumption for yielding of final metal products [1].

Application of additive manufacturing technologies (including titanium industry) allows significant minimisation for coefficient of material usage (more than 0.9) which is a weight ratio between final article and initial raw material (reciprocal of this factor is called "buy-to-fly" parameter) [2]. As a result raw material consumption, number of production steps, and final machining processes will significantly be reduced. However, essential part for additive manufacturing is synthesis of titanium powders with required shapes and definite chemical compositions.

Titanium alloy powder manufacture with the above parameters is one of the most costly processes in non-ferrous metallurgy. Solution for this problem would greatly reduce production cost creating competitive technology.

The main method for titanium alloy (for example VT-6, TiAl-V) powder synthesis is pulverisation of melts [3]. This technology includes: titanium sponge manufacture, its mixing with master alloys, compacting of sponge block, its melting to ingot, ingot processing to required work piece, and finally work piece remelting with pulverisation to metal powder.

The major problems in synthesis of titanium alloys are controlled addition of alloying elements, their even distribution in base metal, and also narrow size distribution of the powders. Concluding the above it is feasible to say that this technology is complicated and expensive.

The largest requirements are especially applied for key article parts. They include homogeneity of chemical composition and even distribution of mechanical properties. In addition sufficiently high demands are introduced to particle shapes.

Required metal structure and its chemical homogeneity related to mechanical properties are directly bound to technology. Currently there is a number of additive manufacturing methods which differ in metal powder feeding into article formation zone and by applied energy type [4]. Each technique needs definite powder size and preferable particle shape. The former is defined by applied energy method (Fig. 1) For example, selective laser melting (SLM) has optimum particle size 20-45 microns. Usage of larger particles will yield significant increase in power of the laser unit. Quality problem for melted spherical particles will exist as well [5].

During electron beam melting powder particles with the size range below 45  $\mu\text{m}$  might be blown away from reaction zone by intensive heat flows [6].

The vast majority of 3D printers are using spherical titanium alloy powders [7]. These powders have better flow ability, allow channel feeding, and minimise active material surface. These materials might be obtained using different methods: atomisation of molten metal, centrifugal pulverisation, inert gas or vacuum spraying [8]. It were reported works related to usage of non-spherical powders for 3D printing [9,10]. Every described method for preparation of titanium alloy powders has own advantages and disadvantages (Table 1).

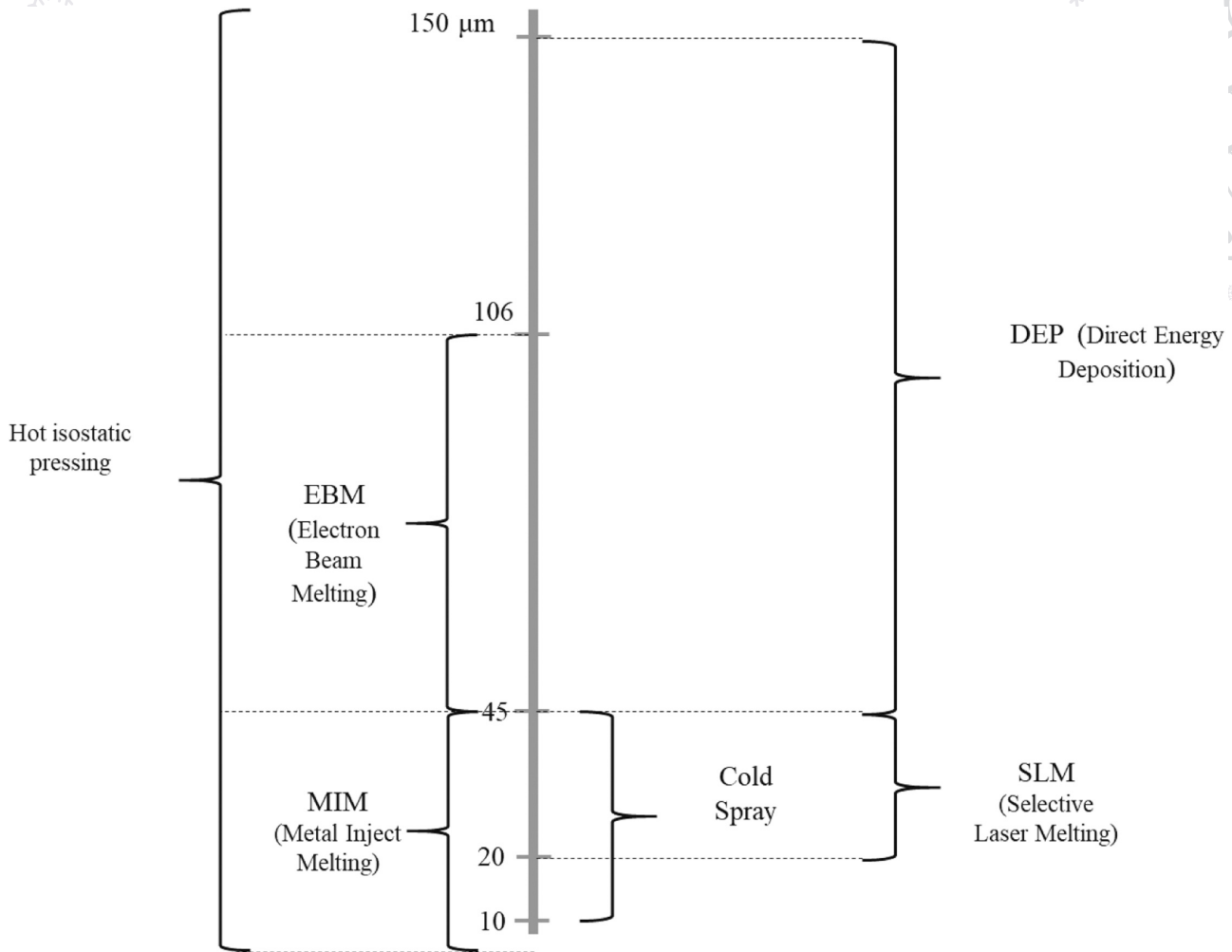


Fig. 1. Typical sizes of titanium alloy powders used in additive manufacturing processes

Table 1

#### Key characteristics of methods for production of titanium powders

Method	Raw material	Particle size, μm	Advantages	Disadvantages
Gas atomisation (GA)	Titanium sponge, ingots, rods	<300	Wide range of alloys and produced materials	Satellites, porosity, significant material loss in gas flow
Plasma atomisation (PA)	Wire	<300	Small number of satellites, high actual yield of small fractions, high purity	Very expensive powders with high requirements
Centrifugal pulverisation (PREP)	Rod	<50-350	Absence of satellites, high purity, high quality shape	Low actual yield of small size fractions
Hydrogenation/de-hydrogenation (HDH)	Titanium sponge, ingots, rods, waste, scrap	5-250	Wide range of alloys and produced materials, possibility of obtaining very small particles in required size interval	Non-spherical shape of particles, elevated concentration of hydrogen in powders

The most high quality titanium alloy powders are obtained by centrifugal spraying. However, actual yield of these powders with the size below 80 microns is insuff-

icient: only 20-30% [11]. The most effective method for small size material production is HDH. This technology generates non-spherical titanium alloy powders in wide

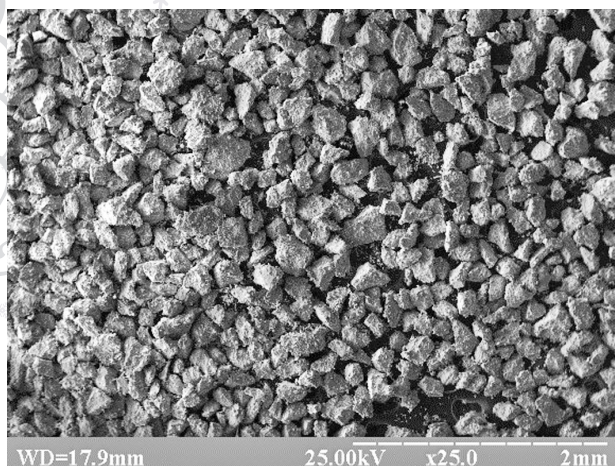


Fig. 2. External view of titanium alloy powders produced by HDH method

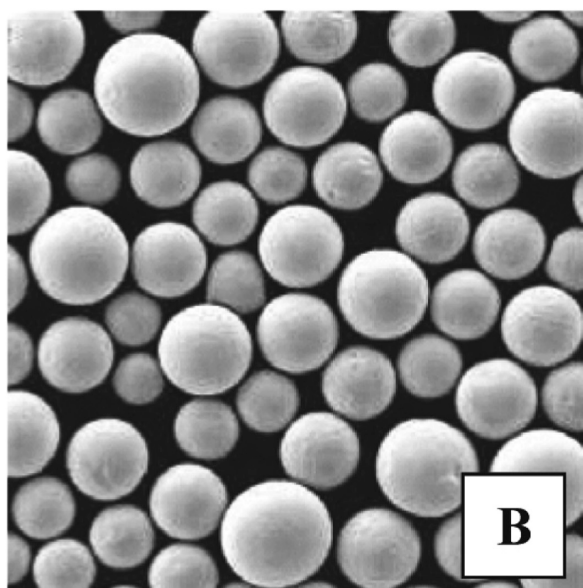
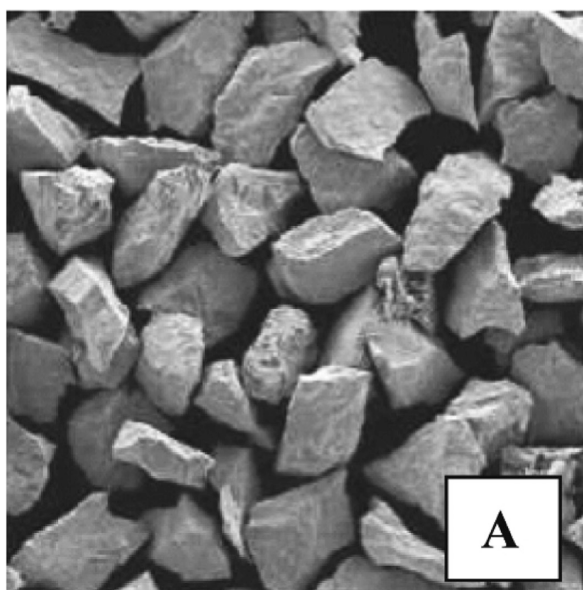


Fig. 3. External view of HDH powders after plasma treatment [13]

interval of sizes (Fig. 2). In addition hydrogenation/dehydrogenation method enables manufacturing of high quality titanium as well as its different alloy powders. Also HDH technology allows usage of titanium alloy waste and alloyed titanium sponge as raw materials [12]. This significantly decreases production cost.

However, the majority of additive technology equipment manufacturers uses spherical powders since non-spherical ones have unsatisfactory flow ability. To make non-spherical “low-cost” powders more competitive in the market it has been suggested to do their spheroidisation [10]. Plasma treatment allows smoothing of sharp grain edges yielding more spherical appearance. This significantly increases flow ability of the powder.

It is important to say that in the majority of cases size range of HDH powders does not change after plasma treatment [14,15].

Table 2 shows that particle size has not been changed, powder density was increased 2.5 fold, and it has appeared measurable flow ability. Despite of the latter parameter is still lower compared to one of spherical powders it is sufficient for usage in majority of industrial 3D printers. Decrease in impurity concentrations is presumably caused by heat treatment of material and reduction of surface area for titanium powder.

Considering all the above we have proposed technological scheme for production of spherical titanium alloy powders (Fig. 4). The powders are intended for usage (3D printing) in aircraft building industry. Local materials and technologies will be employed for powder manufacture. According to the proposed scheme titanium alloy work pieces are made from titanium sponge. Work pieces can be produced by VAR or EBM methods using titanium sponge mixed with master alloys or alloyed titanium sponge [10, 12].

Titanium waste with required chemical composition could also be used as raw material. This significantly decreases production cost. Hydrogenation is conducted with the objective for increasing titanium brittleness. As a result percentage of small fractions (below 200  $\mu\text{m}$ ) could be more than 85%. After crushing and screening of powders degassing of the material for excessive hydrogen removal is needed. Then non-spherical titanium alloy powders are treated by plasma. This operation yields partial melting of sharp grain edges and dendrite parts of the particles. Plasma treatment results spheroidisation of materials and also eliminates volatile impurities [15]. Such titanium alloy powders are suitable for usage in the majority of industrial and laboratory 3D printers.

### Conclusions

Obtaining of «low-cost» titanium alloy powders which fit majority of industrial demands for additive technologies requires complex technological scheme consisted as three stages:

Spheroidisation of titanium powders in argon plasma (TEKNA Ltd)

Properties	Before plasma treatment	After plasma treatment
Tap density	1.0 g/cm <sup>3</sup>	2.6 g/cm <sup>3</sup>
Production rate	–	10 kg/h at 100 kW
Particle size	–140+400 mesh /40 100 μm	–140+400 mesh /40 100 μm
Hall flow test	No flow	37s/50g
[O] ppm	2050	1800
[C] ppm	160	120
[H] ppm	166	114
[N] ppm	90	90
[Cl] ppm	1200	360
[Al] ppm	80	58

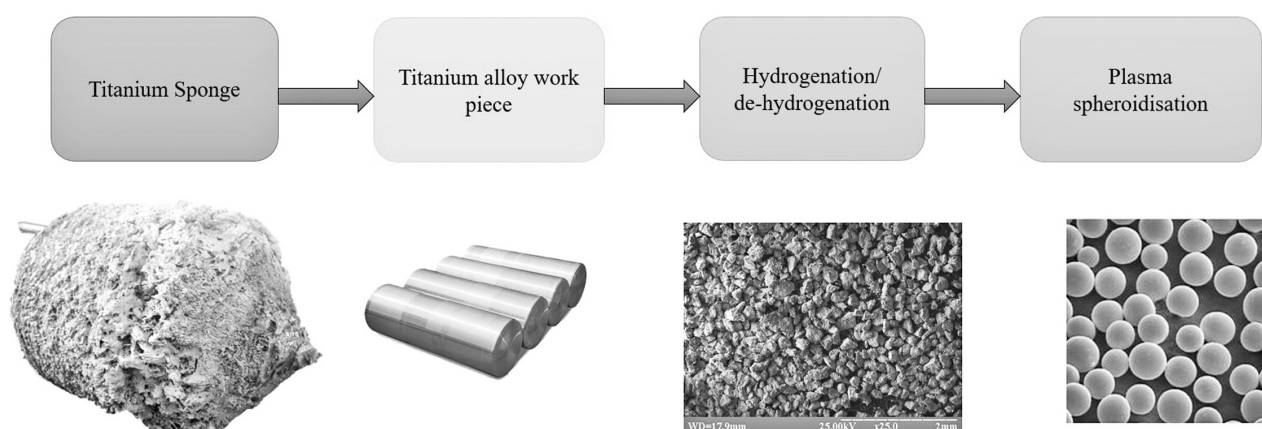


Fig. 4. Technological scheme of manufacture titanium alloy powders for aircraft building industry

1 – preparation of work piece for HDH process – titanium alloy ingot, alloyed titanium sponge or titanium alloy waste;

2 – synthesis of titanium alloy powders with definite fractional composition by HDH method – hydrogenation, crushing /screening, degassing

3 – plasma spheroidisation of non-spherical powders

The offered technology produces spherical titanium alloy powders with required quality and competitive production cost

### Abbreviations

HDH – Hydrogenation-dehydrogenation  
 PS – Plasma spheroidisation  
 GA – Gas atomization  
 PREP – Plasma Rotate Electrode Process  
 VAR – Vacuum arc remelting  
 EBM – Electron beam melting

### References

[1] Main directions for material and power saving in metallurgy/ G. M. Druzhinin, L. A. Zainullin, M. D. Kazyaev,

N. A. Spirin, Yu. G. Yaroshenko, M. V. Gubinsky // V.E. Grum-Grzhimailo's creative heritage: past, present, future: proceedings of international scientific and practical conference (27-29 March 2014, Yekaterinburg). –Yekaterinburg : UrFU, 2014. – part 1. – pp. 205-212.

[2] Zlenko M.A. Additive technologies in machine building / Zlenko M.A., Popovich A.A., Mutylyna I.N. – Sankt-Petersburg: Poly-technical university, 2013. – 221 pp. ISSN 0135-3152.

[3] Roskill report. Titanium Metal: Market Outlook to 2018. Sixth Edition, 2013 // Copyright © Roskill Information Services Ltd. ISBN 978 0 86214 595 8.

[4] Frazier, W.E. Metal Additive Manufacturing: A Review // Journal of Materials Engineering and Performance (2014) 23: 1917. <https://doi.org/10.1007/s11665-014-0958-z>.

[5] C. Körner (2016) Additive manufacturing of metallic components by selective electron beam melting – a review, International Materials Reviews, 61:5, 361-377. <https://doi.org/10.1080/09506608.2016.1176289>

[6] Drescher P, Seitz H (2015). Processability of an amorphous metal alloy powder by electron beam melting. Rte Journal – Fachforum für Rapid Technologie, Vol. 2015 (urn:nbn:de:0009-2-42364).

- [7] Zhigang Zak Fang, James D. Paramore, Pei Sun, K. S. Ravi Chandran, Ying Zhang, Yang Xia, Fei Cao, Mark Koopman & Michael Free (2017): Powder metallurgy of titanium –past, present, and future, International Materials Reviews. <https://doi.org/10.1080/09506608.2017.1366003>
- [8] Sun, P., Fang, Z.Z., Zhang, Y. et al. ., “Review of the Methods for Production of Spherical Ti and Ti Alloy Powder,” JOM (2017) 69:1853. <https://doi.org/10.1007/s11837-017-2513-5>
- [9] Nesterenkov V. M., Matveichuk V. A., Rusynik M. O. Production of industrial articles using electron beam technologies for 3D printing – Automatic welding, No 1, 2018, pp. 5-10. <https://doi.org/10.15407/as2018.01.05>
- [10] New technological schemes for synthesis of «LOW-COST» titanium powders used in additive processes. T.B. Yanko, A. V. Ovchinnikov, M.V. Khaznaferov// Titanium: Sc.-tech. Journ. – M., – ISSN 2075-2903// 2016 No 2 – pp. 31-36.
- [11] W. J. Sames, F. A. List, S. Pannala, R. R. Dehoff & S. S. Babu (2016): The metallurgy and processing science of metal additive manufacturing, International Materials Reviews <http://dx.doi.org/10.1080/09506608.2015.111664912>
- [12] Yanko T.B., Ovchinnikov A.V. Application of titanium sponge, doped with aluminum and vanadium / Titanium: Sc.-tech. Journ. – M., – ISSN 2075-2903// 2017 № 4 – pp. 44-49.
- [13] BISSETT, H.; VAN DER WALT, I.J.; HAVENGA, J.L. and NEL, J.T. Titanium and zirconium metal powder spheroidization by thermal plasma processes. J. S. Afr. Inst. Min. Metall. [online]. 2015, vol.115, n.10, pp.937-942. ISSN 2411-9717
- [14] D.P. Barbis, R.M. Gasior, G.P. Walker, J.A. Capone, and T.S. Schaeffer, Titanium Powder Metallurgy: Science, Technology and Applications, ed. M. Qian and F.H. Froes (Oxford: Butterworth-Heinemann, 2015), pp. 101–105.
- [15] R. Vert, R. Pontone, R. Dolbec, L. Dionne and M.I. Boulos Induction plasma technology applied to powder manufacturing: example of titanium-based materials / 22nd International Symposium on Plasma Chemistry July 5-10, 2015; Antwerp, Belgium <http://www.ispc-conference.org/ispcproc/ispc22/P-II-7-32.pdf>

УДК 669.295

**Янко Т. Б.<sup>1</sup>, Овчинников О. В.<sup>1</sup>, Коржик В. М.<sup>2</sup>, Лютик М. П.<sup>2</sup>**

<sup>1</sup> АТ «Інститут титану». Україна, м. Запоріжжя

<sup>2</sup> ООО Науково-виробничий центр «Плазер». Україна, м. Київ

## ТЕХНОЛОГІЧНА СХЕМА ОТРИМАННЯ ПОРОШКІВ ТИТАНОВИХ СПЛАВІВ АВІАЦІЙНОГО ПРИЗНАЧЕННЯ ДЛЯ 3Д ДРУКУ

*Розглянуто особливості адитивних технологій та представлені основні характеристики методів отримання титанових порошків. Наведені типові розміри порошків титанового сплаву, що використовуються в адитивних процесах. Показано, що найбільш ефективним способом одержання тонких титанових порошків є технологія гідрування-дегідрування (HDH). Однак, щоб отримати необхідні параметри плинності та сферичності, слід використовувати технологію сфероїдизації плазми (PS). Запропоновано технологічну схему виробництва сферичних порошків титанових сплавів для авіаційних застосувань за допомогою комплексного методу HDH та PS. [dx.doi.org/10.29010/085.7]*

Ключові слова:

### Література

- [1] Основные направления ресурсоэкономосбережения в металлургии / Г. М. Дружинин, Л. А. Зайнуллин, М. Д. Казяев, Н. А. Спириин, Ю. Г. Ярошенко, М. В. Губинский // Творческое наследие В. Е. Грум-Гржимайло: прошлое, современное состояние, будущее: сборник докладов международной научно-практической конференции (27-29 марта 2014 г., г. Екатеринбург). — Екатеринбург : УрФУ, 2014. — Ч. 1. — С. 205-212.
- [2] Зленко М.А. Аддитивные технологии в машиностроении / Зленко М.А., Попович А.А., Мутьялина И.Н. – Санкт-Петербург: Издательство политехнического университета, 2013. – 221 с.

- [3] Roskill report. Titanium Metal: Market Outlook to 2018. Sixth Edition, 2013 // Copyright © Roskill Information Services Ltd. ISBN 978 0 86214 595 8.
- [4] Frazier, W.E. Metal Additive Manufacturing: A Review // Journal of Materials Engineering and Performance (2014) 23: 1917. <https://doi.org/10.1007/s11665-014-0958-z>.
- [5] C. Körner (2016) Additive manufacturing of metallic components by selective electron beam melting – a review, International Materials Reviews, 61:5, 361-377. <https://doi.org/10.1080/09506608.2016.1176289>
- [6] Drescher P, Seitz H (2015). Processability of an amorphous metal alloy powder by electron beam melting. Rte Journal – Fachforum für Rapid Technologie, Vol. 2015 (urn:nbn:de:0009-2-42364).
- [7] Zhigang Zak Fang, James D. Paramore, Pei Sun, K. S. Ravi Chandran, Ying Zhang, Yang Xia, Fei Cao, Mark Koopman & Michael Free (2017): Powder metallurgy of titanium –past, present, and future, International Materials Reviews. <https://doi.org/10.1080/09506608.2017.1366003>
- [8] Sun, P., Fang, Z.Z., Zhang, Y. et al. ., “Review of the Methods for Production of Spherical Ti and Ti Alloy Powder,” JOM (2017) 69:1853. <https://doi.org/10.1007/s11837-017-2513-5>
- [9] Нестеренков В. М., Матвейчук В. А., Русыник М. О. Получение промышленных изделий с применением электронно-лучевых технологий для 3D печати – Автоматическая сварка, № 1, 2018, с. 5-10.
- [10] Новые технологические схемы получения «LOW-COST» порошков титана для аддитивных процессов. Т.Б. Янко, О. В. Овчинников, М.В. Хазнаферов // Титан: Науч.-техн. Журн. – М., – ISSN 2075-2903// 2016 № 2 – стр. 31-36.
- [11] W. J. Sames, F. A. List, S. Pannala, R. R. Dehoff & S. S. Babu (2016): The metallurgy and processing science of metal additive manufacturing, International Materials Reviews. <http://dx.doi.org/10.1080/09506608.2015.111664912>
- [12] Янко Т.Б., Овчинников А.В. Применение титана губчатого, легированного алюминием и ванадием // Титан: Науч.-техн. Журн. – М., – ISSN 2075-2903// 2017 № 4 – стр. 44-49.
- [13] BISSETT, H.; VAN DER WALT, I.J.; HAVENGA, J.L. and NEL, J.T. Titanium and zirconium metal powder spheroidization by thermal plasma processes. J. S. Afr. Inst. Min. Metall. [online]. 2015, vol.115, n.10, pp.937-942. ISSN 2411-9717
- [14] D.P. Barbis, R.M. Gasior, G.P. Walker, J.A. Capone, and T.S. Schaeffer, Titanium Powder Metallurgy: Science, Technology and Applications, ed. M. Qian and F.H. Froes (Oxford: Butterworth-Heinemann, 2015), pp. 101–105.
- [15] R. Vert, R. Pontone, R. Dolbec, L. Dionne and M.I. Boulos Induction plasma technology applied to powder manufacturing: example of titanium-based materials / 22nd International Symposium on Plasma Chemistry July 5-10, 2015; Antwerp, Belgium. <http://www.ispc-conference.org/ispcproc/ispc22/P-II-7-32.pdf>