

CRYSTAL-LATTICE DEFECTS

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Features of Multicomponent Diffusion of Alloying Elements in Titanium Metastable β -Alloys at Continuous Rapid Heating

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Features of a competitive diffusion of individual alloying elements in high-temperature β -phase of titanium alloys of the metastable β -class under non-equilibrium conditions of continuous rapid heating are investigated using a few commercial alloys. As established, the rate of diffusion redistribution of alloying elements in β -phase depends not so much on their total concentration (expressed by the integral content of β -stabilizing elements in molybdenum equivalent C_0^{Mo}), but on the rates of diffusion of individual elements. Iron concentration is homogenized thought high-temperature β -phase at first, chromium concentration equalizes somewhat slower, and the concentration of β -stabilizers of isomorphous type (like vanadium or molybdenum) smoothes most slowly. This leads to the fact that, similarly to carbon steels, in the titanium alloys of metastable β -class under non-equilibrium conditions of rapid heating in the beginning the para- (partial) and then the ortho- (complete) equilibrium distributions are formed for β -stabilizers of eutectoid and isomorphous type, respectively.

Key words: titanium alloys, metastable β -phase, phase transformations, alloying elements, diffusion, chemical inhomogeneity.

Особливості конкурентної дифузії окремих леґувальних елементів у високотемпературній β -фазі у титанових стопах метастабільного β -класу у нерівноважних умовах неперервного швидкісного нагрівання досліджено з використанням декількох промислових стопів. Встановлено, що швидкість дифузійного перерозподілу леґувальних елементів у β -фазі зале-

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жить не стільки від їхньої загальної концентрації (яка може бути виражена інтегральним вмістом β -стабілізованих елементів через молібденовий еквівалент C_0^{Mo}), скільки від швидкості дифузії окремих легувальних елементів. Найшвидше при нагріванні до температур однофазної β -області вирівнюється розподіл у β -фазі Феруму, концентрація Хрому вирівнюється трохи повільніше, а концентрація β -стабілізаторів ізоморфного типу таких як Ванадій або Молібден згладжується найповільніше. Це приводить до того, що подібно вуглецевій сталі у титанових стопах метастабільного β -класу у нерівноважних умовах швидкого нагрівання має місце явище встановлення спочатку пара- (часткового) і тільки потім орто- (повного) рівноважного розподілу у високотемпературній β -фазі β -стабілізаторів евтектоїдного та ізоморфного типу відповідно.

Ключові слова: титанові стопи, метастабільна β -фаза, фазові перетворення, легувальні елементи, дифузія, хімічна неоднорідність.

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1. INTRODUCTION

Titanium alloys are important structural materials due to unique set of properties uniting high specific and fatigue strength, impact toughness and corrosion resistance with some others special service properties [1, 2]. The balance of properties is set by the entire history of manufacturing, in which controlled by diffusion phase out and structural transformations play an important role.

The partitioning of alloying elements between phases in titanium alloys at equilibrium conditions has been studied in detail (*e.g.* [3–5] among recent works). At the same time, element partitioning under non-equilibrium conditions has been much less studied.

As it is shown in the previous investigations, in the titanium alloys of the martensite type (*i.e.* those in which martensite phases form upon quenching [1, 2, 6]) in non-equilibrium conditions the beta stabilizers (elements which stabilize the β -phase) act ‘cooperatively’, and their collective behaviour can be described by means of molybdenum equivalent C_0^{Mo} [7]. This coefficient allows taking into account the contribution of various alloying elements in β -phase stabilization upon quenching from the single-phase β -field through known ratio between molybdenum and other elements [7, 8]. Most commonly the molybdenum equivalent is calculated as¹

¹ Unlike other authors, we do not take into account the presence of aluminium (with a minus sign), since in such a case the total amount of β -stabilizers should drop below a critical level (for example, in alloys like VT22 or Ti–5–5–5–3 essentially lower than 11.5% Mo), which would lead to non-fixation of the metastable β -phase upon quenching from temperatures of single-phase β -field that does not actually happen.

$$C_0^{\text{Mo}} = 1.0(\% \text{ wt.})\text{Mo} + 0.67\% \text{V} + 0.44\% \text{W} + 0.28\% \text{Nb} + \quad (1) \\ + 0.22\% \text{Ta} + 2.9\% \text{Fe} + 1.6\% \text{Cr}.$$

This generalizing approach to the impact of all β -stabilizers allowed to describe the influence of alloying elements on various properties and processes, such as the dependence of martensite start temperature M_s on chemical composition [7], formation of chemical inhomogeneity in the high-temperature β -phase upon non-equilibrium rapid heating [8], and even the effect of total content of β -stabilizers on the mechanical properties which can be achieved by heat treatment [9].

As shown in [10], Rapid Heat Treatment (RHT) allows to achieve the highest strength levels in high-alloyed alloys of the martensite type VT23 and VT16 ($C_0^{\text{Mo}} \cong 8\text{--}9.5\%$), whereas after standard furnace heat treatment maximum strength is obtained in alloys which have $C_0^{\text{Mo}} \cong \cong 11.5\text{--}13\%$, *i.e.* on the border between martensite and metastable β -alloys (in the latter ones metastable β -phase is fixed upon quenching). However, the previous investigations showed that in these alloys, as well as in alloys with higher content of β -stabilizers, diffusion processes during heat treatment and their consequences (thermokinetic conditions of recrystallization, decomposition of metastable phases, β -grain growth, mechanical properties, *etc.*) cannot be associated with general characteristics of alloying, including the molybdenum equivalent [9–12]. Preliminary calculations using DICTRA software package also showed that at similar total concentrations of β -stabilizers (over 11.5% wt. in molybdenum equivalent) various alloying elements in different ways affect the rate of diffusion of other elements [13], though it is practically impossible to determine any general dependence. Based on the above, the purpose of this study is to determine the physical role of interference of various alloying elements during their diffusion upon non equilibrium heating conditions in metastable β alloys with $C_0^{\text{Mo}} \geq 11.5\%$.

2. MATERIALS AND METHODS

The following three alloys are selected as the research objects:

1. TIMETAL-LCB (Ti–1.5% wt. Al–4.5% Fe–6.8% Mo; $C_0^{\text{Mo}} = 19.9\%$, $T_{\alpha+\beta \rightarrow \beta} = 790^\circ\text{C}$).
2. An actual analogue of the above alloy in which molybdenum is replaced by a similar amount of chromium: Ti–3.0(% wt.)Al–4.5Fe–7.2Cr ($C_0^{\text{Mo}} = 24.6\%$, $T_{\alpha+\beta \rightarrow \beta} = 815^\circ\text{C}$).
3. Ti–15–3–3–3 alloy (Ti–15(% wt.)V–3Al–3Cr–3Sn; $C_0^{\text{Mo}} = 15.4\%$, $T_{\alpha+\beta \rightarrow \beta} = 760^\circ\text{C}$).

First of all, the alloys are investigated in an annealed two-phase $\alpha + \beta$ condition. Then the alloys are rapidly heated by electric current

at a rate of 5°C/s to various temperatures of the single-phase β -field.

The foils for TEM studies are prepared by double-jet electropolishing in 60% methanol, 35% butanol, 5% perchloric acid electrolyte at -40°C . Analytical TEM-methods using a JEM-2000FXII microscope (JEOL) equipped with an EDS Link microanalyzer and STEM attachment are applied. The accelerating voltage is 200 kV. The spot size (diameter of incident electron beam) is 3 nm. Automatic drift correction is used to make sure electron beam did not shift during the measurements.

The diffusion processes of α -(Al) and β -stabilizers (isomorphous V, Mo, Nb, and eutectoid Cr, Fe, Mn) under non-equilibrium conditions of rapid heating depending on the alloying system of industrial titanium alloys of metastable β -class are studied.

3. RESULTS AND DISCUSSION

3.1. TIMETAL-LCB Alloy

The microstructure of the alloy in the initial, *i.e.* annealed equilibrium two-phase $\alpha + \beta$ state is shown in Fig. 1. As seen, it is characterized by relatively fine β -phase grains with α -phase particles (0.5–1 μm in size) of various morphology inside.

The distribution of alloying elements between the phases is obtained (Fig. 2, *a*), and the same data are shown in terms of molybdenum equivalent (Fig. 2, *b*). The content of iron and molybdenum in the α -phase is minimal (less than 0.5% wt.), whereas in the β -phase it reaches 5.8 and 9%, respectively. As regards the integral content of β -phase stabilizing elements, it corresponds to the molybdenum equivalent of 1 and 25% wt. in the α -phase and β -phase, respectively. It is also worth mentioning the relatively narrow transition zone across the interfacial

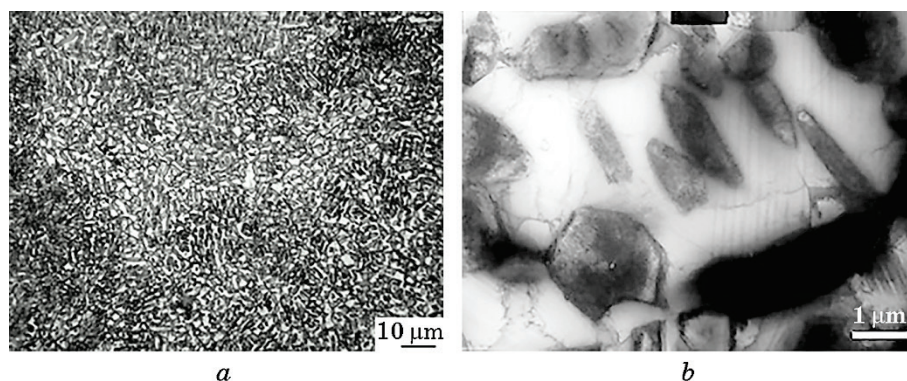


Fig. 1. Initial microstructure of TIMETAL-LCB alloy: *a*—OM, *b*—TEM.

α/β boundary (not wider than 30–50 nm), which indicates the high accuracy of the performed measurements.

The evolution of microstructure of the alloy upon continuous rapid heating at a rate of 5°C/s to temperatures of 800°C and 830°C with subsequent quenching in water (to fix current structural and phase state), as well as the distribution of alloying elements after heating, are shown in Fig. 3. It should be noted that after heating to 800°C the alloy is still in two-phase $\alpha + \beta$ state with an increased amount of β -phase compared to the initial condition (Figs. 3, *a* and *b*). The content of iron in the β -phase is by about 1% wt. lower than in the initial state, whereas the molybdenum concentration significantly drops nearby the interfacial $\alpha + \beta$ boundary and is low in the α -phase (Fig. 3, *c*).

However, this depletion of the boundary zones becomes less apparent when the concentration of the β -stabilizing elements is replotted in terms of molybdenum equivalent (Fig. 3, *d*). Heating to 830°C corresponds to the transformation of the entire volume of the alloy into a single-phase β -state (Fig. 3, *f*): for this alloy with the given microstructure and applied heating rate the temperature of polymorphic $\alpha + \beta_0 \rightarrow \beta$ equals to 815–820°C, although on OM-images polishing and chemical etching revealed the former grain boundaries (Fig. 3, *e*).

In our opinion, this effect on OM-samples can be explained by the residual inhomogeneity in the distribution of alloying elements (Fig. 3, *h*). The distributions of iron and molybdenum in the metastable β -phase are different: the iron distributed almost uniformly, its concentration corresponds to the average content of this element in the alloy (more than 4%), whereas Mo-content changes from 4.8% in the centre of the former α -phase particles up to 7% in the volume of pri-

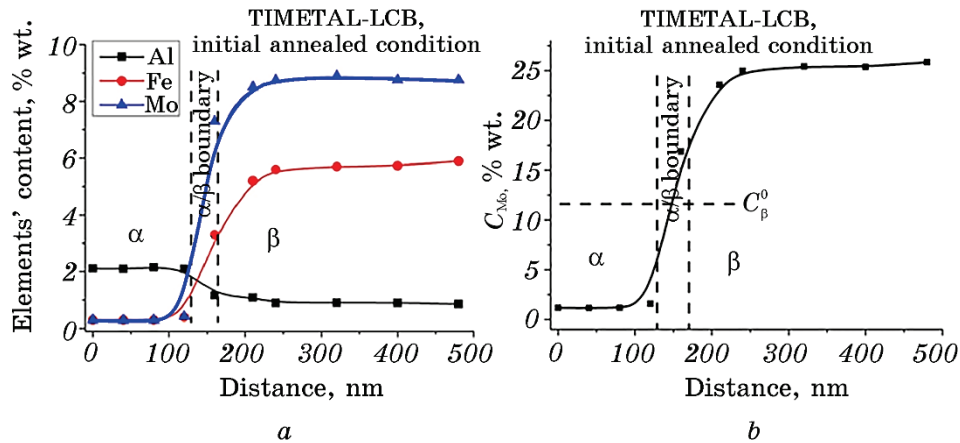


Fig. 2. Distribution of individual alloying elements (*a*) and β -stabilizers in terms of molybdenum equivalent (*b*) between the α - and β -phases in TIMETAL-LCB alloy in initial condition.

mary β -phase grains.

After recalculation of the content of β -stabilizers to molybdenum equivalent this inhomogeneity somewhat smoothies due to more intense redistribution of iron in the metastable β -phase (Fig. 3, *g*), and the concentration of β -stabilizers exceeds the critical value $C_{\beta}^0 = 11.5\%$ Mo in the entire volume [1]. One can determine the approximate locations of the former α/β interphase boundaries by the changes in molybdenum concentration.

These differences in the diffusion of iron and molybdenum, which are not observed in similar experiments on VT23 alloy with subcritical composition (with $C_{\text{Mo}} = 7\text{--}9\%$ wt. Mo), can be explained by the significantly different rates of diffusion of these elements in the α - and β -titanium: the rate of diffusion of iron is approximately three orders of magnitude higher than that of molybdenum [14]. Due to this, the con-

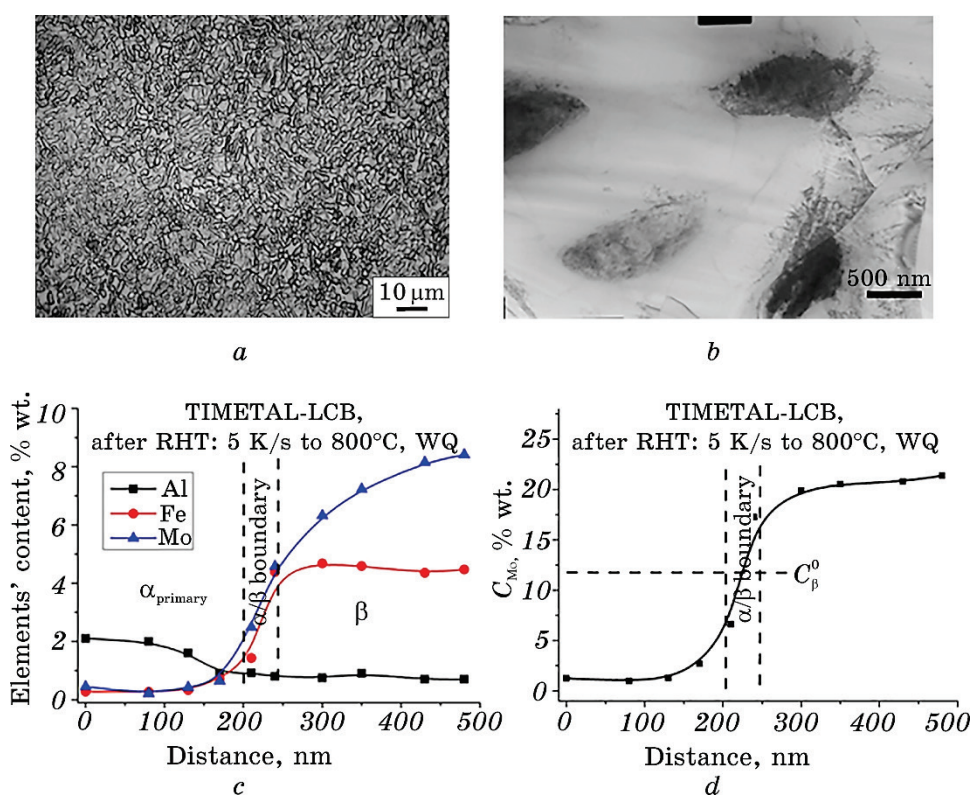
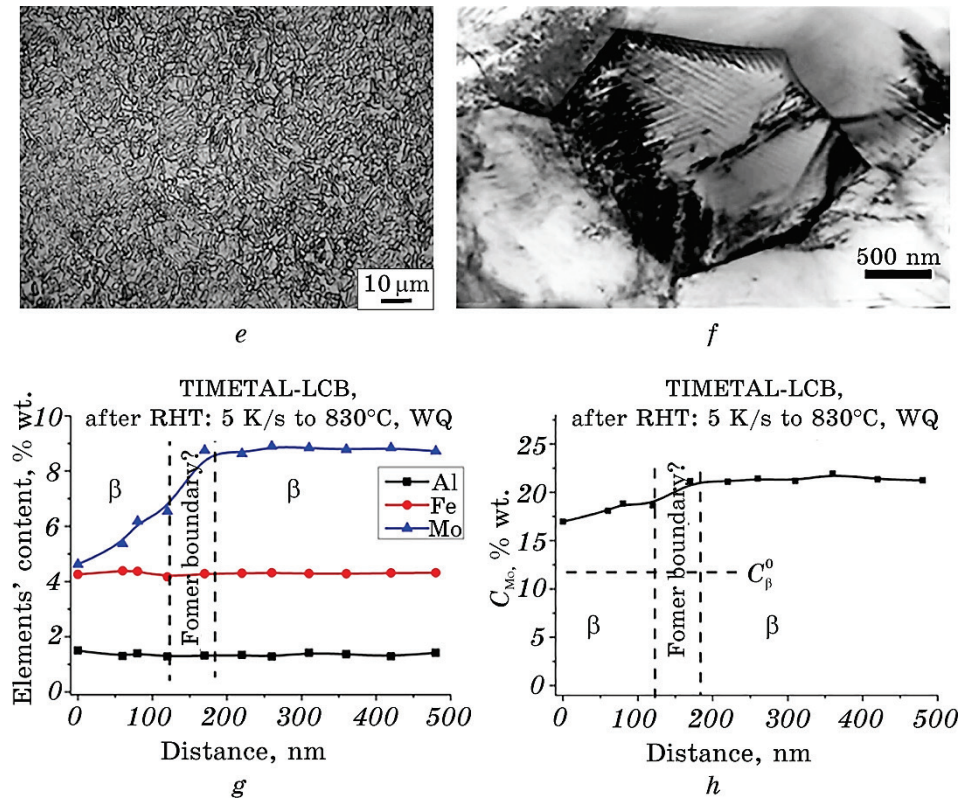


Fig. 3. Microstructure (*a*, *e*—OM, *b*, *f*—TEM), distribution of individual alloying elements (*c*, *g*), and integral distribution of β -stabilizers in terms of molybdenum equivalent (*d*, *h*) between two phases or in the β -phase of TIMETAL-LCB alloy after rapid heating with a rate of 5°C/s up to 800°C (*a*–*d*) and 830°C (*e*–*h*).



Continuation of Fig. 3.

centration of iron during rapid continuous heating is smoothed out between the phases, and in the high-temperature β -phase it is equalized much faster compared to molybdenum. Similar situation is previously observed for carbon steels, in which faster carbon redistribution as compared to metal alloying elements is revealed, and this phenomenon is called para- and ortho-equilibrium [15].

The fact that the diffusion behaviour of iron in titanium is somewhat similar to diffusion of carbon in iron is also suggested by some researchers which found out that iron diffuses not through substitutional but through interstitial sites in titanium lattice [16].

3.2. Ti-3(% wt.)AL-4.5Fe-7.2Cr Alloy

This alloy is even more economically alloyed analogue of the above discussed TIMETAL-LCB alloy, it has eutectoid β -stabilizers (iron and chromium), and is designed to be used primarily for non-aerospace products. A typical microstructure of the alloy annealed in $\alpha + \beta$ field is

shown in Fig. 4, *a* and *b*, the distribution of alloying elements in this initial state is given in Fig. 4, *c* and *d*.

As seen, the original microstructure of the alloy is somewhat finer as compared to TIMETAL-LCB alloy, which is supposedly explained by the features of the given alloying system: the rate of diffusion of chromium is about 2 orders of magnitude higher than that of molybdenum, but an order of magnitude lower compared to iron.

Upon continuous heating up to 800°C (as in the previous case, this temperature corresponds to the upper boundary of the $\alpha + \beta$ region, Fig. 5, *a*), comparatively broad transient zone is formed between the α - and β -phases, and the character of redistribution of both iron and chromium is virtually the same (Fig. 5, *b* and *c*).

It should also be mentioned that an inhomogeneous distribution of chromium is detected in individual β -grains.

After heating into the single-phase β -field (830°C, Fig. 5, *d*) there is

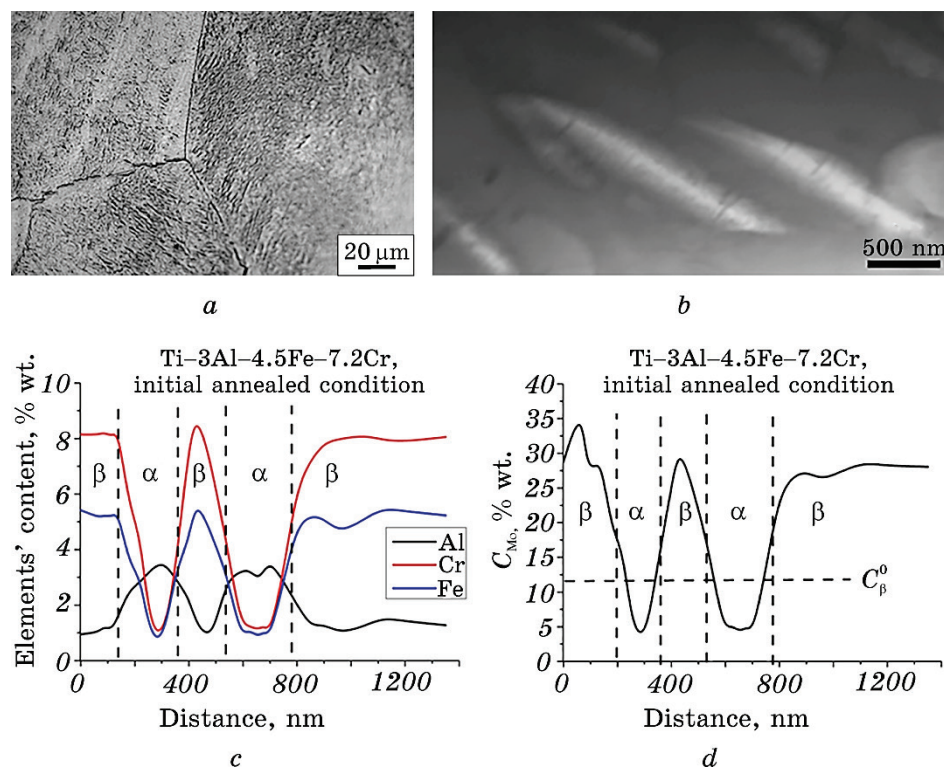


Fig. 4. Microstructure (*a*—OM, *b*—STEM), distribution of individual alloying elements (*c*) and integral distribution of β -stabilizers in terms of molybdenum equivalent (*d*) between two phases of Ti-3Al-4.5Fe-7.2Cr alloy in initial annealed state.

a certain lag in the homogenization of chromium compared to iron (Fig. 5, *e*), and the zones where the minimum concentration of chromium is observed can correspond to the former α -phase in the original microstructure.

Thus, comparing the results for the TIMETAL-LCB and Ti-3Al-4.5Fe-7.2Cr alloys, it can be concluded that, due to the highest rate of diffusion, iron redistributes during polymorphic $\alpha + \beta_0 \rightarrow \beta$ transformation faster than chromium, and much faster than molybdenum.

In other words, unlike the two-phase titanium alloys of subcritical composition with $C_{Mo} < 11.5\%$, in which metastable β -phase is not fixed by quenching from the single-phase β -field and all alloying elements act 'cooperatively', in alloys with $C_{Mo} > 11.5\%$ there is some 'competition' between the alloying elements, and their redistribution proceeds depending on the rate of diffusion.

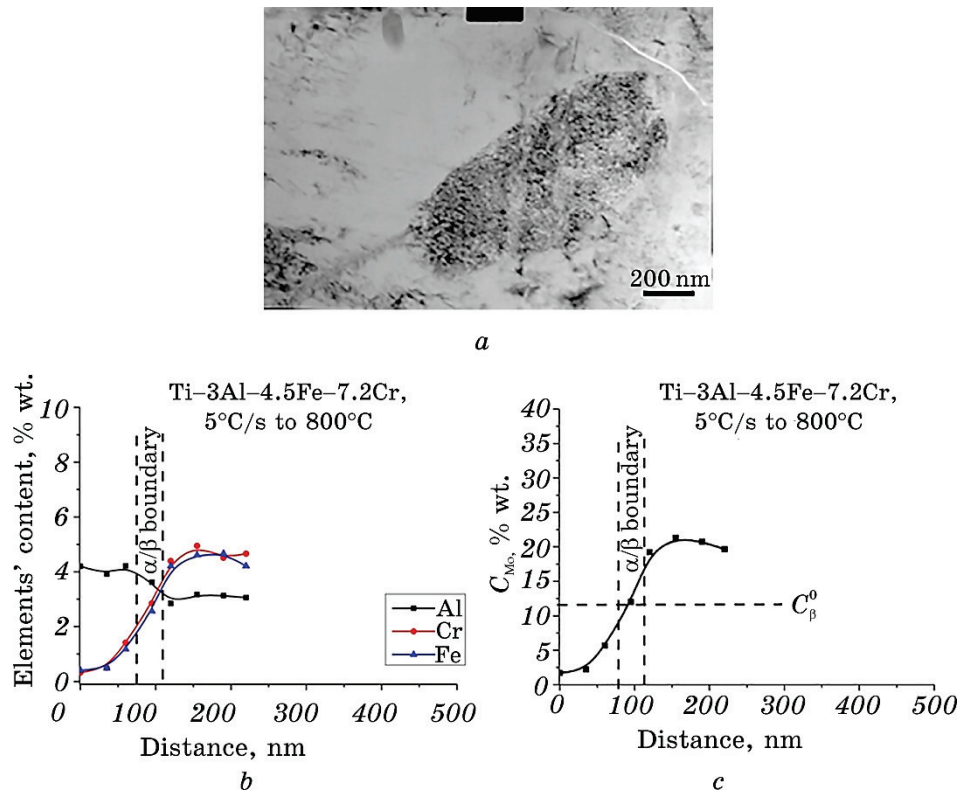
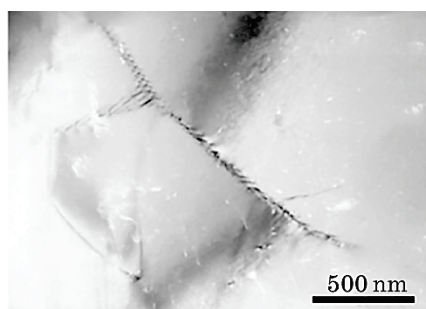
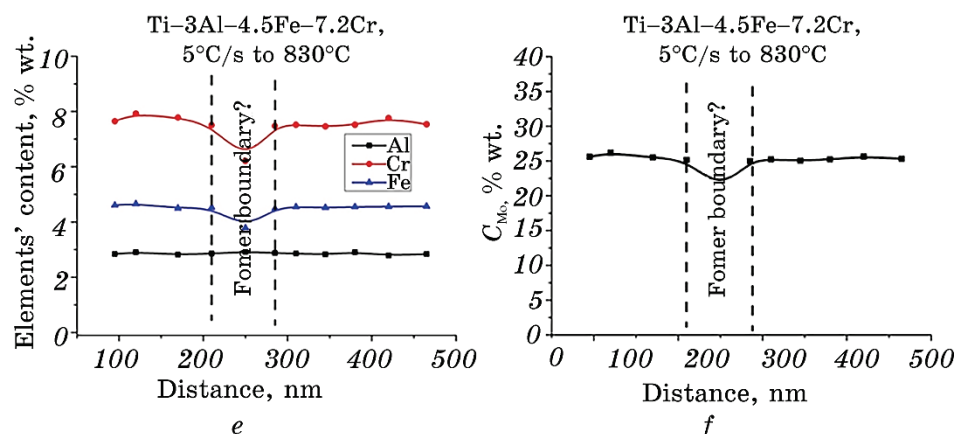


Fig. 5. Microstructure (*a*, *d*—TEM), distribution of individual alloying elements (*b*, *e*), and integral distribution of β -stabilizers in terms of molybdenum equivalent (*c*, *f*) between two phases or in the β -phase of Ti-3Al-4.5Fe-7.2Cr alloy after rapid heating with a rate of 5°C/s up to 800°C (*a*–*c*) and 830°C (*d*–*f*).



d



Continuation of Fig. 5.

3.3. Ti-15-3 Alloy

In contrast to the TIMETAL-LCB and Ti-3Al-4.5Fe-7.2Cr alloys discussed above, Ti-15-3 alloy is comparatively highly alloyed (Ti-15% wt. V-3Al-3Cr-3Sn) and contains both β -isomorphous and β -eutectoid elements. The predominant content of β -isomorphous vanadium which has comparatively low rate of diffusion in titanium matrix leads to the fact that this alloy is 'lazier' in relation to diffusion-controlled processes as compared to two previously discussed alloys.

One consequence of this is the formation of comparatively fine $\alpha + \beta$ microstructure after annealing (even prolonged) at upper temperatures of the $\alpha + \beta$ field (Figs. 6, *a* and *b*). Due to this in relatively thin α -phase plates it is possible to obtain 2 analyzed points in the best case, and measured chemical composition is characterized by relatively large variations (Figs. 6, *c* and *d*).

After heating under the same scheme as the two previous alloys the polymorphic $\alpha + \beta_0 \rightarrow \beta$ transformation is completed, and the thin α -

plates dissolved comparatively quickly (Fig. 7, *a*). As a result, the chromium content is practically uniform throughout the alloy, and only slight fluctuations are observed in the vanadium distribution, possibly at the sites of the former α -phase particles (Fig. 7, *b*).

For comparative analysis of the obtained results we used some data (Table 1) which describe integral content of β -stabilizers ($C_0^{M_0}$), the temperature of completion of the $\alpha + \beta_0 \rightarrow \beta$ transformation (under close to equilibrium heating conditions), and microstructure (α -phase particle thickness in the initial state b_α) of the studied alloys. As seen, the integral content of β -stabilizers is the lowest in Ti-15-3 alloy and the highest in Ti-3Al-7.2Cr-4.5Fe alloy. Nevertheless, the combination of relatively low content of β -stabilizers with high rate of diffusion of iron in TIMETAL-LCB alloy made it possible to obtain the coarsest α -phase plates, whereas in more alloyed Ti-3Al-7.2Cr-4.5Fe

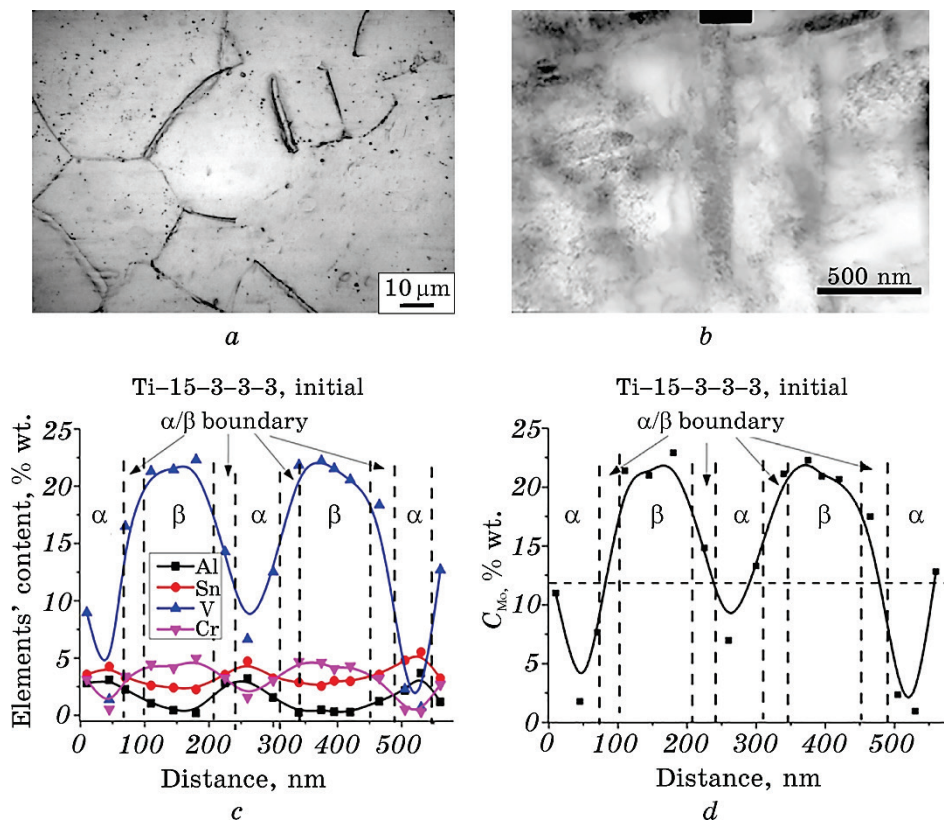


Fig. 6. Microstructure (*a*—OM, *b*—TEM), distribution of individual alloying elements (*c*) and integral distribution of β -stabilizers in terms of molybdenum equivalent (*d*) between two phases of Ti-15-3-3-3 alloy in initial annealed state.

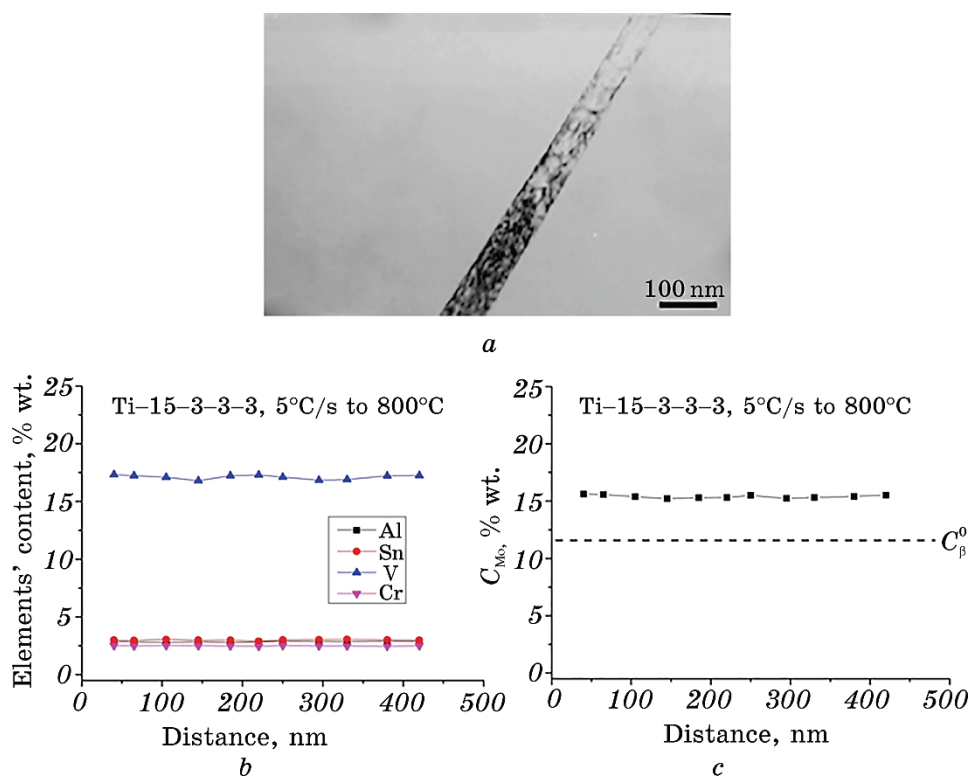


Fig. 7. Microstructure (a —TEM), distribution of individual alloying elements (b), and integral distribution of β -stabilizers in terms of molybdenum equivalent (c) in the β -phase of Ti-15-3-3-3 alloy after rapid heating with a rate of 5°C/s up to 800°C.

TABLE 1. Some characteristics of the studied alloys.

| Alloy (chem. comp., % wt.) | C_0^{Mo} , % | $\alpha + \beta_0 \rightarrow \beta$ temp., °C | b_α , nm | b_α / C_0^{Mo} , nm/% |
|---------------------------------------|-------------------|---|--------------------|---------------------------------|
| TIMETAL-LCB (Ti-1.5Al-6.8Mo-4.5Fe) | 19.9 | 790 | $\cong 400-600$ | 25 |
| Ti-3Al-7.2Cr-4.5Fe alloy | 24.6 | 815 | $\cong 200-250$ | 10 |
| Ti-15-3 (Ti-15V-3Al-3Cr-3Sn) | 15.4 | 780 | $\cong 60-70$ | 4.5 |

which contains two β -stabilizers with high rates of diffusion the α -plates are twice thinner.

The finest α -phase particles are observed in Ti-15-3 alloy due to slow diffusion of vanadium and low temperature of the $\alpha + \beta_0 \rightarrow \beta$ transfor-

mation, and these particles completely dissolved with homogeneous β -phase formation after overheating 20°C above the equilibrium temperature of the transformation completion. A comparison of the alloys by the ratio of α -plates thickness to the integral content of β -stabilizers (b_α/C_0^{Mo}) shows that this parameter decreases in a sequence TIMETAL-LCB \rightarrow Ti-3Al-7.2Cr-4.5Fe \rightarrow Ti-15-3.

4. CONCLUSIONS

1. There is a competitive diffusion of individual alloying elements in titanium alloys of the metastable β -class under non-equilibrium conditions of rapid heating.
2. The rate of diffusion redistribution of alloying elements depends not so much on their total concentration (expressed by the integral content of β -stabilizing elements, molybdenum equivalent), but on the rates of diffusion of individual elements. Iron concentration is homogenized at first, chromium concentration equalizes somewhat slower, and the concentration of β -stabilizers of isomorphous type smoothes most slowly.
3. By analogy with carbon steels, in the titanium alloys of metastable β -class under non-equilibrium conditions of rapid heating para- (partial) and ortho- (complete) equilibrium are formed for β -stabilizers of eutectoid and isomorphous type, respectively.

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