



The migration behavior of the fourth period transition metals in liquid Al: An *ab initio* molecular dynamics study



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ARTICLE INFO

Article history:

Received 17 August 2016

Received in revised form 22 December 2016

Accepted 1 January 2017

Available online 27 January 2017

Keywords:

AIMD

Local structure

Diffusion coefficient

ABSTRACT

The fourth period transition metals (FPTM) atoms were chosen as solute elements of Al binary alloy to be analyzed. The local structures around solute atoms, diffusion coefficients and the electronic densities of states of solute atoms in dilute Al-FPTM molten alloys were studied by *ab initio* molecular dynamics simulation. We find that the local structures around solute atoms from Sc to Zn varies dramatically which are corresponding to the various electronic densities of states of solute atoms. The different local structures lead to the various migration behaviors of solute atoms. The diffusivity of solute atoms are related to the packing density of local structure, while the local environment (1551 bonded pair) plays a more fatal role in determining the diffusion coefficient.

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1. Introduction

The fourth period transition metals (FPTMs) are the most common alloying elements in Al alloy [1]. The diffusion of these alloying elements in the melt plays an important role in the growth of the crystal [2,3]. The heterogeneity of microstructure and composition caused by the segregation of the alloying elements in the ingot also has the significant influence to the properties of alloy. Understanding the mechanism of the diffusion of alloying elements during the segregation process is the persistent pursuit for metallurgists. Eswaremoorthy's research [4] had revealed that during the solidification process of Al-Si-Cu-Mg alloy, the maximum concentration of Cu was at the point a small distance away from solid-liquid interface while the concentration of Si changed gradually. This phenomenon is mainly derived from the various migration behaviors of different solute elements. Many studies have shown that the dynamical properties and structural properties has a strong correlation. The research of Tanaka and co-workers [5–7] has revealed that there exist a correlation between the structural signatures and dynamical properties in colloidal liquid which determines the phase-transition. Jakse and Pasturel [8–14] also found that the diffusion coefficient and viscosity are influenced

by the local structures in liquid metal. They discovered the Stoke-Einstein relation breakdown in some Al-rich liquid alloys result from the effective radius of particles (R_{SE}) has changed by alloying effects which lead to various local structure around solute atoms. But the concentration in Refs. [6–10] is still a little high. Our previous work [15] had indicated that the diffusion coefficients of the solute atoms are closely related to the local structure around them in very dilute liquid alloys. In this study, for extending previous work, we investigated the local structure characters around all FPTMs solute atoms in the Al melt and researched the correlation between the variation of the diffusivity and changing of local structure of the FPTMs solute atoms, then tried to explain the influence law of diffusivity affected by local structure. However, the challenges of directly detecting molten structure have been beyond the capabilities of experimentalists. Characterization of the local structures around a certain atom in the melt is harder than one can imagine. *Ab initio* molecular dynamics (AIMD) make researching of the metallic melt at atomic level become possible. In previous work, it was proved that AIMD is powerful to research the melt characters [16–23] and widely accepted.

In the present work, to simplify the model, dilute binary alloys of Al-FPTMs are taken to analyze the local structure around solute atoms in Al melt. AIMD simulations of the molten dilute binary alloy were carried out from 943 K to 1273 K. The computational details are described in the following section, the results and discussions are presented in Section 3, and the conclusion is given in the last part.

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2. Computational method

All the simulation were based on the density functional theory (DFT) using the Vienna *Ab-initio* Simulation Package (VASP) in canonical NVT ensemble with Nosé-Hoover thermostat [16,17,24,25]. The plane-wave cutoff was set as 270 eV and exchange-correlation potentials were calculated using generalized gradient approximation (GGA) with a PW91 parameters [16,26–28]. The Brillouin zone of supercell was sampled by a single k -point (Γ).

The cubic box containing 108 atoms employ with the periodic boundary condition, containing 107 Al atoms and one solute atom randomly distributing in a cubic supercell and equilibrated at 943 K, 1073 K, 1173 K and 1273 K, respectively. The densities of the liquid Al alloy were obtained by some trial calculations to ensure the total pressure (the sum of the ideal gas part and external pressure) less than 200 MPa. The atomic densities of each system were calculated for temperatures from 943 K to 1273 K and shown in Table 1. Because including one atom in pure liquid Al does not modify its equilibrium density significantly, the experimental values of densities of pure Al are used as comparison for evaluating the validity of simulation. The results show the densities of our simulation at 943 K, 1073 K and 1173 K are about 4% less than the experimental values [29,30]. In this work, all simulations were run at each temperature for 10,000 calculation steps with the time step of 3 fs and the last 5000 configurations were used for the analysis of structural properties and dynamical properties. For suppressing the vibrational motion and thermal noise, the inherent structures [10,13,31] are employed to analyze the local ordering in using the Honeycutt and Andersen analysis. The way to get inherent structures is to extract 10 configurations regularly spaced in time among the last 5000 configurations, and then the steepest-descent energy-minimization procedure with the conjugate gradient method is carried out for each selected configurations.

The electronic density of states of molten Al-FPTMs is also calculated in this paper. This method has been successfully employed in researching of solid crystal structures [32–34] such as the moments of the density of states can provide a robust and transparent means for the characterization of crystal structures and local atomic configurations [35]. But there is no certain structure in liquid phase, So we try to use the electronic densities of states with various band filling to explain the affinity between Al and FPTM atoms qualitatively. In the calculation of electronic density of states, the k -point mesh was set as a $3 \times 3 \times 3$ Monkhorst–Pack and the plane-wave cutoff was set as 370 eV. For getting more accurate result, we calculated the DOS generated from ten configurations in last 3 ps. The electronic density of states of Al-TM systems is obtained by averaging over these DOS.

3. Result and discussion

3.1. Pair-correlation function analysis

The mainly used method for describing a liquid structure is pair-correlation function (PCF) [36,37] defined by Eq. (1).

$$g(r) = \frac{l^3}{N_A N_B} \left\langle \sum_{i=1}^{N_A} \frac{n_{iB}(r, \Delta r)}{4\pi r^2 \Delta r} \right\rangle \quad (1)$$

where l means the length of the supercell, N_A and N_B is the numbers of two kinds of atoms in the system, n_{iB} is the number of B atoms in the sphere shell with radius from r to $r + \Delta r$ referred to the atom i , the angle brackets represents the time average.

The PCFs of the systems of Al-FPTMs at 943 K, 1073 K, 1173 K and 1273 K are calculated. For clearly demonstrating the differences among these systems, only the PCFs at 1173 K are plotted in Fig. 1a, and the PCFs of different systems shifted away from each other by 1 unit along the x-axis are shown in Fig. 1b. The intensity of the primary peak can be used to characterize the atoms stacking configuration and quantitatively reflect the strength of affinity between two kinds of atoms [15,38], the position of the peak reflects the equilibrium bond length between the atoms and also indicates the size of the short-range order. The results in Fig. 1 shows that the position of the first peak and the first minimum of Fe-Al system is 2.45 Å and 3.40 Å (± 0.05 Å) (see Fig. 1a). The values of the position of the first peaks and the second peaks, as well as the first and second minima of Al-Co and Al-Ni systems are same as the ones of Al-Fe system. This result implies that the equilibrium bonding lengths of Al-Fe, Al-Co and Al-Ni are almost same, and the short-range orders related to these three elements have the same magnitude at geometric scale. Fig. 1a also presents the PCFs of Mn, Cr, Cu, Zn, Sc, V and Ti in Al melt. The position of first peaks of this column is at 2.52, 2.56, 2.63, 2.65, 2.90, 2.70, 2.78 Å (± 0.05 Å), respectively. The first minimums of PCFs of those systems are at 3.65, 3.70, 3.40, 3.75, 4.16, 3.90 and 4.15 Å (± 0.05 Å), respectively. The intensity of the first peak increases first and then decreases with the atomic number increasing of solute atoms as shown in Fig. 1b which illustrates a parabolic behavior. The intensity of Al-Fe is strongest in all systems which indicate the affinity between Fe and Al atoms is the strongest, i.e. the cluster around Fe atom should have the most compact and stable structure. Among Al-FPTM systems, the intensity of the first peak of $g_{Al-Zn}(r)$ system is the lowest, which reveals that the interaction between atoms Zn and Al is the weakest. Therefore, the cluster around Zn has the loosest structure in Al melt. The flattened second peak means the adjacent structure away from cutting distance around Zn is quite loose. The loose local structure of Zn atom mainly caused by the particular peripheral electron configuration of Zn, Zn atom has four electric shells; ten electrons occupy orbit 3d and two for 4s. Compared with other FPTMs elements, the charge transfer between atoms Zn and Al is more difficult. The PCFs of Cd and Hg which possess the similar peripheral electron configuration with Zn are also investigated. PCFs of Cd, Zn and Hg is analogous to each other, shows the direct contribution from outer electron configuration to the loose structure.

The partial coordination number N_{AB} of each system was calculated from PCF with Eq. (2) [39,40] and listed in Table 2.

$$N_{AB} = \int_0^{r_{cut}} 4\pi r^2 \rho_B g_{AB}(r) dr \quad (2)$$

where ρ_B is the atomic concentration of element B, r_{cut} is the cut-off distance with the value of the first minimum in each system.

Table 1
Atomic densities (atom/Å³) of each system from 943 K to 1273 K.

System	Al ₁₀₇ Ni	Al ₁₀₇ Co	Al ₁₀₇ Fe	Al ₁₀₇ Cu	Al ₁₀₇ Zn	Al ₁₀₇ Sc	Al ₁₀₇ Mn	Al ₁₀₇ Cr	Al ₁₀₇ V	Al ₁₀₇ Ti
AD _{943K}	0.0509	0.0512	0.0514	0.0508	0.0507	0.0514	0.0510	0.0510	0.0511	0.0508
AD _{1073K}	0.0500	0.0502	0.0508	0.0500	0.0498	0.0507	0.0505	0.0500	0.0503	0.0505
AD _{1173K}	0.0494	0.0494	0.0500	0.0493	0.0493	0.0497	0.0496	0.0493	0.0496	0.0494
AD _{1273K}	0.0485	0.0487	0.0490	0.0487	0.0488	0.0490	0.0486	0.0488	0.0489	0.0486

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