



ARCHIVES
of
FOUNDRY ENGINEERING

ISSN (2299-2944)

Volume 21

Issue 3/2021

27 – 32



10.24425/afe.2021.136109

4/3

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Interaction of Titanium with Ceramic Molds in the Conditions of Electron Beam Casting Technology

P. Kaliuzhnyi *, M. Voron, O. Mykhniian, A. Tymoshenko, O. Neima, O. Iangol

Physico-Technological Institute of Metals and Alloys of the National Academy of Sciences of Ukraine, Ukraine

* Corresponding author: Email address: kpb.ptima@gmail.com

Received 21.04.2021; accepted in revised form 24.06.2021

Abstract

For the manufacture of near net shape complex titanium products, it is necessary to use investment casting process. Melting of titanium is promising to carry out by electron beam casting technology, which allows for specific processing of the melt, and accordingly control the structure and properties of castings of titanium alloys. However, the casting of titanium in ceramic molds is usually accompanied by a reaction of the melt with the mold. In this regard, the aim of the work was to study the interaction of titanium melt with ceramics of shell molds in the conditions of electron beam casting technology. Ceramic molds were made by using the following refractory materials – fused corundum Al_2O_3 , zircon $ZrSiO_4$ and yttria-stabilized zirconium oxide ZrO_2 , and ethyl silicate as a binder. Melting and casting of CP titanium was performed in an electron beam foundry. Samples were made from the obtained castings and electron microscopic metallography was performed. The presence and morphology of the altered structure, on the sample surface, were evaluated and the degree and nature of their interaction were determined. It was found that the molds with face layers of zirconium oxide (Z1) and zircon (ZS1) and backup layers of corundum showed the smallest interaction with the titanium melt. Corundum interacts with titanium to form a non-continuous reaction layer with thickness of 400-500 μm . For shell molds with face and backup layers of zircon on the surface of the castings, a reaction layer with thickness of 500-600 μm is formed. In addition, zirconium-silicon eutectic was detected in these layers.

Keywords: Investment casting, Electron beam casting technology, Titanium, Ceramic shell molds

1. Introduction

The most high-tech industries of nowadays, such as aerospace, energy, engineering, military-industrial complex, medicine and some others, require special materials that would have a specific combination of physical, chemical and mechanical properties. Such materials include titanium and its alloys. These types of materials are characterized by very high specific strength, corrosion resistance, low modulus of elasticity, high hardness, heat resistance, biocompatibility [1-6].

In modern world, titanium products are often made by multi-stage deformation and machining of large ingots and slabs. This

technological cycle causes a high cost of final products and requires alternatives and more profitable technical and economical solutions. One of the examples of technologies for obtaining cheap quality products and semi-finished products from titanium and its alloys is using of foundry technologies, which, to date, are still not common. Among the effective technologies for titanium casting can be distinguished vacuum-induction, vacuum-arc and electron beam casting technology [6-10].

One of the promising methods of obtaining titanium castings is the electron beam casting technology (EBCT) developed at the PTIMA NAS of Ukraine. During many years of research, the principles of smelting complex alloyed titanium alloys with a high

concentration of refractory components and components prone to intense evaporation have been established. EBCT allows to apply the wide range of melting modes and to carry out specific force treatment of the melt, which consists in the simultaneous action of the electron beam and electromagnetic mixing of the liquid metal. Due to this fact, this method makes it possible to obtain titanium castings, the structure of which consists of small equilibrium grains and the mechanical characteristics of the metal are close to the characteristics of the wrought metal [10-13].

In the conditions of EBCT more often graphite, copper or steel permanent molds are used. Such molds are usually used to obtain relatively thick-walled castings of simple configuration [11, 14]. The manufacture of thin-walled castings of complex geometry is possible with using of investment casting process.

To ensure the required level of quality of finished products made of titanium and its alloys obtained in ceramic shell molds, it is necessary to take into account the fact that titanium in the molten state is a chemically very active metal and melts based on it actively interact with most refractory materials. Therefore, the main effective solution to this problem is the use of the method of casting in ceramic molds, provided the use of maximally inert refractory materials for the manufacture of shells and reliable ceramic mixtures to ensure mechanical and thermophysical properties of the mold in general. Such materials can be oxides of aluminum, zirconium, yttrium, beryllium, magnesium, calcium, titanium carbides, hafnium, and calcium zirconate [5, 15].

In practice, titanium castings are most often obtained in corundum ceramic molds. Zircon is also sometimes used as a material for ceramic molds [16-18]. However, such castings are of low quality, because on their surface a layer saturated with impurities is formed, which has a higher hardness and greater defect than the base metal [19]. Therefore, it must be removed, especially from parts that have to work in conditions of long-term alternating loads and vibrations. Literature review shows that to obtain titanium products with a smaller thickness of the defective layer in the face layer of ceramic molds used more inert than corundum, zirconium oxide and quite expensive yttrium oxide.

A lot of works is devoted to the study of the interaction of titanium with various materials of ceramic molds [15-24], but in most studies the conditions of experiments differ (metal melting methods, sample weight, alloy grade, atmosphere in which the pouring was performed), and therefore the results - the thickness of the reactive layer of titanium products for the same materials of ceramic molds may differ by an order of magnitude. Melting and pouring of titanium in an electron-beam foundry takes place under high vacuum conditions (≤ 1.33 Pa), which can cause thermal dissociation of mold refractory oxides and as a result affect the nature of the interaction of ceramic molds with titanium melt. Therefore, the urgent task is to determine the interaction of titanium with ceramic molds in terms of electron beam casting technology.

2. Research methodology

Taking into account the theoretical analysis and the cost of materials for practical research, fused corundum Al_2O_3 , zircon ZrSiO_4 and yttria-stabilized zirconium oxide ZrO_2 were chosen as refractories. Hydrolyzed ethyl silicate (40% SiO_2) was used as a binder. To obtain the face layer (1-2 layers) used the primary slurry,

for other layers (3-9) the secondary slurry, the compositions of which are given in table. 1.

Table 1.

Composition of ceramic shell molds used in experiments

Sample code	Slurry type	Filler	Stucco
A1	Primary	Al_2O_3 5-20 μm	Al_2O_3 28-40 μm
	Secondary	Al_2O_3 15-40 μm	Al_2O_3 0,2-0,63 mm
Z1	Primary	ZrO_2 9-30 μm	ZrO_2 63-100 μm
	Secondary	Al_2O_3 15-40 μm	Al_2O_3 0,2-0,63 mm
Z2	Primary	ZrO_2 9-30 μm	ZrO_2 63-100 μm
	Secondary	ZrSiO_4 40-63 μm	ZrSiO_4 0,16-0,4 mm
ZS1	Primary	ZrSiO_4 16-45 μm	ZrSiO_4 63-100 μm
	Secondary	Al_2O_3 15-40 μm	Al_2O_3 0,2-0,63 mm
ZS2	Primary	ZrSiO_4 16-45 μm	ZrSiO_4 63-100 μm
	Secondary	ZrSiO_4 40-63 μm	ZrSiO_4 0,16-0,4 mm

Samples for research were cylinders $\text{Ø}20$ mm and a length of 120 mm. Foamed polystyrene patterns of samples were glued to the riser, forming a cluster. Ceramic shell molds were made by traditional investment casting technology. The cluster was dipped in the slurry and sprinkled with stucco, forming layer by layer of ceramic shell.

The first layer was dried in air for 24 hours, the second and subsequent layers - at least 6 hours. As a result of drying, the liquid component of the slurry was removed and the binder solidified. After receiving 8 layers on the pattern, a fixing layer was applied. Next, the molds were dried and two-stage firing of the patterns in a furnace was performed. At the low-temperature stage (gradual heating to 250 °C) compaction, melting and partial gasification of foamed polystyrene took place, thus preventing cracking of the shell mold. And the high-temperature stage of firing was combined with the process of calcination of the ceramic mold at 1000 °C, during which the removal of the polystyrene remnants, gas and moisture residues from the ceramic and sintering of the binder. The pattern tree with face layers and ready made ceramic mold are presented in Figure 1.



Fig. 1. Pattern with face coat (a) and ceramic shell mould (b)

Melting of technically pure titanium CP-Ti and pouring it into ceramic molds was performed in an electron beam foundry EPLU-4, a scheme and general view of which is presented in Figure 2. For experiments, water-cooled copper crucible (3) with a system of electromagnetic mixing of the melt, which is a side structure of two induction coils, was used. The metal in the crucible was heated and melted by an electron beam generated by an electron beam thermocathodic gun (5). Electromagnetic stirring of the melt helped to equalize the temperature and homogenize the chemical composition throughout the melt.

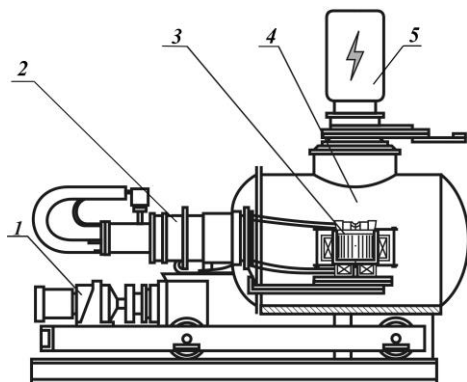


Fig. 2. Scheme and general view of the foundry EPLU-4:
 1 - the movement mechanism of a cover; 2 - the mechanism of crucible rotation; 3 - crucible; 4 - vacuum chamber; 5 - electron-change gun

The ceramic mold was fixed in the vacuum chamber (4) at an angle of 90 degrees to the axis of the crucible. A graphite drain sock was placed between the crucible and the ceramic basin, which serves to direct the metal jet into the center of the casting basin. Then the cover of the vacuum chamber was closed by means of mechanism (1) and air was pumped out. The working pressure in the chamber of the installation was not more than 1.33 Pa (10^{-2} mm

Hg). After the titanium was melted, it was poured into an unheated ceramic mold by turning the skull crucible using mechanism (2). The mass of titanium castings (one of which is shown in Figure 3) obtained in ceramic molds was 2.5-2.7 kg.

The study of the interaction of liquid titanium with the surface of ceramic molds in the casting production in the conditions of the electron beam foundry was performed by analyzing the microstructure of cast samples. To study the structure, the samples were cut from the obtained cylindrical castings and sections were made from them according to the standard method.



Fig. 3. Casting of CP titanium obtained in ceramic mold

The microstructure was manifested using Kroll's herb - an aqueous solution of 2% HNO_3 and 2% HF. The microstructure of the samples was examined on a Tescan Vega 3 electron microscope with a Bruker EDX attachment to determine the local chemical analysis of the phases.

3. Results and discussion

The macrostructure of all samples is characterized by equiaxial grains 1-1.5 mm in size, which indicates a fairly rapid crystallization of the melt in ceramic molds. The microstructure of the samples has the characteristics of a cast structure, but is quite uniform. The relatively large size of the alpha-phase colonies indicate a slow rate of polymorphic transformation. During the phase recrystallization, the growth of alpha plates is inhibited due to the small size of the primary beta phase, which provides a positive effect on the mechanical properties of the cast metal.

The microstructure of the castings surface obtained by casting into various ceramic molds is presented in Figures 4 and 5. On all structures of the surface layer of castings can be observed areas of individual clear plates of the α -phase, which, judging by the separation and shape could be formed as the primary phase due to oxygen saturation in the interaction of the melt with ceramics.

The structure of castings, which were obtained in corundum shell molds A1, shows a fairly high activity of interaction between titanium melt and ceramic. So on the surface of the samples, the structure of which is shown in Figure 4 (b) and Figure 5 (a), there is a solid α -layer with a thickness of 400-500 μm . In another sample (Figure 4 (a)) there is a discontinuous layer of large areas of α -plates, the thickness of which ranges from 250 to 550 μm .

The structure of castings obtained in shell molds from zirconium oxide shows less interaction of the titanium melt with

the mold material compared to corundum molds. For the casting obtained in the Z1 mold (Figures 4 (c) and 5 (b)), the depth of large individual grains of the α -phase is 200-350 μm from the contact surface. In the case of using the Z2 mold (Figure 4 (d), Figure 5 (c)) the thickness of the α -case was 300-400 μm . The structure of the reaction layer in both cases has a homogeneous solid character throughout the contact zone.

The study of the interaction of liquid titanium with zirconium molds shows contradictory results. Castings obtained in the ZS1 mold (Figure 4 (d), Figure 5 (d)) have a relatively small thickness of the α -case - 150-200 μm , and in the ZS2 mold (Figure 4 (e), Figure 5 (d)) - 500-600 μm . It should be noted that in the case of the use of zircon for facecoat when separating the ceramic from the surface of the casting, a fragile contact layer was observed. This fragile layer made it easy to separate ceramics from metal, but the surface of the castings was characterized by increased roughness and the presence of surface holes. In addition, the formation on the casting surface of gas holes (Figure 4 (e)) can be caused by impurities of various oxides, which, although in small quantities, are present in zircon, which could also adversely affect the interaction of titanium with zircon.

Comparing the studied types of molds, it was found that molds with a face layer of zirconium oxide and zircon and the backup layers of corundum (ie Z1 and ZS1) showed the least interaction

with the titanium melt. At the same time less thermodynamically stable zircon showed the best result. This effect can be explained by the mechanism presented in [17] - the reaction products between titanium and zircon, present in the outer reaction layer, prevent the transport of harmful elements, and therefore a thinner diffusion layer is formed.

A more detailed study of the outer layer of titanium castings obtained in ZS2 molds with a zircon face layer showed the presence of single sections of silicon eutectic, which could be formed by reaction with zircon particles. The image of eutectic inclusions is presented in Figure 5 (f). Chemical composition of the eutectic: Ti-12,5Si-3Zr. Eutectic inclusions are located at a depth of 250-350 μm from the surface.

It is claimed that regardless of the refractory filler when using a binder based on SiO_2 , such mold will interact with the titanium melt. However, in [24] it was shown that when using heat-resistant yttrium oxide, the thickness of the reaction layer is affected by the concentration of SiO_2 in the binder. In [22], in the study of various binders for corundum molds, it was concluded that it would be good if the use of silica in free or combined form as a binder could be minimized to reduce the interaction of the metal surface with the mold. Therefore, there is a need to continue these studies to reduce the amount of SiO_2 in the binder.

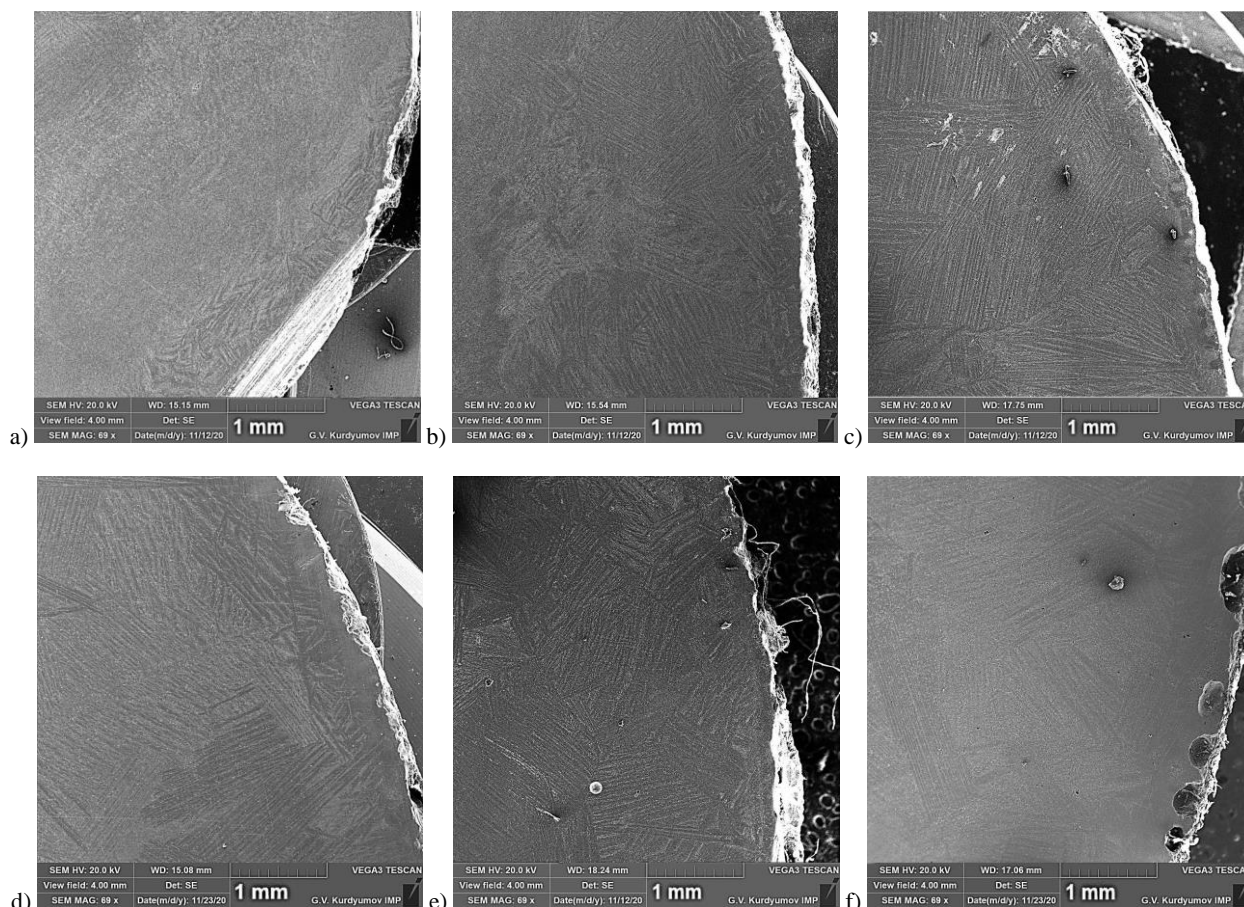


Fig. 4. Microstructure of CP-Ti casting obtained in mold: A1 (a) and (b), Z1 (c), Z2 (d), ZS1 (e), ZS2 (f) (magnification $\times 69$)

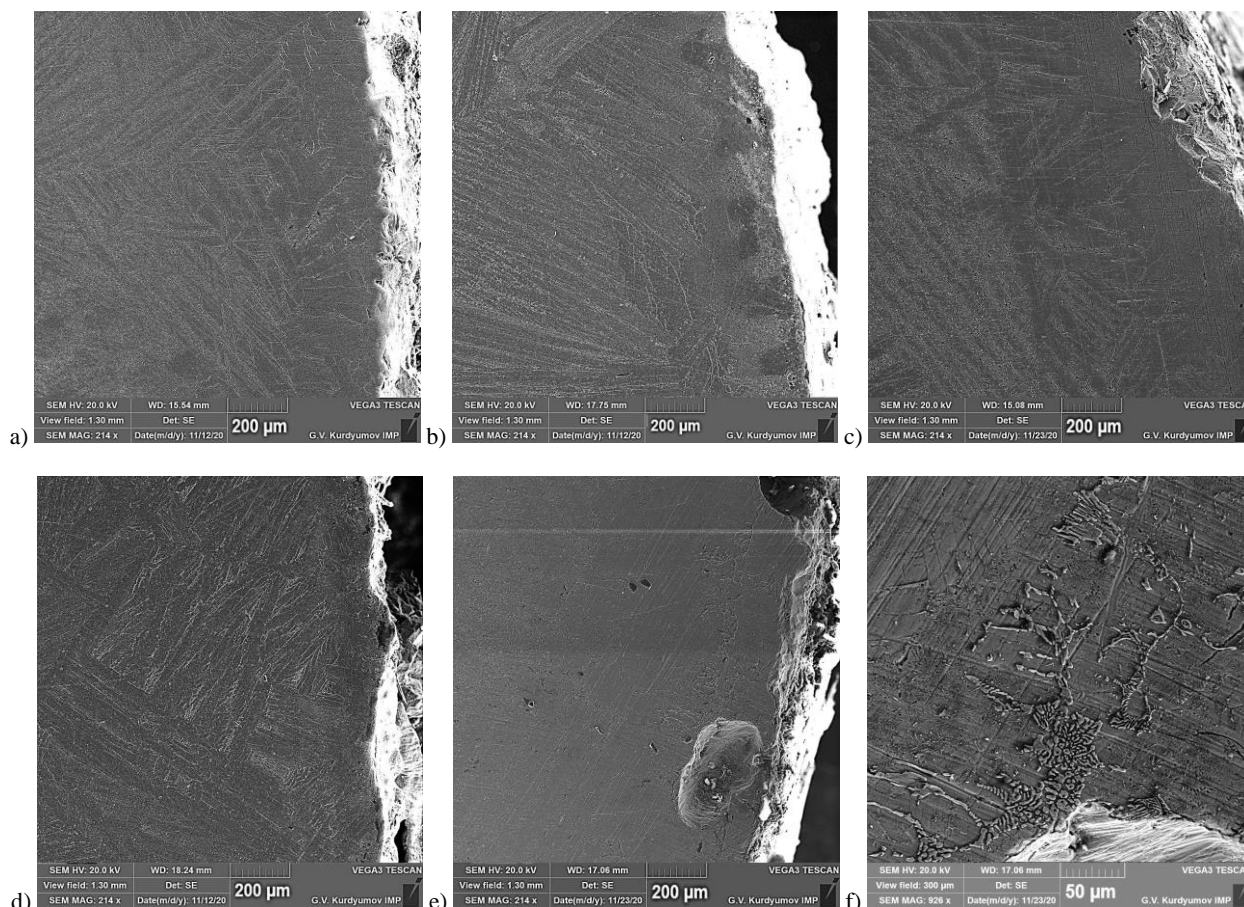


Fig. 5. Microstructure of CP-Ti casting obtained in mold: Al (a), Z1 (b), Z2 (c), ZS1 (d), ZS2 (e) (magnification x214) and inclusion of eutectic in the surface layers of the sample (f)

The interaction could also be influenced by the fact that a larger filler was used in the secondary suspension with zircon, and therefore the ceramic could contain more binder, and hence SiO_2 . In suspensions with Al_2O_3 , a powder of smaller fractions was used, which gave better reproduction of the surface of the castings than when using zirconium oxide and zircon. It should also be noted that despite the combination of different materials (for the face and backup layers), the molds did not have cracks and had sufficient strength to form and pour titanium alloy in them. Vibration treatment [25] or other known methods can be recommended for finishing of titanium castings with a small reaction layer.

4. Conclusions

The results of the study of the interaction of CP titanium with materials of ceramic molds (Al_2O_3 , ZrSiO_4 and yttria-stabilized ZrO_2) in conditions of electron beam casting technology can be summarized as follows:

- 1) The degree of interaction of the titanium melt with ceramic shell materials, determined by the change in size of individual clear α -phase plates formed on the surface of castings, showed that the least interaction with titanium is

characterized by molds with face layers of zirconium oxide and zircon and backup layers with corundum.

- 2) Corundum as a contact layer exhibits good properties, but the surface of the titanium casting is characterized by an uneven structure after interaction with it.
- 3) Shell molds with zircon show ambiguous results. In one case, a relatively small α -case (up to 200 μm thick) is formed on the surface of the castings. Otherwise, a significant reaction layer (up to 600 μm) containing zirconium-silicon eutectic is formed.

Given the high properties of titanium alloys of electron beam smelting, it is necessary to continue work in the direction of finding materials of ceramic molds that would ensure the formation of a minimal reaction surface layer of the casting.

Acknowledgements

This study was supported by a grant of the National Academy of Sciences of Ukraine to research laboratories / groups of young scientists (state registration No 0120U100114).

Reference

- [1] Agripa, H. & Botef, I. (2019). Modern Production Methods for Titanium Alloys: A Review. In Maciej Motyka (Eds.) *Titanium Alloys – Novel Aspects of Their Manufacturing and Processing* (pp. 1-14). UK: IntechOpen. DOI: 10.5772/intechopen.81712.
- [2] Cviker, U. (1979). *Titan i ego splavy*. Moscow: Metallurgija, 512. (in Russian).
- [3] Il'in, A.A., Kolachev, B.A., Pol'kin, I.S. (2009). *Titanovye splavy: Sostav, struktura, svojstva. Spravochnik*. Moskva: VILS-MATI, 520. (in Russian).
- [4] Banerjee, D. & Williams, J.C. (2013). Perspectives on titanium science and technology. *Acta Materialia*. 6(3), 844-879. doi.org/10.1016/j.actamat.2012.10.043.
- [5] Saha, R. L., Jacob, K.T. (1986). Casting of titanium and its alloys. *Defense science journal*. 36(2), 121-141.
- [6] Suzuki, K. (2001). An Introduction to the extraction, melting and casting technologies of titanium alloys. *Metals and Materials International*. 7(6), 587-604. DOI: 10.1007/BF03179258.
- [7] Cen, M. J., Liu, Y., Chen, X., Zhang, H.W. & Li, Y.X. (2019). Inclusions in melting process of titanium and titanium alloys. *China Foundry*. 16(4), 223-231. doi.org/10.1007/s41230-019-9046-1.
- [8] Smalcerz, A., Blacha, L. & Łabaj, J. (2021). Aluminium loss during Ti-Al-X alloy smelting using the VIM technology. *Archives of Foundry Engineering*. 21(1), 11-17. DOI: 10.24425/afe.2021.136072.
- [9] Paton, B.E., Trigub, N.P., Ahonin, S.V., Zhuk, G.V. (2006). *Jelektronno-luchevaja plavka titana*. Kyiv: Naukova dumka, 248. (in Russian).
- [10] Ladohin, S.V. (Ed.). (2007). *Jelektronno-luchevaja plavka v litejnom proizvodstve*. Kyiv: Stal', 626. (in Russian).
- [11] Ladohin, S.V., Levickij, N.I., Lapshuk, T.V., Drozd, E.A., Matviec, E.A. & Voron, M.M. (2015). Primenenie jelektronno-luchevoj plavki dlja poluchenija izdelij medicinskogo naznachenija. *Metal and casting of Ukraine*. 4, 7-11. (in Russian).
- [12] Voron, M.M., Drozd, E.A., Matviec, E.A. & Suhenko, V.Ju. (2018). Vlijanie temperatury litejnoj formy na strukturu i svojstva otlivok titanovogo splava VT6 jelektronno-luchevoj viplavki. *Metal and casting of Ukraine*. 1-2, 40-44. (in Russian).
- [13] Voron, M.M., Levytskyi, M.I. & Lapshuk, T.V. (2015). Structure and properties of lytic alloys of Ti-Al-V electron-variable smelting system. *Metaloznavstvo ta obrobka metaliv*. 2, 29-37. (in Ukrainian).
- [14] Levickij, N.I., Ladohin, S.V., Miroshnichenko, V.I., Matviec, E.A. & Lapshuk T.V. (2008). Ispol'zovanie metallicheskih form dlja poluchenija slitkov i otlivok iz titanovyh splavov pri jelektronno-luchevoj garnisazhnoj plavke. *Metal and casting of Ukraine*. 7-8, 50-52. (in Russian).
- [15] Nikitchenko, M.N., Semukov, A.S., Saulin, D.V. & Jaburov, A.Ju. (2017). Izuchenie termodinamicheskoy vozmozhnosti vzaimodejstviya materialov lit'evoy formy s metallom pri lit'e titanovyh splavov. *Vestnik Permskogo nacional'nogo issledovatel'skogo politehnicheskogo universiteta. Himicheskaja tehnologija i biotehnologija*. 4, 249-263. (in Russian).
- [16] Altindis, M., Hagemann, K., Polaczek, A.B. & Krupp, U. (2011). Investigation of the Effects of Different Types of Investments on the Alpha-Case Layer of Ti6Al7Nb Castings. *Advanced Engineering Materials*. 13(4), 319-324. DOI: 10.1002/adem.201000264.
- [17] Chamorro, X., Herrero-Dorca, N., Rodríguez, P. P., Andrés, U. & Azpilgain, Z. (2017). α -Case formation in Ti-6Al-4V investment casting using ZrSiO₄ and Al₂O₃ moulds. *Journal of Materials Processing Technology*. 243, 75-81. doi.org/10.1016/j.jmatprotec.2016.12.007.
- [18] Neto, R.L., Duarte, T.P., Alves, J.L. & Barrigana, T.G. (2017). The influence of face coat material on reactivity and fluidity of the Ti6Al4V and TiAl alloys during investment casting. *Proceedings of the Institution of Mechanical Engineers, Part L: Journal of Materials: Design and Applications*. 231(1-2), 38-48. doi.org/10.1177/1464420716681824.
- [19] Saulin, D., Poylov, V., Uglev, N. (2020). Effusion Mechanism of α -Layer Formation in Vacuum Casting of Titanium Alloys. *IOP Conference Series: Materials Science and Engineering*. 969, 012060, 1-12. doi.org/10.1088/1757-899X/969/1/012060.
- [20] Uwanyuze, S., Kanyo, J., Myrick, S. & Schafföner, S. (2021). A review on alpha case formation and modeling of mass transfer during investment casting of titanium alloys. *Journal of Alloys and Compounds*. 865, June 2021, 158558, 1-19. doi.org/10.1016/j.jallcom.2020.158558/
- [21] Guilin, Y., Nan, L., Yousheng, L., Yining, W. (2007). The effects of different types of investments on the alpha-case layer of titanium castings. *The Journal of prosthetic dentistry*. 97(3), 157-164. doi.org/10.1016/j.prosdent.2007.01.005
- [22] Kim, M.G., Kim, S.K. & Kim, Y.J. (2002). Effect of mold material and binder on metal-mold interfacial reaction for investment castings of titanium alloys. *Materials Transactions*. 43(4), 745-750. doi.org/10.2320/matertrans.43.745.
- [23] Sun, S.C., Zhao, E.T., Hu, C., Yu, J.R., An, Y.K. & Guan, R.G. (2020). Characteristics of interfacial reactions between Ti-6Al-4V alloy and ZrO₂ ceramic mold. *China Foundry*. 17(6), 409-415. doi.org/10.1007/s41230-020-0106-3.
- [24] Farsani, M.A. & Gholamipour, R. (2020). Silica-Free Zirconia-Based Primary Slurry for Titanium Investment Casting. *International Journal of Metalcasting*. 14(1), 92-97. DOI: 10.1007/s40962-019-00335-y.
- [25] Bańkowski, D. & Spadło, S. (2020). Research on the Influence of Vibratory Machining on Titanium Alloys Properties. *Archives of Foundry Engineering*. 20(3), 47-52. DOI: 10.24425/afe.2020.133329.