

Study on Sn-Sb alloy by Ab-Initio Molecular Dynamic Simulation

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Abstract. Sn-Sb alloy was the secondary resources of tin and antimony in metal recovery process and massively exist in the smelting and refining of crude tin. Vacuum distillation can effectively separate and recycle tin. *Ab-initio* molecular dynamics can reveal the microscopic atomic motion and provide theoretical basis for the separation of Sn-Sb alloy. The author calculated the Radial distribution function (RDF), coordination number (CN), Mean square displacement (MSD), diffusion coefficient (DC) and structure factor of the Sn-Sb system. The results showed that the *Ab-initio* molecular dynamics simulation can forecast the best experimental conditions in vacuum distillation.

1. Introduction

Tin and antimony were widely used in the fields of information technology industry, biological industry, new material industry and so on with excellent physical and chemical properties [1-4]. But tin and antimony resources storage guarantee period worldwide was shorter, while the consumption of tin and antimony persistently high, simply rely on ore mining has been impossible, and vigorously develop renewable resources was one of the solutions of the contradiction between the shortage of mineral resources and consumption growth.

Sn-Sb alloy was the secondary resources of tin and antimony in metal recovery process. Also exist in the smelting and refining of crude tin [5]. Vacuum distillation was a new kind of field metallurgy method, which carried out in a closed container with the characteristics of high efficiency and clean [6]. It can effectively solve the problems such as long process, high energy consumption, low yield and poor economic benefit in traditional metallurgy method of separation of alloy. Vacuum distillation has been widely used in the separation of alloys and the refining of crude metals [7]. Kunming University of Science and Technology has been engaged in small scale, expanded and industrialized experiments of alloy separation for many years and achieved good results in those experiments [8-9]. However, there was less research work on theoretical basis and further work was needed.



In recent years, with the rapid growth of computer operation speed and the relevant theories, more and more calculation methods have been used in the research of reaction dynamics and material science such as quantum chemistry, quantum dynamics simulation, *Ab-initio* molecular dynamics(AIMD) simulation, etc [10]. These studied include electronic structure, reaction kinetics, mass transfer process and so on [11]. Manaa [12] simulated the nitromethane under compression (cell volume compressed to about 70% under the zero pressure initial value) and the initial decomposition reaction was the proton transfer process between molecules by using molecular dynamics method which based on density functional theory. Shu Kai [13] calculated the structures of the Sn_4As_3 and SnAs compounds in the plane-wave pseudopotential method which based on the DFT. In addition, computer simulation was becoming an important method to study the dynamics of metallurgical reaction due to the difficulty of high temperature experiment and the complexity of multiphase reaction [14]. Therefore, the author carried out the *Ab-initio* molecular dynamics with Sn-Sb alloy, in order to provide theoretical basis in separation of Sn-Sb alloy.

2. Computational Methods

In this paper, the author adopted Materials Studio, which develop by Cambridge Serial Total Energy Package code of Materials Studio. Adopting CASTEP Modular to calculate the alloy structure and electronic properties of Sn-Sb alloy which based on density functional theory within the generalized gradient approximation (GGA)^[15] using the Perdew Burke Ernzerhof (PBE) functional^[16-17]. Using Perdew, Burke, Ernzerhof to revise the exchange gradient and describing the interaction of electrons by Ultrasoft Pseudopotential. Computer calculation applied canonical ensemble with the Nosé-Hoover thermostat for temperature control and Andersen for pressure control [18-19].

In this work, the author accorded to the molar composition of raw materials to build the Sn-Sb system in Materials Studio. Disrupting these atoms randomly in the simple-cubic supercell as the initial configuration. Then, set as 5ps with a time step of 1fs and carried out NPT ensemble at the temperature of 1173K, 1273K, 1373K, 1473K, 1573K, 1673K and system pressure of 5pa during the simulation.

3. Results And Discussion

3.1. Radial distribution function (RDF) and coordination number (CN)

In statistical mechanics, the radial distribution describes how density varies as a function of distance from a reference particle. The coordination number can be obtained by radial distribution function, the coordination number of each atom can be expressed as:

$$N(r) = \frac{4\pi N}{V} \int_0^r r^2 g(r) dr \quad (1)$$

Where r was the first minimum of total $g(r)$, N was the coordination number of the first coordination layer.

Fig.1 showed the $g_{\text{Sn-Sb}}(r)$, $g_{\text{Sb-Sb}}(r)$ and $g_{\text{Sn-Sn}}(r)$ systems in Sn-Sb alloy at different temperatures. In Fig.1 (a), the short distance was always equal to zero in the radial distribution function, because there was a strong repulsion between atoms. With the increased of r , the subsequent small peaks gradually weaken, which showed the important characteristics of the short-range order and long-range disorder of the alloy melt. The results showed that the similarity of liquid and solid in the first nearest neighbor. Obviously, with the increase of temperature, the peak value of the first peak had little change, but the peak width became narrower, the results showed that the short-range order of Sn-Sb alloy melt decreases with the increase of temperature. At the same time, many small peaks between the highest peak and the second peak gradually disappear with the increase of temperature. It was shown that the thermal motion of molecules in the system increased with the increase of temperature,

and reflected that the average distance between atoms was slightly larger than that at low temperature in real space, which led the decrease of the order degree.

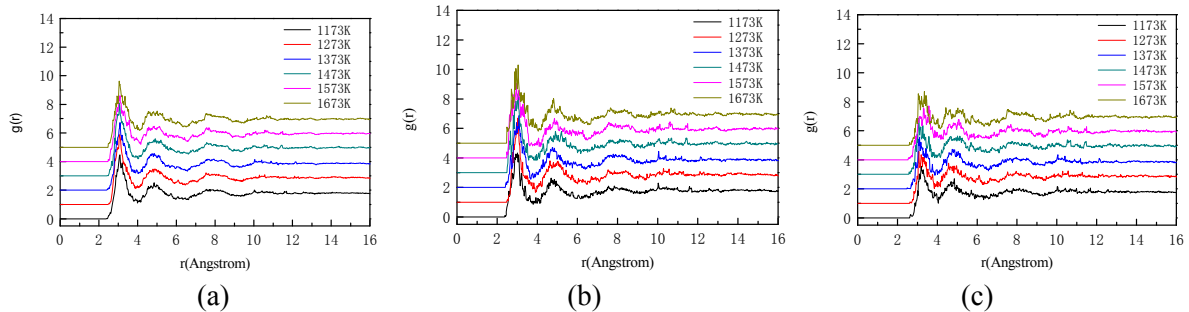


Fig.1 The Radial distribution function of Sn-Sb system: (a) $g_{\text{Sn-Sb}}(r)$; (b) $g_{\text{Sb-Sb}}(r)$; (c) $g_{\text{Sn-Sn}}(r)$

The $g_{\text{Sb-Sb}}(r)$ was similar to the $g_{\text{Sn-Sn}}(r)$. Both of them have many small peaks at the first peak and after peaks. And these peaks disappeared with the increase of temperature, because the decrease of the order degree.

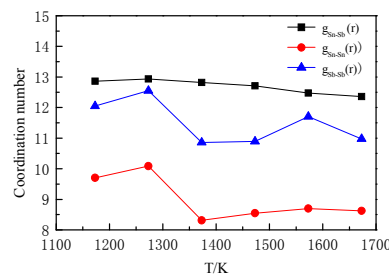


Fig.2 The coordination number of $g_{\text{Sn-Sb}}(r)$ and $g_{\text{Al-Al}}(r)$ systems

Coordination numbers can be calculated with Eq. (1), which are shown in Fig.2. The coordination numbers were reduced from 12.05 to 10.97 and 9.70 to 8.62 in $g_{\text{Sb-Sb}}(r)$ and $g_{\text{Sn-Sn}}(r)$ respectively with the temperature changed from 1173K to 1673K, which showed that the interaction between particles was weakening with the increase of temperature. From the numerical point of view, the reduction of the total coordination number in the system was small, which showed that the interaction between particles in the alloy remains at a relatively stable level. But the coordination numbers was the smallest when temperature was 1473K in $g_{\text{Sn-Sb}}(r)$, $g_{\text{Sb-Sb}}(r)$ and $g_{\text{Sn-Sn}}(r)$. It showed that interaction between particles was strong at 1473K.

3.2. Mean square displacement (MSD) and diffusion coefficient (DC)

Mean square displacement was the square of total vector, and it can also represent the net displacement of the atom after many beats. When the system was liquid, diffusion coefficient was 1/6 gradient of mean square displacement. The diffusion coefficient can be expressed as:

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

Fig.3 showed the total MSD in Sn-Sb alloy at different temperatures. The MSD increased with the increase of temperature in the Sn-Sb alloy largely. When the temperature increased from 1173K to 1373K, the MSD in the system increased continuously. When the temperature reached at 1473K and 1673K, the MSD in the system was larger and different from other temperature, but the MSD of

1573K decreased. It can be concluded that the molecular motion acutely at 1473K and 1673K than other temperature, in general, molecular motion was the most acute at 1473K in Sn-Sb alloy.

The MSD of Sb, Sn are shown in Fig.3 (b)(c) respectively. All in all, the maximum diffusion coefficient was at 1473K in Sn-Sb alloy. The diffusion coefficient which calculated by MSD are shown in Table 1. The variation of diffusion coefficient was consistent with MSD.

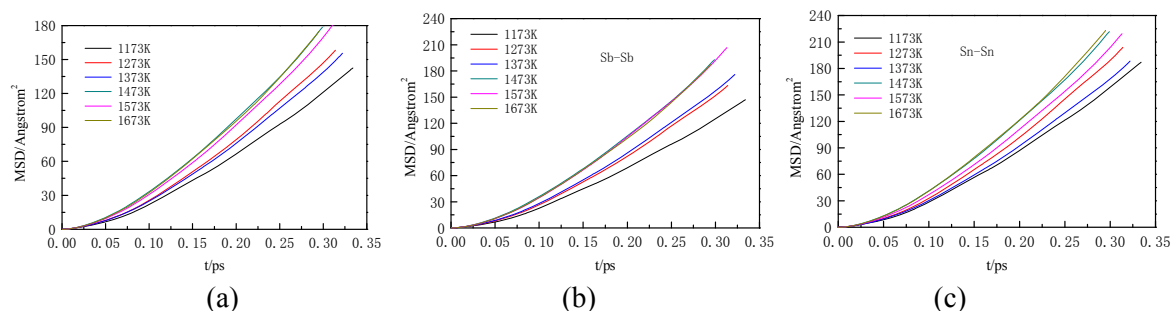


Fig.3 The Mean square displacement of Sn-Sb system: (a) total Mean square displacement; (b) Sb-Sb; (c) Sn-Sn

3.3. Structure factor

The relationship between structure factor and radial distribution function was based on Fourier transform. The basis was that they came from the same structural information. As can be seen from the Fig.4, structure factors $S_{Sb-Sb}(k)$ and $S_{Sn-Sn}(k)$ had a common structure, which can obviously observe the first peak at $k=0.16\text{\AA}^{-1}$. And it can observe many small shoulder-peak on the right side of the first peak, which indicated that there was a local ordered structure induced by covalent bond in the melt. The structure factors of $S_{Sn-Sb}(k)$ are little difference from $S_{Sb-Sb}(k)$ and $S_{Sn-Sn}(k)$, but among of them had same structure. Comprehensive consideration the first peak, shoulder-peak in $S_{Sn-Sb}(k)$, $S_{Sb-Sb}(k)$ and $S_{Sn-Sn}(k)$, with the increase of temperature, the peak value of the first peak changed slightly, but the overall downward trend, so the degree of order in the molten alloy decreased with the increase of temperature.

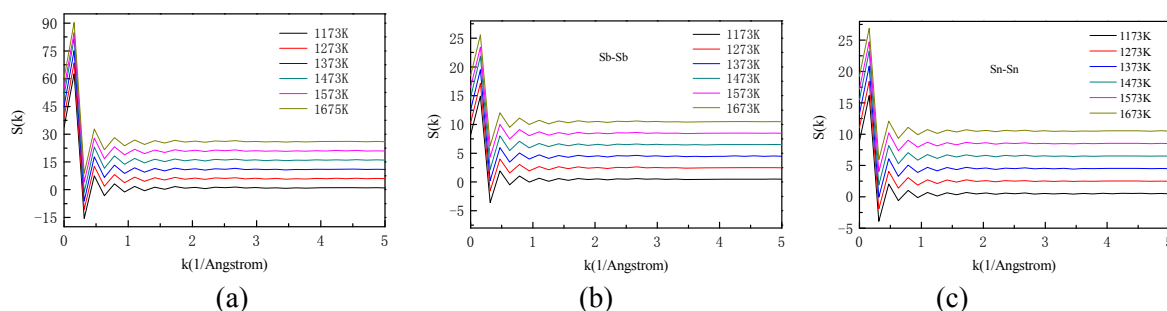


Fig.4 The Structure factor of Sn-Sb system: (a) total Structure factor; (b) Sb-Sb; (c) Sn-Sn

4. Conclusions

Ab-initio molecular dynamics for the Sn-Sb system were carried out. The author simulated and calculated the Radial distribution function (RDF), coordination number (CN), Mean square displacement (MSD), diffusion coefficient (DC) and structure factor of the Sn-Sb system. The results showed that molecular diffusion was faster and moving quickly at 1473K, it suitable for distillation experiments at this temperature. The *Ab-initio* molecular dynamics simulation can be used to elucidate the reaction mechanism from the microscopic point of view and forecast the best experimental conditions in vacuum distillation. It provided an efficient and convenient idea to guide the process of vacuum metallurgy.

Acknowledgements

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