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Self-diffusion in melts of Ni-Al and Ti-Al systems: molecular dynamics study

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Self-diffusion in liquid alloys of Ni-Al and Ti-Al systems, depending on the concentration of the components, as well as in pure metals Al, Ni, and Ti, has been studied using the molecular dynamics method. Knowledge of the diffusion parameters in melts of binary systems, such as Ni-Al and Ti-Al, is necessary for a more detailed understanding and prediction of the processes occurring during combustion synthesis and in the manufacture of wares by melt casting. For the considered systems, self-diffusion characteristics (activation energy and preexponential factor in the corresponding Arrhenius equation) are found separately for atoms of different types. Good agreement of diffusion characteristics with experimental data was obtained for pure metal melts, which indicates the physical realism of the molecular dynamics model and EAM potentials used. In addition to pure metals, three component ratios were considered for each system: $A_{75}B_{25}$, $A_{50}B_{50}$ and $A_{25}B_{75}$. According to the data obtained, the activation energy of diffusion substantially depends on the concentration of the components, and the highest, among the considered compositions, for $Ni_{75}Al_{25}$ for Ni-Al system and for $Ti_{50}Al_{50}$ for Ti-Al system. At the same time, no significant predominance of diffusion mobility of atoms of different types was observed for all the mixture compositions considered.

Keywords: molecular dynamics, diffusion, activation energy, alloy, melt.

УДК: 538.931

Самодиффузия в расплавах систем Ni-Al и Ti-Al: молекулярно-динамическое исследование

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Методом молекулярной динамики проведено исследование самодиффузии в жидких сплавах систем Ni-Al и Ti-Al в зависимости от концентрации компонентов, а также в чистых металлах Al, Ni и Ti. Знание параметров диффузии в расплавах бинарных систем, таких как Ni-Al и Ti-Al, необходимо для более детального понимания и прогнозирования процессов, происходящих при высокотемпературном синтезе и при изготовлении деталей путем отливки из расплава. Для рассмотренных систем отдельно для атомов разного сорта найдены характеристики самодиффузии (энергия активации и предэкспоненциальный множитель в соответствующем уравнении Аррениуса). Для расплавов чистых металлов получено хорошее согласие диффузионных характеристик с экспериментальными данными, что говорит в пользу физической реалистичности молекулярно-динамической модели и используемых EAM потенциалов. Помимо чистых металлов, для каждой системы рассматривалось три соотношения компонентов: $A_{75}B_{25}$, $A_{50}B_{50}$ и $A_{25}B_{75}$. Согласно полученным данным, энергия активации диффузии существенно зависит от концентрации компонентов и наибольшая, среди рассмотренных составов, для $Ni_{75}Al_{25}$ для системы Ni-Al и $Ti_{50}Al_{50}$ для системы Ti-Al. При этом не было замечено существенного преобладания диффузионной подвижности атомов разного сорта для всех рассмотренных составов смесей.

Ключевые слова: молекулярная динамика, диффузия, энергия активации, сплав, расплав.

1. Introduction

Intermetallic compounds of Ni-Al and Ti-Al systems and alloys based on them, due to the combination of properties such as low density, high yield strength at elevated temperatures, good resistance to oxidation and corrosion, have a high potential for their use as high-temperature structural materials [1–4]. The technology for producing intermetallic compounds and alloys is based on diffusion, the process of which in such systems is complex and multifactorial. In the diffusion zone at the interface of two metals, for example, in the process of combustion synthesis, both solid ordered and disordered phases can be present simultaneously, as well as liquid mixtures with different content of components [5–7]. In this case, diffusion characteristics, such as the activation energy of diffusion, differ significantly not only in the indicated phases, but also depend on the concentration of the components in a simple mixture [7–10]. Besides, one of the popular technological methods for obtaining products from intermetallic compounds is solidification from a melt [11]. It is known that the microstructure and properties of solidified alloys are largely determined by the processes of mass transport in the liquid state. Knowledge of the diffusion parameters in melts of binary systems, such as Ni-Al and Ti-Al, is necessary for a more detailed understanding and prediction of the processes occurring during high-temperature synthesis and in the manufacture of wares by melt casting.

Experimental study of diffusion in liquid alloys is a difficult task. This is due to a number of difficulties associated with conducting such studies: high temperature, chemical reactivity, crystallization caused by container walls, lack of suitable isotopes in the case of Al [12,13]. In this case, the most effective is the application of the molecular dynamics method, which directly allows to study various transport and thermodynamic properties of alloys in a wide temperature range at a clearly specified ratio of components.

The aim of this work was to obtain self-diffusion characteristics for liquid alloys of Ni-Al and Ti-Al systems, depending on the concentration of the components, using the molecular dynamics method.

2. Description of the model

EAM potentials from [14] were used to describe interatomic interactions in Ni-Al system in the molecular dynamics model, and from [15] for Ti-Al system. These potentials were obtained in [14,15] on the basis of comparison with both experimental and *ab initio* data on various properties and structures of the corresponding metals and intermetallic compounds. They have proven themselves in various studies and have been successfully tested in a wide range of mechanical and structural-energy properties of the alloys of the systems under consideration [14–18].

Computational cells contained 80 thousand atoms and have the form of rectangular parallelepipeds (Fig. 1). Periodic boundary conditions were used on all axes, wherein an additional free space was created along one of the axes (above and below in Fig. 1) so that the melt could freely change its volume with a change in temperature and initial melting of the start crystal. The melt structure in the model was created by setting the temperature of the computational cell significantly higher than the melting temperature and holding it for a time sufficient for complete destruction of the crystal lattice, melting of the entire cell, and completion of all processes associated with relaxation of the structure after the phase transition.

To find the diffusion characteristics in this work, we used the kinematic method [19]. It consists in finding the temperature dependence of the diffusion coefficient $D(T)$ and then determining from the obtained dependence of the diffusion activation energy and the preexponential factor in the corresponding Arrhenius equation. The self-diffusion coefficient was calculated using the Einstein ratio:

$$D = \frac{\left\langle \Delta r^2 \right\rangle}{6t}, \qquad (1)$$

where $\langle \Delta r^2 \rangle$ is the root-mean-square displacement of atoms relative to the initial positions, t is time.

The diffusion coefficient in the simulated melt was determined from the displacement of atoms only in the shaded zone in Fig. 1 in order to exclude the influence of the free surface. Molecular dynamics experiments to determine the diffusion coefficient had a duration of 0.5 ns. The temperature in the model was set through the initial velocities of atoms according to the Maxwell-Boltzmann distribution [20,21]. To keep the temperature constant during the simulation, a Nose-Hoover thermostat was used. The time integration step in the molecular dynamics method was 2 fs.

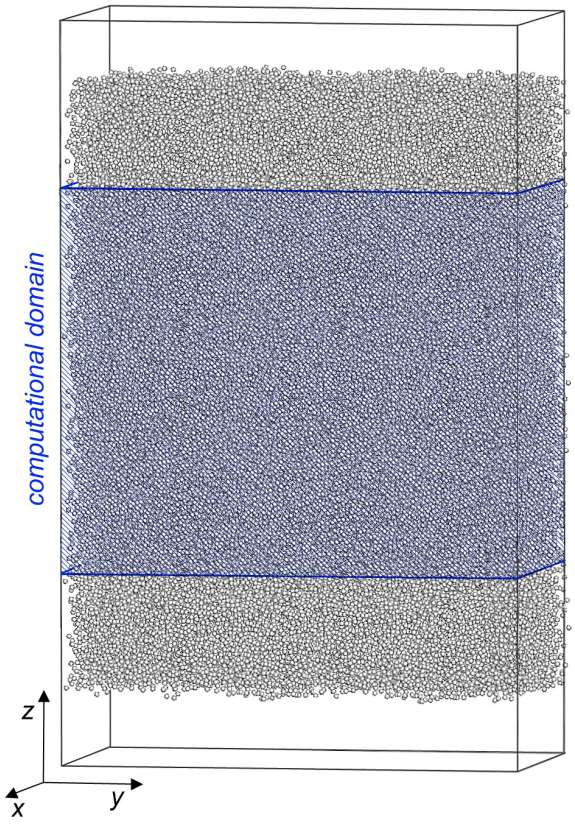


Fig. 1. The model for studying self-diffusion in a melt (diffusion was estimated from the displacement of atoms in the shaded region).

3. Results and discussion

The used EAM potentials describe quite well the various properties of the metals under consideration, including the melting point and thermal expansion coefficient [14–18]. In our model, the melting temperatures of the metals Ni, Ti, and Al were 1705, 1995 and 1045 K respectively, which is close to the reference data: 1726, 1943 and 933 K. The diffusion coefficient was measured in a wide temperature range, the width of which for different compositions was usually equal to or exceeded 1000 K (usually from the melting point to plus 1000–1200 K).

Fig. 2 shows the dependences of $\ln D$ on $10^3/T$ obtained in the model for liquid mixtures of Ni-Al (Fig. 2 a) and Ti-Al (Fig. 2 b), as well as for pure metals Al, Ni, and Ti. All found diffusion coefficients had values in the range of 10^{-8}–10^{-9} m²/s, which for the temperatures under consideration is in good agreement with experimental works and data of other authors for melts [13, 22–25]. All the dependences obtained are strictly linear, which indicates that the same diffusion mechanism with the same activation energy operates in the temperature range under consideration.

According to the Arrhenius equation, the self-diffusion activation energy can be determined from the slope of the linear dependence:

$$Q = -k\frac{d\ln D}{d\left(T^{-1}\right)} = -k\cdot \mathrm{tg}\,\alpha, \qquad (2)$$

where k is the Boltzmann constant.

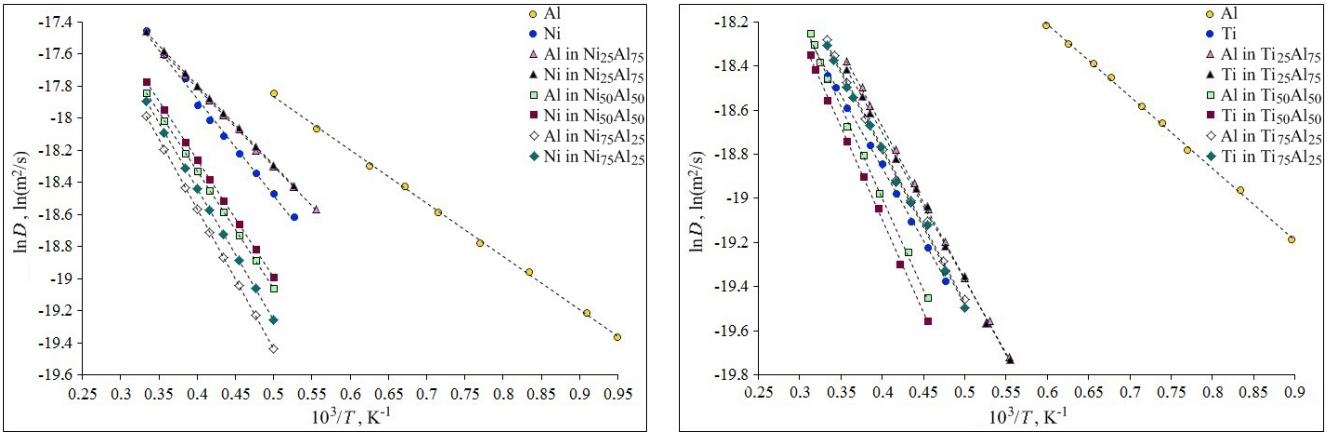
Herewith the pre-exponential factor is calculated by the intersection of the line with the ordinate axis:

$$\ln D_0 = \ln D(0) \qquad (3)$$

The found values of Q and D_0 are shown in Table 1. The activation energy of diffusion in liquid Al, Ni, and Ti almost coincided with the data of real experiments [22–25] (in Table 1 they are below the values obtained in the model), which indicates the realism of the potentials used [14,15]. The activation energy in alloys, as expected, significantly depends on the concentration of the components. This dependence is non-monotonic and, among the considered compositions, has a maximum for Ni-Al system at the ratio of the components $Ni_{75}Al_{25}$ (0.69 eV for Ni and 0.71 eV for Al), for Ti-Al system — at the ratio $Ti_{50}Al_{50}$ (0.72 eV for the atoms of both components). This behavior is explained by the dependence of the average energy of atoms in the corresponding mixtures: for the indicated ratios, the depths of potential wells in which the atoms are located are largest [14,15], which is reflected in the height of the energy barrier and, accordingly, the activation energy of self-diffusion. It should be noted that no significant prevalence of diffusion of one or another component was observed for all the considered mixture compositions — the diffusion characteristics for atoms of different types turned out to be close under the same conditions. The average energy of atoms in the mixture and the depth of potential wells in which the atoms are located correlate, as is known, with the melting temperature of the corresponding alloys, and therefore the obtained

Table 1. Diffusion parameters for melts of Ni-Al and Ti-Al systems.

Ni-Al	Q, eV	D_0, m²/s	Ti-Al	Q, eV	D_0, m²/s
Al in Al	0.28 0.274 [22] 0.280 [23]	$0.88\cdot10^{-7}$ $1.79\cdot10^{-7}$ [22]	Al in Al	–	–
Ni in Ni	0.52 0.47 [24]	$1.71\cdot10^{-7}$ $0.77\cdot10^{-7}$ [24]	Ti in Ti	0.57 0.563 [25]	$0.89\cdot10^{-7}$ $1.14\cdot10^{-7}$ [25]
Al in $Ni_{75}Al_{25}$	0.71	$2.79\cdot10^{-7}$	Al in $Ti_{75}Al_{25}$	0.60	$1.17\cdot10^{-7}$
Ni in $Ni_{75}Al_{25}$	0.69	$2.56\cdot10^{-7}$	Ti in $Ti_{75}Al_{25}$	0.60	$1.15\cdot10^{-7}$
Al in $Ni_{50}Al_{50}$	0.61	$2.04\cdot10^{-7}$	Al in $Ti_{50}Al_{50}$	0.72	$1.54\cdot10^{-7}$
Ni in $Ni_{50}Al_{50}$	0.62	$2.18\cdot10^{-7}$	Ti in $Ti_{50}Al_{50}$	0.72	$1.47\cdot10^{-7}$
Al in $Ni_{25}Al_{75}$	0.44	$1.31\cdot10^{-7}$	Al in $Ti_{25}Al_{75}$	0.59	$1.21\cdot10^{-7}$
Ni in $Ni_{25}Al_{75}$	0.43	$1.38\cdot10^{-7}$	Ti in $Ti_{25}Al_{75}$	0.57	$1.08\cdot10^{-7}$



a b

Fig. 2. (Color online) Dependences of $\ln D$ on $10^3/T$ for liquid mixtures of Ni-Al (a), Ti-Al (b) and pure metals Al, Ni, and Ti.

dependences of the activation energy on the concentration of the components approximately repeat the phase diagrams of the systems under consideration.

4. Conclusion

Using the molecular dynamics method, self-diffusion in liquid alloys of Ni-Al and Ti-Al systems, as well as in pure metals Al, Ni, and Ti, has been studied depending on the concentration of the components. For the considered systems, activation energy and preexponential factor in the corresponding Arrhenius equation are calculated separately for atoms of different types. Good agreement of diffusion characteristics with experimental data was obtained for pure metal melts, which indicates the physical realism of the used molecular dynamics model and EAM potentials.

In addition to pure metals, three component ratios were considered for each system: $A_{75}B_{25}$, $A_{50}B_{50}$ and $A_{25}B_{75}$. According to the data obtained, the activation energy of diffusion substantially depends on the concentration of the components and has a maximum for Ni-Al system at the ratio of the components $Ni_{75}Al_{25}$, for Ti-Al system — at the ratio $Ti_{50}Al_{50}$. For the indicated ratios, the depths of potential wells in which the atoms are located in melts are largest, which is reflected in the height of the energy barrier and, accordingly, the activation energy of self-diffusion. No significant predominance of diffusion of one or another component was observed for all the mixture compositions considered — the diffusion characteristics for atoms of different types turned out to be close under the same conditions.

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