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# Influence of the orientation of Ti–Al interphase boundary on the mutual diffusion rate at the solid and liquid states of aluminium: molecular dynamics simulation

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The influence of the orientation of Ti–Al interphase boundary on the intensity of mutual diffusion at solid-phase and solid-liquid-phase contacts was studied by the method of molecular dynamics. Four orientations of the boundary with respect to the Ti (hcp) and Al (fcc) lattices were considered: (0001):(111), (0001):(001), (10 $\bar{1}$ 0):(111), (10 $\bar{1}$ 1):(001). At solid-phase contact, an important phenomenon influencing the intensity of mutual diffusion was the formation, due to the mismatch of the lattices of Ti and Al, of grain boundaries in Al parallel to the interphase boundary. This boundary was both the main source and sink of structural defects, including vacancies required for diffusion to proceed. In the case of solid-liquid-phase contact, after melting of aluminium, part of it near the interphase boundary remained in the crystalline state, repeating the titanium lattice. That is, the boundary between the crystal and the liquid metal was shifted by two or three atomic planes deep into the aluminium. For the considered orientations, concentration curves were obtained after simulating mutual diffusion at different temperatures. The flatter parts of the curves, which are responsible for the diffusion of Ti atoms deep into liquid Al, turned out to be similar for all orientations. However, the parts related to the diffusion of Al atoms into crystalline Ti were different: diffusion of Al atoms in Ti proceeded more intensively with the orientation of the boundary (0001) and more slowly with the orientations (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1).

**Keywords:** molecular dynamics, diffusion, interphase boundary, titan, aluminum.

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## 1. Introduction

Intermetallic compounds of the Ti–Al systems and alloys on their basis, thanks to a combination of such properties as low density, high yield stress at increased temperatures, good oxidation and corrosion resistance, have a high potential of application as high-temperature structural materials, in particular, for aerospace and automobile industries [1–5]. The main technology for the making of intermetallides and alloys is diffusion, which in such systems has a complex and multiple-factor nature. Both solid ordered and disordered phases and liquid mixtures with a different content of components can be simultaneously present in the diffusion zone on the Ti and Al boundary, e.g. during high-temperature synthesis [6–9]. The knowledge of diffusion kinetics, characteristics and mechanisms of diffusion in metal systems, in particular, in the Ti–Al system, is necessary for a more detailed understanding of processes which take place during high-temperature synthesis, and is important for the whole area of research and creation of intermetallides and binary alloys.

Our previous papers [10,11] deal with a study of self-diffusion of Ti and Al atoms in liquid and hard Ti–Al alloys separately. We considered ordered and disordered alloys

consisting of Ti<sub>75</sub>Al<sub>25</sub>, Ti<sub>50</sub>Al<sub>50</sub>, Ti<sub>25</sub>Al<sub>75</sub>, as well as pure Ti and Al metals. The following self-diffusion characteristics, in particular, were obtained for the considered systems: diffusion activation energy and pre-exponential factor in the corresponding Arrhenius equation.

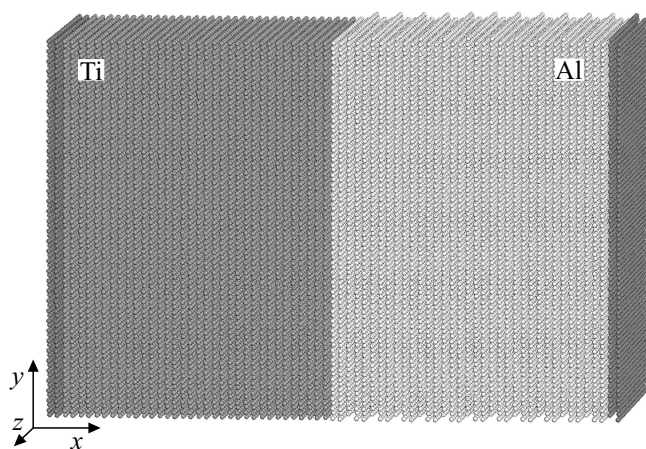
This paper deals with a molecular dynamics simulation of the influence of interphase boundary orientation in relation to Ti and Al crystal lattice on the rate of mutual diffusion under solid-phase and solid-liquid phase contacts, that is at temperatures below and above the Al melting temperature, but below the Ti melting temperature.

## 2. Model description

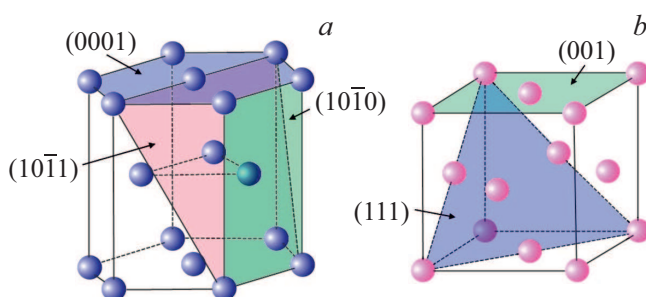
Interatomic interactions in the Ti–Al system in the molecular dynamic model using EAM potentials of Zope and Mishin [12], obtained by comparing the experimental data and results of *ab initio* calculations in relation to various properties and structure of Ti, Al metals and Ti<sub>3</sub>Al and TiAl intermetallides. They have been proved in the course of various studied and have been successfully tried in a wide range of mechanical and structural-energy properties of Ti–Al alloys [10–14].

Computational cells contained about 120 thousand atoms and had the shape of rectangular parallelepipeds (Fig. 1). The interphase boundary was created at the computational cell center along the  $YZ$  plane. An infinite cell repetition was simulated along the  $Y$  and  $Z$  axes, that is periodic boundary conditions were imposed. Thereat, sizes along these axes were chosen so that they are divisible, with the minimum possible deviation, by repeat periods of Ti and Al crystal lattices simultaneously. Thereat, we also took into account the different thermal expansion of metals for each specific temperature at which simulation was performed. Rigid conditions were imposed along the  $X$  axis: atoms on the left and right butts of the computational cell in Fig. 1 (dark-grey color) remained immobile during the computer experiment.

Four orientations of the Ti–Al boundary in relation to the Ti (HCP) and Al (FCC) crystal lattices were considered: 1)  $(0001):(111)$ ; 2)  $(0001):(001)$ ; 3)  $(10\bar{1}0):(111)$ ; 4)  $(10\bar{1}1):(001)$ . Aluminum was initially created in the crystalline state. Fig. 2 shows the images of these atomic planes. It is considered that the most close-packed plane is plane  $(0001)$  — an equivalent of plane  $(111)$  in a FCC-lattice. But not all is so unambiguous here. The thing is that



**Figure 1.** Computational cell for simulation of mutual diffusion on the Ti–Al boundary before temperature assignment (dark-grey atoms on the cell butts were immobile during simulation).



**Figure 2.** Considered orientations of the interphase boundary in relation to the HCP crystal lattice of Ti (a) and FCC lattice of Al (b).

Density of atomic plane filling

№	Orientation IPB (Ti:Al)	Strictly in plane (in a layer 0.1 Å thick)	In a layer 1 Å thick
1	$(0001):(111)$	90.7%:90.7%	90.7%:90.7%
2	$(0001):(001)$	90.7%:78.6%	90.7%:78.6%
3	$(10\bar{1}0):(111)$	49.5%:90.7%	99.0%:90.7%
4	$(10\bar{1}1):(001)$	44.5%:78.6%	86.8%:78.6%

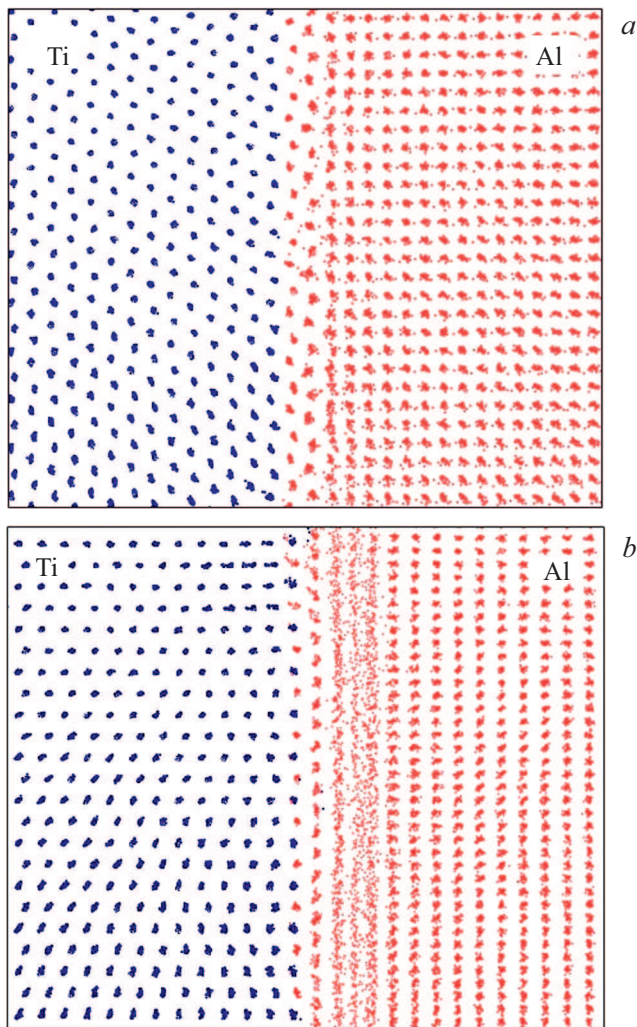
this is true if atom density strictly in the given plane is taken into account. If atoms are taken into account in a layer, for instance, 1 Å thick, the greatest packing density will be in case of orientation  $(10\bar{1}0)$  (almost 99%). The table gives the values of density of atomic plane density strictly in the plane and in a layer 1 Å thick. Atomic radius in the density calculation was equal to half the distance to the nearest neighbors in a perfect crystal.

Temperature in the model was specified via initial atom velocities according to the Maxwell distribution [15,16]. A Noze–Hoover thermostat was used to maintain a constant temperature during simulation. The step of time integration in the molecular dynamics method was equal to 2 fs. Simulation of mutual diffusion was performed at different temperatures below and above the aluminum melting temperatures, from 500 to 1700 K. The used potential, among other things, describe the Ti and Al melting temperature well: in the molecular dynamic model they are equal to 1995 and 990 K respectively (reference values: 1943 and 933 K). The aluminum melted in the model significantly faster than diffusion, and its influence was insignificant. Accounting of thermal expansion due to a phase transition was mandatory in computer experiments that included aluminum melting.

### 3. Solid-phase contact on the Ti–Al boundary

Simulation of mutual diffusion was preceded by relaxation of the structure of the created computational cell, during which the structure on the interphase boundary passed to a state corresponding to the minimum potential energy. Relaxation was accelerated by specifying a relatively low temperature, insufficient for mutual diffusion within a short relaxation time.

An important peculiarity of structure formation near the Ti–Al interphase boundary was noted at the relaxation stage. When the Ti and Al crystalline structures mismatched, lattice irregularities due to this mismatch formed as a grain boundary in aluminum, parallel to the interphase boundary (Fig. 3). The interphase boundary of defects, as a rule, did not contain and „pushed“ them out to the grain boundary in aluminum.



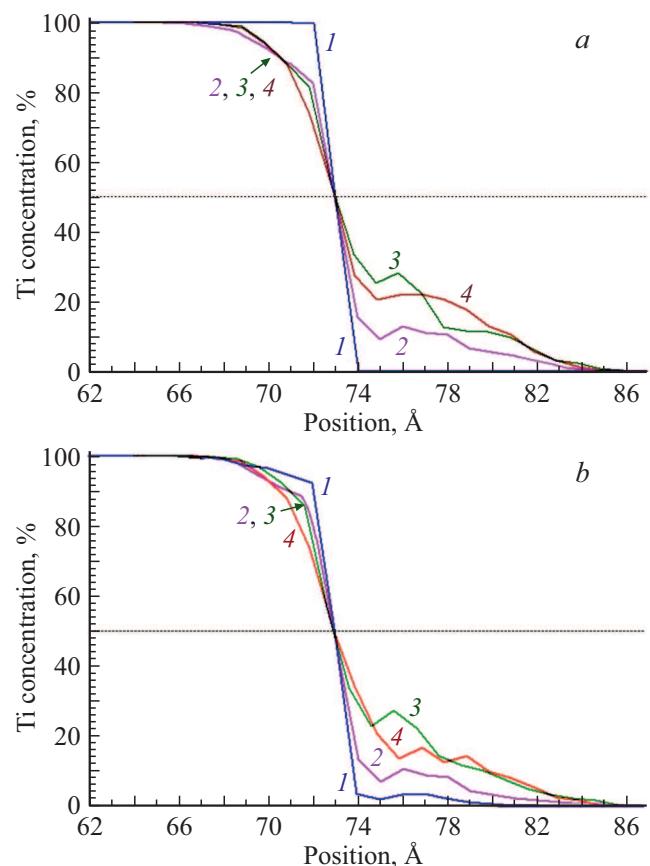
**Figure 3.** Formation of a grain boundary in Al parallel to the interphase boundary: *a*) orientation  $(10\bar{1}1):(100)$ ; *b*) orientation  $(10\bar{1}0):(111)$ . The structures were obtained after simulation at 500 K for 50 ps.

We have already observed this peculiarity of the structure of interphase boundaries for the Ni–Al boundaries in [17], where we simulated a plastic deformation near the IPB in a two-dimensional model. We also noted there that plastic shears (dislocations) are initiated on similar grain boundaries in aluminum, and not on the interphase boundary itself. Evidently, such behavior is conditioned by stronger bonds of Ti and Al atoms (like Ni and Al) as compared to Al–Al bonds. It will be shown below that the grain boundary (GB) in aluminum is important in solid diffusion.

Injection of additional defects into the interphase boundary (IPB), e.g. vacancies, due to the above-mentioned phenomenon, did not lead to significant influence on mutual diffusion. At the beginning of simulation, they left the interphase boundary and migrated to aluminum. Fig. 4 shows the concentration curves obtained by diffusion simulation for 3000 ps at 900 K for all the considered orientations without

vacancy injection into the IPB (Fig. 4, *a*) and with injection of 6 vacancies into the IPB at the beginning of simulation (Fig. 4, *b*). Curves of Ti atoms concentration distribution in the computational cell were plotted by analyzing the concentration in a comparatively thin layer 3 Å thick when this layer moved to 1 Å along the X axis. It can be seen that even six vacancies exerted almost no impact on diffusion, except the 1-st orientation which has the highest degree of coupling of Ti and Al crystal lattice and is the only one of the four considered orientations when a grain boundary did not form in Al. The influence of vacancies in this case is explained by the fact that diffusion under a solid-phase contact did not take place at all without any other defects with the given IPB orientation. This was also noted by the authors of [18], who explained it by high similarity of the atomic planes (0001) in Ti and (111) in Al (distances between the nearest atoms in these planes are very close for both metals: 2.951 and 2.864 Å at absolute zero respectively; this difference becomes even smaller under heating).

Diffusion did not take place for orientation 1 without injection of vacancies into the IPB at the initial stage, as can be seen in Fig. 4, *a*. For all the other three orientations, including the 2-nd one, i.e. with the same IPB orientation



**Figure 4.** Distribution of Ti atoms concentration in computational cells after simulation for 3000 ps at 900 K: *a*) without injection of vacancies into the IPB; *b*) with injection of 6 vacancies into the IPB at the beginning of simulation. The digits in the figure denote the considered IPB orientation (Table).



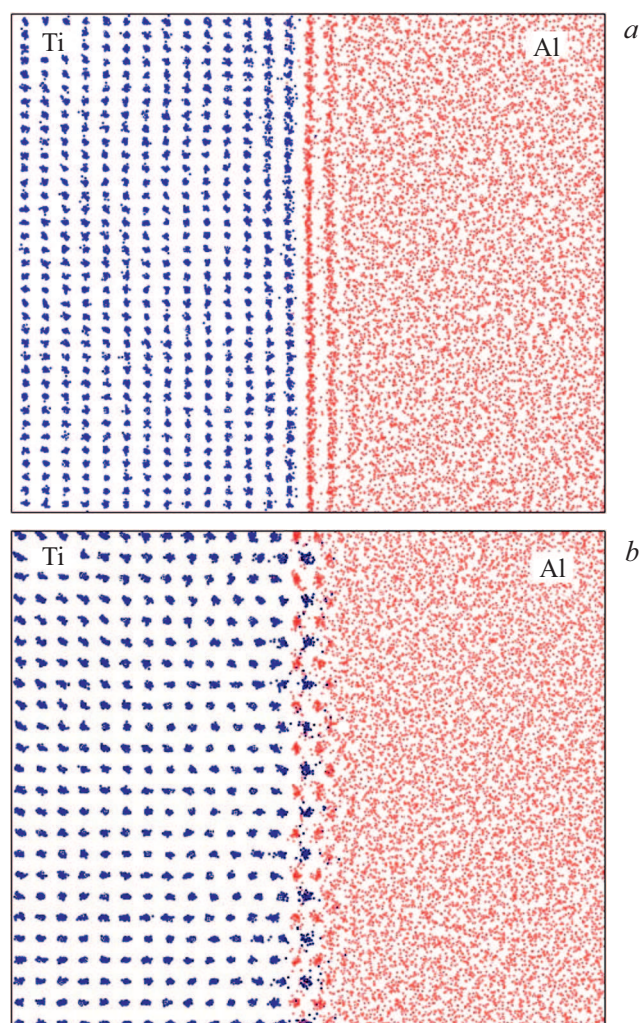
in relation to the Ti lattice (0001), but with a different orientation in relation to Al (001), the curve run was approximately similar in the left part which characterizes diffusion in the Ti lattice. Diffusion was faster, as we can see, in the Al region — Ti atoms penetrated deeper into Al as compared to penetration of Al atoms into the Ti lattice. This was in a great extent due to the presence of a grain boundary in Al, which has already been mentioned above. Diffusion in its region was faster than in the crystal lattice — this is confirmed by the curve rises in the areas of the GB. Moreover, the grain boundary in this case was also important in diffusion of Al atoms into the Ti lattice, being a „supplier“ of vacancies into this region. Thus, rate of mutual diffusion at the stage of the Ti–Al solid-phase contact is first of all affected by a grain boundary in Al, caused by a mismatch of the Ti and Al lattices.

#### 4. Solid-liquid phase contact on the Ti–Al boundary

After melting, a part of aluminum near the interphase boundary remained in the crystalline state, exactly repeating the titanium lattice. That is, the solid and liquid phase boundary in fact moved to two-three atomic planes deep into aluminum. Fig. 5 shows examples of this phenomenon. This is again explained by the fact that the Ti–Al bond is stronger than the Al–Al bond, due to which, in particular, melting temperatures of Ti–Al intermetallics exceed the aluminum melting temperature. Therefore, the considered temperatures are insufficient to break down the Ti–Al bonds on the interphase boundary. Because of this, separation of Ti atoms and their entrainment into liquid aluminum, evidently, becomes complicated and is not so fast as in case of a direct contact between titanium and the liquid phase.

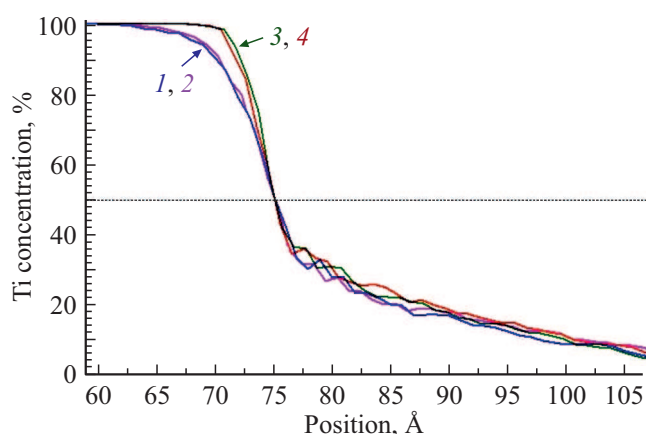
Despite the above-mentioned phenomenon, mutual diffusion on the Ti–Al boundary under a solid-liquid phase contact was considerably faster than under a solid-phase contact. In this case we observed a more significant prevalence of diffusion of Ti atoms deep into liquid Al as compared to diffusion of Al atoms into crystalline Ti, which is explained, first of all, by different physical states of Ti and Al.

Fig. 6 shows the concentration curves obtained at 1500 K after simulation for 300 ps for four considered orientations of the interphase boundary. The initial orientation of the Al lattice on the IPB after aluminum melting did not matter — as seen from the figure, the curves for orientations 1 and 2 are almost the same. The obtained concentration curves are qualitatively similar to the ones obtained experimentally for the given system [8]. The right gently sloping part shows diffusion of Ti atoms deep into liquid Al. Rate of such diffusion, evidently, does not depend on orientation of the interphase boundary and is the same for all the four considered orientations. A change from the gently sloping to a steeper curve pattern in the middle corresponds



**Figure 5.** Formation of a crystalline structure in Al near the interphase boundary at temperatures above the aluminum melting temperature (1300 K in this case): *a*) orientation (0001); *b*) orientation (10 $\bar{1}$ 0).

to diffusion on the interphase boundary in its crystalline region. Diffusion there is considerably slower, which affects the curve slope angle. It should be noted that this region begins considerably earlier than the 50% concentration, which is due to the above-mentioned phenomenon of crystal lattice retention in aluminum near the interphase boundary. However, differences can be distinctly seen for the considered orientations further, in the region that characterizes the penetration of Al atoms into crystalline Ti and rate of mutual diffusion in it. Diffusion of Al atoms deep into Ti was the fastest in case of the most „close-packed“ and „smooth“ orientation of the interphase boundary — (0001) (1 and 2 in Fig. 6). „Looser“ packing (3 — (10 $\bar{1}$ 0) and 4 — (10 $\bar{1}$ 1) in Fig. 4) turned out to be more „resistant“ to penetration of Al atoms — the concentration curves in these cases are considerably steeper than for the first two orientations.



**Figure 6.** Distribution of Ti atoms concentration in computational cells after simulation for 300 ps at 1500 K. The digits in the figure denote the considered IPB orientation (Table).

A similar influence of interphase boundary orientation is observed during motion of the crystallization front, i.e. the boundary of the growing crystal in the melt, in metals [19–22]: crystallization from the boundary that has a relatively „looser“ orientation (100) in a FCC lattice, moves in 1.3–1.5 times faster than from the boundary that has the densest orientation (111). Such behavior can be explained by a different depth of potential well ins where atoms are located on the interphase boundary. The main role the near the interphase boundary of metals under a solid-liquid phase contact, like on the liquid–crystal boundary, is played by the magnitude of different of free atom energies near the boundary in the liquid phase and the crystal „embedded“ into the boundary. This magnitude can be compared to the adatom energy on the corresponding free crystal surface, or to the activation energy of its migration along the given surface. For instance, computer simulation in [23] showed that the energy of adatom diffusion along the free surface (100) of FCC-metals is almost two times larger than along surface (111). In all likelihood, this affects the probability of vacancy transport from liquid Al into the crystalline Ti phase.

We did not observe a significant correlation of the rate of mutual diffusion with density of atom packing not strictly in the crystal lattice plane, but in a layer 1 Å thick (the table). The most remarkable of the considered orientations in all cases was the orientation (0001) in relation to the Ti lattice, especially the 1-st orientation (0001):(111) in case of a solid-phase contact.

## 5. Conclusion

The molecular dynamics method was used to study the influence of interphase boundary orientation in relation to Ti and Al crystal lattices on rate of mutual diffusion under solid-phase and solid-liquid phase contacts. Four orientations of the Ti–Al boundary in relation to the Ti (HCP)

and Al (FCC) lattices were considered: (0001):(111), (0001):(001), (10 $\bar{1}$ 0):(111), (10 $\bar{1}$ 1):(001). It was found that boundary orientation affects the diffusion rate both under a solid-phase contact and at a temperature above the aluminum melting temperature. Thereat, the influence mechanism is different in both cases and, while diffusion rate in the first case was the lowest with the orientation (0001):(111), in the second case the orientation (0001), on the opposite, had the highest rate of aluminum diffusion in crystalline titanium. An important phenomenon under a solid-phase contact was the formation, due to a mismatch of the Ti and Al lattices, of a grain boundary in Al, parallel to the interphase boundary. This boundary was simultaneously the main source and drain of structural defects, including vacancies, which were required for diffusion. A grain boundary in Al did not form in case of the orientation (0001):(111), with a high degree of coupling of the Ti and Al lattices on the interphase boundary, only the formation of a coarse grid of mismatch dislocation was observed.

In the case of a solid-liquid phase contact, its part near the interphase boundary after melting remained in the crystalline state, repeating the titanium lattice, i.e. the crystal and liquid metal boundary moved by two-three atomic planes deep into the aluminum. The parts that characterize diffusion of Ti in liquid Al on the concentration curves, obtained for the considered orientations, turned out to be similar. However, the parts related to diffusion of Al atoms in crystalline Ti had clear differences: diffusion of Al atoms into Ti was faster with the orientation (0001) and slower with comparatively „looser“ orientations (10 $\bar{1}$ 0) and (10 $\bar{1}$ 1).

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## Conflict of interest

The authors declare that they have no conflict of interest.

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