Effusion Mechanism of α-Layer Formation in Vacuum Casting of Titanium Alloys

D V Saulin, V Z Poylov and N P Uglev
The Department of chemical technologies, Perm National Research Polytechnic University, 29, Komsomolskii av., Perm, 614000, Russia
E-mail: Ouglev@mail.ru

Abstract. The formation of the so-called α-layer when casting titanium alloys significantly impairs the mechanical properties of the metal and leads to the need for additional product surface treatment. It is known that simultaneously with the change in mechanical properties, the composition of the casting surface layer is often changed, and the composition change depth, as a rule, does not coincide with the depth of α-layer formed. The reason for α-layer formation, most often, is considered to be the introduction of foreign elements into the crystal lattice of a metal casting. According to our assumption, the mechanism of α-layer formation is two-stage, and it is associated with an intense diffusive effect on the melt structure in the casting outer layer, resulting from its boiling in vacuum during pouring into porous ceramic shells (CS). The paper suggests possible mechanism for composition changing of the surface α-layer in titanium castings due to the secondary processes of effusion saturation of the metal surface with reverse vapor flows coming from the porous ceramic shell after solidification of the casting. In this case, the primary process is the saturation of the CS pores due to the effusion of metal vapors during the boiling of the poured melt due to the high intrinsic vapor pressure exceeding the pressure in the foundry furnace. Chemical interaction of the alloy component vapors with the CS material leads to the volatile components: silicon, silicon II oxide, zirconium II oxide, saturating the metal surface layer due to reverse secondary effusion. The paper presents experimental results on α-layer formation when casting BT5Л alloy in CS having different composition and porosity. The research results confirm the assumption about both the diffusion mechanism of α-layer formation and the effusion mechanism of changes in its composition.

1. Introduction
When casting products made of titanium alloys, the surface layer is often formed that differs in mechanical properties and composition from the material in the casting volume (core). It is difficult to machine, has high hardness and brittleness, and is a source of cracks during solidification and operation of the product. The condition of the casting outer layer is controlled on a cross-section of the sample to a depth of at least 500 microns by Vickers microhardness determination, followed by removal of the detected α-layer by chemical etching or mechanical treatment [1, 2].

A lot of papers have been devoted to study of α-layer formation causes [3, 4]. It is believed that the casting process is accompanied by oxidation and saturation of the casting surface layer with oxygen due to interaction with residual gases, or due to chemical reactions with the shell material. The influence of many factors: material of the mold face layer; temperature of the form before pouring;
duration of exposure at high temperature; cooling rate; distribution of the components in the surface layer of castings; size and position CS in the centrifugal field during the pouring of the melt, etc. However, it is currently impossible to say that the mechanism of $\alpha$-layer formation of the during titanium alloys casting in CS is clear to the end, although a number of semi-empirical recommendations have been formulated that significantly reduce the probability of its formation.

In this regard, this paper analyzes the possible causes of $\alpha$-layer formation and formulates a new hypothesis of such formation, based on experimental data.

2. A brief overview of possible mechanisms of $\alpha$-layer formation

Let's consider the most probable mechanisms of this effect:

1. Inheritance of the structure when passing the state diagram of the alloy from top to bottom at the temperature when cooling the casting.

2. Influence of the second component on polymorphic transformations in the alloy.

3. Chemical interaction of alloy components with residual oxygen in the furnace volume.

4. Interaction of the melt with gases released during desorption from CS.

5. Release of gases dissolved in the melt during the crystallization.

6. Chemical interaction of the alloy components with CS material.

7. The influence of microstructure and syngony of the CS front layer components on the formation of surface crystal seed during solidification of the alloy.

Mechanism 1: in accordance with Ti-Al diagram, in a case of slow cooling and equilibrium crystallization of the BT5L melt containing 5% w/w of Al, in the composition of the first equilibrium crystals at the “cold” wall of the ceramic form, the aluminum content in the casting should be approximately 7%, and until the Figure urative point of the alloy passes the solidus temperature, the composition of the wall layer should have increased concentrations of aluminum, while in the subsequent layers of the wall, the melt will be enriched with titanium [5]. For alloys containing 20% w/w of Al, on the contrary, the wall layer should be enriched with titanium. When the melt is further cooled below the solidus temperature, the phase compositions will be located first in the $\beta$-Ti region, and then in the $\alpha$-Ti region. In practice, the composition of the casting wall layer does not correspond to this rule, which indicates the non-equilibrium cooling of the entire alloy volume. When the melt is rapidly cooled, which is typical for the process of industrial casting of titanium alloys in cold ceramic shells, the BT5L alloy seems to immediately fall into the $\alpha$-Ti zone, while it may partially remain “trapped” $\beta$-Ti zones that affect the casting mechanical properties. But this state should be characteristic of the entire casting volume, and not just for the surface layer. In addition, there are no correlations with the initial temperature and thermal conductivity of the shell. When using CS with high thermal conductivity, for example, from graphite, the degree of non-equilibrium of the crystallization process, and $\alpha$-layer size in this case should increase. This should also occur when reducing the size of the casting - the smaller mass of the casting, the faster it cools. The latter two dependencies are contrary to experimental data. It should also be noted that the maximum content of aluminum in the surface layer often exceeds the theoretically possible value by almost twice (Figure 1). Given that aluminum and other components are not always contained in the casting surface layer, it can be assumed that they are formed due to a secondary, external process.

Mechanism 2: It is known that impurities of the second component affect the rate of transition of a substance from one to another allotropic state [5]. When changing the parameters of the crystal lattice, the sample may crack. It should be noted that cracking is also found in the surface layers of titanium castings, which are most enriched with impurities of foreign elements in comparison with deeper layers of metal. Such effect allows to link the properties of the casting surface layer with changes in its structure due to changes in composition. However, cracking does not always occur, and it is not clear why $\alpha$-layer is often present, but there is no extraneous component. For example, from the analysis of curves in Figure 1, 2, it follows that the main drop in the concentration of aluminum occurs at the first 40 microns of the casting depth, after which it does not change, while the microhardness of the same
sample continues to decrease up to 500 microns. Strange is the fact that the hardness increases in the direction of the casting wall, where the content of a relatively soft component is greater:

**Figure 1.** Distribution of aluminum (upper curve) and silicon in surface layers of ВТ5Л titanium alloy.

**Figure 2.** Hardness in $\alpha$-layer (Microhardness Tester FM-300, USA).

Thus, the hardness of $\alpha$-layer of titanium castings samples does not correlate with the concentration of aluminum. Therefore, the excess aluminum and silicon contained in the alloy are not the cause of the formation of $\alpha$-layer in this case.

This result suggests that the reason for the change in hardness is the variable structure of the cast alloy acquired when the sample solidifies, the characteristics of which are functionally and independently related to the distance from the external surface of the sample, and not to the content of impurities of foreign elements.

**Mechanism 3:** when holding the solid sample of titanium alloy in air at an elevated temperature (700-800°C), it is gradually saturated with oxygen, and the saturation rate increases significantly with increasing temperature, which is associated with an increase in the rate of diffusion of oxygen atoms into the metal volume. The external gas-saturated $\alpha$-layer has an increased microhardness, which decreases with a decrease in the oxygen content. The thickness of $\alpha$-layer also gradually increases, reaching 100 microns in 500–1000 hours. A clear logarithmic relationship between microhardness and oxygen content in the titanium alloy has been revealed, which was shown in [6]. When applied to the actual casting conditions of titanium alloys, an unresolved issue in the interpretation of these results is the source of oxygen, possibly diffusing into the melt from the interface. If this question does not arise during heat treatment of solid castings in an oxygen-containing atmosphere, then in the case of casting the alloy in ceramic shells in a vacuum ($10^{-3}$ mm Hg) or purified argon, the source of oxygen is not clear. The temperature of the molten metal is within 1700 °C, aluminum and titanium are intensively vaporized during melting and are chemically very active chemical elements, so they perform the functions of a getter inside the vacuum furnace, completely absorbing residual oxygen, water vapor, and probably also residual nitrogen. At the above operating pressure, no more than 3–4 mg of oxygen can remain in the volume of the centrifugal vacuum furnace ($\approx 10$ m$^3$), which is sufficient to form $\alpha$-layer with a thickness of no more than 1 µm, distributed over the total surface of all the loaded workpieces, and even then, provided that all the residual oxygen passes into the melt.

**Mechanism 4.** Gases that can be adsorbed on the surface of the pores of ceramic shells include oxygen and nitrogen in the air. Since they have relatively low critical condensation temperatures well below the operating temperature of the CS, capillary condensation is completely excluded. Thus, oxygen can be adsorbed practically only in the form of a monomolecular layer. We will
make a rough, overestimated assessment of the amount of residual oxygen introduced into the furnace volume in the adsorbed form. Let’s assume that adsorption at one atmosphere leads to the formation of a monomolecular layer of oxygen on the entire inner surface of the ceramic with a density corresponding to the liquid state. When applying the vacuum, the adsorption capacity is proportionally reduced by 5-6 orders of magnitude. Research of foundry ceramics (“Sorbi” MS device for determining the surface) showed that its specific surface, with the porosity of 5%, corresponds to 1.9 m²/g, which, in terms of the entire volume of ceramics at full load of the furnace, is estimated to be no more than 0.5·10⁶ m². The average pore diameter is 26 nm. After vacuuming the furnace volume, no more than 1.2 mg of oxygen can remain on the ceramic surface. At the time of casting metal into molds, the vacuum in the furnace, indeed, for a short time deteriorates due to the desorption of gases, but then quickly recovers. However, it is most likely that this is due to the desorption of water vapor rather than oxygen, since ceramics have some hygroscopicity. When the mold is heated at the time of filling, desorbed gases will mostly move in the pores as a Knudsen flow towards the evacuated volume of the furnace, rather than towards the dead end created by the melt. In any case, the oxygen pressure at the melt surface will be in the range of 10⁻³–10⁻⁴ mm Hg, which will not allow the mechanism 4 to have any noticeable significance in the formation of α-layer.

Mechanism 5. The release of dissolved gases during the crystallization of the melt is quite likely, but it should be taken into account that during electron-arc metal remelting in vacuum, the melt enters the storage crucible in fairly small drops with a developed surface and has the high temperature that leads to complete evaporation of foreign volatile components. Therefore, in our opinion, mechanism 5 cannot make a significant contribution to the formation of α-layer.

Mechanism 6: it is assumed that the metal oxides that make up the ceramic shell of the mold, depending on the composition, can partially physically dissolve in the molten titanium in molecular form (with subsequent dissociation), or chemically interact with the melt to form both metal titanites and pure components, such as silicon. For example, in [3] we present the results of the influence study of the ceramic face layer composition on the characteristics of α-layer. It is shown that the oxygen content in the metal boundary layer increases sharply with simultaneous drop in the concentration of titanium, and fluctuations in the content of aluminum and zirconium are insignificant. The results are interpreted as oxygen insertion into the metal layer, accompanied by distortion of the alloy crystal lattice, leading to a significant change in the mechanical characteristics of the metal in the boundary layer. The depth of penetration of both oxygen and other impurities is determined by the diffusion coefficients and the duration of phase contact, and most often, at a significantly shorter length than α-layer (see mechanism 2). It should be noted that solid reaction products formed at the first moment at the interface, especially those that are not soluble in the metal melt, will block the further flow of the reaction due to a sharp decrease in the rate of diffusion supply of components to the contact zone. The latter is confirmed experimentally - for example, it is shown [7] that when a pure titanium melt contacts a ceramic material made of TiO₂ and TiAl₃, simple dissolution or chemical interaction does not occur, which is confirmed by the absence of α-layer, although titanium oxides are completely soluble in liquid titanium (see the Ti-O diagram [5]).

Thermodynamic analysis [8, 9] showed that a very limited number of oxides remain chemically inert to titanium at casting temperatures, among which ZrO₂ and Y₂O₃ are of the greatest interest, which are recommended in foreign literature as materials that guarantee a reduction in the thickness of α-layer (Figure 3).

However, despite the significant inertia of the materials, α-layer is formed in this case, although on a small scale. Thus, it is independently shown that the mechanism of formation is not related to chemical interactions in the system. You should notice the fact that during casting in a vacuum furnace, or in a furnace filled with clean argon gas, the cooling rate of the melt poured into cold form is quite high, causing the duration of contact of the melt with the mold material estimated by the equation of Newton-Richman, subject to delays due to crystallization is 6 to 10
minutes, after which the metal solidifies. With further cooling of the solid casting, taking into account the difference in the expansion coefficients of metal and ceramics, we should expect the loss of physical contact between the metal and the wall and termination of possible chemical reactions between them [10]. Even when using components capable of chemical reactions with titanium for CS formation, chemical reactions seem to be strongly hindered not only by a lack of contact time, but also by mass transfer difficulties. So, as an example, it should be pointed out that when casting titanium alloys in chemically active graphite shells (or shells coated with graphite), α-layer is minimal.

Mechanism 7. The influence of the seed on the crystallization process in melts is not in doubt. In this case, the syngony of the introduced seed crystal must be at least isomorphic to the resulting phase. A decrease in the number of seeds usually leads to an increase in the average size of new crystals formed. Given that CS wall material uses granular materials with the grain size of up to 100 microns, we should expect a large-crystal structure directly from the surface of the resulting casting. In fact, the coarse-grained structure of the metal appears in the casting not from the surface layer, but somewhat deeper. It is significant that the microhardness of the sample decreases smoothly both within a single crystal and in the case of a polycrystalline structure of the surface layer of the casting (Figure 4). Thus, we can conclude that the dependence of the hardness on the layer depth is the result of an external general physical factor that does not depend on the macrostructure of the condensed matter.

The crystallization front at the boundary of the liquid and solid phases usually has a sharp break and does not allow an exponential distribution of the substance properties over the depth, which occurs when studying the hardness within α-layer (Figure 3, 4, 6). Strange, also, is the fact that the positive effect on α-layer is provided by materials with different syngony – ZrO2, Y2O3, pyrocarbon (graphite), from which we can conclude that there is no specific effect of these components on the embryo formation during the crystallization of the titanium alloy. Therefore, mechanism 7 also cannot claim to be the general physical cause of the formation of α-layer.

![Figure 3](image3.png)

**Figure 3.** Changes in the micro-hardness of titanium alloys in casting α-layer if casting into ceramic molds made of yttrium and zirconium oxides (the temperature of the ceramic mold before casting is 400°C [3]).

![Figure 4](image4.png)

**Figure 4.** Microstructure and distribution of hardness HV, kg/mm² by the depth of BT5J alloy sample.

Thus, it should be recognized that none of the mechanisms discussed above can claim to fully explain the effect of α-layer, which is the result of some external general physical phenomenon that appears in the liquid during the crystallization.
3. Proposed mechanism of formation of α-layer

One of the general factors that were not previously considered related to the casting conditions of titanium alloys in centrifugal machines is the intrinsic vapor pressure of the molten metal. The condensing vapor of metals and oxides thereof is collected on the chamber walls and in vacuum filters in the form of dust in sufficiently large quantities, which makes it possible to consider the evaporation of the melt during casting a fairly significant factor in the casting process. Calculation of natural vapor pressure of BT5Л alloy from temperature based on reference data [11] at temperatures close to 1700 °C leads to the value of 1.2 mm Hg, while the additive contribution of titanium is approximately $5 \times 10^{-3}$ mm Hg. In any case, the melt poured into a ceramic shell with open pores, and is under mechanical pressure (in the lower part of the gating system up to 10 atm) due to centripetal acceleration, is under the external pressure of the surrounding gas $1 \cdot 10^3$–$10^4$ mm Hg, which is significantly lower than its own vapor pressure over the metal. The latter is just the condition for boiling the liquid. Under the influence of high mechanical pressure, the metal partially enters the pores of the ceramic, forming convex menisci, with a curvature less than critical, which does not allow it to flow into the pores, since it does not wet the CS material. The metal “boils in the pores”, while powerful diffusion flows are formed in the conjugated layers of the casting, which violate the structure of the melt near the surface [12]. It is clear that when the mechanical pressure of the metal increases in the zones most remote from the center of rotation, the curvature of the meniscus, which provides a counterbalancing Laplace counter-pressure, increases. It is known from the general thermodynamic laws that the pressure in the liquid also affects the intensity of evaporation of the melt. When boiling, the metal is further cooled and the outer layer of the melt passes in the quenching mode into a solid non-equilibrium state with a disturbed structure. Thus, in our opinion, α-layer is formed having the properties significantly different from the normal crystalline metal.

Figure 5 shows typical results of the study of the cross-section composition of used CSs after BT5Л alloy casting in them in industrial conditions. The results confirm the effusion of titanium vapors into the ceramics pores, and effusion intensity depends on the density. It should be noted that the metal vapor flow is very significant - during the period of filling and cooling of the part, the amount of effusive titanium was up to 1.1 mg per 1 cm$^2$ of the shell. We have not identified the condensed aluminum on the background of ceramic corundum, but its flow is much larger, and it leads to a fairly fast blocking of the through pores of CS. The depth of this visually noticeable “aliting” of CS is 2–3 mm. Different intensity of steam flows from the melt in CS with different density (porosity) is accompanied by quantitatively different violations in the structure of the surface metal layers of castings, which appear as α-layer through the dependence of microhardness on the distance to the casting surface (Figure 6).

The fact of structure violation of the substance under the influence of diffusion flows is known [13].

Additional experiments on the influence of the porosity of the shell on the regularities of the formation of α-layer were carried out.

4. Experimental methods and results

Experimental samples were made from a model mass in the form of cylinders with a rounded end having diameter of 10 mm, a length of 60 mm, which were soldered to a common gate with a diameter of 50 mm. Previously, the samples were coated with the two-layer protective coating up to 400 microns thick, containing various components that lead to changes in the characteristics of α-layer. After that, 8–10 layers of ordinary ceramic suspension of corundum powder of different sizes were applied to the prepared block. Own binder of the protective layer was prepared on the basis of silica sol and alumina sol. After standard drying procedures, model melting and CS firing, BT5Л titanium alloy was poured into the finished ceramic molds on the ДВЛ-200P centrifugal unit. Experimental samples were cut approximately in the middle and the microhardness and composition of the surface layer were determined using Microhardness Tester FM-300 (USA), and a scanning electron microscope S-3400N, Hitachi, (Japan) with the Brookner unit for quantitative X-ray spectral analysis. Figure 7–18 below shows the results of synchronous analysis.
of Vickers microhardness and composition of a number of samples made of BT5JI alloy. The value of α-layer (the microhardness drop at distance of 400 microns and the length of this layer) is considered by us as an indicator of the intensity of the boiling of the melt associated with the amount of metal trapped in the form of vapors into the ceramic shell.

![Figure 5](image1.png)  
**Figure 5.** Titanium content in the surface layers of used ceramic shells of various densities.

![Figure 6](image2.png)  
**Figure 6.** HV microhardness in surface layers of BT5JI parts cast in ceramic shells of different densities.

In some of the drawings below, the content of aluminum and other components is shifted up by 60-70%, which allows extend the scope and present the results more clearly. A slight change in the composition of the surface layer of the metal (Figure 8) is visible only to a depth of 20 microns. At the same time, the length of α-layer (Figure 7) is much greater. This pattern is observed for all experimental data, including those presented in this paper, which further confirms the assumption that α-layer is not directly related to the composition of the casting in this area.

![Figure 7](image3.png)  
**Figure 7.** Change in microhardness with the distance to the casting boundary.

![Figure 8](image4.png)  
**Figure 8.** The composition of the surface layer (Al) +70%.

Attention is drawn to the fact of the multidirectional deviation of the concentration of aluminum in the range from 0 to 100 microns in the experiments in Figure 8 and 10 (synchronously with aluminum, the same is seen for titanium). In accordance with the previously described idea of the formation mechanism of α-layer, it can be imagined that in the case of intensive effusion of aluminum into the
pores of ceramics, which exceeds the effusion of titanium by several hundred times, their concentration in the adjacent layer decreases faster than that of titanium. In accordance with the balance equation, the part of titanium increases, which is shown in Figure 8. In the next experiment (Figure 9, 10), smaller graphite particles were used, which led to better sealing of the pores and condensation of liquid aluminum in them, as a result of which it accumulated in the wall layers of the CS, restored some of the silicon that is part of the binder, and together with it returned as vapors to the pores of the casting (Figure 10). It is clear that in the case of (Figure 8), a much smaller amount of aluminum vapor returned back, since the pores were open both ways.

![Figure 9. Change in microhardness with the distance to the casting boundary.](image)

![Figure 10. The composition of the surface layer (Al, Si) +70%.](image)

Similar processes are observed when using zirconium oxide as a facial protective layer, both in a mixture with aluminum oxide, and in pure form (Figure 11–14). However, in this case, alumina sol was used as a binder [14–17], so in this experiment series, silicon was not detected in α-layer. It should be noted that in this case, the protective ceramic layer had a significant porosity, so that the amount of evaporated aluminum (and titanium) in the pores of the ceramic is significantly higher than what was observed in the first two experiments (the estimated proportions of displaced aluminum in the layer up to 100 microns are indicated in the Figures in %). Sample 4 (Figure 12) was about twice as close to the axis of rotation as sample 5 (Figure 14), so the melt pressure in the latter case was about twice as high. Perhaps an increase in pressure in the liquid metal can be explained by the decrease in evaporation in this case.

When conducting an experiment using pure zirconium oxide as the front layer (Figure 16), the sample was placed in a low-pressure zone. Almost unimpeded access of aluminum vapors to zirconium oxide led to an intensive chemical reaction with almost complete exhaustion of aluminum. Instead, an almost balanced amount of volatile chemical reaction products returned to the casting. Thus, we can conclude that the second condition for the formation of an intense steam flow from a liquid metal into a ceramic shell is the possibility of chemical interaction of aluminum and ceramic components with the formation of volatile products [18–21].

Additional verification of the possibility of chemical reactions with inert fluorite (Figure 18) and magnesium oxide, when using a silica-based binder, confirmed the above regularities.
Figure 11. Change in microhardness with the distance to the casting boundary.

Figure 12. The composition of the surface layer.

Figure 13. Change in microhardness with the distance to the casting boundary.

Figure 14. The composition of the surface layer.

Figure 15. Change in microhardness with the distance to the casting boundary.

Figure 16. The composition of the surface layer (Al, Zr, O) + 60%.
5. Discussion of experiment results
Based on the mechanism of formation of α-layer proposed in section 2, we can assume the following mechanism for changing the composition of the surface layer of the casting: as a result of the boiling process, the aluminum contained in the alloy begins to evaporate into the pores of the shell, taking part of the titanium with it [21]. Further, in the volume of the porous ceramic shell, aluminum condensation occurs, which, under vacuum conditions, accumulates and seals the through pores of the shell. Due to high temperatures, all condensed aluminum in the pores is in a liquid state. The process of casting solidification takes place when the pores of the CS are completely blocked from the side of the poured melt. With a further decrease in temperature, due to different expansion coefficients, the solid part is separated from the surface of the ceramic to form a gap. At the same time, Al, which is located in the pores of CS, retains its liquid state for a long time. The pressure of aluminum vapor at these temperatures is significant, and significantly exceeds the pressure in the casting furnace [11], so it can move for a considerable time (1-2 hours) in the form of a molecular (atomic) flow through the gap between the CS and the metal casting to the low-pressure zone of the furnace. Thus, an increased concentration of Al vapors is formed on the outer surface of the metal, leading to the effusion of its atoms into the pores of the surface layer of the solid casting. In other words, a secondary alitization process is taking place, which causes an increase in the concentration of aluminum within some external part of α-layer.

In the case of CS containing silicon oxide (when used as a silica binder), a chemical reaction takes place inside the ceramic [9]:

$$\text{SiO}_2 + \text{Al}(g) = \text{Si}(g) + \text{Al}_2\text{O}_3.$$  

(1)

It is clear that in this case, the amount of free aluminum capable of secondary alitization decreases in proportion to the reaction loss (1), which is observed in Figure 16, in contrast to the results of the experiment in Figure 10, where the decrease in the proportion of titanium almost completely corresponds to an increase in the proportion of aluminum in the surface layer. It is also possible that a reaction occurs with the formation of a volatile SiO incomplete oxide, but it should be expected that oxygen appears in the outer layers of the casting. The pressure of silicon vapors at high temperatures is much higher than that of aluminum, so the process of silicification of the metal part with silicon vapors occurs by the same mechanism. A similar situation occurs in the case of using zirconium dioxide in CS together with a binder based on an almost inert alumina sol.

Figure 17. Change in microhardness with the distance to the casting boundary.

Figure 18. The composition of the surface layer (Al, Si) +70%.
Despite the exceptionally low vapor pressure of pure zirconium, it enters the casting by the same mechanism as a gaseous incomplete oxide formed by the reaction:

$$3\text{ZrO}_2 + 2\text{Al(g)} = \text{ZrO(g)} + \text{Al}_2\text{O}_3. \quad (2)$$

It should be noted that aluminum can also form volatile oxides at high temperatures that can carry oxygen into the outer layer of the casting [21].

6. Conclusion on the work

Thus, the main way to reduce the intensity of the formation of $\alpha$-layer is to reduce the flow of metal vapors in the CS during casting by reducing the porosity of ceramics, which corresponds to the empirical recommendations known from the literature for casting titanium alloys. This rule is automatically triggered when using fine-grained materials (grain size less than 1 micron) for CS, such as ZrO2, Y2O3, MgO, pyrolytic carbon (graphite), which show the best results with respect to $\alpha$-layer.

We tested this assumption in a special experiment with a different method of applying a two-layer coating of aluminum and yttrium oxides (Figure 19):

![Figure 19: The value of $\alpha$-layer when using different combinations of oxides in both protective layers applied to the CS: 23 - First layer $\text{Al}_2\text{O}_3$, second - $\text{Y}_2\text{O}_3$; 24 - First - $\text{Y}_2\text{O}_3$, second - $\text{Al}_2\text{O}_3$.](image)

Of greatest interest are the results for sample 24, which demonstrate almost no $\alpha$-layer. It is significant that changes in the order of alternating layers of a porous sublayer with thickness of 200 microns made of corundum F1000 (sample 23) were sufficient for the effusive flow of aluminum vapors into this layer from the surface of the boiling melt to cause an intense conjugate diffusion flow in the near-surface layer of the casting with a violation of the metal structure and the formation of unacceptable $\alpha$-layer.

References
[1] Prokhorov A M 1995 Chemical encyclopedia (Moscow: Great Russian Encyclopedia)
[2] Leyen C and Peters M 2003 Titanium and Titanium Alloys. Fundamentals and Applications (Weinheim: Wiley-VCH Verlag)
[3] Zhao E, Kong F, Chen Yu and Li B 2011 Trans. of Nonfer. Met. Soc. of China B 21 348–352
[4] Saha R L, Nandy T K, Misra R D K and Jacob K 1989 Bull. Mater. Sci B 12 481–493
[5] Lyakishev N P 1996 State diagrams of double metal systems (Moscow: Mashinostroenie)
[6] Leyens C 2014 Oxidation and Alpha–Case Phenomena in Titanium Alloys used in Aerospace Industry (Luleå University of Technology SE–971 87 Luleå)
[7] Si-Young S, Bong-Jae C, Beom-Suck H, Han-Jun O and Young-Jig K 2008 J. Mater. Sci. Technol B 24 70–74
[8] Ganeev A A, Demenok A O, Bakerin S V, Kulakov B A, Mukhamadeev I R and Garipov A R 2016 Bulletin of the South Ural State University (Metallurgy) B 16 70–78
[9] Nikitchenko M N, Semukov A S, Saulin D V and Jaburov A Yu 2017 Bulletin of PNRPU. Chemical technology and biotechnology B 4 249–263
[10] Chretien J, King M, Proia W and Rudolf S 2010 Titanium Alpha Case Prevention (Worcester Polytec. Inst)
[11] Kikoin I K 1976 Tables of physical quantities. Handbook (Moscow: Atomizdat)
[12] Ouglev N P, Poilov V Z and Smirnov S A 2017 Foundry B 8 2–8
[13] Beyer W J 2000 Non-Cryst. Solids B 2 845-849
[14] Si-Young S, Bong-Jae C, Sang-Ho N, Chang-Su H, Yong-Mun R, Beom-Suck H and Young-Jig K 2007 Advanced Materials Research Online B 26–28 519–522
[15] Chennakesava R A 2016 Int. J. of Advanced Research B 4 101–106
[16] Mukhamadeev I R, Demenok O B, Ganeev A A, Pavlynich S P and Alikin P V 2015 Bulletin of the South Ural State University (Metallurgy) B 15 95–104
[17] Myoung-Gyun K, Shae K K and Young-Jig K 2002 The Jap. Inst. of Met. Material Transactions B 43 745–750
[18] Bauristhene A M, Mutombo K, Stumpf W E 2013 J. of The Southern African Institute of Mining and Metallurgy B 113 357–361
[19] Mutombo K, Mazibuko N E, Rossow P 2011 ITA Conference 1–25
[20] Branscomb T 2015 ITA Conference 1–10
[21] Kostomarov D V 2011 Melts B 4 89–96

Acknowledgments
The research was carried out using scientific equipment of the “Center for science-intensive chemical technologies and physical and chemical research” of PNRPU in accordance with the project of the Perm REC (RFMEFI62120X0038) “Rational subsoil use”.