



DOI: 10.31643/2023/6445.10

Engineering and Technology

Ceramic molds based on yttrium oxide for the casting of titanium alloys

^{1*}Chukmanova M.T., ¹Panichkin A.V., ¹Mamayeva A.A., ¹Kenzhaliyev B.K., ²Azlan M.N.

¹Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty, Kazakhstan

²University Pendidikan Sultan Idris, Malaysia

* Corresponding author email: chukmanova_m@mail.ru

Received: May 21, 2022
Peer-reviewed: February 22, 2022
Accepted: July 27, 2022

ABSTRACT

The effect of various binding agents based on aqueous solutions of nitric acid, yttrium nitrate and orthophosphoric acid and yttrium hydroxide gel on the physical and mechanical properties of casting molds based on Y_2O_3 has been studied. It is shown that the most promising binding agent for yttrium oxide casting molds is a phosphate bond. The data describing the curing mechanism of phosphate-bonded molding mass is presented. The influence of the concentration of binding agent solutions on the strength characteristics of molding materials after curing and heat treatment is shown. Information about the interaction of yttrium oxide powder molds with phosphate-binding with titanium melt of VT1-0 and VT6 grades is presented. The obtained data allowed us to describe the advantages and disadvantages of the developed molding compound. A method for producing casting molds based on yttrium oxide powder with a yttrium phosphate-binding agent was developed based on this research.

Keywords: molding mixture, yttrium oxide, binding agent, casting mold, titanium alloy

Chukmanova Marzhan Tursyngaliyevna

Information about authors:

Junior researcher, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. E-mail: chukmanova_m@mail.ru, ORCID ID: <https://orcid.org/0000-0002-9626-3205>

Panichkin Alexander Vladimirovich

Candidate of technical sciences, Senior Researcher, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. E-mail: abpanichkin@mail.ru; ORCID ID: <https://orcid.org/0000-0002-2403-8949>

Mamayeva Axaule Alipovna

Candidate of physical and mathematical sciences, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. E-mail: ak78@mail.ru, ORCID ID: <https://orcid.org/0000-0002-9659-8152>

Kenzhaliyev Bagdaulet Kenzhaliyevich

Doctor of Technical Sciences, Professor, General Director-Chairman of the Management Board of the JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: bagdaulet_k@satbayev.university, ORCID ID: <https://orcid.org/0000-0003-1474-8354>

Azlan M.N.

Physics Department, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, Tanjung Malim, Perak, 35900, Malaysia. Email: azlanmn@fsmt.ups.edu.my; ORCID ID: <https://orcid.org/0000-0002-2792-4145>

Introduction

Investment casting is one of the most efficient and cost-effective manufacturing methods for titanium alloys of various complexity and with weights ranging from a few grams to tens of kilograms. The manufacture of high-quality titanium products with a minimum of surface defects is possible only when using casting molds obtained from refractory materials inert concerning titanium melts. This requirement and the high melting point of titanium alloys do not allow the use of most materials traditionally used in the foundry of non-ferrous and ferrous metals.

Forming material or its components, if they are not sufficiently resistant to titanium melts, will

develop physical and chemical processes between them, leading to the dissolution of the mold elements, redox reactions, and wetting and capillary phenomena when receiving the castings. These processes lead to defects in the castings: burning, formation of an alpha layer, porosity, and poor filling of narrow channels with melt. This contributes to higher machining costs and higher rejection rates and makes it impossible to produce thin-walled castings. A gas-saturated layer can lead to the emergence and spreading of cracks, which reduces the operational reliability of the titanium casting. For this purpose, the initial refractory molding and binder materials that are inert with respect to the titanium melt should be used for casting.

Mixtures based on fused aluminum oxide (electrocorundum), magnesite, zirconium dioxide, and graphite have been used in the industry for casting titanium alloys. The low chemical activity or inertness of refractory oxides MgO, ZrO₂, Al₂O₃, CaO, and Y₂O₃ for titanium melts and titanium alloys has been shown in the works of of [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13]]. However, such oxides react in varying degrees with the titanium melt [14], which can cause burn-in and limit the wall thickness of the castings. Y₂O₃ interacts with the titanium melt to a lesser degree than the above oxides, and this can be explained by the fact that their contact, due to the reduction of the titanium oxide, produces metallic yttrium, which is extremely insoluble in the melt. A barrier layer is formed, reducing the rate of interaction between them.

REMET® UK offers a water-dispersed aluminum oxide binder, Remal20, which has solution stability in a certain pH range, to form the face layer of the refractory shell for casting titanium alloys. It is known that aluminum oxide interacts very actively with the titanium melt, which will prevent the melt from filling the thin channels. In addition, ceramic layers obtained from zirconium oxide with Remal20 bonding are characterized by relatively low strength and crack formation [15]. Tetsui et al. and Zhao et al. (reference) found in experiments on casting titanium alloys into molds made of various refractory materials that the least oxygen enrichment in titanium parts occurs when Y₂O₃ is used as the face layer [1]. Contamination studies of directionally solidified alloy Ti46Al8Nb and other titanium alloys in Al₂O₃, Y₂O₃, and CaO crucibles were performed [[16], [17], [18], [19], [20]].

Electrocorundum molds are widely used in the aircraft industry to manufacture castings, which are produced by investment models on an ethyl silicate binder. However, this technology also produces a surface layer on the surface of the titanium castings that is saturated with impurities and negatively affects the characteristics of the castings (alpha layer). In addition, a significant disadvantage of these binding agents is their high cost, low eco-friendliness, and low survivability, which limits their use for large castings from titanium alloys [20], [21]. One of the main problems in producing Y₂O₃ casting molds is the inability to use binding agents based on silicon dioxide and aluminosilicates, which cause a reaction with titanium alloys with the formation of cracks on the casting surface and a very hard alpha layer of 0.3-0.6 mm thickness [22]. The work [23]

shows the formation of an alpha layer with a width of 0.45-0.55 mm, when used as the first layer of ceramic shells of calcium oxide stabilized with zirconium oxide or yttrium oxide stabilized with zirconium oxide. This surface layer results from the reaction of Ti with metal oxides of the ceramic shells, which consists of brittle intermetallic compounds that significantly impair the mechanical properties of the castings. [24]. To overcome this problem, titanium alloys should be embedded in special ceramic casings that prevent or significantly reduce this reaction.

Further research on the selection of a binding agent for the production of ceramic molds from Y₂O₃ for the manufacture of castings from titanium and titanium-based alloys is necessary in this regard. Reducing the thickness of the alpha layer when producing castings from titanium alloys can only be achieved by casting in molds made entirely or partially (face layer) of materials that are inert in relation to titanium. The development of such materials will provide the required quality of the casting surface, which will make it possible to produce titanium castings with a relief surface. The lack of research on the development of binding agents inert to titanium melts for molds based on yttrium oxide hinders the development of technologies for casting titanium alloys. In this regard, studies were performed to find binding agents for the production of Y₂O₃ casting molds by the method of investment casting. The results of these studies are given in this article.

Experimental part

It is necessary to develop molding materials characterized by good fluidity, harden after model pouring, and do not interact with titanium melts, and provide high mold strength to obtain complex configuration castings from titanium alloys using wax models, including those made by additive technologies.

We set the following requirements when developing binding agents for Y₂O₃ powders:

- the binding agent must be stable up to the casting temperature of the titanium alloy, or at decomposition, it must provide high strength to the casting molds;
- the binding agent must interact weakly with the titanium melt;
- the binding agent should be based on yttrium compounds. Curing the molding mixture from Y₂O₃

powders should occur within an acceptable time interval (from 0.25 to 24 hours).

The possibility of using compounds as binders is considered:

- formed by the interaction of Y_2O_3 with solutions HNO_3 and $Y(NO_3)_3$
- forming yttrium hydroxide $Y(OH)_3$ - yttrium acetate $Y(CH_3COO)_3$
- not decomposing when heated - yttrium phosphate YPO_4 .

Recrystallization of yttrium oxide powders increases their chemical resistance to both yttrium nitrate and orthophosphoric acid solutions, and titanium melts due to a decrease in surface energy. The initial yttrium oxide used as a filler of the molding material was subjected to heat treatment in a tubular furnace in an argon flow to remove hydrated water and decompose yttrium carbonate which recrystallization of the powder developed. It was found that the minimum temperature at which recrystallization of chemically deposited yttrium oxide powders begins is 1300 °C, this process actively proceeds above 1500 °C, above 1700 °C their sintering develops (Figure 1).

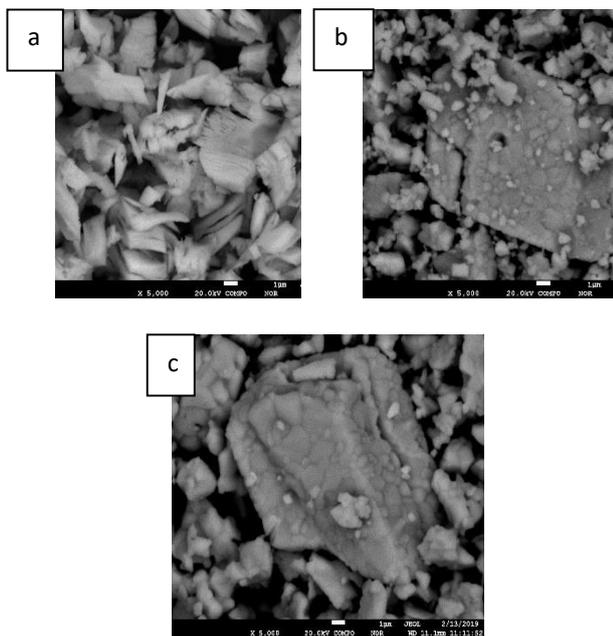


Figure 1 – Recrystallization of yttrium oxide powder during annealing: (a) initial state; (b) 1500 °C, 2 hours; (c) 1650 °C, 2 hours

Evaluation of the possibility of using solutions of HNO_3 and $Y(NO_3)_3$. The conducted research has shown that when Y_2O_3 powder is mixed with an aqueous nitric acid solution with a concentration of 0.5-2 mol/l or with an aqueous $Y(NO_3)_3$ solution with

a concentration of 2-10 mol/l at a T/L ratio of 2:1, an interaction develops between them, which leads to the solidification of the mixture. The curing speed improves from 10 to 2 minutes with an increase in solution concentration in the specified interval. The hardened mixture at room temperature is characterized by high strength, however, when heated above 400 °C, such materials lose strength and crumble. This makes it impossible to use HNO_3 and $Y(NO_3)_3$ solutions as binding agents in the production of casting molds based on Y_2O_3 powders.

Evaluation of the possibility of using yttrium hydroxide $Y(OH)_3$ as a binding agent in the production of Y_2O_3 -based molds. It is known that the precipitation of yttrium hydroxide from aqueous solutions of yttrium acetate $Y(CH_3COO)_3$ forms a gel. Separation of the gel and ammonium acetate solution was performed by dilution with water in a ratio of 1/1, stirring and subsequent centrifugation at a centrifuge spindle speed of 2500 rpm for 10 min with the separation of the gel from the solution. It was found that the water content in it is 73%, when drying yttrium hydroxide gel at 180 °C for 1 hour. Only 10% yttrium oxide remained of the initial gel mass after calcination of the remaining material at 900 °C.

Three layers of yttrium hydroxide gel and yttrium oxide gel were applied to the surface of molding models in the amounts of 25 and 50 wt% to evaluate the possibility of using yttrium hydroxide gel as a binding agent for the first and subsequent layers of molding materials. The model was dried for 1 day after applying each layer, and then the surface was photographed. Figure 2 shows the structure of the obtained shells on the surface of the models after the application of 3 layers of the mixture.

High water content during drying causes cracking of even thin gel films up to 0.2 mm, applied to both smooth and rough surfaces of the model (Figure. 2a). Mixtures of gel with yttrium oxide powder in amounts of 50 and 75 wt% also crack when dried (Figures 2 b-c). However, the number and width of cracks decrease as the proportion of yttrium oxide increases. But the high viscosity of such mixtures requires their mechanical application to the surface of the model and excludes the possibility of spraying. High shrinkage with crack

formation makes it impossible to use $Y(OH)_3$ gel as a bond for yttrium oxide-based molding materials.

Using as a concentrated binding solution (10%) yttrium acetate does not provide the required level of strength of the mixture with Y_2O_3 in the ratio W/T 1:2 after drying. The layer of such material on the model surface increases in thickness by at least 40% due to $Y(OH)_3$ gel formation during subsequent ammonia drying. This causes the face layer to crack and chip off the surface of the model during subsequent drying, which makes the use of yttrium acetate solution as a binding agent useless.

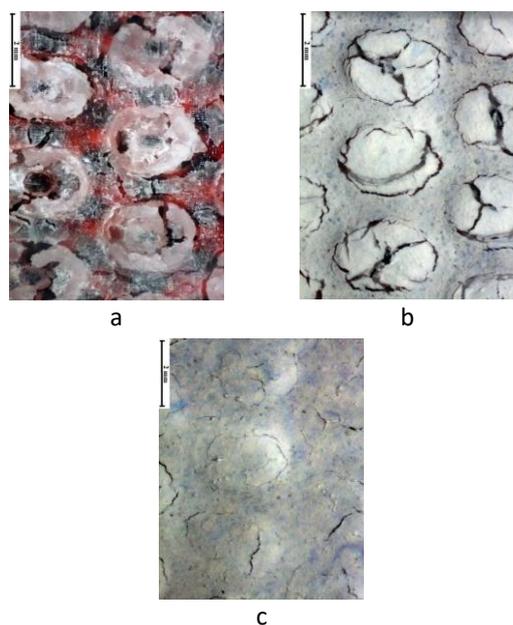


Figure 2 – Crack formation in hydroxide-based shells: (a) $Y(OH)_3$ gel; (b) 50% $Y(OH)_3$ gel +50% Y_2O_3 ; (c) 2nd layer 25% $Y(OH)_3$ gel+75% Y_2O_3

Study of the possibility of using yttrium phosphate as a binding agent. It is known that yttrium phosphate is formed by the interaction of yttrium nitrate and phosphoric acid in an ammonia atmosphere in the following reaction:



We used chemically precipitated yttrium oxide powder with a dispersion of fewer than 10 μm , an aqueous solution of yttrium nitrate, and orthophosphoric acid as the initial raw materials in the experiments. It was found during preliminary experiments that mixing yttrium oxide powders with a mixture of yttrium nitrate and orthophosphoric acid in a short time (up to 5 minutes) resulted in the curing of the molding mixture, which did not allow

to fill the flask with the model and remove air bubbles from it. The solution to this problem was to pretreat the mixture of yttrium nitrate and phosphoric acid solutions for at least 24 hours at room temperature. The curing of mixtures of Y_2O_3 with $Y(NO_3)_3 + H_3PO_4$ solution followed from 10 minutes to 8 hours, depending on the concentration of the solution. The temperature of preliminary annealing of Y_2O_3 , in this case, did not have a significant effect on the curing rate of the molding mixture.

Cylindrical samples with a mixture of pre-baked yttrium oxide powder at 1300-1700 $^{\circ}C$ and an aqueous solution of yttrium nitrate with a concentration from 80 g/l to 333.3 g/l and orthophosphoric acid from 14 g/l to 52 g/l were prepared to determine the effect of the concentration of yttrium nitrate and orthophosphoric acid on the structure and strength of the molding materials. We took a stoichiometric ratio of $Y(NO_3)_3$ and H_3PO_4 according to the reaction equation (1). The ratio W/T was taken no more than 1:2. The mold with the samples was left at room temperature for 24 hours to cure the mixture, then the samples were removed from the mold and dried in ammonia medium at room temperature for 1 day and then in a normal atmosphere at 90-95 $^{\circ}C$ for 0.4 days. The ceramic forms were calcined in a resistance shaft furnace at 600 $^{\circ}C$ and 900 $^{\circ}C$ for 3 hours. Heating to the target temperature was performed at a rate of 3 deg/min. The purpose of the heat treatment was to remove crystalline moisture, decompose ammonium nitrate and yttrium nitrate that did not interact.

Cylindrical samples made of yttrium oxide molding mixture were tested in compression on a Shimadzu AG 100kNx electromechanical testing machine with a 1 mm/min loading speed.

Casting into ceramic molds was performed using titanium alloys VT1-0 and VT6 in a UIPV-0.001 vacuum induction furnace with melt discharge through the bottom.

We investigated the structure of the near-surface and alpha layers of molding materials and cylindrical castings obtained using the developed molding materials by optical and scanning electron microscopy (SEM) and microprobe analysis using a JEOL JXA-8230 microprobe analyzer. The structure was studied using the backscattered electron mode (COMPO). The thickness of the alpha layer was determined by measuring the microhardness from the surface to the center of the casting using a PMT-3 microhardness tester at a load of 50 g.

Research Results and Discussion

The molding mixture had the consistency of thick sour cream when the ratio of a yttrium oxide powder to an aqueous solution by weight is 2:1, and, when vibrations were applied, well filled the flask with a model installed in it to obtain a shape with the required wall thickness and surface relief. In this case, air bubbles were well removed from the mold cavity. The introduction of orthophosphoric acid with a concentration of 21.5 g/l to 43.0 g/l into the composition of an aqueous solution of yttrium nitrate with 125 to 250 g/l provided a solidification period of the mixture from 2 hours to 15 minutes. Increasing the concentration of binders $Y(NO_3)_3$ and H_3PO_4 more than 250 g/l and 43 g/l, respectively, led to self-heating of the mixture and its rapid hardening, which did not allow to complete the molding process.

A graph of the dependence of the strength limit of the molding compound on the concentration of the binder $Y(NO_3)_3$ and H_3PO_4 was drawn according to the results of tests of the obtained cylindrical samples. The analysis of the graph (Figure 3) shows that with increasing binder concentrations of $Y(NO_3)_3$ and H_3PO_4 from 80 and 14 g/l to 167 and 28.7 g/l respectively, the strength of the molding compound increases, and decreases with further increase. This may be due to the fact that as the concentration of these substances increases, the proportion of binding agents formed becomes higher. Curing time is shortened to a few minutes if the concentration is above a certain value and air bubbles are not effectively removed from the mixture during vibration. This reduces the strength of the material. The strength of the molding material decreases after ammonia drying and heat treatment at 600 and 900 °C. At the same time, the strength of the molding material naturally grows with an increase in the concentration of components in the binding agent. A significant decrease in strength after annealing at 900 °C is observed in the mixture with concentrations of 333 and 54.7 g/l $Y(NO_3)_3$ and H_3PO_4 , respectively, the reason for which is the high porosity of such material.

The curing mechanism of the molding mixture based on yttrium oxide powder with a binding agent based on an aqueous solution of yttrium nitrate and orthophosphoric acid is considered based on the analysis of the material structure after curing, X-ray diffraction analysis and infrared spectra of the material obtained during various stages of curing at room temperature.

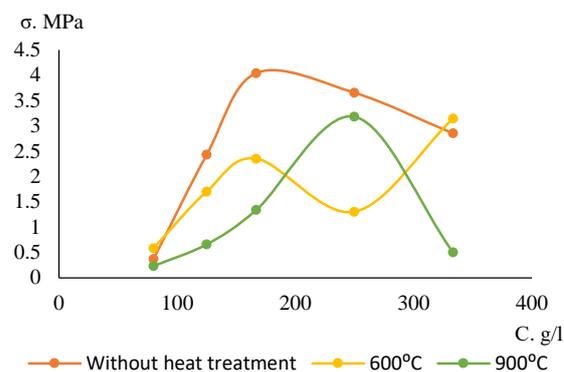


Figure 3 – Dependence of the effect of the concentration of $Y(NO_3)_3$ in the binding agent and H_3PO_4 in aqueous solutions on the strength limit of the molding compound

IR spectra of the sample obtained by mixing Y_2O_3 powder with a binding solution of $Y(NO_3)_3$ and H_3PO_4 167.0 g/l and 28.7 g/l were taken immediately after mixing and then after 1, 2, 3 hours and 3 days. The images were taken on an Avatar 370 CsI FT-IR spectrometer, in the spectral range of $4000-300\text{ cm}^{-1}$ from tablet preparations prepared by pressing 200 mg of KBr with 2 mg of sample. Experiment set-top box is Transmission E.S.P.

As follows from the data obtained, regardless of the exposure time, the spectra of such a sample (Figure 4a) contain lines characteristic of the following compounds:

yttrium oxide Y_2O_3 – 561, 464, 418, 399, 341, 310 cm^{-1} [25]; valence $\nu(OH)$ - 3405 cm^{-1} and deformation δHOH - 1635 cm^{-1} vibrations of water molecules [26]; yttrium orthophosphate YPO_4 - 1040, 634 cm^{-1} [25]; xenotime YPO_4 - 1076, 634 cm^{-1} [27]; group $[CO_3]^{2-}$ – 1474, 1458, 839, 825 cm^{-1} [26, 29, 30]; group $[NO_3]^-$ – 1763, 1384, 1346, 1040, 792 cm^{-1} [[25], [29], [30], [31]]. The band at 746 cm^{-1} can be referred to yttrium orthophosphate dihydrate $YPO_4 \cdot 2H_2O$ [28], a band in this range of the spectrum is also observed in the spectra of nitrate hydrates of rare earth elements [[29], [30]]. There is a band at wave number 391 cm^{-1} in the range of Y-O valence vibrations in the spectrum of the sample; this band probably corresponds to the $Me^{3+}-O$ bond in the carbonate [32].

Comparison of the spectra taken immediately after mixing, after 3 hours and after 3 days showed changes in the intensity of the lines (Figure 4b), indicating changes in the phase composition of the sample. The following changes are observed:

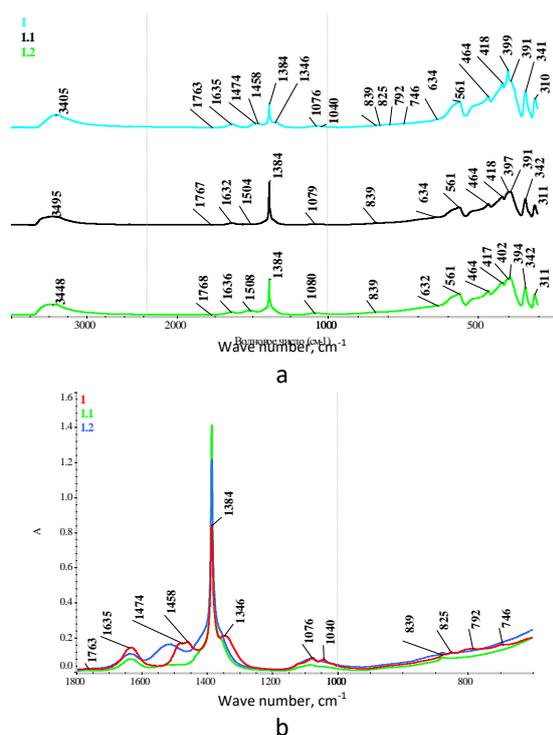


Figure 4 – Infrared spectra: (a) No. 1 suspension immediately after mixing; (b) No. 1.1 - after 3 hours; No. 1.2 - after 3 days

1. Shift of the maximum of the valence band ν_3 of the $[CO_3]^{2-}$ ion to the high frequency range (1-1474, 1458 cm^{-1} ; 1.1 - 1504 cm^{-1} ; 1.2 - 1508 cm^{-1}), and variation of the absorption intensity. The lowest intensity of the valence vibration band ν_3 of the $[CO_3]^{2-}$ ion was recorded in the spectrum of sample 1.1.

2. Varying the intensity of the valence band ν_3 of the $[NO_3]^-$ ion.

3. Varying absorption intensities in the range of Y-O valence vibrations.

4. Displacement of the maximum of valence vibrations $\nu(OH)$:

sample 1- 3405 cm^{-1} ; sample 1.1- 3495 cm^{-1} ; sample 1.2- 3448 cm^{-1} .

This indicates that the processes of yttrium phosphate formation develop before ammonia drying and are associated with the reaction of yttrium nitrate with yttrium oxide and phosphoric acid.

X-ray phase analysis of such a molding compound after curing for 3 hours indicates the formation of yttrium nitrate hexahydrate (Figure 5). Its formation occurs due to the interaction of yttrium oxide and nitrate. The lines characteristic of yttrium phosphate does not appear on radiographs after ammonia drying, indicating its formation in X-ray amorphous form.

The data obtained indicate that the bond between Y_2O_3 powders is formed already at the stage of mixture curing at room temperature (Fig. 6a). Lamellar crystals of yttrium phosphate are formed after ammonia drying, intertwining with each other and binding Y_2O_3 particles (Figure 6b). This structure is maintained during further heat treatment (Figures 6c and d). It is likely that the decrease in strength of the cured molding compound after heat treatment can be explained first by the decay of ammonium nitrate, and then at 900 °C by the beginning of recrystallization of yttrium phosphate needle crystals.

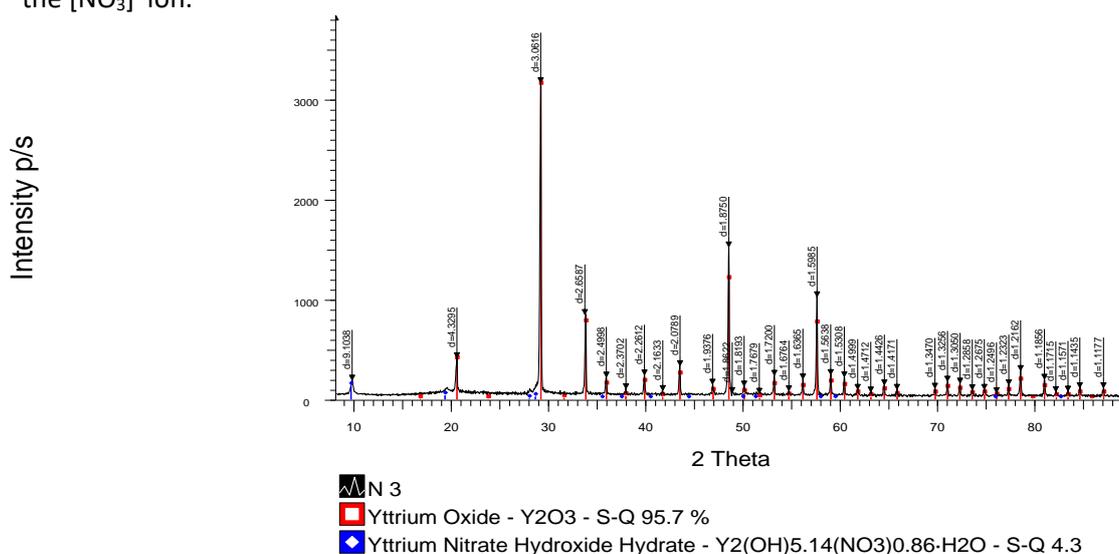


Figure 5 – X-ray diffraction pattern of the resulting mixture based on $Y(NO_3)_3 + H_3PO_4 + Y_2O_3$ without ammonia drying

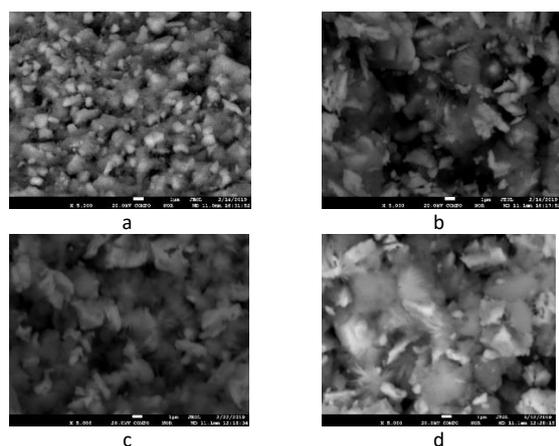


Figure 6 – Changes in the structure of molding mixture based on yttrium oxide and binder $Y(NO_3)_3$ 167,0 g/l H_3PO_4 = 28,7 g/l at different stages of treatment: (a) after curing at room temperature; (b) after ammonia drying; (c) after heat treatment at 600 °C; (d) after heat treatment at 900 °C

It has been established, based on studies of the effect of the concentration of yttrium nitrate and phosphoric acid solutions on the strength of the molding materials obtained, that the optimal concentration of yttrium nitrate and orthophosphoric acid solutions for producing Y_2O_3 -based molds is 167.0 g/l and 28.7 g/l, respectively.

Production of castings into molds based on Y_2O_3 and binder YPO_4 . Casting molds were made on the basis of the developed molding mixture, into which castings of titanium grade VT1-0 and titanium alloy VT6 were obtained. Casting was performed in a mold at room temperature and heated to 550 °C. The diagram of the casting unit, the casting mold, and the resulting casting are shown in Figure 7. Metallographic, electron microscopic, and microprobe examinations were performed to study the formation of an alpha layer and annealing layer on the surface of the castings.

The formation of the alpha layer occurs primarily due to the dissolution of oxygen, which titanium releases, reducing or dissolving in itself the metal oxides that make up the basis of the molding materials. The formation of an alpha layer seriously affects the mechanical properties, the structure of the surface layer of the metal and the dimensional accuracy of the castings. The thickness of such a layer depends on the chemical stability of the mold material and the contact period between the liquid titanium and the mold. The structure and thickness

of the alpha layer must therefore be studied first when examining the structure of the castings.

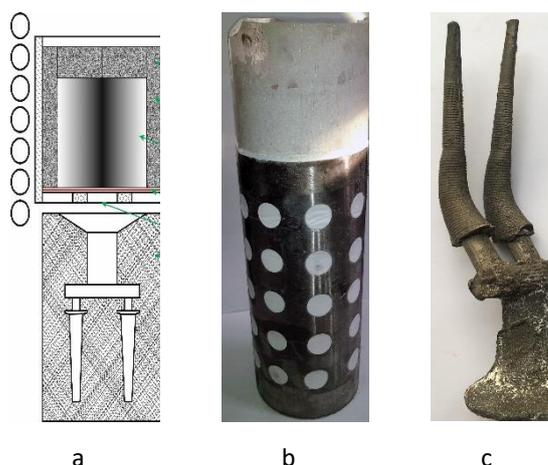


Figure 7 – Diagram of the melting unit of the UIPV-0.001 vacuum induction furnace (a), casting mold (b), casting of blanks of the femoral component of the hip endoprosthesis, obtained from titanium alloy VT6 (c): (1) titanium cylinder; (2) casting mold; (3) - tantalum foil; (4) perforated graphite ring; (5) quartz glass body; (6) lining of yttrium oxide powder

Figure 8 shows the microstructure of the burn-in layer and the near-surface layer formed when casting the alloy VT6 and titanium grade VT1-0 in a mold based on yttrium oxide with a phosphate bond at the mold temperature of 25 °C and 550 °C. The analysis of the structure shows that with an increase in the temperature of the mold, the thickness of the burn-in significantly increases (from ~60 μm to 300 μm). In addition, the surface topography is distorted when casting in a heated casting mold. Microprobe analysis of the burn-in zone indicates that when the melt comes into contact with the mold material due to wetting, titanium penetrates the channels and reacts. Yttrium oxide reduction develops, after which yttrium and oxygen diffuse into the near-surface layer. Oxygen dissolves to form an alpha layer, and yttrium, after crystallization of the melt, is released as a separate phase along the grain boundaries. Titanium surface is covered by a thin oxide film in the air, so in microprobe analysis by EDS and WDS analysis methods there is a big error of oxygen measurement in the alpha layer. In this regard, the most revealing way to determine its thickness is to measure the microhardness along the cross section from the surface deep into the casting.

The microhardness measurements performed on the PMT-3 microhardness tester showed that when casting titanium alloy VT6 into cold and hot molds and titanium VT1-0 into a cold mold made of yttrium oxide, the thickness of the alpha layer does not exceed 550 μm (Fig. 9). This allows us to conclude that there is an insignificant change in the properties of the titanium casting due to the reaction interaction with the mold material. The burn-in layer that forms on the casting surface is poorly separated and can only be effectively removed by sandblasting.

The main disadvantage of casting molds from the developed molding material based on yttrium oxide is the formation of single pores $\varnothing < 0.8$ mm in the alpha layer. Thermal analysis of the mold material, which underwent all stages of processing at 900 $^{\circ}\text{C}$, was performed to identify the causes of porosity formation in the alpha layer. The studies were performed on a synchronous thermal analyzer TG-DTA / DSC STA449 F3 Jupiter[®] "NETZSCH". The furnace space was evacuated before heating (achievable vacuum level $\sim 92\%$) and then purged with inert gas for 5 minutes. Heating was done to $\sim 1500^{\circ}\text{C}$ at a rate of 15 $^{\circ}\text{C}/\text{min}$. Cooling was performed at a rate of 170 $^{\circ}\text{C}/\text{min}$. The total volume of incoming gas was kept within 90ml/min. The results obtained with the STA 449 F3 Jupiter were processed using the NETZSCH Proteus software.

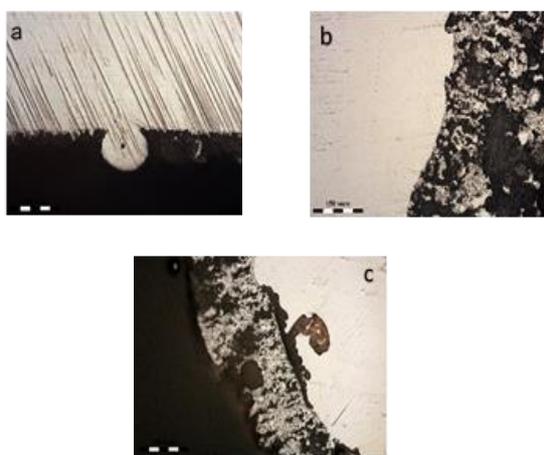


Figure 8 – Cross-sectional structure of burn-in layer and near-surface area of VT1-0 and VT6 titanium castings, formed during casting in Y_2O_3 molds with phosphate-bonding ($\times 250$): (a) VT6 mould heated to 25 $^{\circ}\text{C}$; (b) VT6 mould heated to 550 $^{\circ}\text{C}$; (c) VT1-0 mould heated to 25 $^{\circ}\text{C}$

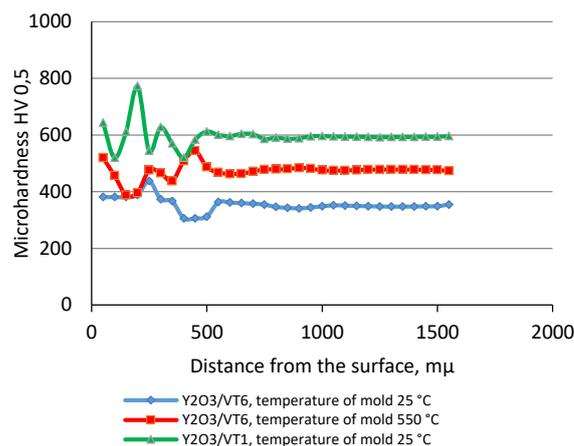


Figure 9 – Change in microhardness over the cross-section of the alpha layer of castings from VT1-0 titanium and VT6 titanium alloy, obtained by casting into molds from yttrium oxide with a phosphate binder

Figure 10 shows that when the molding compound is heated to 1500 $^{\circ}\text{C}$, the decrease in weight is 0.25%. The main decrease in weight is caused by the dehydration process, which develops most intensively at 196.20 $^{\circ}\text{C}$. Further weight loss occurs gradually and is probably associated with the processes of gradual decomposition of yttrium phosphate. The mold material does not undergo a phase transition when heated. Sintering processes begin at temperatures above 1380 $^{\circ}\text{C}$. This indicates that the only reason for the formation of porosity in castings can be the reaction of the phosphate bond with the titanium melt. Presumably, the phosphorus is reduced to its elemental state and evaporates to form micro-cavities as a result of a series of reductive reactions between titanium and YPO_4 (Figure 8c). This may be due to the low solubility of phosphorus in titanium, less than 0.3% at 1495 $^{\circ}\text{C}$. Accordingly, a maximum reduction of yttrium phosphate content in the yttrium oxide-based molding mass is necessary.

In addition, it has been found that if the melt is poured after the heat-treated mold has been exposed to a normal atmosphere, the likelihood of pores in the central part of the casting increases significantly. This is due to the active absorption of moisture and carbon dioxide by yttrium oxide from the air.

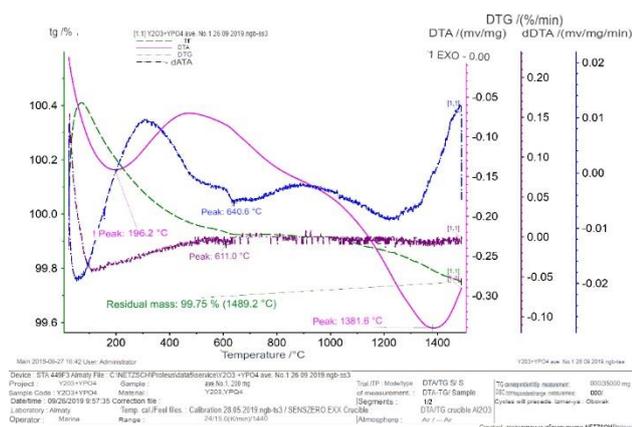


Figure 10 – Thermogram of heating the molding compound based on Y_2O_3 and YPO_4 binder

Conclusions

The use of nitric acid or yttrium nitrate solutions as binding agents for yttrium oxide powders is not promising due to the fact that the forms lose strength after thermal decomposition of yttrium nitrate hexahydrate.

Using a mixture of yttrium oxide and yttrium hydroxide as a face layer is not promising due to the fact that during drying the yttrium hydroxide gel undergoes high shrinkage, which leads to the formation of numerous cracks in the face layer. Similarly, yttrium acetate solution cannot be used as a binding agent for Y_2O_3 powder, due to the low strength of such a molding compound and the subsequent ammonia drying of the yttrium hydroxide gel formation leads to significant swelling of the resulting mold and its subsequent destruction;

A new composition and modes of subsequent processing of molding compound based on yttrium oxide and binding agent from yttrium nitrate solution and orthophosphoric acid, which allow to produce casting molds for casting titanium and titanium alloys with high strength level, have been developed. The mechanism of solidification of the molding compound is described by the following

processes: the formation of yttrium nitrate hexahydrate in the first stage due to the interaction of yttrium oxide and nitrate, which binds the filler particles in the period from 0.25 to 3 hours after mixing the components; conversion of yttrium nitrate hexahydrate into yttrium phosphate with needle-shaped crystals in a second stage after ammonia drying. The molds of such a mixture retain their strength after heat treatment at $900^\circ C$ and do not undergo polymorphic transformations when reheated. Mass loss on heating to $1500^\circ C$ does not exceed 0.25%.

Casting of VT1-0 and VT6 alloys into molds from the developed mixture results in the formation of an alpha layer up to 550 microns thick on the casting surface, which is associated with the reduction of yttrium oxide by titanium melt with subsequent dissolution of oxygen in the reaction zone. The microhardness increases naturally in this layer. Single pores up to 0.8 mm in size are formed in the alpha layer due to the interaction of titanium melt with yttrium phosphate. A burn-in layer with high adhesion is formed on the surface of the castings. It can be removed by sandblasting. Titanium molds must be cast directly after heat treatment or measures must be taken to protect the molds from interaction with the atmosphere due to the large surface area of yttrium oxide powders and their interaction with atmospheric carbon dioxide and moisture.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgments

The research was performed with the financial support of the Committee for Science of the Ministry of Education and Science of the Republic of Kazakhstan under grant funding No. AR05130722.

Cite this article as: Chukmanova MT, Panichkin AV, Mamayeva AA, Kenzhaliyev BK, Azlan MN. Ceramic molds based on yttrium oxide for the casting of titanium alloys. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*. 2023;324(1):71-82. <https://doi.org/10.31643/2023/6445.10>

Титан қорытпаларын құюға арналған иттрий оксиді негізіндегі керамикалық қалыптар

¹Чукманова М.Т., ¹Паничкин А.В., ¹Мамаева А.А., ¹Кенжалиев Б.К., ²Азлан М.Н

¹Металлургия және кен байыту институты АҚ, Сәтбаев университеті, Алматы, Қазақстан

²Сұлтан Ыдырыс атындағы білім беру университеті, Малайзия

<p>Мақала келді: 21 мамыр 2021 Сараптамадан өтті: 22 ақпан 2022 Қабылданды: 27 шілде 2022</p>	<p>ТҮЙІНДЕМЕ</p> <p>Y₂O₃ негізіндегі құю қалыптарының физика-механикалық қасиеттеріне азот қышқылының, иттрий нитраты мен ортофосфор қышқылының және иттрий гидроксиді гелінің сулы ерітінділері негізіндегі әртүрлі байланыстырғыш заттардың әсері зерттелді. Иттрий оксидінен құйма қалыптарды алу үшін ең перспективалық байланыстырғыш фосфатты байланыстырғыш екені көрсетілген. Фосфатты байланысы бар қалыптау қосылысының қатаю механизмін сипаттайтын деректер берілген. Қалыптау материалдарының қатаю және термиялық өңдеуден кейінгі беріктік сипаттамаларына байланыстырушы ерітінділер концентрациясының әсері көрсетілген. Иттрий оксиді ұнтағынан жасалған құю қалыптарының BT1-0 және BT6 маркалы титан балқымасы бар фосфатты байланыстырғышпен әрекеттесуі туралы ақпарат берілген. Алынған мәліметтер әзірленген қалыптау қоспасының артықшылықтары мен кемшіліктерін сипаттауға мүмкіндік берді. Жүргізілген зерттеулердің негізінде иттрий оксиді ұнтағы негізінде иттрий фосфатының байланыстырғышы бар құю қалыптарын жасау әдісі әзірленді.</p> <p>Түйін сөздер: қалыптау қоспасы, иттрий оксиді, байланыстырғыш, құю қалыптары, титан қорытпасы</p>
<p>Чукманова Маржан Турсынғалиевна</p>	<p>Авторлар туралы ақпарат: Кіші ғылыми қызметкер, <i>Металлургия және кен байыту институты АҚ, Алматы, Қазақстан, E-mail: chukmanova_m@mail.ru, ORCID https://orcid.org/0000-0002-9626-3205</i></p>
<p>Паничкин Александр Владимирович</p>	<p>Техника ғылымының кандидаты, аға ғылыми қызметкер, <i>Металлургия және кен байыту институты АҚ, Алматы, Қазақстан, E-mail: abpanichkin@mail.ru, ORCID ID: https://orcid.org/0000-0002-2403-8949</i></p>
<p>Мамаева Аксауле Алиповна</p>	<p>Физика-математика ғылымының кандидаты, <i>Металлургия және кен байыту институты АҚ, Алматы, Қазақстан, E-mail: ak78@mail.ru, ORCID ID: https://orcid.org/0000-0002-9659-8152</i></p>
<p>Кенжалиев Багдаулет Кенжалиевич</p>	<p>Т.ғ.д., проф., бас директор – Басқарма Төрағасы, <i>"Металлургия және кен байыту институты" АҚ, Алматы, Қазақстан, Email: bagdaulet_k@satbayev.university, ORCID ID: https://orcid.org/0000-0003-1474-8354</i></p>
<p>Азлан М.Н.</p>	<p>физика кафедрасы, жаратылыстану-математика факультеті, <i>Университет Пендидикан Сұлтан Идрис, Танджунг Малим, Перак, 35900, Малайзия. Email: azlanmn@fsmt.ups.edu.my; ORCID ID: https://orcid.org/0000-0002-2792-4145</i></p>

Керамические литейные формы на основе оксида иттрия для литья титановых сплавов

¹Чукманова М.Т., ¹Паничкин А.В., ¹Мамаева А.А., ¹Кенжалиев Б.К., ²Азлан М.Н.

¹АО Институт металлургии и обогащения, Satbayev University, Алматы, Қазақстан

²Образовательный университет Султана Идриса, Малайзия

<p>Поступила: 21 мая 2021 Рецензирование: 22 февраля 2022 Принята в печать: 27 июля 2022</p>	<p>АННОТАЦИЯ</p> <p>Проведены исследования влияния различных связующих на основе водных растворов азотной кислоты, нитрата иттрия и ортофосфорной кислоты, геля гидроксида иттрия на физико-механические свойства литейных форм на основе Y₂O₃. Показано, что наиболее перспективным связующим для получения литейных форм из оксида иттрия является фосфатная связка. Приведены данные, описывающие механизм отверждения формовочной массы с фосфатной связкой. Показано влияние концентрации связующих растворов на прочностные характеристики формовочных материалов после затвердевания и термообработки. Представлена информация о взаимодействии литейных форм из порошка оксида иттрия с фосфатной связкой с титановым расплавом марок BT1-0 и BT6. Полученные данные позволили описать достоинства и недостатки разработанной формовочной смеси. На основании проведенных исследований разработан способ по изготовлению литейных форм на основе порошка оксида иттрия со связующим из фосфата иттрия.</p> <p>Ключевые слова: формовочная смесь, оксид иттрия, связующее, литейная форма, титановый сплав</p>
--	---

Чукманова Маржан Турсынғалиевна	Информация об авторах: Младший научный сотрудник, АО «Институт металлургии и обогащения», Алматы, Казахстан, E-mail: chukmanova_m@mail.ru, ORCID https://orcid.org/0000-0002-9626-3205
Паничкин Александр Владимирович	Кандидат технических наук, старший научный сотрудник, АО «Институт металлургии и обогащения», Алматы, Казахстан, E-mail: abpanichkin@mail.ru, ORCID ID: https://orcid.org/0000-0002-2403-8949
Мамаева Аксауле Алиповна	кандидат физико-математических наук, АО «Институт металлургии и обогащения», Алматы, Казахстан, E-mail: ak78@mail.ru, ORCID https://orcid.org/0000-0002-9659-8152
Кенжалиев Багдаулет Кенжалиевич	Д.т.н., проф., генеральный директор – Председатель правления АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: bagdaulet_k@satbayev.university, ORCID https://orcid.org/0000-0003-1474-8354
Азлан М.Н.	Кафедра физики, факультет естественных наук и математики Университета Пендидикан Султан Идрис, Танджунг Малим, Перак, 35900, Малайзия. Email: azlanmn@fsm.tps.edu.my; ORCID ID: https://orcid.org/0000-0002-2792-4145

References

- [1] Wei YM, Lu ZG, Li XY, Guo X. Interface reaction during titanium alloys investment casting by residue gas in ceramic mold. *Rare Met.* 2019;38:327-335.
- [2] Fan J, Liang L, Liu, Zh Li, Yu Li, Y, Gao H, et al. Recent research and development of mould materials for casting TiAl alloys. *Materials Science and Technology.* 2019;35:891-899. <https://doi.org/10.1080/02670836.2019.1598667>
- [3] Cui R, Zhang H, Tang X, Ma L, Zhang H, Gong Sh. Interactions between γ -TiAl melt and Y₂O₃ ceramic material during directional solidification proces. *Nonferrous Metals Society of China.* 2011;21:2415-2420. [https://doi.org/10.1016/S1003-6326\(11\)61029-7](https://doi.org/10.1016/S1003-6326(11)61029-7)
- [4] Shcherbakova G, Varfolomeev M, Storozhenko P. Solution to Technological Problems of Raising the Reliability and Quality of Castings Based on Titanium Alloys. *Trans Tech Publications, Switzerland. Materials Science Forum.* 2019;946:258-264. <https://doi.org/10.4028/www.scientific.net/MSF.946.258>
- [5] Varfolomeev MS, Moiseev VS, Shcherbakova GI. Perspective ceramic composite materials based on aluminumyttrium binder composition. In: *Journal of Physics. 15th International Scientific and Technical Conference Rapid Solidification Materials and Coatings (RSMC-2018).* 2018 October 16-17; Moscow, Russian Federation. (Vol. 1121) 012032. <https://doi.org/10.1088/1742-6596/1121/1/012032>
- [6] Tetsui T, Kobayashi T, Mori T, Kishimoto T, Harada H. Evaluation of Yttria Applicability as a Crucible for Induction Melting of TiAl Alloy. *Materials Transactions.* 2010;9:1656-1662. <https://doi.org/10.2320/matertrans.MAW201002>
- [7] Cheng X, Yuan C, Blackburn S, Withey PA. Influence of Al₂O₃ concentration in yttria based face coats for investment casting Ti-45Al-2Mn-2Nb-0*2TiB alloy. *Materials Science and Technology.* 2014;30:1758-1764. <https://doi.org/10.1179/1743284713Y.0000000467>
- [8] Tetsui T, Kobayashi T, Ueno T, Harada H. Consideration of the influence of contamination from oxide crucibles on TiAl cast material, and the possibility of achieving low-purity TiAl precision cast turbine wheels. *Intermetallics.* 2012;31:274-281. <http://dx.doi.org/10.1016/j.intermet.2012.07.019>
- [9] Xiude L, Xiangyi X, Hong Zh, Tiebang Zh, Jinshan L. Interface Reaction between Ceramic Moulds and High Nb-TiAl Alloys. *Rare Metal Materials and Engineering.* 2013;42:1568-1571.
- [10] Lin B, Liu R, Jia Q, Cui Y, Withey PA, Yang R. Effect of yttria inclusion on room temperature tensile properties of investment cast TiAl. *Materials Science and Engineering A.* 2018;712:73-79. <https://doi.org/10.1016/j.msea.2017.11.100>
- [11] Panichkin AV, Uskenbayeva A, Imanbayeva A, Temirgaliyev S, Dzhumabekov D. Vzaimodeistvie titanovykh rasplavov s razlichnymi tugoplavkimi soedineniyami [Interaction of titanium alloys with various refractory compounds]. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources.* 2016;3:84-90. (in Russ.).
- [12] Kenzhaliyev BK, Chukmanova MT. Technologii izgotovleniya individual'no razrabatyvaemykh endoprotezov iz titanovykh splavov [Technologies for manufacturing individually developed endoprosthesis from titanium alloys]. *Mezhdunarodnaya nauchno-prakticheskaya konferenciya "Effektivnye tehnologii proizvodstva cvetnykh, redkih i blagorodnykh metallov"* [Proceedings of International scientific and practical conference "The Effective Technologies of Non-Ferrous, Rare and Precious Metals Manufacturing] *Almaty.* 2018;364-367. (in Russ.). <https://doi.org/10.31643/2018-7.36>

- [13] Бирюкова АА, Тихонова ТА, Боронина АВ, Акчулакова СТ. Процессы минералообразования и спекания магнезиальносиликатных композиций системы MgO-SiO. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*. 2011;5.
- [14] Panichkin A, Imanbayeva A, Imbarova A. Titanium melt interaction with the refractory oxides of some metals. *Kompleksnoe Ispolzovanie Mineralnogo Syra = Complex Use of Mineral Resources*. 2019;2:51-60. <https://doi.org/10.31643/2019/6445.16>.
- [15] Rassohina L, Bityutskaya O, Parfenovich P, Narskiy A. Study of the properties of latex binder «Remal 20» and suspensions for the manufacture of shell shape in the production of castings from γ -TiAl alloys. *Novosti materialovedeniya. Nauka i tehnika*. 2015;4:43-51.
- [16] Lapin J, Gabalcová Z, Pelachová T. Effect of Y₂O₃ crucibles on contamination of directionally solidified intermetallic Ti-46Al-8Nb alloy. *Intermetallics*. 2011;19:396-403. doi:10.1016/j.intermet.2010.11.007.
- [17] Zhang H, Tang X, Zhou C, Zhang S. Comparison of directional solidification of γ -TiAl alloys in conventional Al₂O₃ and novel Y₂O₃-coated Al₂O₃ crucibles. *Journal of the European Ceramic Society*. 2013;33:925-934. <https://doi.org/10.1016/j.jeurceramsoc.2012.11.006>
- [18] Fan J, Liu J, Wu S, Tian S, Gao H, Wang S, et al. Microstructure formation and interface characteristics of directionally solidified TiAl-Si alloys in alumina crucibles with a new Y₂O₃ skull-aided technology. *Scientific Reports*. 2017;7. <https://doi.org/10.1038/srep45198>
- [19] Fan J, Liu J, Tian S, Wu S, Wang S, Gao H, et al. Effect of solidification parameters on microstructural characteristics and mechanical properties of directionally solidified binary TiAl alloy. *Journal of Alloys and Compounds*. 2015;650:8-14. <https://doi.org/10.1016/j.jallcom.2015.05.160>
- [20] Fan J, Zhang C, Wu S, Gao H, Wang X, Guo J, et al. Effects of solidification parameters on the growth direction of α phase in directionally solidified Ti-49Al alloy. *Intermetallics*. 2017;90:113-118. <https://doi.org/10.1016/j.intermet.2017.07.008>
- [21] Mukhamadeev I, Demenok O, Ganeev A, Pavlinich S, Alikin P. Vybór svyazuyshih na vodnoi osnove dlya oblochkovykh form lit'ya po vyplavyaemym modelyam titanovykh splavov [The Choice of Water-Based Binder for Shell Molds of the Investment Casting of Titanium Alloys]. *Bulletin of the South Ural State University. Ser. Metallurgy*. 2015;3:95-104. (in Russ).
- [22] Sung SY, Kim YJ. Alpha-case formation mechanism on titanium investment castings. *Materials Science and Engineering A*. 2005;405:173-177. <https://doi.org/10.1016/j.msea.2005.05.092>
- [23] Duarte TP, Neto RJ, Félix R, Lino J. Optimization of Ceramic Shells for Contact with Reactive Alloys. *Materials Science Forum*. 2008;587-588:157-161. <https://doi.org/10.4028/www.scientific.net/MSF.587-588.157>
- [24] Ding HS, Guo JJ, Jia J, Fu HZ. Thermodynamic and Kinetic Consideration of Selecting Mould Materials for Casting Titanium Alloys. In: Hamburg, organizer. *Proc. of the 10th World Conf. on Titanium*. 2003;1:439 - 446.
- [25] Iurchenko A, Kustova G, Bacanov C. Kolebatel'nye spektry neorganicheskikh soedinenii [Vibrational spectra of inorganic compounds]. Novosibirsk: Nauka. 1987;145. (in Russ.).
- [26] Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. A Wiley-Interscience Publication. 1986.
- [27] Boldyrev AI. *Infrakrasnye spektry mineralov [Infrared spectra of minerals]* Moskva: Nedra, 1976; 200. (in Russ.).
- [28] Pechkovskii V, Mel'nikova R, Dziuba E, Barannikova T, Nikanovich M. *Atlas infrakrasnykh spektrov fosfátov [Atlas of infrared spectra of phosphates]*. Moskva: Nauka. 1981;248. (in Russ.).
- [29] Aldrich H. *Organometallic, Inorganic, Boron, Deuterium Compounds (632 spectra)*. Nicolet Instrument Corp. 1995.
- [30] Aldrich H. *FT-IR Collection Edition II (18454 spectra)* Thermo Fisher Scientific Inc. for Nicolet FT-IR. 2008.
- [31] Kazicyna L, Kupletskaya N. *Primenenie UV-, IK, I YMR-spektroskopii v organicheskoi khimii [Application of UV, IR and NMR spectroscopy in organic chemistry]*. Moskva. 1971;264. (in Russ.).
- [32] Solntseva LS, Sidorenko GA, Solntsev BP. *Primeneniye IK-spektroskopii k izucheniyu kharaktera svyazi i koordinatsii kationov po kislorodu i galogenam v mineralakh [Application of IR spectroscopy to the study of the nature of the bond and coordination of cations in oxygen and halogens in minerals]* *Konstitutsiya i svoystva mineralov = Constitution and properties of minerals*. 1972;6:30-46. (in Russ.).