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Dynamic process of H-controlled oxygen concentration in LBE: A first-principles study

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HIGHLIGHTS

- The behaviors of H in LBE are investigated.
- We clearly explain the dynamic process of the interaction between H and O in LBE.
- The equilibrium concentrations of H, H_2, HO, O and H_2O in LBE at different temperatures are predicted.
- The mechanism of H-controlled O concentration in LBE is revealed.

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ABSTRACT

First-principles molecular dynamics simulations have been performed to study the behaviors of H and the dynamic process of H-controlled O concentration in the liquid lead bismuth eutectic (LBE). Our calculations show that H_2 molecules in LBE are dissociated to be diffusive H atoms, taking the forms of H-metal clusters. Meanwhile, H prefers to interact with O in LBE to form HO radicals and H_2O molecules, reducing the O concentration in LBE. With the mass action analysis, we quantitatively predict the variation of the O concentration in LBE with the amount of the introduced H_2 at different temperatures. Our results are practical for the H-controlled O concentration in LBE experiments.

1. Introduction

Liquid lead bismuth eutectic (LBE) is regarded as a good candidate for the coolant materials in accelerator driven subcritical reactor systems (ADS), due to its favorable thermo-physical and neutronic properties [1]. As we know, LBE in ADS is encapsulated by the so-called structural materials, such as stainless steels T91, 316L, oxide dispersion strengthened (ODS) steel and so on. A critical issue in ADS is that structural materials suffer the serious dissolution corrosion from the encapsulated LBE [2,3]. Meanwhile, the corroded fragments blocked up the flow of LBE, and threatened the safety of the system [4,5]. To ensure the long-term run of ADS, surface treatment, such as coating Al and its alloys (FeCrAl, FeCrAlY) as well as Al_2O_3, were used to provide corrosion resistance [6–9]. However, such coating surface could easily spall off from the surface in the service period [10]. Alternately, a popular approach to prevent the dissolution of the structural material is to directly generate a protective oxide layer on the surface of the stainless steel [10,11], which could be formed through the interaction of O in LBE with the metal at the steel surface [10]. Recently, the corrosion behaviors of LBE on various structural materials were extensive investigated in experiment, which provided much valuable data for exploring anticorrosion materials [12–18]. For instance, the oxide on the surface was found to characterize the double-layer structure where the inner layer was Fe–Cr spinel and the outer layer was magnetite. Meanwhile, the thickness of oxide scale showed a time-dependent parabolic trend, displaying the diffusion-rate-controlled oxide feature in the growth [14]. More importantly, it was found the formation of protective oxide layer correlated tightly with the concentration of O in LBE. For example, in liquid Pb, the steel

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surface could not be oxidized to form the protective layer if the concentration of O was lower than 10^{-7}at.% [19]; In contrast, if the concentration of O in LBE was high, the excess O atoms reacted with the metal atoms in LBE to form the particles of PbO and Bi_2O_3, altering the properties of LBE. Therefore, properly controlling the concentration of O in LBE is a crucial issue in ADS.

So far, the main way to control the concentration of O in LBE is to inject H_2 or the mixed H_2/H_2O gas with proper ratio into LBE [20]. Actually, many experiments on controlling O concentration in LBE have been carried out [19,21–23], but how to effectively control the concentration of O in LBE still remains a challenge [20]. Basically, controlling O concentration in LBE is relevant to the formation and the decomposition of H_2O in LBE, which is essentially related to the interaction between H and O in LBE. In the present paper, we perform first-principles MD simulations to investigate the dynamic interaction behaviors between O in LBE and the introduced H. We find that H prefers to interact with O in LBE to form HO radicals or H_2O molecules, and the produced HO radicals play an important role in modulating the O concentration in LBE. With the mass action analysis, variation of O concentration in LBE with the introduced H is quantitatively predicted.

2. Models and methods

The calculations are performed within the density functional theory as implemented in the SIESTA code [24]. The local density approximation (LDA) is adopted to deal with exchange-correlation potential. The norm-conserving pseudopotentials that are generated from the Troullier-Martins scheme [25–27], are used to represent the valence electrons. Sankey finite-range pseudo atomic orbitals (PAOs) [28] are utilized as the split-valence double-ζ basis set (DZ) for the valence electrons of all atoms involved.

To simulate the liquid LBE, we construct a cubic supercell consisting of 28 Pb atoms and 36 Bi atoms, in which the concentration of Pb is 43.75at.%. The concentration of Pb in our chosen supercell matches that in the experiment [4]. Periodical boundary conditions are imposed in three directions in our calculations. The Monkhorst-Pack scheme is used to sample the Brillouin zone [29], and the $2 \times 2 \times 2$ mesh in $\mathbf{k}$ space is adopted, which is converged in our calculations. The molecular dynamics with the Nosé–Hoover thermostat, a deterministic algorithm to achieve a constant temperature, is employed [30,31]. We set cutoff energy for plane wave to be 150 R y and the time interval of 1.0 fs for each MD step.

To verify the reliability of our employed method and the structural model for LBE, the pair function of Pb/Bi in our supercell was calculated [32]. Our calculated pair function agrees well with that from the experiment [33]. Besides, the formation energy of an H_2O molecule is calculated to be −2.591 eV, being in good agreement with the experimental value (−2.506 eV) [34]. These agreements confirm that our chosen method and the generated structural model for LBE are appropriate to deal with the concerned systems. In addition, a larger-sized supercell containing 56Pb and 72Bi atoms is used to take a test calculation, and the obtained results are quite similar to those from the supercell consisting of 28Pb atoms and 36Bi atoms. For instance, the energy difference between an O atom in LBE calculated from the 64-atom supercell and that from the 128-atom supercell is less than 0.06 eV. This confirms that the obtained results from our chosen supercell are valid.

3. Results and discussions

3.1. The behavior of H in LBE

Firstly, an H_2 molecule is introduced in LBE, and MD simulations are performed for this system at 500 K, 800 K and 1000 K respectively. We find that H_2 dissociates into two atomic H in LBE in less than 40 ps. After each system reaches its thermal equilibrium, the additional 100 ps of MD simulations are performed at each given temperature, from which the local structures near the H atoms are carefully examined. Fig. 1 displays the computed pair functions of H–Pb and H–Bi in the systems. As well known, the pair function, g(r), depicts the density of atoms near a certain atom in the system. From Fig. 1, one can see that the main peak in the pair function curve for H–Pb is much higher than that for H–Bi at each considered temperature. This feature demonstrates that there are much more Pb atoms around the H atoms in LBE. With increasing temperature, the height of the main peak in the pair function curve for H–Pb decreases, whereas that for H–Bi increases slightly. This implies that the number of Pb atoms which are the first neighbors of the H atom decreases, but that of Bi atoms increases.

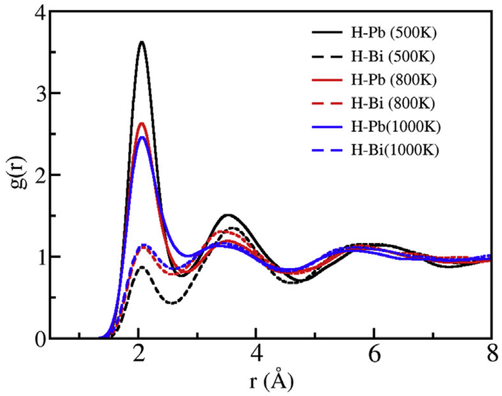

Fig. 1. Pair functions of H–Pb and H–Bi at 500 K, 800 K and 1000 K, respectively.

By checking the configurations around the H atoms in our MD simulations, we find that five typical clusters containing the H atoms (H-metal clusters) appear frequently, as shown in Fig. 2. Among these H-metal clusters, H–Pb_2, H–PbBi and H–Bi_2 characterize the feature of the H atoms locating at the center sites between the two metal atoms. For the other two typical clusters, the H atoms locate at the center sites of the three or four metal atoms. The cases with three metal atoms surrounding the H atoms are denoted as H-Pb_iBi_{3-i} with i ranging from 0 to 3. Physically, the more stable the local structure is, the more frequently this structure appears at a certain temperature. We then statistically calculate the frequency

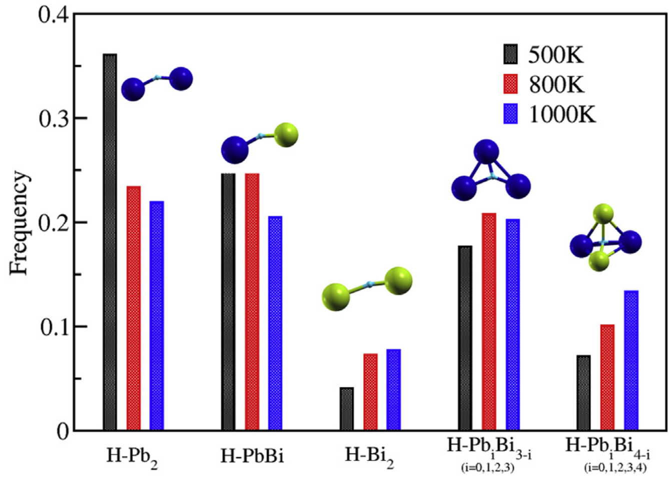

Fig. 2. The frequencies of occurrence for five typical clusters observed in LBE at different temperatures.