First-principles molecular dynamics simulation on interatomic interaction of Fe crystal with Pb and Bi atoms

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Abstract

The interaction mechanism between Fe crystals and Pb and Bi atoms was investigated using the first-principles molecular dynamics theory based on the density functional theory, which was the first step of an analytical approach to the simulation of steel corrosion in high temperature lead–bismuth (Pb–Bi) cooled fast breeder reactors and accelerator driven systems. The Vanderbilt ultrasoft pseudopotentials for Fe, Pb and Bi elements were calculated with the exchange and correlation corrections by the local density approximation. Crystal lattice constants calculated using the potentials agreed well with experimental ones. Using the calculated pseudopotentials, the first-principles molecular dynamics simulations were performed to investigate the interatomic interaction between Fe crystal and Pb, Bi atoms. The result shows the reasonable motions of Pb and Bi atoms near the surface of the Fe crystal and those of Fe atoms in the crystal.

Keywords: First-principles molecular dynamics simulation; Density functional theory; Fe crystals; Pb–Bi eutectic

1. Introduction

Compatibility of structural materials with lead–bismuth (Pb–Bi) has been one of the key issues for the development of Pb–Bi cooled fast reactors and accelerator driven systems (ADS). The corrosion behaviors of steels in high temperature Pb–Bi have been investigated experimentally so far, but the interaction mechanism between the steels and Pb–Bi has not been made clear yet. Thus, the interatomic (intermolecular) interactions between iron crystals, steels and Pb–Bi melt were studied using the molecular dynamics method with the appropriate interatomic potentials [1,2]. In these references, the simple pairwise empirical interatomic potentials, i.e. the Born–Mayer potential and the Morse potential, were used in the first simulation. However, the same types of the potentials, e.g. the Born–Mayer potential, were unavailable for all the interacting atoms, and the interactions between different species of atoms: Fe–Pb, Fe–Bi and Pb–Bi were approximated by means of the mixing rule. It is necessary to take into account the interatomic interactions between the metallic ions which are emerged in the free-electron gas in the potentials of metals. This kind of interatomic potentials have not been constructed precisely for mixed metal systems of steel and Pb–Bi melt, although they have been constructed for some pure metals of Fe, Al, Cu, Na, K, etc. [3].

The correlation between the ionic configuration and the electronic states plays an important role in the metal systems. It is necessary to avoid the problem of the potential between two atoms mentioned above for the description of the metal system. It is expected that the metal systems can be described more effectively and successfully with the first-principles molecular dynamics simulation, since the interatomic forces are not calculated by the derivatives of the interatomic potentials but by the first-principles theory in the first-principles molecular...
dynamics simulation. The first-principles molecular dynamics simulation based on the density functional theory was applied to only a small system of liquid Na–Pb alloys so far, since the system size is limited to tens to hundreds of atoms because of the computing cost [4].

In the present study, the first-principles molecular dynamics method based on the density functional theory was used to investigate the interaction between the steel and Pb–Bi melt. As the first step, only one Pb atom and one Bi atom were included in the system to examine the performance of the method. The Pb and Bi atoms were located above the surface of a Fe crystal, and the changes in the charge-density distributions of the atoms, the motions of the Pb and Bi atoms to the surface of the Fe crystal and the structure deformation of the Fe crystal were simulated.

2. Numerical procedure of first-principles molecular dynamics simulation

Within the ultrasoft pseudopotential, the Kohn–Sham equation for the total energy [5] is written as

\[ E_{tot} = \sum_{\phi} \{ \psi_{\phi} \} \{ f_{\phi} \} \{ R_{i} \} \]

\[ = E_{kin} + E_{NL} + E_{ion} + E_{H} + E_{xc} + E_{Ewald}, \tag{1} \]

where \( E_{kin} \) is the kinetic energy for electrons, \( E_{NL} \) is the nonlocal potential energy, \( E_{ion} \) is the local ionic potential energy, \( E_{H} \) is the Coulombic repulsive interaction energy between electrons, \( E_{xc} \) is the exchange and correlation energy and \( E_{Ewald} \) is the Coulombic repulsive interaction energy between valence charges of atoms.

The electronic structures and the forces exerted on atoms were determined by the band calculation based on the density functional theory with the local density approximation for the exchange and correlation interaction. In the band calculation, the wavefunctions were represented by the linear combination of the plane-waves. The motions of the Fe, Pb and Bi atoms were simulated by the molecular dynamics method using the velocity Verlet algorithm for solving the Newton’s equation \( F_I = m_I (\dddot{r}_I / \dot{t}^2) \), where \( F_I \) was the force exerted on atom \( I \) of mass \( m_I \), and \( r_I \) was the position vector. The temperature was kept constant at 773 K by the Nosé-Hoover method during the simulation. This is the typical temperature in the Pb–Bi cooled fast breeder reactor (FBR) and ADS.

The first-principles molecular dynamics simulation was carried out by using the multiscale molecular dynamics simulator CAMUS [6] and the first-principles band calculation program PHASE [7]. An atomic configuration was given, and the force exerted on each atom was calculated in PHASE, and transferred to CAMUS. The positions and the velocities of the atoms were updated in CAMUS, and then the new atomic configuration was determined. The motions of atoms were described by repeating this procedure.

In order to confirm the adequacy of the Vanderbilt ultrasoft pseudopotentials [8] which were constructed from the calculations of the electronic structure of a single atom, the lattice constants of Fe, Pb, Bi crystals were calculated by using the pseudopotentials and compared with...
the experimental lattice ones. The Fourier components of the wavefunctions were also calculated to find a proper cutoff wave number in the plane-wave expansion of the wavefunction. From the calculated result of the energy of the Fe crystal, the stable lattice constants of the Fe crystal was determined to be 5.32 Bohr (2.81 Å). The difference between the calculated lattice constant and the experimental one of 5.41 Bohr (2.86 Å) is about 1.7%, which indicates the good agreement between the calculated and experimental lattice constants. The lattice constants of the Pb and Bi atoms were 9.24 (4.89 Å) and 8.53 Bohr (4.51 Å), respectively. They agreed well with the experimental values. The cutoff wave numbers of Fe, Pb, Bi atoms were determined to be about 6.0 (11.3 Å⁻¹), 5.0 (9.5 Å⁻¹) and 5.0 Bohr⁻¹ (9.5 Å⁻¹), respectively.

3. First-principles molecular dynamics simulation for motions of Pb and Bi on Fe crystal surface

3.1. Motion of Pb on Fe crystal surface

The motion of Pb atom on Fe crystal surface was simulated by the first-principles molecular dynamics method with the pseudopotentials discussed in the previous section. In the simulations, two initial configurations were used. The Pb atom was located just above the Fe atom of the surface in the atomic configuration of Fig. 1(a), and it was located just above the center of four neighboring Fe atoms on the surface in another case. The distance between the Pb atom and Fe surface was set to be 5.37 Bohr (2.84 Å), and the initial velocity of Pb atom was (0.0, 0.0, −0.1) eV. The Fe cluster was constructed with 6×6×5 layers. The periodic boundary condition was used in x- and y-directions, and the lower edge of the Fe crystal was fixed during the simulation. The vacuum region of 16 Bohr (7.9 Å) thickness was put in the z-directions. The cutoff wave number was set to be 6.0 Bohr⁻¹ (11.3 Å⁻¹).

The distance between the Fe surface and the Pb atom is shown as a function of time (≡t) in Fig. 2. When the Pb atom was located just above the Fe atom of the surface, the distance between the Fe surface and the Pb atom decreases as increasing t, and it takes the minimum value of about 3.4 Bohr (1.79 Å) at t = 150 fs. Since the distance between the Pb atom and the Fe surface is nearly constant in the time span of 150< t < 200 fs, the Pb atom may be adsorbed of the Fe surface. When the Pb atom is located just above the center of four neighboring Fe atoms in the surface, the distance of the Fe surface and the Pb atom takes the minimum value of 2.8 Bohr (1.48 Å) at t = 110 fs, and it is shorter than that between the Fe surface and the Pb atom located just above the Fe atom of the surface. This means that the Pb atom is accessible when it is located just above the center of four neighboring Fe atoms in the surface. Fig. 1 shows that, when the Pb atom is located just above the Fe atom on the surface, the Fe atom just below the Pb atom goes down as the Pb atom approaches the surface. This means that the structural change of the Fe surface is brought about due to the adsorption of the Pb atom.

3.2. Motion of Bi on Fe crystal surface

Fig. 3 shows that the structural change of the Fe crystal induced by the approach of the Bi atom is similar to that in the case of the Pb atom, but it is more notable compared
with the case of the Pb atom. The magnitude of the lattice deformation may be closely related to the numbers of valence charges in the ionic states, Pb\(^{2+}\) and Bi\(^{3+}\). Because of larger number of the valence charges, the repulsive interaction between the Fe surface and the Bi ion is stronger than that between the Fe surface and the Pb ion, which causes greater lattice deformation of the Fe surface. As a consequence of the lattice deformation, the Bi atom becomes much accessible to the Fe surface. By comparing Figs. 2 and 4, it is found that the Bi atom approaches the Fe surface more closely than Pb atom.

### 3.3. Motion of Pb and Bi on Fe crystal surface

Fig. 5 shows that, due to the repulsive interaction between the Pb atom and the Bi atom, they are separated from each other as \(t\) increases, and no longer exist just above the Fe atoms of the surface in the atomic configurations of \(t \geq 100\) fs. Fig. 6 shows that the distances between the Fe surface and the adsorbed atoms are different from those in the case of single atom adsorption. These calculated results indicate that the interaction between the Pb atom and the Bi atom plays an important role on the adsorption process.

### 4. Conclusion

The effects of the interatomic interaction on the motions of the Fe, Pb and Bi atoms are made clear by means of the simulation using the first-principles molecular dynamics method based on the density functional theory. The calculated result shows the structural changes induced by the interaction between Fe, Pb and Bi atoms. The adsorption of Bi atom changes the structure of Fe surface more greatly than the Pb atom. When the Pb and Bi atoms are located on the Fe surface, the dynamics of the Pb and Bi atom is different from those in the cases of single atom adsorption. Therefore, the interaction of the Pb atom with the Bi atom may be one of key factors in the Pb–Bi adsorption process.

The microscopic properties of the interaction between the Fe surface and the heavy metals such as Pb and Bi are clarified. The fundamental phenomena discussed in this study may be an important clue to solve more complicated problems for the interaction between the metallic surface and the atoms of the heavy metal.

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