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Molecular dynamics simulations on local structure and diffusion in liquid $\text{Ti}_x\text{Al}_{1-x}$ alloys

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ABSTRACT

The microscopic structure and dynamics of liquid $\text{Ti}_x\text{Al}_{1-x}$ alloys together with pure liquid Ti and Al metals were investigated by means of molecular dynamics simulations. This work gives the structural properties, including pair-correlation function, bond-angle distribution function, HA and Voronoi indices, and their composition dependence. The dynamical properties have also been studied. The calculated pair-correlation function, bond-angle distribution function, and HA and Voronoi indices suggest that the stoichiometric composition $\text{Ti}_{0.75}\text{Al}_{0.25}$ exhibits a different local structure order compared with other concentrations, which help us understand the appearance of the minimum diffusion coefficient at this composition. These results indicate that the mobility of atoms strongly depends on their atomic local structure.

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1. Introduction

Ti–Al alloys are attractive for a broad range of applications to aerospace and automobile engines due to their high strength, high melting temperature, desirable oxidation and creep resistances, combined with low density [1–3]. As is well known, short-range order in liquid is of great importance to understand crystallization and glass formation as well as properties of the liquid itself. The icosahedral short-range order has been found to develop in amorphous alloys by simulations and experiments. A number of experiments and molecular dynamics simulations have been studied including the transition from amorphous structure to crystal structure, associated with the variations in the internal energy and atomic structure [3–8], though recent molecular dynamics simulations studies suggest that the modes are closely related to the local atomic structure [4,5]. For example, Pei et al. [5] reported that amorphous $\text{Ti}_x\text{Al}_{1-x}$ has the strongest crystallization ability at $x=0.25$. Han et al. [4] calculated the density and specific heat of liquid Ti–Al alloys at temperatures above and below the melting temperature in a wide composition range using molecular dynamics simulations. They found that both the density and specific heat show highly nonideal behaviors, indicating that the Neumann–Kopp rule does not apply. However, the local structure and diffusion in liquid $\text{Ti}_x\text{Al}_{1-x}$ alloys are still far from being understood completely.

In this paper, with the embedded atom method (EAM) potential for the Ti–Al system, we carried out molecular dynamics simulations

to study the structural change of liquid $\text{Ti}_x\text{Al}_{1-x}$. We calculated the pair-correlation distribution, bond-angle distribution, and HA and Voronoi indices, in the hope of theoretically obtaining some detailed microscopic structural information on liquid Ti–Al system. For comparison, we have studied the structural properties of pure liquid Ti and Al. In order to investigate the correlation between local atomic structure and the dynamical properties in the system, we have also investigated the diffusion behavior.

2. Computational methods

We have performed molecular dynamics (MD) simulation using the LAMMPS code [9,10]. The EAM potential [11,12] was used in our simulations to consider the many-body effect due to metallic bonding. We adopt the EAM potential for Ti–Al alloy that was recently developed by Zope and Mishin [13] by fitting to a large database of both experimental and *ab initio* data. The NPT (constant pressure and temperature) ensemble was used and controlled with the Nose–Hoover algorithm. The MD simulations were performed on a three-dimensional super-cubic cell containing 4000 atoms under periodic boundary conditions. The system was melted and equilibrated at the temperature 2200 K for 350 ps under the pressure of 0 Pa, then cooled down to 2000 K and run for 50 ps to guarantee an equilibrium liquid state. A time step of 2 fs was used.

3. Results and discussion

The pair-correlation function $g(r)$ is an important physical quantity because various properties of liquid materials can be

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estimated from the pair-correction function when coupled with an appropriate theory. Fig. 1(a) shows the total pair-correlation functions of five different concentrations together with pure liquid Al and Ti at temperature 2000 K. Apparently, there are two peaks in the pair-correlation functions $g(r)$ for liquid Ti_xAl_{1-x} ($x=0.0, 0.1, 0.25, 0.5, 0.75, 0.9, 1.0$). With increasing Ti concentration, the position of the first peak is almost unchanged. However, as can be seen from Fig. 1(b), the height of the first peak increases and then decreases with increasing Ti concentration. The peak of the height of the first peak curve is found at the composition of Ti-75 at%Al, which indicates an increasing degree short-range order in this composition.

The bond-angle distribution function $g_3(\theta)$ is one type of three-body distribution function. The angle is formed by a pair of vectors drawn from a reference atom to any other two atoms within a sphere of cutoff radius r_{cutoff} . To gain further insight into the structural change with composition of liquid Ti_xAl_{1-x} we calculated the total bond-angle distribution functions by $\sin \theta$ with the cutoff radii of 3.8 Å, which corresponds to the first minimum in the pair-correlation function. Fig. 2(a) shows the bond-angle distribution at different compositions of liquid Ti_xAl_{1-x} together with pure liquid Al

and Ti. It can be found that the bond-angle distribution function shows two peaks. The first peak position is around 54° and almost invariable with changing Ti concentration. The second peak is located around 108° and its position is also almost invariable with the variation of composition. It is well known that when the interatomic interaction is isotropic and the atoms are packed in a closed-packed form the $g_3(\theta)$ should show peaks around 60° and 120° . Here the 54° peak indicates a feature of the typical simple liquid structure. But the height of the first peak increases with the increase of Ti concentration, arrives at the maximum value at $x=0.75$ and then decreases (see Fig. 2(b)). This indicates that close-packed structure of atoms in liquid Ti_xAl_{1-x} becomes more closed-packed at $x=0.75$.

To obtain a three-dimensional description of the local atomic configuration of liquid Ti_xAl_{1-x} , we use the common-neighbor analysis by HA index [14]. In this technique, pairs of atoms have been classified by the relationship among their neighbors into four indices of integer. The first one indicates whether the pair of atoms is closer than a specified cutoff distance, chosen at the first minimum of $g(r)$. The first integer is 1 if the pair is bonded and 2 otherwise, the second integer represents the number of neighbors shared by the pair atoms, the third integer represents the number of bonds among the

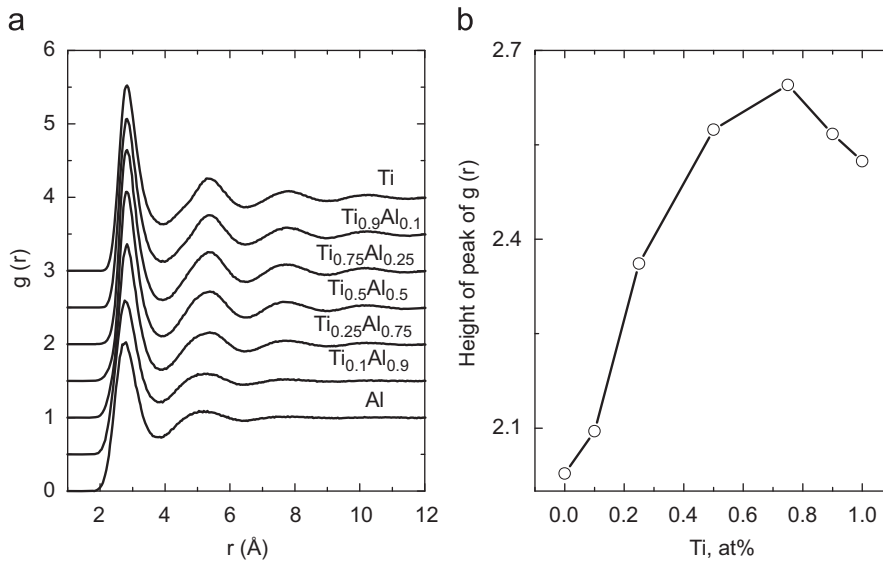


Fig. 1. Pair-correlation function of liquid Ti_xAl_{1-x} at the temperature 2000 K: (a) total pair-correlation function and (b) Al concentration-dependent height of the first peak in $g(r)$ of the simulated Ti_xAl_{1-x} .

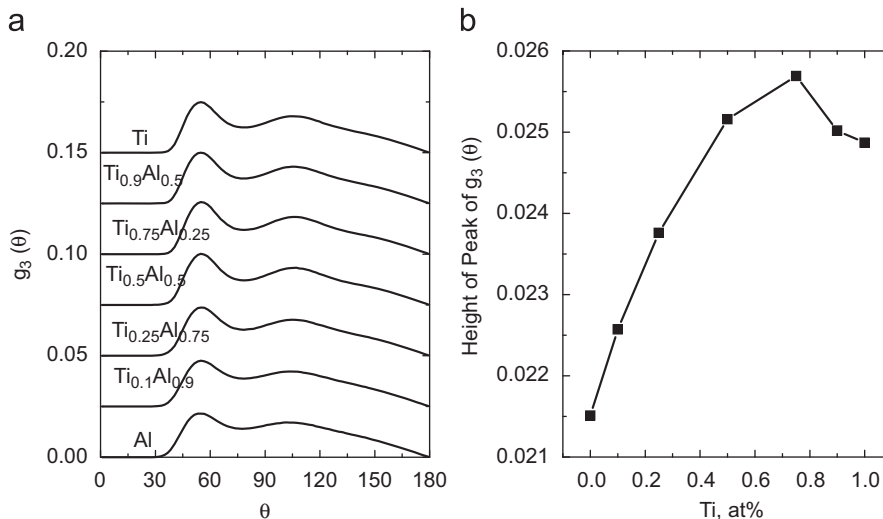


Fig. 2. (a) Bond-angle distribution function of liquid Ti_xAl_{1-x} at the temperature 2000 K and (b) Ti concentration-dependent height of the first peak in $g_3(r)$ of the simulated Ti_xAl_{1-x} .

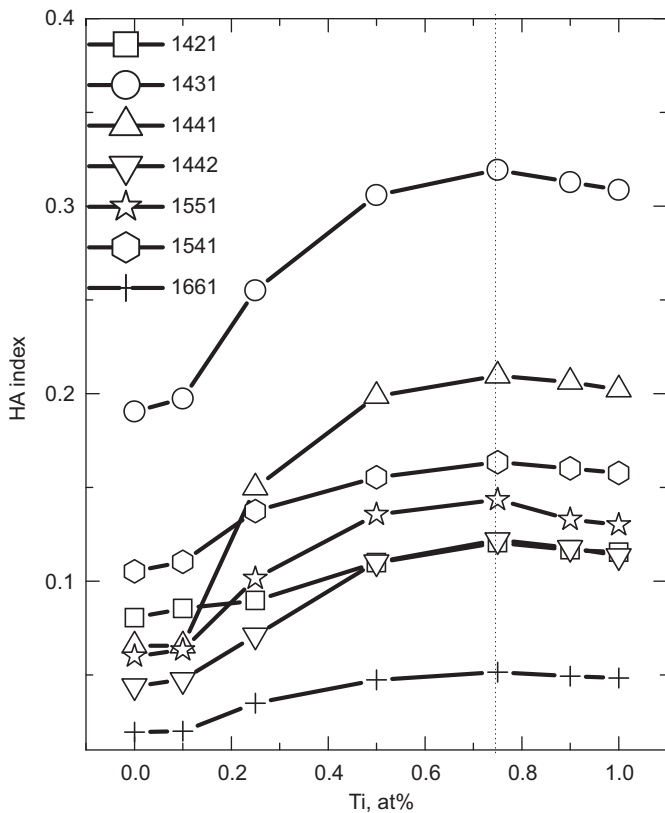


Fig. 3. Relative number of those main bonded pairs as a function of Ti concentration.

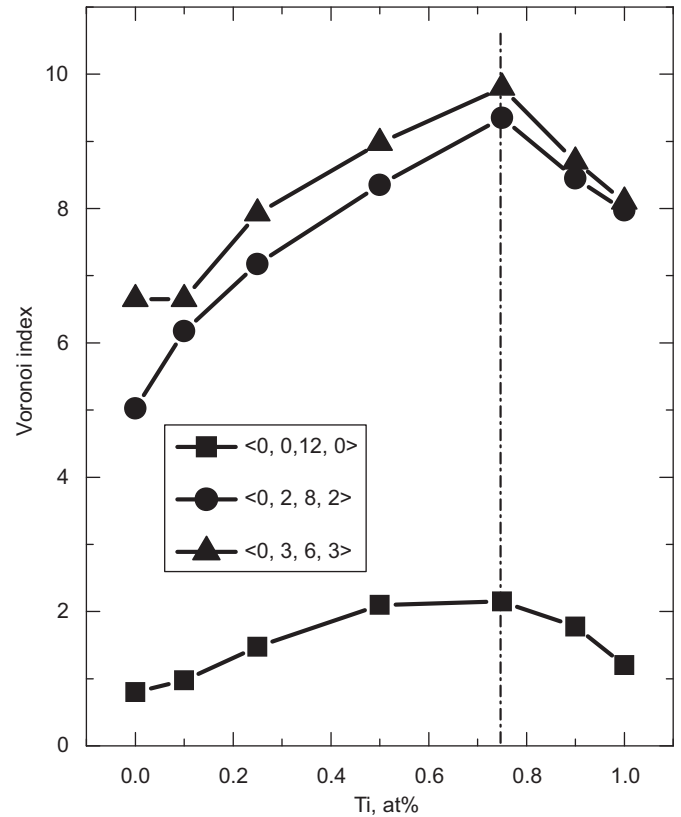


Fig. 4. Fraction of domination Voronoi polyhedral at various x .

shared neighbors and the fourth integer is used to distinguish the pair atoms when the former three integers are not sufficient. Counting all kinds of types of atom pairs show that each of the various phases of bulk system has its own signature that characterizes its local structure. The 1421 pair represents the fcc-like local structure, the 1422 pair characterizes the hcp-like local structure, the 1441 and 1661 pairs characterize the bcc-like local structure, the 1551 pair characterizes the icosahedral short-range order, and the 1541 and 1431 pairs characterize the defect and disorder icosahedral local structure, respectively. Fig. 3 shows the results of some HA indices as a function of Ti concentration. We observe most of the defect and disorder icosahedral local structure (the 1541 and 1431 pairs) and the icosahedral short-range order (the 1551 pair) at different compositions of liquid Ti_xAl_{1-x} together with pure liquid Al and Ti. In addition, there exist the 1421, 1441, 1442 and 1661 pairs. It is obvious that these indices increase with the increase of Ti concentration, arrive at the maximum value at $x=0.75$ and then decrease. It implies that the short-range order is the strongest in this composition.

To further characterize the geometric feature of the atomic configuration, we explore the local atomic packing of the simulated liquid configuration in virtue of the Voronoi tessellation method [15,16]. The Voronoi index $\langle n_3, n_4, n_5, \dots \rangle$ designates and differentiates the types of the coordinate polyhedron, where n denotes the number of i -edged faces of the Voronoi polyhedron. The total number of faces of the Voronoi polyhedron equals to the coordination number (CN) of the central atom. The local ordering is found to strongly depend on the Ti concentration, in terms of the dominant types of Voronoi polyhedra. The fractions of icosahedra (Voronoi index $\langle 0,0,12,0 \rangle$) and the distorted icosahedra ($\langle 0,2,8,2 \rangle$ and $\langle 0,3,6,3 \rangle$) are shown in Fig. 4. One can see that the fractions of icosahedra (Voronoi index $\langle 0,0,12,0 \rangle$) and the distorted icosahedra ($\langle 0,2,8,2 \rangle$ and $\langle 0,3,6,3 \rangle$) first increase, arrive at the maximum value at $x=0.75$

and then decrease. It indicates that ordering is the most pronounced in liquid $Ti_{0.75}Al_{0.25}$ alloys, in full agreement with the previous HA index.

The information of microscopic atomic motion can also be obtained. The diffusion behavior of $Ti_{1-x}Al_x$ has been studied by calculating the time-dependent mean-square displacement (MSD). MSD is defined as $\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N \langle |r_i(t) - r_i(0)|^2 \rangle$, where $r_i(t)$ is atomic position of atom i at time t and $\langle \rangle$ represents the thermal average. As is well known, in liquid state, slope is proportional to the diffusion coefficient (D) according to the so-called Einstein relationship, $\langle \Delta r(t)^2 \rangle \rightarrow 6Dt + C$, where C is a constant. Fig. 5(a) shows the typical behavior of MSD versus time t in liquid state. MSD always increases with time, implying that atomic diffusivity in the $Ti_{0.75}Al_{0.25}$ alloy is slower. The reduced atomic diffusivity in Ti_xAl_{1-x} liquid alloys would retard its local atomic rearrangements. To show the effect on atomic diffusivity more clearly, we plot the diffusion coefficient (D) as a function of Ti concentration in Fig. 5(b). It is obvious that the diffusion coefficient (D) decreases and then increases. The minimum is found at the composition of Ti-75%Al. This suggests that the motion of atoms is the slowest in this case. From the above results of local cluster structures analyzed by the HA index and Voronoi tessellation methods, the lower atomic mobility in Ti-75%Al liquid alloy could be due to the high concentrations of the icosahedra and distorted icosahedra clusters.

4. Conclusions

In summary, based on molecular dynamics simulations, we have investigated the pair-correlation functions, the bond-angle distribution functions, HA and Voronoi indices, and the mean-square displacements on liquid Ti_xAl_{1-x} alloys together with pure

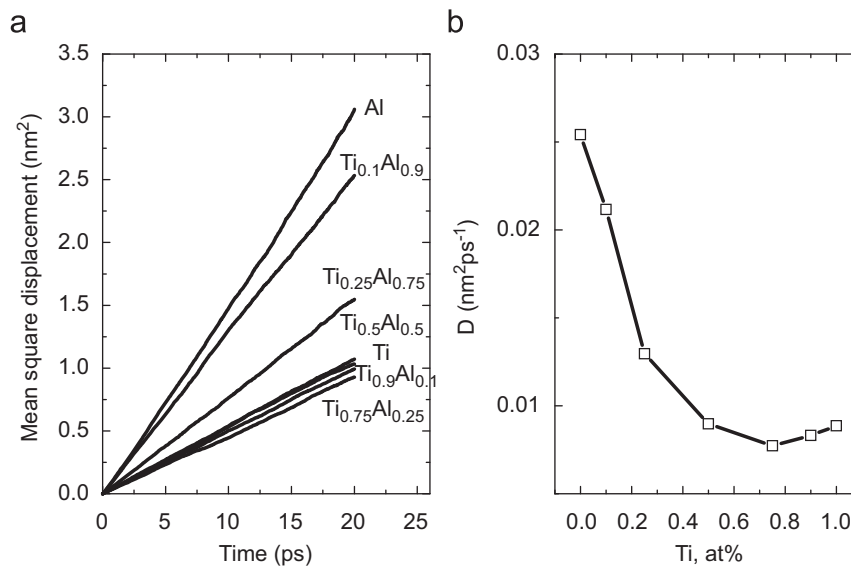


Fig. 5. (a) Variation of the mean-square displacement (MSD) with time t and (b) the diffusion coefficient D as a function of Ti concentration.

liquid Ti and Al metals. The calculated pair-correlation function, bond-angle distribution function, HA and Voronoi indices show that the stoichiometric composition Ti_{0.75}Al_{0.25} exhibits a different local structural order compared with other concentrations, which help us to understand the appearance of the minimum diffusion coefficient at this composition. From the analysis of MSD, we find that there is a strong correlation between the local structure and the mobility of the atom.

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