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Kinetic and thermodynamic properties of liquid zinc: An *ab initio* molecular dynamics study

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ABSTRACT

In this paper, structure, dynamic and kinetics properties of the liquid zinc were calculated by *ab initio* molecular dynamics simulations. Temperature dependence of self-diffusion coefficient, shear viscosity and surface tension were investigated in the range from 420 to 550 °C. The pair correlation functions calculated in this study are in good agreement with those previous results by other scholars. The calculated results indicate that both of self-diffusion coefficient and shear viscosity have very good compatibility with Arrhenius relationship. Moreover, the formula exhibiting temperature dependence of the surface tension had been established in order to evaluate the surface tension at any given temperature in this paper.

1. Introduction

Hot dip galvanizing is now considered as one of the most widely effective techniques for improvement of corrosion resistance in the iron and steel materials [1]. However, corrosion of the immersed equipment components such as sink rollers and immersion heaters was an inevitable problem in the continuous hot dip galvanizing process. Therefore, it is of great significance to put a lot of efforts into studying the structure and physical properties of liquid zinc. Since corrosion of the metal materials in the environment begins at the surface of the metal, the surface tension is an important thermodynamic parameter which reflects the surface state of the material, and affects the corrosion behavior of the material [2–4]. Furthermore, it is one of the key factors affecting the interphase mass transfer and the reaction of the heterogeneous system. In addition, for high-temperature melts, the surface and interfacial properties of the materials also play a dominant role in the interfacial reaction and separation process, as are the basis for studying the kinetics of the interfacial reaction. Moreover, it is worth to mention that viscosity and diffusion [5] is also a significant physical properties of the liquid metal. For measurement of the viscosity, a number of methods, such as the traditional capillary method, rotation method and vibration method has been recently developed [6]. However, experimental measurement of these physical parameters such as tension and viscosity of the liquid metal is relatively hard and inaccurate. One reason is that the metal is easy to be oxidized and volatile when temperature approaching above the melting point. Therefore, establishment of an adequate theoretical model is very crucial for simulating the microstructure of the liquid metal.

Due to the recent development of the *ab initio* molecular dynamics simulations (AIMD) [7], it becomes undoubtedly an effective method for investigating the structure and dynamical properties of metallic liquids alloy [8,9,10]. Li et al. [11] calculated the liquid structure of $Zn_{95}Fe_5$ alloy, accompanying with formation and evolution of the $FeZn_{13}$ phase during hot dip galvanizing by AIMD. And Gu et al. [12] also used AIMD and revealed the structure and electronic properties of GaSb and InSb alloys. In contrast, theoretical studies of liquid zinc have been performed mostly by using classical molecular-dynamics method [13]. There are very few investigations on the diffusion and viscosity of metallic melts by AIMD [14,15]. Moreover, the information about surface tension of the metal melts is scarcely available in the previous literatures by AIMD method.

In this paper, in order to gain more insight into the thermodynamic and kinetic properties of liquid zinc over a range of temperatures, we have performed *ab initio* molecular dynamics simulations. This work aims at theoretical calculation of surface tension, viscosity, wettability to reflect the surface state of the metal, which is expected to provide the foundation for exploring the interfacial and corrosion behavior of the materials.

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2. Computational details

The simulations were carried out by *ab initio* calculation based on density function theory (DFT), using the Vienna *ab initio* simulation package (VASP) [16] along with the projector augmented-wave method [17]. The generalized gradient approximation (GGA) of PBE was used for the exchange-correlation functional. The gamma point is used for Brillouin zone sampling, and a cutoff energy of 277 eV has been applied for the plane-wave expansion. For simulations with this size, a single k-point was more than adequate for performing accurate reciprocal-space summations. All the dynamical simulations were carried out in the canonical ensemble (NVT) by means of a Nosé [18] thermostat to control temperature.

The simulation system contains 216 atoms in a cubic box with random positions and periodic boundary conditions. It is worth mentioning that number of atoms has been examined by increasing over 216, but two system sizes give the same results for structural properties. The number density was carefully adjusted so as for the external pressure to approach zero, as is rather good for both structural information and energy. The simulation temperature was set at 420 °C, which is the melting point of zinc in experiment. In order to ensure the system at 420 °C as liquid state in molecular dynamics simulation, we have obtained when the system at 420 °C, the atomic structure configuration is formed mainly with the 1551, 1541 and 1431 bond-types. It is a typical liquid characteristic. In the subsequent analysis, in order to confirm it is appropriate to regard the system at 420 °C as liquid state in molecular dynamics simulation, the properties of the melting point between other theoretical and calculated values will be focused on. The setting temperatures and densities are shown in Table 1. The equation of motion was solved using the Verlet algorithm in the velocity form with a time step of 3 fs. The starting configuration was allowed to iterate for beyond 15 ps to reach equilibrium of the system and reliability of simulations. The system had been verified that sizes of the supercells and times of simulation were of sufficient magnitude. In order to obtain good statistical precision, the last 2500 configurations were collected for structural analysis.

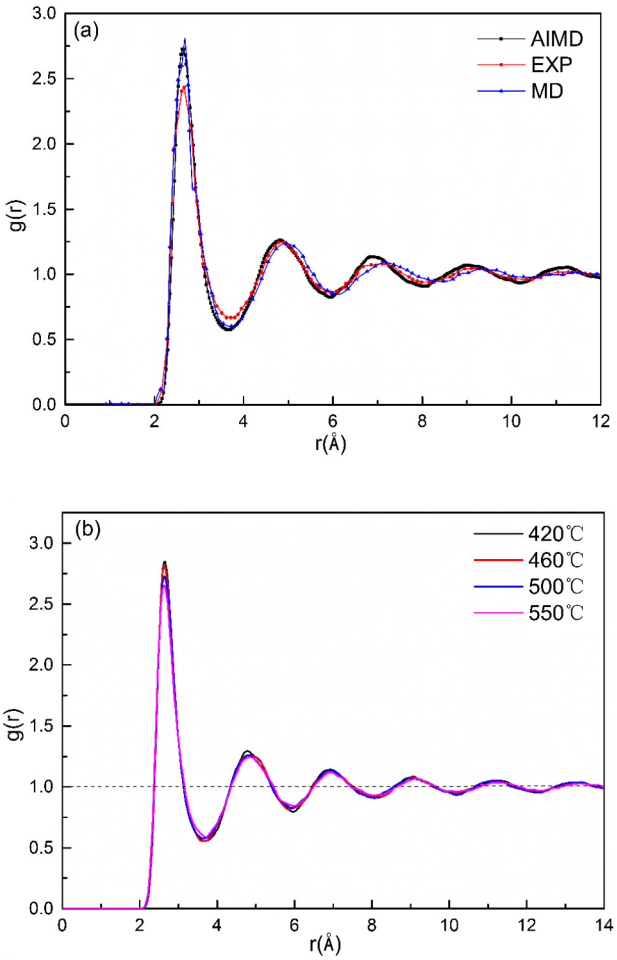

Fig. 1. Pair-correlation functions of liquid zinc at different temperatures. (a) Comparison of the pair-correlation calculation for liquid zinc at 500 °C with the experimental result by Waseda [19] and molecular dynamics calculations by Lin [13]. (b) Temperature dependence of the pair distribution functions calculated in this study.

3. Results and discussions

3.1. Structure properties

Better insight into the liquid structure can be provided by calculating the pair correlation function $g(r)$. Fig. 1(a) shows comparison of the calculated pair correlation functions of zinc with the experimental result obtained by Waseda [19] and the theoretical result of molecular dynamics calculations by Lin [13]. The pair correlation function of zinc at 500 °C calculated in this study shows very good agreement with those previous studies [13,19]. It is observed that position of the first peak is in good agreement with that experimental result, but the height of the first peak is slightly biased. This experimentally determined g(r) is subject to a greater uncertainty due to the limited q-range where the experiments performed, and so somewhat differences between the experiment and calculations are generated. Furthermore, four sets of data of pair correlation functions of liquid zinc at different temperature have been shown in Fig. 1(b). It can be seen that the pair correlation functions of liquid metal all have the characteristics of shock, and tends to the unit when the atomic distance becomes large. Such a uniform feature implies the typical liquid state is maintained above 420 °C. In addition, with increasing the temperature, height of the first peak of $g(r)$ becomes lower, indicating that the degree of short-range order in the system decreases, however, its position does not change when varying the temperature. As showed in Table 2, when compared to experimental measurement, the structural information near the melting point calculated by AIMD is in reasonable agreement with the corresponding experimental results [6]. It indicates that AIMD is a feasible method for calculation of the liquid structure of zinc and the corresponding parameters selected in AIMD are also reasonable.

3.2. Kinetics properties

The diffusion coefficient plays an essential part to comprehend the diffusion process dynamically. For this reason, the self-

Table 1
Temperature and density for *ab initio* molecular dynamics simulations.

Temperature (°C)	420	425	435	460	469	479	500	550
Density (g/cm^3)	6.535	6.536	6.544	6.507	6.506	6.510	6.468	6.436