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ПЛОТНОСТЬ ЖАРОПРОЧНЫХ ТИТАНОВЫХ СПЛАВОВ, ЛЕГИРОВАННЫХ ЛАНТАНОМ И РЕНИЕМ

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Аннотация. С использованием компьютерной программы Thermo-Calc теоретически рассчитан фазовый и поэлементный состав жаропрочных титановых сплавов Ti-5Al-5Mo-5V-3Cr, Ti-5Al-5Mo-5V-3La и Ti-5Al-5Mo-5V-3Re в широком температурном интервале и построены диаграммы их состояния. Отмечено, что в сплавах Ti-5Al-5Mo-5V-3Cr наблюдается четырехфазное превращение, замена в указанном сплаве хрома на лантан приводит к резкому сокращению образующихся фаз, а добавление к сплаву рения повышает температуру начала образования двухфазной области до 850 ^{0}C. Методами удельных объемов рассчитаны плотности этих сплавов при разных температурах. Отмечено, что значение плотностей β-фазы, обогащённой молибденом и хромом, заметно выше плотности α-фазы, содержащей повышенное количество алюминия, и эта разница растет с уменьшением температуры, в отличие от сплавов Ti-5Al-5Mo-5V-3Re, где рений, концентрируясь в основном в α-фазе, уменьшает это различие до 1 %. Большие значения плотностей β_2- и λ-фаз в сплавах Ti-5Al-5Mo-5V-3Cr обусловлены высоким содержанием в них молибдена, ванадия и хрома.

Ключевые слова: жаропрочные титановые сплавы; лантан; рений; удельные объемы; плотность; фазовое строение.

ЛАНТАН ЖАНА РЕНИЙ КОШУЛГАН ЫСЫККА ЧЫДАМДУУ ТИТАН ЭРИТМЕЛЕРИНИН ТЫГЫЗДЫГЫ

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Аннотация. Макалада Thermo-Calc компьютердик программасын колдонуу менен ысыкка чыдамдуу титан эритмелери Ti-5Al-5Mo-5V-3Cr, Ti-5Al-5Mo-5V-3La жана Ti-5Al-5Mo-5V-3Re фазалык жана элементтер боюнча курамы теориялык жактан кең температуралык диапазондо эсептелген жана алардын абалынын диаграммалары түзүлгөн. Ti-5Al-5Mo-5V-3Cr эритмелеринде төрт фазалуу трансформация байкалып, көрсөтүлгөн эритмеде хромдун ордун лантан менен алмаштыруу пайда болгон фазалардын кескин кыскарышына алып келери белгиленген, ал эми эритмеге ренийди кошуу эки фазалуу аймактын башталышынын температурасын 850 ^{0}Cге чейин жогорулатат. Ар кандай температураларда салыштырма көлөмдөрү ыкмалары менен ушул эритмелердин тыгыздыгы эсептелген. Молибден жана хром менен байытылган β-фазасынын тыгыздыгынын мааниси алюминийдин көбөйгөн өлчөмүн камтыган α-фазасынын тыгыздыгынан байкаларлык жогору экендиги белгиленет, жана бул айырмачылык температуранын төмөндөшү менен көбөйөт, Ti-5Al-5Mo-5V-3Re эритмелеринен айырмаланып, мында негизинен α-фазада топтолгон рений бул айырманы 1%ке чейин азайтат. Ti-5Al-5Mo-5V-3Cr эритмелериндеги β_2- жана λ-фазалардын тыгыздыгынын чоң маанилери алардагы молибдендин, ванадийдин жана хромдун көп болушу менен шартталган.

Түйүндүү сөздөр: ысыкка чыдамдуу титан эритмелери; лантан; рений; салыштырма көлөмдөр; тыгыздык; фазалык түзүлүш.

DENSITY OF HEAT-RESISTANT TITANIUM ALLOYS DOPED WITH LANTHANUM AND RHENIUM

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Abstract. The phase and elemental composition of Ti-5Al-5Mo-5V-3Cr, Ti-5Al-5Mo-5V-3La and Ti-5Al-5Mo-5V-3Re heat resistant titanium alloys in a wide temperature interval and their state diagrams have been theoretically calculated using

the Thermo-Calc computer program. It is noted that in alloys Ti-5Al-5Mo-5V-3Cr, four-phase transformation is observed, replacement in the specified alloy of chromium by lanthanum leads to a sharp reduction of the phases formed, and the addition to the alloy of rhenium increases the temperature of the beginning of the two-phase region formation to 850 °C. The densities of these alloys at different temperatures are calculated using specific volume methods. It is noted that the value of the densities of the β-phase enriched with molybdenum and chromium is noticeably higher than the density of the α-phase containing an increased amount of aluminum, and this difference increases with decreasing temperature, unlike Ti-5Al-5Mo-5V-3Re alloys, where rhenium concentrating mainly in the α-phase reduces this difference to 1%. The high densities of the β_2- and λ - phases in Ti-5Al-5Mo-5V-3Cr alloys are due to the high content of molybdenum, vanadium and chromium in them.

Keywords: heat-resistant titanium alloys; lanthanum; rhenium; specific volumes; density; phase structure.

The main advantages of titanium alloys are their high specific strength and corrosion resistance [1, 2]. To increase the strength, heat resistance and technological plasticity of titanium alloys, aluminum is primarily used as alloying elements. It strengthens the α-phase, being an α-stabilizer and reduces the density of alloys. Along with α-stabilizers, elements that stabilize the β-phase are used [3–6]. Depending on the content of these elements, it is possible to obtain alloys with a β and (α+β) structure. The advantage of two-phase, (α+β)-alloys is their ability to harden during heat treatment, which makes it possible to obtain a significant gain in strength and heat resistance [7–9].

In most cases, β-stabilizers are elements with a large atomic weight, such as molybdenum, chromium and others. One of the new aspects in this direction can be considered alloys with the addition of rare earth metals, as well as rhenium, which change the phase structure of alloys and allow significantly raising the operating temperature of products [10–13]. Such doping significantly increases the density of these alloys, resulting in problems associated with an increase in the mass of products. Therefore, knowledge of their physico-chemical characteristics and especially in a wide temperature range is a very urgent task.

The aim of the work is to conduct a qualitative and quantitative analysis of the phase composition of heat-resistant titanium alloys of the Ti-5Al-5Mo-5V-3Cr type, as well as alloys in which chromium is replaced by lanthanum or rhenium, by computer modeling methods and calculation of their density taking into account the fractions of each phase, the crystal structure of the main lattice, temperature and temperature coefficient of expansion of all the elements that constituting the alloy.

To construct phase diagrams, a specialized Thermo-Calc computer program (TCW5 version) with the TTTIAL1 database was used: Thermotech TiAl-based Alloys Database [14, 15], which allows predicting the behavior of titanium alloys depending on composition and temperature in areas where experimental data are not available.

As the earlier studies have shown the model calculations of the density of titanium alloys Ti-5Al-5Mo-5V-3Cr and Ti-5Al-5Mo-5V-1Re made by the methods of specific volumes have a good agreement with the experimental results [16], which was used in this work.

The essence of the method is that the total volume of the alloy V_{al} consists of the sum of the volumes of the components that make up the alloy.

$$V_{al} = \sum_i V_i ,$$

where $V_i = \frac{m_i}{\rho_i}$ – is the volume occupied by Ti, Al, Mo, V, Cr, and Re atoms, and m_i and ρ_i are their mass and density, respectively.

With this in mind, the calculated dependence of the alloy density will have the following form:

$$\frac{M_{al}}{\rho} = \sum_i \frac{m_i}{\rho_i} .$$

Since $m_i = \eta_i * M_{al}$, the density value, after some simple transformations of the above expression, can be written in the following form:

$$\rho = \frac{1}{\sum_i \frac{\eta_i}{\rho_i}},$$

where *i* – is Ti, Al, Mo, V, Cr, La or Re, and η and ρ are their mass fraction in the alloy and density, respectively.

In the expanded form, this expression takes the following form:

$$\rho_i = 1 / (\frac{\eta_{Ti}}{\rho_{Ti}} + \frac{\eta_{Al}}{\rho_{Al}} + \frac{\eta_{Mo}}{\rho_{Mo}} + \frac{\eta_V}{\rho_V} + \frac{\eta_{Cr}}{\rho_{Cr}} + \frac{\eta_{\mathrm{Re}}}{\rho_{\mathrm{Re}}}). \quad (1)$$

The obtained calculated values are given for the room temperature of 20–25 °C. Since the heat-resistant alloys under consideration are expected to operate at elevated temperatures, it is therefore of some interest to consider the change in the density characteristics in a wide temperature range.

With increasing temperature, the density of all metals and alloys in the solid state decreases. Strictly speaking, the graph of the $\rho = f(t)$ function is not a straight line for a solid state, however, experimental data with small errors are usually well approximated by straight-line dependencies even in a wide temperature range. Therefore, the reference books usually provide an average linear dependence of

density on temperature [17, 18]:

$$\rho_t = \rho_{20}(1 - b(t - 20)),$$

where ρ_{20}, ρ_t – is the density of the metal at 20 °C and the temperature under consideration; *b* – is the coefficient that can be taken for technical calculations $b = 3k$, *k* – is the temperature coefficient of linear expansion, t – is the temperature.

To calculate the density of alloys at different temperatures, it is necessary to substitute the obtained values of individual metal densities at the temperatures under consideration into formula 1.

In the case of multiphase alloys, we first calculate the densities of each phase taking into account the chemical composition of the elements according to formula (1), and then calculate the density of the alloy according to the following formula:

$$\rho_i = 1 / (\frac{\eta_\alpha}{\rho_\alpha} + \frac{\eta_\beta}{\rho_\beta} + \frac{\eta_{(\alpha,\beta)}}{\rho_{\alpha,\beta}}), \quad (2)$$

where η_α, η_β, $\eta_{(\alpha,\beta)}$ – content in the alloy *α* and *β*-phase, or some sort of intermediate *(α, β)* phase component, andρ_α, ρ_β, $\rho_{(\alpha,\beta)}$, – their density, respectively.

Using formula (2) will reduce the error in determining the density of a multiphase alloy having differences in phase densities.

Titanium, like iron, is a polymorphic metal and has a phase transformation at a temperature of 882 °C. Below this temperature, a hexagonal close-packed(HCP) crystal lattice of α – titanium is stable, and above it is a body-centered cubic (BCC) lattice of β – titanium [18].

The calculations of phase diagrams of multicomponent alloys of the Ti-5Al-5Mo-5V-3Cr system using temperature and concentration dependences of the component distribution coefficients are carried out, and their phase states are considered when replacing chromium with lanthanum and rhenium.

The calculated theoretical values of fractions and phase compositions of Ti-5Al-5Mo-5V-3Cr alloys at characteristic temperatures are given in table 1.

The calculation in these ranges showed the presence of the following phases: α – solid solution based on the HCP lattice (α-Ti); β – solid solution based on the BCC lattice (β-Ti); β2 – solid solution with an increased content of β-stabilizers; λ – phase based on the compound TiX_2 (Laves phase). Large amounts of phases and phase transitions are also observed in some other titanium alloys [19].

Table 1 – Quantitative parameters of the phase composition of Ti-5Al-5Mo-5V-3Cr alloy at characteristic temperatures

T, ^{0}C	Phase	QM, % (mass.)	Element content, % (mass)				
			Ti	Al	Mo	V	Cr
1000	β	100	81,9	5,12	4,89	5,14	2,95
800	β	100	81,9	5,12	4,89	5,14	2,95
700	β	98,43	81,74	5,1	4,96	5,21	2,99
	α	1,57	90,9	7,59	0,3	0,95	0,26
600	β	61,06	76,01	4,14	7,75	7,59	4,5
	α	38,93	91,65	6,83	0,31	0,93	0,27
500	β	40,68	68,43	3,29	10,78	10,72	6,88
	α	59,32	92,22	6,55	0,27	0,72	0,26
400	β	22,38	68,62	1,21	12,86	13,27	4,04
	β_2	1,44	25,73	0,24	26,85	31,39	15,69
	α	73,5	89,24	6,53	1,85	1,61	0,83
	λ	2,66	10,62	1,24	19,22	23,27	45,85

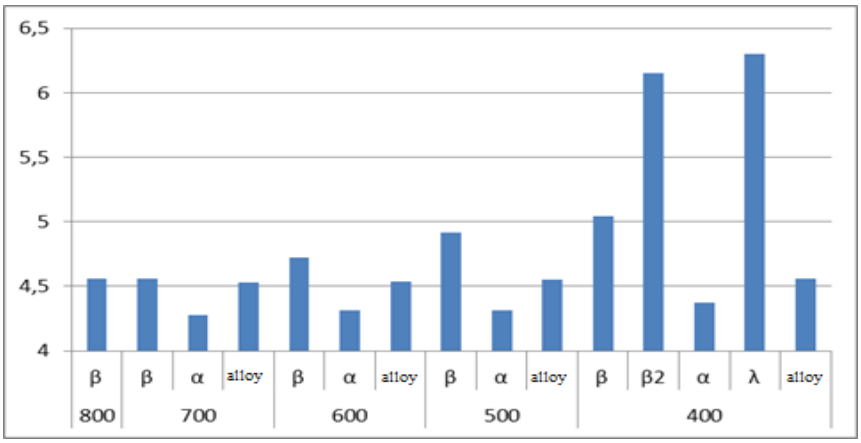

Figure 1 – Calculated values of phase densities and alloys of Ti-5Al-5Mo-5V-3Cr systems at different temperatures

The calculated values of the alloy densities and various phases of the Ti-5Al-5 Mo5 V3Cr system performed by the specific volume method at characteristic temperatures are shown in Figure 1.

It is expected that the *α* phase containing an increased amount of aluminum is noticeably lighter than the *β* phase enriched with molybdenum and chromium in the entire temperature range. The difference in the densities of the *α* and *β* phases of the same alloys is approximately 6.5–15 % and increases with decreasing temperature. The abnormally large values of the densities of the β_2- and λ-phases in the alloys under consideration are due to their low content in the alloy of 1.5–2.5 %, which allowed them to diffuse a relatively large amount of molybdenum, vanadium and chromium, and the λ-phase (Laves phase) is traditionally considered the densest phase of alloys, in our case it is almost half it consists of chromium.

Doping of titanium alloys with rare earth metals leads to significant improvements in their properties [10, 12]. Table 2 shows the calculated values of the fractions and phase compositions of Ti-5Al-5 Mo-5V-3La alloys depending on the composition and temperature.

Table 2 – Calculated values of quantitative fractions and phase compositions of Ti-5Al-5 Mo-5V-3La alloys at characteristic temperatures

T, ^{0}C	Phase	Q_M, % (mass.)	Element content, % (mass)				
			Ti	Al	Mo	V	La
1000	β	100,0	81,67	5,06	4,97	5,15	3,15
800	β	100,0	81,67	5,06	4,97	5,15	3,15
780	β	96,42	81,79	4,63	5,06	5,25	3,26
	α	3,57	86,16	7,07	2,47	2,39	1,76
700	β	59,78	78,92	3,23	7,06	6,99	3,93
	α	40,22	86,52	7,78	1,86	2,42	1,49
600	β	31,95	76,12	2,13	9,7	8,06	4,2
	α	68,04	84,6	6,5	2,75	3,7	2,42
400	β	12,07	49,65	1,42	15,25	21,61	11,99
	α	87,93	86,37	5,58	3,37	2,9	1,75

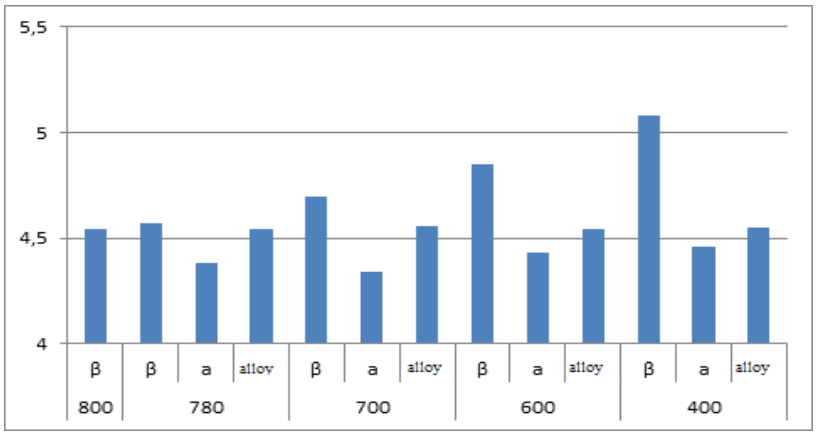

Figure 2 – Calculated values of alloy densities and various phases of Ti-5Al-5Mo-5V-3La systems made by the method of specific volumes at different temperatures

The introduction of lanthanum into the heat-resistant alloy of the Ti-5Al-5Mo-5V-3Cr system leads to a significant change in the phase composition. In the alloy under consideration, a two-phase transformation takes place, instead of three-phase and four-phase for the same systems without lanthanum. No new intermetallides were found in the considered five-dimensional system. Similar reductions in the number of phases were observed for alloys with tantalum and niobium [20], however, in our case, changes occur at lower concentrations of lanthanum.

The calculated values of the densities of alloys and various phases of the Ti-5Al-5 Mo-5V-3La system performed by the method of specific volumes at different temperatures are shown in figure 2.

Here, as in the previous alloy, the value of the β–phase densities is noticeably higher than the α–phase density and this difference increases with a decrease in temperature from 4 % at 780 °C to 20 % at 400 °C. The higher differences in phase densities in these alloys are due to the increased content of lanthanum in the β-phase, which has a relatively high density.

Table 3 – Calculated values of fractions and phase compositions of Ti-5Al-5 Mo-5V-3Re alloys depending on temperature

T, ºC	Phase	Q, % (mass)	Element content, % (mass)				
			Ti	Al	Mo	V	Re
1000	β	100,0	81,68	4,98	5,12	5,08	3,14
900	β	100,0	81,68	4,98	5,12	5,08	3,14
850	β	87,46	81,24	4,93	5,56	5,56	2,71
	α	12,54	84,56	5,32	2,08	2,03	6,01
800	β	49,78	80,69	4,68	6,45	6,99	1,19
	α	50,22	82,65	5,28	3,82	3,24	5,01
700	β	13,58	77,4	4,32	7,99	9,54	0,75
	α	86,41	82,33	5,09	4,68	4,39	3,51
600	α	100,0	81,68	4,98	5,12	5,08	3,14
400	α	100,0	81,68	4,98	5,12	5,08	3,14

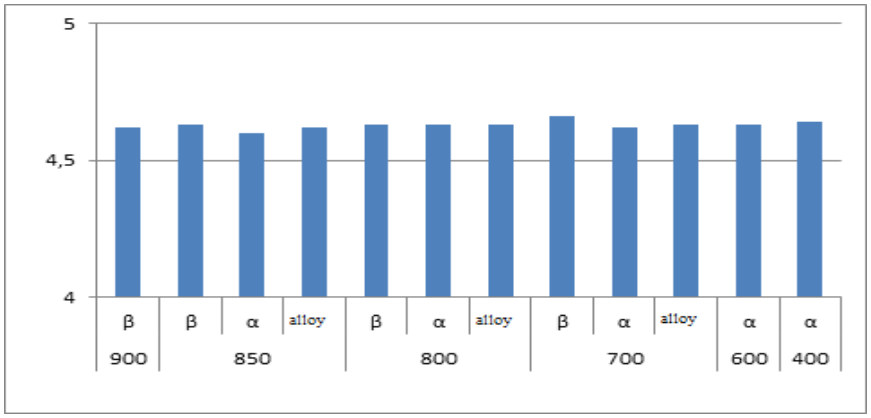

Figure 3 – Calculated values of phase densities and Ti-5Al-5Mo-5V-3Re alloys at different temperatures

To increase the plasticity of these alloys of the Ti-5Al-5Mo-5V-3Cr system, it is necessary to weaken the covalent bond between Ti and Al by alloying elements with a large number of valence electrons. A new aspect in this direction can be considered alloys with the addition of rhenium, which has a large number of collectivized electrons that change the phase structure of alloys and allow to significantly raise the operating temperature of products [13]. Table 3 consider the effect of rhenium on the properties of the alloy when it replaces chromium.

It can be seen from this table that the number of phases in the alloys under consideration has sharply decreased. This confirms the assumption that a large number of free electrons on rhenium atoms can significantly change the structure of the alloy, converting them into a structure with a lower phase content and even into a single-phase region already at 600 °C and below. The two-phase $\alpha + \beta$ region is formed already at 850 °C, which is significantly higher than that of Ti-5Al-5Mo-5V-3Cr alloys. Rhenium, unlike molybdenum, vanadium or chromium, is concentrated in the α -region, and this difference can reach five or more times. The calculated values of the alloy densities and various phases of the Ti-5Al-5 Mo-5V-3Re system at different temperatures are shown in Figure 3.

The difference in the densities of the α- and β-phases in Ti-5Al-5Mo-5V-3Re alloys is relatively small. This is due to the fact that rhenium is concentrated mainly in the α-phase and, due to the large density value, compensates for the total effect of molybdenum, chromium and vanadium, which are mainly in the β phase. At these concentrations of rhenium, it, being mainly in the α-phase, practically equalizes the densities of the α and β phases, bringing their differences to only 1%.

Density calculations of these alloys at different temperatures were carried out using specific volume methods.

It is shown that the density of the β-phase enriched with molybdenum and chromium is noticeably higher than the density of the α-phase containing an increased amount of aluminum, and this difference increases with decreasing temperature. For Ti-5Al-5Mo-5V-3Re alloys, the difference in the densities of the α and β phases is less than 1 %. This is explained by the fact that rhenium, concentrating mainly in the α-phase, compensates for the total effect of the remaining heavy elements in the β-phase.

The abnormally high densities of β_2 and λ-phases in Ti-5Al-5Mo-5V-3Cr alloys are due to the high content of molybdenum, vanadium and chromium in them.

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