Ab Initio MOLECULAR DYNAMIC SIMULATION OF Zn-Al-Fe ALLOYS

H. Zhang [a,b,c], J. Zhao [a,b,c], Z. Pu [a,c,c], Y. Li [a,b,c,*], B.Q. Xu [a,b,c], B. Yang [a,b,c]

[a]* National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, PR China

[b] Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, PR China

[c] The State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming, PR China

Abstract

This paper presents the measurement of the Ab initio molecular dynamics of a Zn-Al-Fe alloy system. The structural and electronic properties of the Zn-Al-Fe alloy at different temperatures are simulated, and the partial density of states, radial distribution function, coordination number, mean square displacement, and diffusion coefficient are obtained. It provides a theoretical analysis of the vacuum separation of Zn-Al-Fe alloys. The simulation results show that when the temperature was 1073 K, the disorder degree of the system was the largest, the diffusion coefficient was 1.29（$10^{-8} m^2 s^{-1}$), and the coordination number was 9.48. It means that the Zn-Al-Fe alloy can be separated into its constituent metals easily by vacuum distillation, and that the optimum temperature to achieve this is 1073 K.

Keywords: Zn-Al-Fe alloys; Vacuum distillation; Ab initio molecular dynamics

1. Introduction

Aluminum alloys have been extensively applied in various fields, owing to their superior performance [1-2]. Among the aluminum alloys, the Zn-Al-Fe alloy is the most widely used alloy [3], and has become the focus of many researchers [4-6]. For example, Zn-Al-Fe alloy is the main component of hot-dip galvanizing slag [7], which is the most convenient and effective solution for preventing steel corrosion. With the rapid development of the automobile industry, more and more steel companies and research institutes are pursuing research and development on hot galvanizing slag steel sheets. However, the wide range of applications of the Zn-Al-Fe alloy results in an increasing amount of alloy being wasted. If these metals are not recycled, it can lead to a huge waste of resources and cause serious pollution in the environment. Therefore, the recovery and separation of useful metals from Zn-Al-Fe alloys scrap can not only bring significant economic benefits but also minimize the negative impacts on the environment.

At present, the methods for recovering valuable metals from the waste of Zn-Al-Fe alloy include the electrolytic method, vacuum distillation, Wurtz method, and chemical methods. Among them, vacuum distillation has the advantages of high metal recovery rate, low energy consumption, simple procedure, and is environment-friendly. However, the mechanism of vacuum distillation for the treatment of Zn-Al-Fe alloy has not been defined clearly yet.

The rapid developments in computer operation speed and the relevant theories of quantum chemistry have produced many novel calculation methods suitable for use in research on reaction dynamics and material sciences such as quantum chemistry, quantum dynamics simulation, *Ab initio* molecular dynamics (AIMD) simulation, etc. [8]. These calculation methods cover topics such as electronic structure, reaction kinetics, mass-transfer processes, and so on [9]. In the research on AIMD, computer simulation is often used for studying the dynamics of metallurgical reactions, as it helps avoid the difficult high-temperature experiments and complex multiphase reactions [10]. In this work, we present the use of AIMD for studying the structure and

interactions of Zn-Al-Fe alloys under vacuum conditions, which can provide a theoretical basis for the vacuum distillation of Zn-Al-Fe alloys.

2. *Ab initio* molecular dynamics

The potential energy of the system can be calculated using quantum mechanics, which is the basic concept of AIMD. The process of AIMD is as follows: first, the density functional theory (DFT) is used for calculating electronic structure and molecular properties, and then the molecular dynamics simulation is performed. The Lagrangian quantity of this method can be expressed as:

$$L = K - U = \frac{1}{2}\sum_{i=1}^{3N} m_i v_i^2 - E\left[\varphi\left(r_1, \cdots, r_{3N}\right)\right] \quad (1)$$

where φ $(r_1,…,r_{3N})$ represents a full set of Kohn–Sham wave functions of a single electron equation under the electronic ground states in the system. The Lagrangian quantity measure indicates that all calculations should be performed in sequence. First, the ground state energy is calculated by AIMD. Second, molecular dynamics simulation is performed and the position of the core is moved forward. The new ground state energy is calculated by AIMD. This calculation is repeated in this order. All methods for moving the position of the nucleus forward, along the track, are defined by classical mechanics. However, if the force that causes the displacement is obtained using DFT methods, these methods are called AIMD. AIMD can be used to calculate some electronic and structural properties of the system, which reflect certain parameters of the system.

2.2.1 Partial density of states (PDOS)

PDOS indicates the allowed number of electrons per unit of energy. It is the distribution of electrons in any energy range [11]. The atomic orbital is mainly divided in terms of energy. The image of PDOS can reflect the distribution of electrons in each orbit and the interactions between atoms. It can also reveal the information on the chemical bonds. PDOS can be regarded to be a reflection of the band structure, because it is intuitive [12]. The electronic PDOS for a given band n is as follows:

$$N_n(E) = \int \frac{d\vec{k}}{4\pi^3} \delta\left[\left(E - E_n(\vec{k})\right)\right] \quad (2)$$

where E is the energy and $\vec{k}$ is the energy band vector. The total DOS can be obtained by performing summation over all bands.

2.2.2 Radial distribution function (RDF) and coordination number

In statistical mechanics, the RDF g(r) in a system of particles (atoms, molecules, colloids, etc.), describes the variation of density as a function of the distance from a reference particle [13]. RDF can be expressed as:

$$g(r) = \frac{2V}{N^2}\left[\sum \delta\left(r - r_{ij}\right)\right] \quad (3)$$

where N is the number of atoms, V is the volume of the system, and r_{ij} is the distance between atoms i and j.

The structural characteristics of the alloy can also be described by the coordination number, which is the number of coordination atoms around the central atom in a compound. The coordination number can be obtained from the RDF. The coordination number of each atom can be expressed as:

$$N(r) = \frac{4\pi N}{V}\int_0^r r^2 g(r)d(r) \quad (4)$$

where r is the first minimum of the total $g(r)$ and N is the coordination number of the first coordination layer.

2.2.3 Mean square displacement (MSD) and diffusion coefficient

Diffusing atoms do not diffuse in a straight line. Instead, they pulsate irregularly between the crystal and the space gaps. However, the displacement will be offset, owing to the positive and negative atomic displacements [14]. MSD is the square of the total vector of the displacement. It can also represent the net displacement of an atom after many beats [15]. MSD can be expressed as:

$$\left[R_\alpha^2(t)\right] = \frac{1}{N_\alpha}\left[\sum_{i=1}^{N_\alpha}\left|R_{i\alpha}(t+\tau) - R_{i\alpha}(\tau)\right|^2\right] \quad (5)$$

where $R_{i\alpha}$ is the coordinate of the atom and α is an arbitrary origin of time. When the system is in the liquid state, the diffusion coefficient is one-sixth the gradient of the MSD. The diffusion coefficient can be expressed as:

$$\lim_{t\to\infty}\left[R_{i\alpha}^2(t)\right] = 6D_{ii}t + C \quad (6)$$

3. Computational methods

The Zn-Al-Fe alloy was simulated using Material Studio, which was developed by the Cambridge Sequential Total Energy Package (CASTEP). CASTEP Modular was used to calculate the alloy structure and electronic properties of the Zn-Al-Fe alloy, based on the DFT within the generalized gradient approximation (GGA) [16], using the Perdew–Burke–Ernzerhof (PBE) functional [17-18]. The composition of the Zn-Al-Fe alloy was Al-15.67wt%Zn-6.69wt%Fe. The mass ratio was converted to a molar ratio of Al-7.9969 at% Zn-3.9968 at% Fe. Thus, the total number of atoms in the cell was 108—96 aluminum atoms, eight zinc atoms, and four iron atoms. The K-points were set as $3 \times 3 \times 3$. The energy cutoff was set as 300 eV. The condition for convergence was: the energy change should be less than 2×10^{-5} eV/atom and the displacement change should be less than 0.0002 Å. The exchange gradient of electrons was corrected using the PBE functional. The interactions of electrons were described using Ultrasoft Pseudopotential. Computer calculations applied the canonical ensemble with the Nosé–Hoover thermostat for temperature control and Andersen for pressure control [19-20].

In this work, the Zn-Al-Fe system was built in Material Studio, based on the molar compositions of the raw materials. The lattice parameter was a=b=c=4.056 Å, $\alpha=\beta=\gamma=90°$. The atoms were randomly dispersed in a simple-cubic supercell, as the initial structural. The initial structure was shown in Figure 1. The total simulation time was set as 5 ps with a time step of 1 fs. The NPT ensemble was used for temperatures of 893 K, 993 K, 1073 K, and 1173 K and a system pressure of 5 Pa, during the simulation.
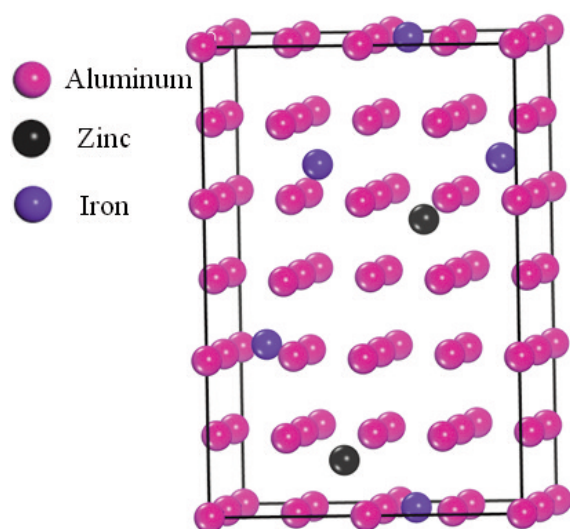

Figure 1. *Initial structural of Zn-Al-Fe alloys*

4. Results and discussion
4.1 RDF and coordination number

Owing to the small number of atoms in the system, the RDF *gZn-Zn(r)* of zinc atom and the RDF *gFe-Fe(r)* of iron atom were unclear. Fig.2 shows the *gZn-Al-Fe(r)* and *gAl-Al(r)* systems in the Zn-Al-Fe alloy, at different temperatures. *gZn-Al-Fe(r)* of is the total RDF, which can also be expressed as gtotal(r). In Fig.2 (a), the short distance is always equal to zero in the RDF, because there is strong repulsion between atoms. With increase in *r*, the subsequent small peaks weaken gradually, which indicates the important characteristics of short-range order and long-range disorder, in the alloy melt. The results show the similarity of liquid and solid in the first nearest neighbor. Obviously, with the increase in temperature, the peak value of the first peak decreases from 2.73 Å (873 K) to 2.49 Å (1073 K and 1173 K), and the peak width becomes narrower. The results show that the short-range order of Zn-Al-Fe alloy melt decreases with the increase in temperature. At the same time, many small peaks between the highest and second-
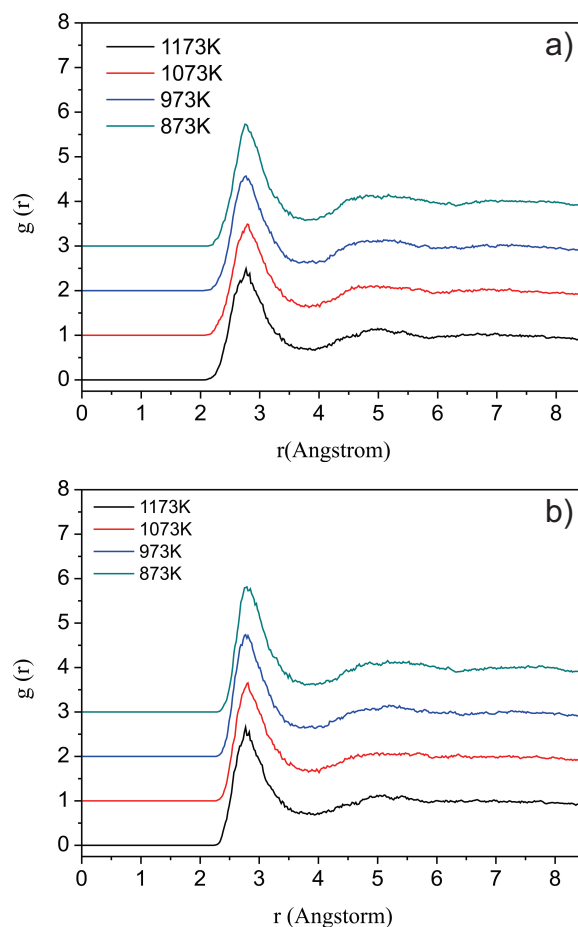

Figure 2. *Radial distribution function of Zn-Al-Fe system: (a) gZn-Al-Fe (r); (b) gAl-Al(r)*

highest peaks disappear gradually with the increase in temperature. It is shown that the thermal motion of molecules in the system increases with the increase in temperature. This indicates that the average distance between atoms is slightly larger than that at 873K in real space, which leads to a decrease in the degree of order.

$g_{Al-Al(r)}$ is similar to $g_{Zn-Al-Fe(r)}$. The coordination numbers can be calculated using Eq. (4), and are shown in Fig. 3. The coordination numbers are reduced from 8.94 to 8.54 and 9.48 to 9.25 for $g_{Al-Al(r)}$ and $g_{Zn-Al-Fe(r)}$, respectively, for a temperature change from 873 K to 1173 K, which shows that the

interactions between particles weaken with the increase in temperature. As the temperature changes from 873 K to 1173 K, the interactions between the particles decrease as the temperature increases. From the numerical point of view, the reduction in the total coordination number in the system is small, which shows that the interactions between particles in the alloy remain at a relatively stable level.

4.2 MSD and diffusion coefficient

Fig.4 shows the total MSD in the Zn-Al-Fe alloy at different temperatures. The MSD increases with the increase in temperature in the Zn-Al-Fe alloy; the maximum MSD is observed at 1073 K. When the temperature increases from 873 K to 973 K, the MSD in the system increases continuously, but the increment is small, and is always at a low level. When the temperature reaches 1073 K, the MSD in the system is the largest and the growth rate increases significantly; however, the MSD at 1173 K is lower. The results obtained through molecular dynamics simulations show that the phase transformation occurs near 1073 K in this Zn-Al-Fe alloy; i.e., the boiling point of this Zn-Al-Fe alloy is near 1073 K. This is in agreement with the phase diagram analysis results, in which the alloy has been produced in the g phase at 1093 K in the phase diagram. The numerical value of MSD in the system will be changed greatly at 1073K.
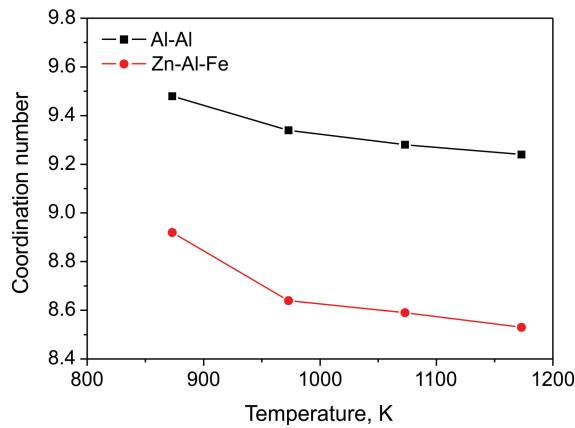
The MSD of aluminum, zinc, and iron are shown

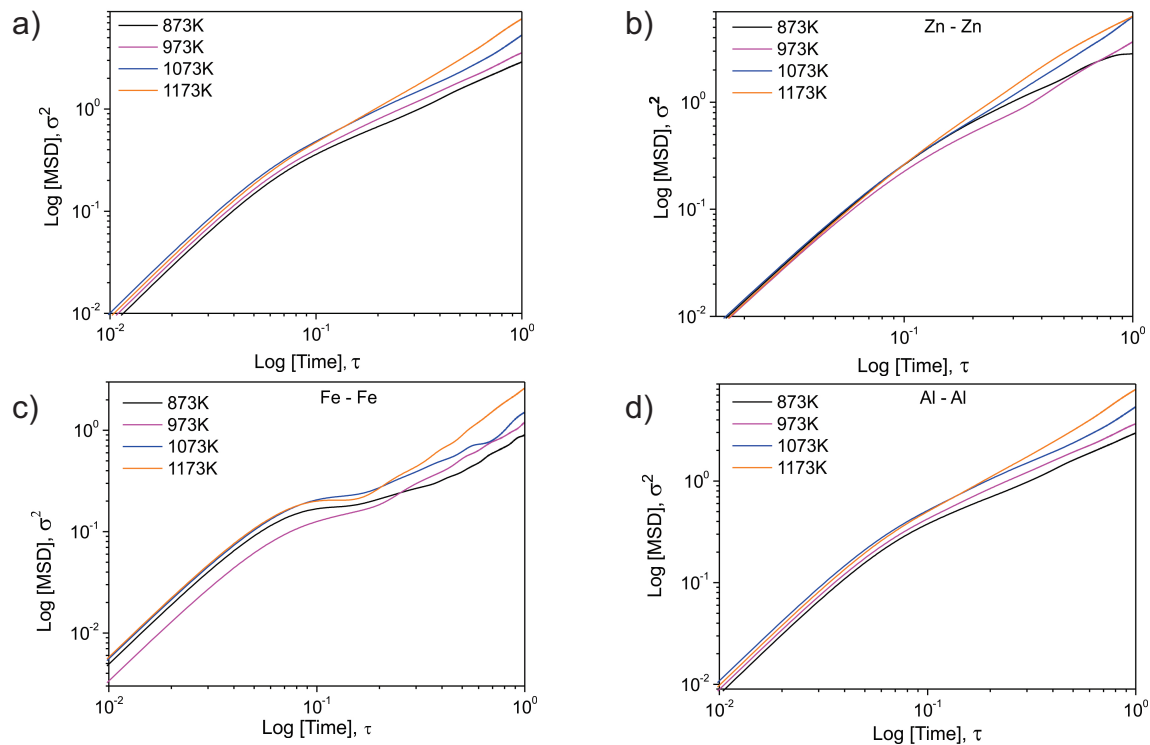**Figure 3.** *Coordination number of $g_{Zn-Al-Fe(r)}$ and $g_{Al-Al(r)}$ systems*

Figure 4. *Mean square displacement (MSD) of Zn-Al-Fe system: (a) Total MSD; (b) Zn–Zn; (c) Fe–Fe; (d) Al–Al*

in Fig.4. The MSD of aluminum atom is similar to the total MSD. Although the change trends for the MSDs of zinc and iron are different from that of the total MSD, the maximum MSDs are observed at 1073 K. The diffusion coefficients calculated using the MSD are shown in Table 1. The variations in the diffusion coefficient are consistent with MSD.

Table 1. *Diffusion coefficients of particles at different temperatures ($10^{-8} m^2 s^{-1}$)*

T/K	873	973	1073	1173
D	0.48	0.58	1.29	0.84
D_{Al-Al}	0.49	0.6	1.34	0.85
D_{Zn-Zn}	0.53	0.63	1.13	1.05
D_{Fe-Fe}	0.19	0.14	0.44	0.22

4.3 Partial density of state (PDOS)

As shown in Fig.5 (a), the total PDOS in the system is smoother and the states become narrower from -10.17 eV ~ 2.18 eV to -9.93 eV ~ 2.16 eV. This is due to the enhanced thermal motion and relatively uniform electron distribution between the band levels. The total PDOS is mainly composed of two peaks, which are contributed by the 3s and 3p orbital electrons from aluminum and 3d orbital electrons from zinc,

respectively. The PDOS at the Fermi level is mainly provided by the 3s and 3p orbital electrons from aluminum, and the PDOS at -7.5 eV is provided by the 3d orbital electron from zinc, which leads to the nearest neighbor distance for zinc atom, aluminum atom and iron atom in the alloy being larger than the sum of their metallic radii. This shows that the interactions between the 3p orbital electrons from aluminum and 3d orbital electrons from zinc and iron are weak. The clusters of these atoms are not obvious or the cluster stability is low. As a result, when the alloy melts under vacuum, zinc can easily evaporate from the alloy without any bond with a larger saturated vapor.

As shown in Fig.5 (b), (c), and (d), the change trends for zinc, aluminum, and iron are similar to that of the total PDOS. The density contributed by the 3p orbital electrons from aluminum mainly focus on a part of the state near the Fermi level and even a part of the density is on the right of EF; however, the 3d orbital electron from zinc is at -7.3 eV, which is on the left of EF, and the 3d orbital electron from iron is at -1 eV, which is again on the left of EF. Meanwhile, there are two peaks on both sides of the Fermi level in the figure of PDOS, and the PDOS between the two peaks is not zero, which state is called pseudogap. Pseudogap reflects the strength of the covalent bond of the system. The wider the pseudogap, the stronger the covalent bond will be. With the increase in temperature, the width and depth of
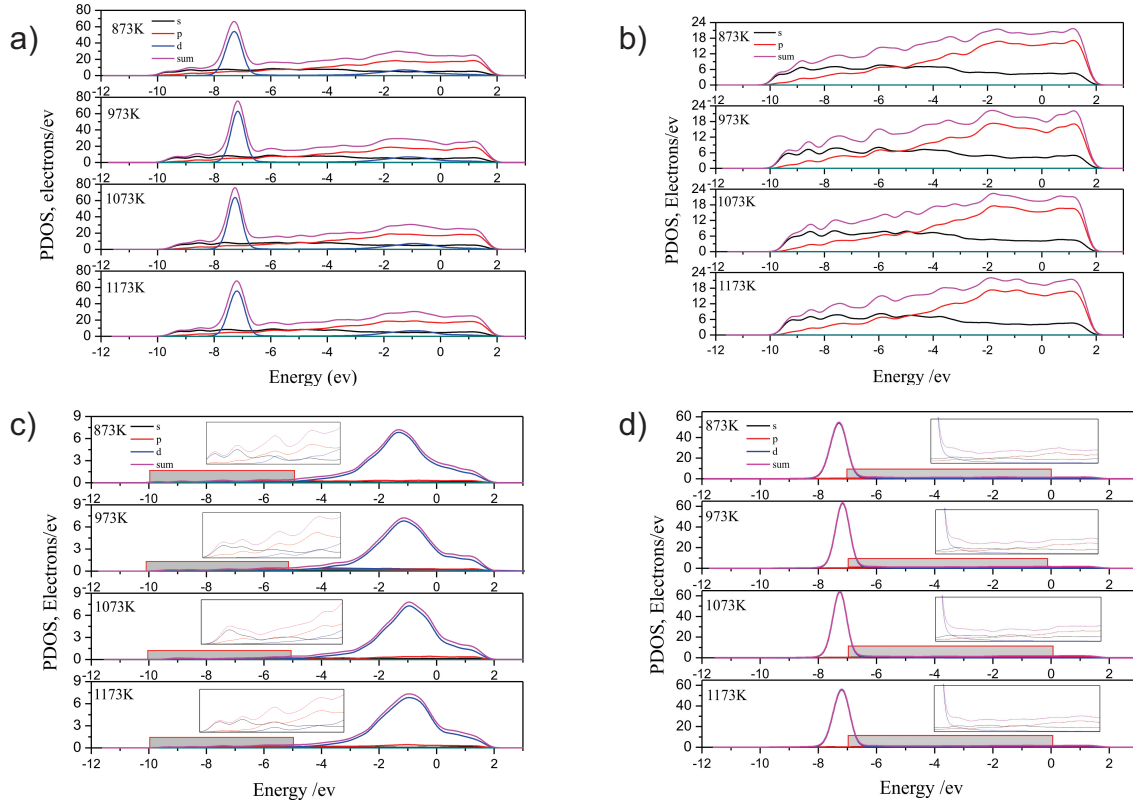

Figure 5. *Partial density of states (PDOS) of Zn-Al-Fe system: (a) Total PDOS; (b) Fe-Fe; (c) Al-Al; (d) Zn-Zn*

the pseudogap reduce. However, combining with the MSD and RDF analyses shows that, when the temperature is 1073 K, these phenomena are the most obvious. The diffusion of atoms in the system is faster and the disorder degree of the system is higher at 1073 K, among the four temperatures.

5. Conclusion

AIMD for the Zn-Al-Fe system were analyzed. The author simulated and calculated the PDOSs, RDFs, coordination numbers, MSDs, and diffusion coefficients of the Zn-Al-Fe system. The results showed that, with the increase in temperature, the disorder degree of the melt increased, the diffusion coefficient increased, and the coordination number decreased. However, when the temperature was 1073 K, the disorder degree of the system was the largest, the diffusion coefficient was 1.29 （$10^{-8}m^2s^{-1}$), and the coordination number was 9.48. AIMD can used to forecast the best experimental conditions for vacuum distillation. It provides an efficient and convenient method to guide vacuum metallurgy.

References

[1] X.-H. Yuan, M.-Y. He, S.-M. Wang, X. Zhao, X.-J. Zhao. Yunnan Metall., 36 (1) (2007) 32-35.

[2] S. Cui, R. Mishra, I.-H. Jung, J. Min. Metall. Sect. B Metall., 54 (2018) 119-131.

[3] V. Raghavan, J. Phase Equilib. Diffus., 29 (5) (2008) 431-433.

[4] Z. Pu, J. Han, Y. Li, B. Yang, Y. Dai, J. Mater. Trans., 59 (3) (2018) 443-449.

[5] C.-H. Bae, J.-H. Lee, C.-S. Han, Korean J. Mater. Res., 20 (1) (2010) 37-41.

[6] D. Beke, I. Gödeny, F. J. Kedves, G. Groma, Acta Metall., 25 (5) (1977) 539-550.

[7] Y. Yang, Doctoral dissertation, Northeastern University (2010).

[8] R. Car, M. Parrinello, Phys. Rev. Lett., 55 (22) (1985) 2471

[9] C. Zhang, Y. Wei, C. Zhu, Chem. Phys. Lett., 408 (4) (2005) 348-353.

[10] Y. Senda, F. Shimojo, K. Hoshino, J. Phys. Condens. Matter, 11 (28) (1999) 5387.

[11] F. Knider, J. Hugel, A.V. Postnikov, J. Phys. Condens. Matter, 19 (19) (2007)196105.

[12] W. Jank, J. Hafner, Phys. Rev. B 41 (3) (1990) 1497-1515.

[13] Y. N. Wu, G. Zhao, C. S. Liu, Z. G. Zhu, J. Phys. Condens. Matter, 18 (19) (2006) 4471-4480.

[14] P. A. Egelstaff: An introduction to the liquid state, Clarendon, New York, 1992, p. 240.

[15] T.K. Gu, J.Y. Qin, X.F. Bian, C.Y. Xu, Y.H. Qi, Phys. Rev. B, 70 (2004) 245214 .

[16] J. P. Perdew, W. Yue, Phys. Rev. B Condens. Matter, 33(12) (1986) 8800-8802.

[17] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 80 (1998) 891.

[18] Y. Zhang, W. Yang, Phys. Rev. Lett., 80 (1998) 890.

[19] S. Nosé, J. Chem. Phys., 81(1) (1984) 511-519.

[20] S. Nosé, Mol. Phys., 52(2) (1984) 255-268.

Ab initio SIMULACIJA MOLEKULARNE DINAMIKE Zn-Al-Fe LEGURA

H. Zhang [a,b,c], J. Zhao [a,b,c], Z. Pu [a,c,c], Y. Li [a,b,c,*], B.Q. Xu [a,b,c], B. Yang [a,b,c]

[a]* Nacionalna inženjerska laboratorija za vakuumsku metalurgiju, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, Kina

[b] Fakultet za metalurško i energetsko inženjerstvo, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, Kina

[c] Glavna državna laboratorija za čisto iskorišćavanje resursa kompleksnih obojenih metala, Univerzitet za nauku i tehnologiju u Kunmingu, Kunming, Kina

Apstrakt

U ovom radu predstavljeno je merenje Ab initio molekularne dinamike Zn-Al-Fe sistema legura. Izvršena je simulacija strukturalnih i elektronskih osobina Zn-Al-Fe legure pri različitim temperaturama, i dobijeni su parcijalna gustina stanja, radijalna distribucijska funkcija, koordinacioni broj, srednje kvadratno odstupanje, kao i koeficijent difuzije. Ovaj rad pruža teoretsku analizu vakuumske separacije Zn-Al-Fe legura. Rezultati simulacije pokazuju da je pri temperaturi od 1073 K poremećaj sistema bio najveći, koeficijent difuzije bio je 1.29 （$10^{-8}m^2s^{-1}$), a koordinacioni broj je bio 9.48. To znači da Zn-Al-Fe legura može biti lako separirana na konstituivne metale vakuumskom destilacijom, a da bi se to postiglo optimalna temperatura je 1073 K.

Ključne reči: Zn-Al-Fe legure; Vakuumska destilacija; Ab initio molekularna dinamika