ISSN: 2616-6445 (Online), ISSN: 2224-5243 (Print)
Kompleksnoe Ispol’zovanie Mineral’nogo Syr’a. №2. 2019 (51-60)

UDC 621.745-621.746
IRSTI 55.15.17
https://doi.org/10.31643/2019/6445.16

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# TITANIUM MELT INTERACTION WITH THE REFRACTORY OXIDES OF SOME METALS

*Received: 27March 2019 / Peerreviewed: 14 April 2019 / Accepted: 13 May 2019*

**Abstract.** This article reviews perspectives of various refractory oxides application, including rare earth elements as fire resistance material to produce tiegels for titanium induction melting and titanium alloys. The interaction of titanium molten with calcium oxide, magnesium, zirconium and the rare earth elements oxides: lanthanum, cerium and yttrium were studied in theory and by testing. In order to assess the possibility of using oxides of these metals in the manufacture of refractories for Ti alloys melting, the thermodynamic calculations were performed using the Outotec HSC Chemistry 8 program. The Gibbs free energy of the reactions of interaction between titanium alloys with the listed oxides was calculated. The Gibbs energy was testified to have positive values in the high temperatures, which in theory means that they can be used as refractory materials in the smelting of titanium. The experiments of short-term interaction of titanium with the oxides of the listed elements were carried out under heating in a vacuum induction furnace. The interaction was evaluated by the change in the titanium structure after melting it in the volume of the pressed oxide powder. In the process of titanium melting with oxides of calcium and magnesium at high temperatures, an intense boiling and splashing is observed.This fact is explained by the titanium restores calcium and magnesium to the state of metal, and the low boiling temperature of calcium and magnesium causes the release of a large amount of metal vapor. Titanium is heavily contaminated by the metals that form these oxides, and, therefore, by oxygen being in contact with $La_2O_3$, $CeO_2$ and $ZrO_2$. The yttrium oxide is testified to be the most resistant to the titanium melting, there is no significant contamination of the molten with yttrium and oxygen, and this increases the titanium hardness by 20%. The experiments have resulted in that it was recommended to use yttrium oxide as a refractory material.

**Keywords:** titanium molten, refractory oxides, refractory material, reactional interaction

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# ИНДУКИЯЛЫҚ БАЛҚЫТУ КЕЗІНДЕ ОТҚА ТӨЗІМДІ КЕЙБІР МЕТАЛЛ ОКСИДТЕРІНІҢ ТИТАНМЕН ӘСЕРЛЕСУІН ЗЕРТТЕУ

**Түйіндеме: Түйіндеме:**Мақаладаәртүрлі сирекжер элементтерінің титанды индуктивті балқытукезінде отқатөзімді материал ретінде отқабырлар жасауда қарастырудың маңыздылығы көрсетілген. Кальций, магний, цирконий оксидтері және сирек-жер элементтерінің: лантан, церия және иттрий оксидтерімен титанның өзара әрекеттесуі теориялық және эксперименталды түрдезе рттелген. Осы металдардың оксидтерінің Ті қорытпаларын балқытуға арналған отқатөзімді материалын өндіруге пайдалану мүмкіндігін бағалау үшін Outotec HSC Chemistry 8 бағдарламасы арқылы термодинамикалық есептеулер жүргізілді. Аталған оксидтермен титанның өзараәрекеттестігі үшін Гиббстің еркін энергиясы есептелген. Гиббс энергиясының жоғары температураларда осы реакциялардағы энергиясы теориялық тұрғыдан олар титанбалқыт укезінде отқатөзімді материалдар ретінде қолданыла алатындығын көрсетеді.Вакуумдық индукциялық пеште жылу жағдайында титанның қысқамерзімді өзараәрекеттестіг ібойынша аталған элементтердің оксидтерімен эксперименттер жүргізілді. Сұйылтылған оксид ұнтағы көлемінде балқығаннан кейін титан құрамының өзгеруімен өзараәрекеттесу бағаланды.Титан еріген кезде кальциймен магний оксидтері мен жанасқанда жоғарытемпературада, интенсивті қайнау және бүрку байқалады. Бұл құбылыс титанның металл күйіне кальций мен магнийді азайтатынын түсіндіреді, ал кальций мен магнийдің төменгі қайнау температурасы металл буларының көпмөлшерін босатады.$La_2O_3$, $CeO_2$ және $ZrO_2$ байланысқан кезде, титан бұлоксидтерді, демек, оттегіні құрайтын металдар мен қаттыластанған. Иттрий оксиді титан балқымасына қатысты ең төзімді болып табылады. Олардың байланыстары кезінде балқыманың иттриймен оттегімен ластануы жоқ, бұл титанның қаттылығын есе 20% арттырады. Эксперименттердің нәтижелері бойынша иттрий оксиді нотқатөзімді материал ретінде пайдалану ұсынылды.

**Түйінсөздер**: индукциялық жылу; титанбалқымасы, отқатөзімді материал, өзарареакциялықәсерлесу.

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# ВЗАИМОДЕЙСТВИЕ ТИТАНОВОГО РАСПЛАВА С ТУГОПЛАВКИМИ ОКСИДАМИ НЕКОТОРЫХ МЕТАЛЛОВ

**Резюме.** В статье показаны перспективы применения различных тугоплавких оксидов, в том числе редкоземельных элементов в качестве огнеупорного материала для изготовления тиглейдляиндукционной плавки титана и титановых сплавов. Теоретически и экспериментально исследовано взаимодействие титанового расплава с оксидами кальция, магния, циркония и оксидами редкоземельных элементов: лантана, церия и иттрия. В целях оценки возможности использования оксидов этих металлов при изготовлении огнеупоров для плавки Ti-сплавов были проведены термодинамические расчеты, с помощью программы Outotec HSC Chemistry 8.Была рассчитана свободная энергия Гиббса реакций взаимодействия титановых сплавов с перечисленными оксидами.Показано, что энергия Гиббса в области высоких температур имеет положительные значения, что теоретически означает возможность использования их в качестве огнеупорных материалов при плавке титана. В условиях нагрева в вакуумной индукционной печи выполнены эксперименты по кратковременному взаимодействию титана с оксидами перечисленных элементов.Взаимодействие оценивали по изменению состава титана после расплавления его в объеме спрессованного порошка оксида.В процессе плавки титановых расплавов с оксидами кальция и магния при высоких температурах наблюдается интенсивное бурление и разбрызгивание. Это явление объяснено тем, что титан восстанавливает кальций и магний до металлического состояния, а низкая температура кипения кальция и магния вызывает выделение большого количества металлического пара. При контакте с $La_2O_3$, $CeO_2$ и $ZrO_2$ титан сильно загрязняется металлами, образующими эти оксиды,а,следовательно и кислородом. Показано, что оксид иттрия является наиболее стойким по отношению к титановому расплаву, происходит не существенное загрязнение расплава иттрием и кислородом, и при этом увеличивается твердость титана на~20%. По результатам экспериментов рекомендовано в качестве огнеупорного материала использовать оксид иттрия.

**Ключевые слова**: титановый расплав, тугоплавкие оксиды, огнеупорный материал, реакционное взаимодействие

**Introduction**. Pure titanium and its alloys have a valuable set of physical and chemical and mechanical properties, such as high strength to density ratio, acceptable ductility at room, elevated and subzero temperatures, good welding capacity, low linear expansion coefficient and good casting properties - high fluidity, low tendency to gas porosity, slight linear and bulk shrinkage (2–3%). At the same time, titanium has a high reactivity in the molten state, which leads to its contamination with impurities that reduce the ductility and viscosity of the metal during the smelting process and when interacting with the crucible material and mold. The refore, during shaped casting, the difficulties arise, firstly, with the need to use equipment for conducting smelting in a protective atmosphere or in a vacuum, and secondly, with the choice of material for molds and crucibles [1-3].

Now the two methods of titanium smelting are used to obtain the large-tonnage castings in industries, such ascathode ray and electric arc. In order to obtain small castings, induction melting in vacuum or inert gas atmosphere is the best possible. This allows obtaining very homogeneous and reproducible castings. The main failure of the existing method of induction melting is that the molten metal interacting with the material of the crucible used is significantly contaminated by impurities [3].

A low-tonnage production is increasingly applies induction melting in the so-called “cold” crucible to resolve this problem [4, 5]. However, despite the fact that the contamination of the melted material is minimized, and the use of this method leads to its chemical and thermal homogenization, the cost of such installations remains extremely high.

Since the middle of the twentieth century, a research has been actively conducted aimed at searching for refractory materials inert to titanium and titanium-containing alloys. Various studies are underway to develop ceramic crucibles suitable for melting titanium alloys.

Thus, according to the research data [6], crucibles from various oxides, carbides, borides, and sulfides were tested, but the results were generally considered unsatisfactory. This is due to the high level of their interaction with titanium melts or poor heat resistance, which leads to the development of cracks and the destruction of crucibles.

According to the results of thermodynamic calculations made by the authors [7], the resistance of refractory materials made of CaO, $Y_2O_3$, $ZrO_2$, $Al_2O_3$, MgO, $SiO_2$ in contact with molten titanium-aluminum alloys was demonstrated to depend on the temperature, aluminum content and the oxygen. Reactional interaction of Ti-Al melt with CaO, $Y_2O_3$, $ZrO_2$ and $Al_2O_3$ and their mixtures have positive values of ΔGr in Ti-Al in the 1000 ° C - 1700 ° C temperature range for all Ti-Al compositions, including pure titanium, which indicates the absence of their chemical interaction and according to the authors allows the use of such materials for the manufacture of crucibles. According to the results of calculations MgO, $SiO_2$can interact with melts containing more than 80 and more than 70 wt. % Ti, respectively.

Mea nwhile, subsequent calculations [8] and a comparison of the Gibbs energy for the formation of various oxides and titanium oxide have resulted in $Y_2O_3$ and CaO can only be resistant to the titanium melts of the above, while CaO will not interact with the titanium melt only after reaching its oxygen concentration of more than 5 wt. %. The calculations performed here found no reaction of Ti-48 wt. % melt with only $Y_2O_3$ and CaO. These results were experimentally confirmed by the example of Ti-6Al-4V and Ti-50Al alloys, while in the case of the use of a crucible of $Y_2O_3$, the oxygen concentration in the alloy was less than 1 wt. %

In [9–14], it was experimentally demonstrated that CaO and $Y_2O_3$ crucibles are characterized by minimal interaction with γ-TiAl titanium melt, especially $Y_2O_3$, while MgO, $ZrO_2$, $Al_2O_3$ crucibles interact with titanium melt [14]. However, due to the high hygroscopicity and the development of a weak reaction, the manufacture of crucibles for induction melting of titanium alloys from CaO did not find practical application, although in [8] it was noted the importance and perspective of producing such crucibles for industrial remelting of wastes from γ-TiAl alloys.

Since $Y_2O_3$ is a relatively expensive material in works [12, 13] it is proposed to use multilayer crucibles where the crucible main material is zirconium oxide stabilized by silicon oxide, calcium and magnesium, and the inner layer is covered with a layer of yttrium oxide 200 micronsfor smelting γ-alloys based on titanium. When the level of porosity is less than 14%, $Y_2O_3$ remains inert to the melt containing titanium, and only a small part goes into its composition [13]. The main failure of crucibles made of $Y_2O_3$ according to the results of the research of the authors [14] is the destruction of their surface upon contact with the melt and the entrainment of particles of refractory material.

Currently, the possibility of using calcium zirconate $CaZrO_3$ and $BaZrO_3$ as a crucible material is widely considered, which, as studies have shown, is comparable to $Y_2O_3$ in resistance to titanium melt [15-17]. However, this material is not resistant to thermal shock and the currently proposed solutions for its reinforcement and cementation are not effective [15-17].

The search for alternative refractory materials based on nitrides for melting γ-TiAl alloys did not give positive results. Thus, in [18, 19], the interaction of AlN and BN crucibles with the Ti – 46Al – 8Nb melt was investigated and it was found that, upon their contact with the melt, a TiN layer is formed at the contact boundary, reducing the rate of further reaction. At this the growth rate of nitrogen concentration in the melt is ~4 times higher than the growth rate of oxygen concentration in the case of using ceramics based on $Y_2O_3$ and ~2 times in the case of $Al_2O_3$ and CaO was demonstrated in [19].

Thus, the problem of refractory materials for induction melting of titanium alloys has not been fully resolved, which makes the further search for materials inert with respect to titanium melts relevant.

It is important to have a deeper realizing of the interaction processes of titanium melts with various refractory oxide compounds. In this respect, oxides of rare-earth metals — cerium and lanthanum are of interest, since Ce and La, like Y, have a low solubility in Ti and do not form intermetallic compounds with it. It is also important to re-examine the interaction of MgO, $ZrO_2$, $Y_2O_3$ with a titanium melt. As provided from the above this paper is aimed at the study of the interaction of titanium with some refractory oxides to assess the possibility of making from them crucibles for melting titanium and titanium alloys in vacuum induction furnaces.

**Research methods.** Thermodynamic calculations of the reactions of the oxides recovery of various metals by titanium in the range from 1000 to 2000 ° C were carried out using the Outotec HSC Chemistry 8 program.

The reaction of titanium alloys with various oxides was calculated by Gibbs free energy (Figure 1). As followed by the results of calculations, the highest ΔG values have reactions with Y2O3, and the lowest with ZrO2.

All selected materials have positive values, which in theory mean their use as crucibles. An interesting fact is that ΔG reactions of Ti with Ce2O3 and La2O3 increase those of CaO.

3Ti+La2O3=3TiO+2La (1)
3Ti+Ce2O3=3TiO+2Ce (2)
3Ti+Y2O3=3TiO+2Y (3)
2Ti+ZrO2=2TiO+Zr (4)
Ti+CaO=TiO+Ca (5)
Ti+MgO=TiO+Mg (6)

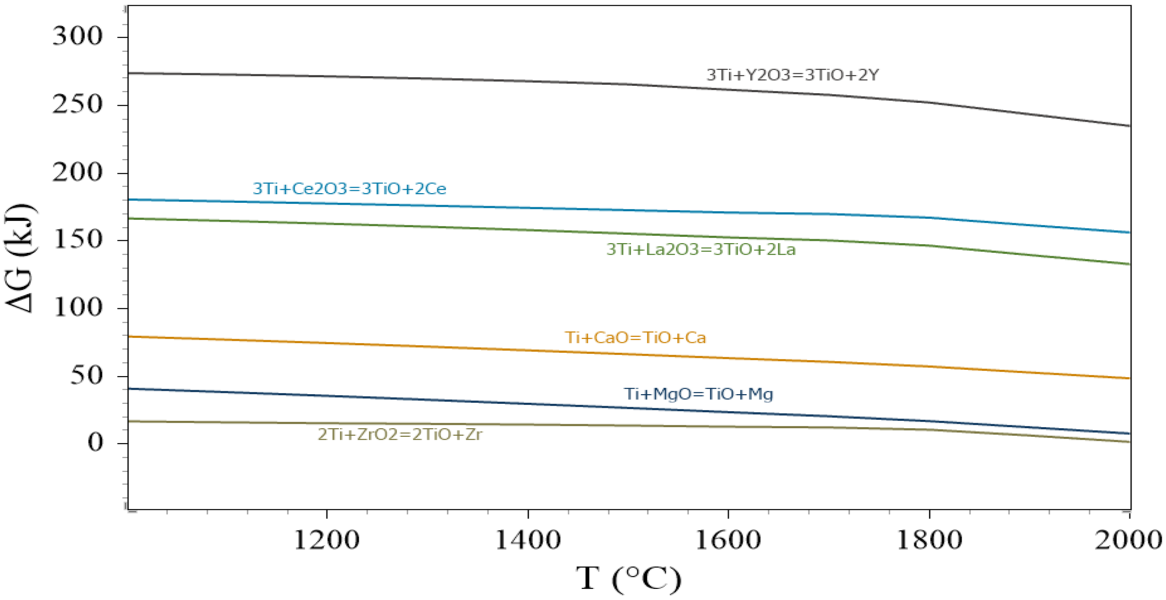
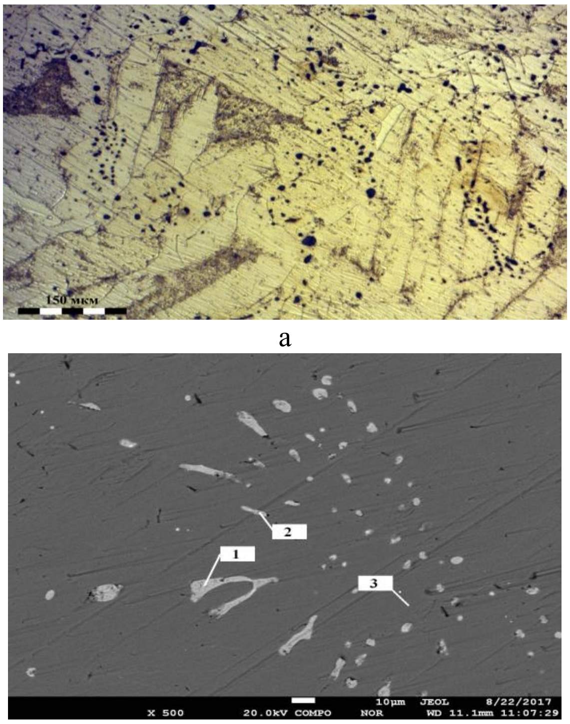


Figure 1 - The dependence of the Gibbs energy recovery reactions ofvarious refractory oxides by titanium

Tests to define interaction the above oxides with the titanium melt were carried out in a vacuum induction melting furnace UIPV-0.001 equipped with an UZG16-10 generator (10 kW) with an operating frequency of 18-20 kHz. To this purpose, the bottom of a cylindrical alundum cruciblea compacted layer of powders of refractory compounds 25-30 mm thick was formed, on the surface of which a cylinder made of VT1-0 titanium ∅40 mm and 40 mm high was installed in the center.Then the space between the crucible walls and the titanium cylinder was filled and sealed with a powder of a refractory compound. After the crucible was installed in the inductor, the furnace chamber was pumped to a level of discharge not less than 133 Pa. An induction furnace was extremely fast heated; for this, the maximum current was set on the inductor to 30A, which allowed the titanium to be converted to a liquid state after 10 minutes from the beginning of the furnace being turned on. The duration of exposure after melting titanium was 60 seconds.

The samples were studied using a NEOPHOT-32 metallographic optical microscope and a JEOL JXA-8230 microprobe analyzer. The phase composition of the samples was determined by X-ray phase analysis using a D8 Advance diffractometer (BRUKER) with Cu-Kα radiation.

**The results and discussion.** The titanium structure testing after the interaction with $La_2O_3$ provided it to be specific to α-alloys and is represented by elongated grains (Figure 2). In addition, the structure reveals numerous allocations of a globular shape, the sizes of which vary from ~2 to 25 μm. Mostly they are observed in the α-phase grains in the form of clusters. Microprobe analysis showed that these emissions are lanthanum, the surface of which in the process of sample preparation is covered with an oxide film.



a

б

a- x250, б- x500

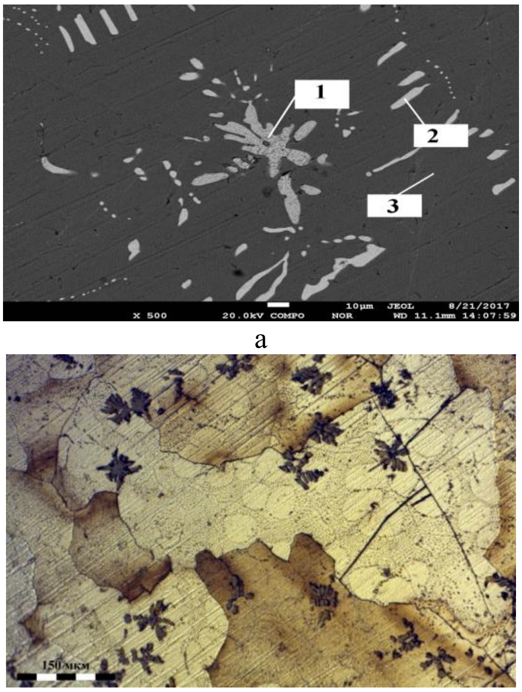
Figure 2 –The VT1-0 titanium microstructure after interaction with the lanthanum oxide

Table 2- Spot chemical analysis of phases as regards Figure 2 (at.%)

| No. | Ti | La | O | C | Cr |
|---|---|---|---|---|---|
| 1 | - | 74,18 | 23,47 | 2,34 | - |
| 2 | 42,43 | 31,13 | 22,29 | 3,22 | 0,93 |
| 3 | 100 | - | - | - | - |

Titanium after interaction with $Ce_2O_3$ is characterized by a polyhedral structure. With in polyhedra, a substructure is observed, which is specific to the cast alloys, crystallized from the melt separation area. In particular, such a substructure includes globular titanium crystals and cerium dendritic precipitates, the space between which is filled with a mechanical mixture of dispersed globular cerium precipitates in a titanium matrix (Figure 3).

After interaction with $Y_2O_3$, titanium has a lamellar structure with a chaotic arrangement of plates, which is typical of α-titanium (Figure 4). Also, not numerous dendritic grains, 20-30 microns in size are found. The microprobe analysis results show that these grains are yttrium oxide. In addition, globular dispersed precipitates of pure yttrium are found along the grain boundaries, while the yttrium does not dissolve in the matrix (Table 4).



а

б

а- x250, б- x500

Figure 3 - VT1-0 titanium microstructure after interaction with cerium oxide

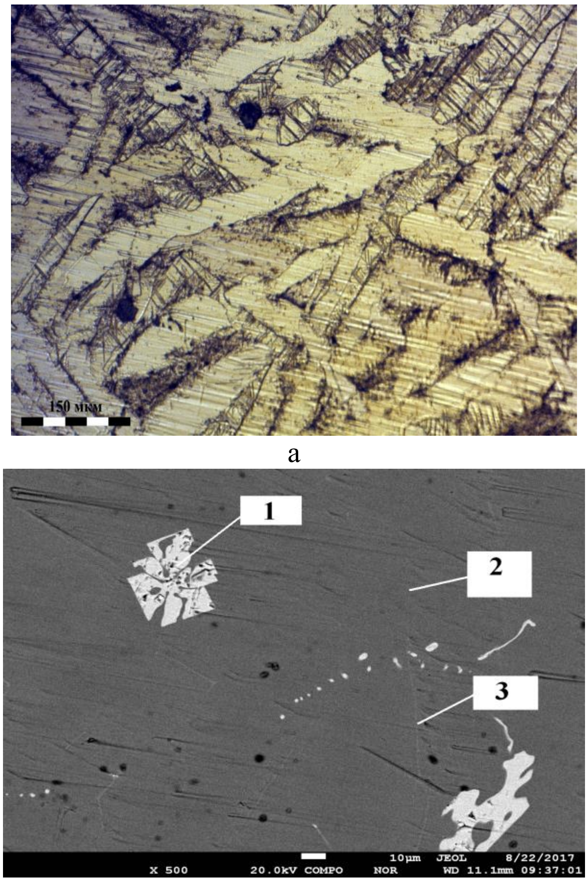
Table 3. Spot chemical analysis of phases as regards Figure 3 (at.%)

| No. | Ti | Ce | O | Al |
|---|---|---|---|---|
| 1 | 1,62 | 78,47 | 18,26 | 1,65 |
| 2 | 27,03 | 50,84 | 22,13 | - |
| 3 | 100 | - | - | - |

Analysis of the sample structure obtained as a result of the titanium melt interaction with zirconium oxide shows that it is formed by elongated lamellar grains predominantly arranged parallel to each other (Figure 5).

Such a structure is typical for high-alloyed α-alloys. Microprobe analysis shows that the alloy contains titanium and a small amount of zirconium, while zirconium is mainly concentrated in the form of a solid solution between the plates.

When titanium melts come in contact with oxides of calcium and magnesium, their intensive boiling and spraying occurs.



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а-x250, б-x500

Figure 4 - VT1-0 titanium microstructure after interaction with yttrium oxide

Table 4. Spot chemical analysis of phases as regards Figure 4 (at.%)

| No. | Ti | Y | O | Fe |
|---|---|---|---|---|
| 1 | 0,94 | 78,7 | 20,37 | - |
| 2 | 100 | - | - | - |
| 3 | 98,25 | 0,5 | - | 1,25 |

This interaction indicates the reduction of calcium and magnesium to the metallic state and their subsequent boiling at ~ 1800 ° C melt temperature, since the boiling point of calcium and magnesium is much lower. (Figure 6)

The results indicate the development of the reaction between the titanium melt and the powders of refractory oxides, which leads to their reduction to the metallic state. Since the rare-earth metals actually do not dissolve in solid titanium, and are not significantly soluble in liquid, they are released as an independent phase during crystallization.When zirconium oxide interacts with titanium, it dissolves in the melt and a solid solution of zirconium and oxygen in titanium is formed during crystallization. More over, due to segregation, zirconium is concentrated in the solid solution along the grain boundaries.

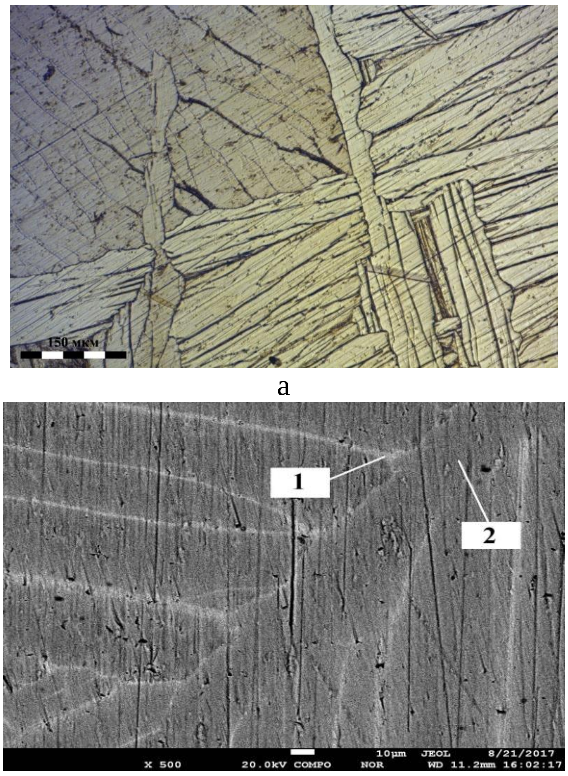

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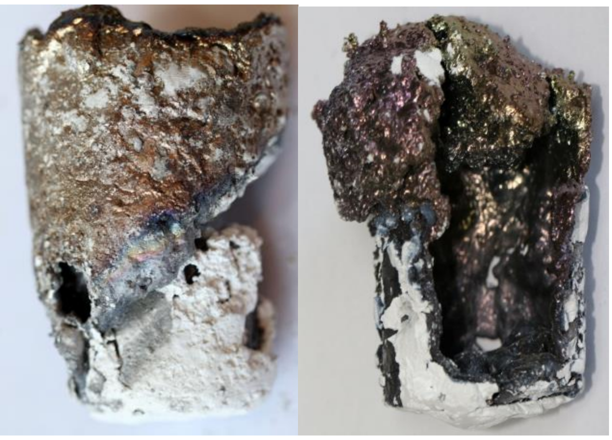
Figure 5 - VT1-0 titanium microstructure after interaction with zirconium oxide

Table 5. Spot chemical analysis of phases as regards Figure 5 (at.%)

| No. | Ti | Zr | O | Fe |
|---|---|---|---|---|
| 1 | 92,28 | 5,62 | - | 2,11 |
| 2 | 97,62 | 2,38 | - | - |



a б

a-CaO, б –MgO

Figure 6 - The titanium melt interaction at a short-term contact (60 s) with oxides of calcium and magnesium

The phase composition of the products formed at the melt / oxide interface was studied to understand the mechanism of titanium melt interaction with the oxides (Table 6).The data obtained show, as a result of the titanium melt and lanthanum oxide powder interaction an intermediate ternary oxide and lower titanium oxide $Ti_2O$ are formed.

The recovery of $CeO_2$ cerium oxide by titanium melt proceeds through the formation of $Ce_2O_3$ lower cerium oxide. When yttrium oxide interacts with the titanium, it is reduced immediately to a metallic state, while titanium is oxidized forming a $Ti_3O$ lower oxide. Upon contact with zirconium oxide, it dissolves in the melt, while oxygen and zirconium diffuse into the melt (Table 6).

Table 6 - Phase structure of the ingot cover after heating

| Combination | Phases,% | | | | |
|---|---|---|---|---|---|
| Ti+$La_2O_3$ | $La_4Ti_9O_{24}$-32,6 | $TiO_{0,48}$-18,3 | $La(OH)_3$-17,9 | $Ti_2O$-16 | Ti-15,2 |
| Ti+$CeO_2$ | $CeO_2$-84,1 | Ce-8,6 | $Ce_2O_3$-4,5 | Ti-2,7 | |
| Ti+$Y_2O_3$ | $Y_2O_3$- 81 | $Ti_3O$-19 | | | |
| Ti+$ZrO_2$ | $ZrO_2$-100 | | | | |

X-ray fluorescence analysis of titanium ingots obtained by smelting oxides in powders showed that when get in contact with $La_2O_3$, $CeO_2$ and $ZrO_2$, a large amount of lanthanum, cerium and zirconium and, consequently, oxygen also passes into the titanium melt (Table 7). The determination of the oxygen content was complicated by the fact that there is always an oxide film on the surface of titanium, and therefore, Table 7 shows the testing and calculated oxygen content. The calculation was based on the content of metals, recovered by titanium from oxides.

Dissolution of oxygen and other elements in the titanium melt when they interact with oxides causes a significant increase in the hardness of the obtained in gots to values more than 2 times higher than the hardness of the original VT1-0 titanium, with the exception of the sample after contact with $Y_2O_3$. Since the cerium and lanthanum cannot significantly affect to reinforce titanium, due to the absence of their mutual solubility in the solid state, the observed non-proportional increase in hardness occurs only due to the dissolution of oxygen, in an amount greater than calculated. Zirconium and oxygen, dissolving in titanium, jointly affect its hardness. Yttrium turning into a small amount in titanium due to sufficiently high strength causes an increase in the hardness of titanium by the type of dispersion hardening, additional hardening occurs due to the dissolution of small amounts of oxygen.

Table 7. Titanium structure after interaction with oxides according to X-ray diffraction analysis data

| Commpositions | Content by X-ray DA, mas.% | | | Calc. content,mas.% | Vickers hardness,HV |
|---|---|---|---|---|---|
| | Ti | O | Me | O | |
| Original titanium | 92,7 | 6,8 | - | 0,0 | 210,5 |
| Ti+$La_2O_3$ | 89,8 | 7,58 | La-2,19 | 0,39 | 475,58 |
| Ti+$CeO_2$ | 87,65 | 9,26 | Ce-2,29 | 0,39 | 556,85 |
| Ti+$Y_2O_3$ | 91,1 | 7,26 | Y-0,92 | 0,25 | 251,69 |
| Ti+$ZrO_2$ | 81,86 | 6,5 | Zr - 2,34 | 0,82 | 446,01 |

Pursuant to data obtained, the best possible refractory material for the manufacture of crucibles for melting titanium alloys is concluded to be yttrium oxide. Since the interaction between the titanium melt and yttrium oxide leads to the dissolution of the latter, the crucibles of the steady-state zirconium oxide coated with a layer of yttrium oxide on the inner surface are not of a high-potential because they will require constant reduction.We consider the most appropriate the production of crucibles entirely of yttrium oxide. Given the high cost of this material, failed crucibles should be recycled. A method was developed for the manufacture of yttrium oxide crucibles by bulk pressing (Figure 7).

Figure 7 - Yttrium oxide crucible of ∅40 mm

**Findings.** As a result of the titanium melt interaction with the oxides of the rare-earth elements, the oxides of lanthanum, cerium and yttrium are revealed to be recovered to the metallic state, forming the separate phases in the melt composition. Calcium and magnesium oxides are similarre covered to the metallic state, but since the boiling point of calcium and magnesium is much lower than the melting point of the titanium, this leads to boiling and splashing of the melt. Zirconium oxide is dissolved in the melt of titanium, there by contaminating it with zirconium and oxygen.

The testing shows that for melting titanium in a vacuum induction furnace as a material for crucibles, the use of yttrium oxide is more appropriate. $Y_2O_3$, which exhibits sufficient thermochemical stability during induction melting of titanium with out significant interaction with the melt.

In this case, there is no significant contamination of the melt with yttrium and oxygen, which leads to an increase in the hardness of titanium by ~20%. Yttrium oxide crucibles were obtained.

The use of such crucibles in the manufacture of personally designed implants melted out by casting method according to investment patterns will further simplify the technology and make it more available [20].

*Completed as part of the project No. AR05130722 "Improving the technology of implants by casting titanium alloys with subsequent application of biocomposites to their surface" of grant funding of MES RK for 2018-2020.*

*The equipment of the National Scientific Laboratory of general use was used in the priority direction "The hydrocarbon and mining and metallurgical sectors technologies and related service industries." The authors are grateful to the leading research associate - B.M.Sukurov.*

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***Cite this article as:*** Panichkin A.V., Imanbayeva A.B., Imbarova A.T. Titanium melt interaction with the refractory oxides of some metals. // Kompleksnoe Ispol'zovanie Mineral'nogo Syr'a. (Complex Use of Mineral Resources). –2019. –No.2. - p. 51-60 https://doi.org/10.31643/2019/6445.16