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分子動力学計算を用いた液体 Pb 中における不純物拡散係数の予測

Prediction of Impurity Diffusion Coefficients in Liquid Pb using Molecular Dynamics Simulations

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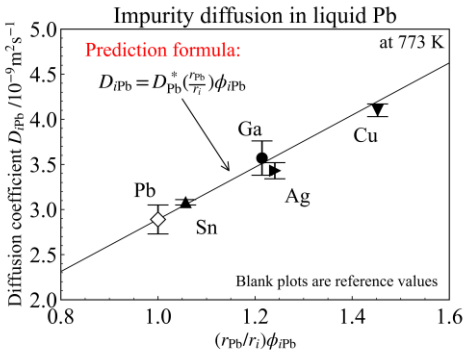
Abstract: This study aims to evaluate the dependence of impurity diffusion coefficients on atomic radii by deriving the directly from partial pair distribution functions obtained via molecular dynamics (MD) simulations. MD simulations of liquid Pb–Cu, –Ga, –Ag, and –Sn were conducted at 773 K using a universal neural network potential. The simulation parameters were adjusted to match the experimental impurity diffusion coefficients for Cu, Ga, Ag, and Sn from the references, all of which were measured at 773 K using the identical shear cell technique. In calculated partial pair distribution functions from MD results, a height of the first peak of partial pair distribution function in between Pb atoms was agreed with the experimental data. However, its position of the first peak was smaller than that. The solute atomic radius in the liquid Pb alloy was defined as the difference between the positions of the first peaks in the solute-solvent and solvent-solvent partial pair distribution functions. The defined atomic radii above were Cu, Ag, Ga, Sn, and Pb in order of smallest to largest, which did not correspond to Ag and Ga in order of largest to smallest diffusion coefficients. Incorporating this definition into the proposed prediction formula yielded impurity diffusion coefficients in liquid Pb that are more accurate with the values derived from the MD method than with the values derived from Gold–Schmidt radii.



Keywords: Shear cell technique, Molecular dynamics simulations, Impurity diffusion coefficients, Liquid Pb

1. Introduction

Impurity diffusion coefficient in liquid metals is critical thermophysical parameter for understanding and modeling mass transport processes. Our research group proposed a prediction formula in which the impurity diffusion coefficient is expressed as the product of the self-diffusion coefficient of a solvent and two factors: (i) the ratio of the atomic radius of the solvent to that of the solute and (ii) a thermodynamic factor[1)]. However, this formula relies on Gold–Schmidt radii derived from crystalline solids and has not been validated directly using the atomic radii of liquids. In this study, a definition of atomic radius using a pair distribution function could be proposed for liquid metals reproduced by molecular dynamics (MD) simulations for predicting the impurity diffusion coefficient. On the other hand, it is unclear what settings should be used in MD simulations

to reproduce this dependence although previous study has confirmed that the impurity diffusion coefficient depends on the atomic radius. This study aims to evaluate the dependence of impurity diffusion coefficients on atomic radii by deriving the directly from partial pair distribution functions obtained via MD simulations.

2. Computational Procedures

The MD simulations of liquid Pb-1 at.%Cu, -2 at.%Ga, -2 at.%Ag, and -2 at.%Sn at 773 K were performed using a universal neural network potential (Matlantis)[2]. 13500 atoms arranged in a cubic simulation box with standard periodic boundary conditions have been considered. The conditions of MD simulations were determined so that the impurity diffusion coefficients should agree with the experimental data[3–5] using the identical shear cell technique as the same operation in microgravity experiments[3]. Before running the targeted calculation, the thermal equilibrium process was carried out to the simulation box according to the following procedure. First, the liquid sample was simulated at 573 K during 3000 fs using NPT ensemble. After the thermal equilibrium process, the targeted calculation was running during 10000 fs using NVT and then time series data of atomic position was obtained.

3. Results

From the position data, the partial pair distribution functions $g_{ij}(r)$ were calculated. **Figure 1** shows the calculated partial pair distribution functions of Pb-1 at.%Cu with experimental data[6]. In **Fig. 1**, the height of the first peak of partial pair distribution function in between Pb atoms was agreed with the experimental data. However, its position of the first peak was smaller than that, which indicates a parallel shift of the pair distribution function of Pb. Similar results were obtained for the values of Pb in the other partial pair distribution function in between Pb atoms. **Figure 2** shows the calculated impurity diffusion coefficients of Cu, Ga, Ag, and Sn in liquid Pb via MD simulations and referenced self-diffusion coefficient of Pb[7].

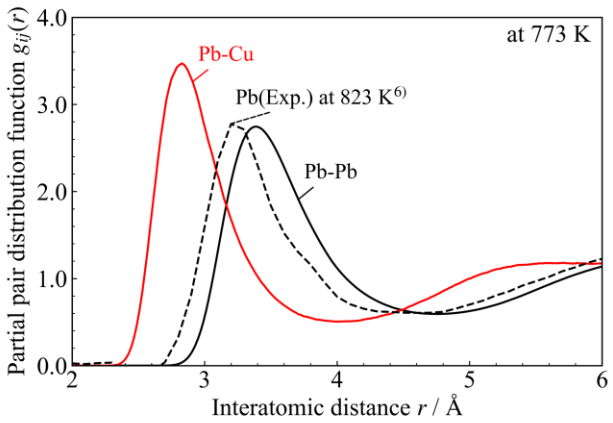


Figure 1. Calculated partial pair distribution functions in Pb-1 at.%Cu at 773 K. The dashed line presents the experimental data in liquid Pb.

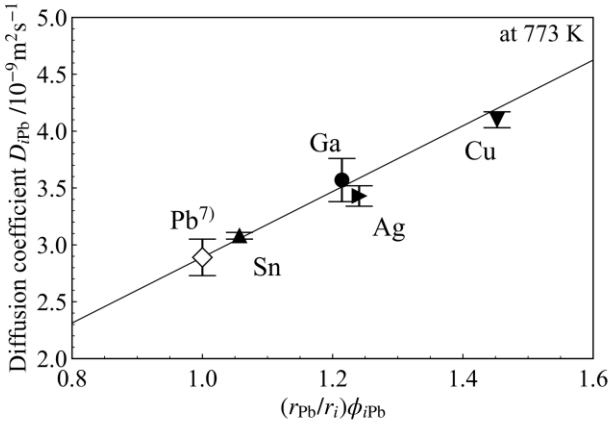


Figure 2. Calculated impurity diffusion coefficient in liquid Pb D_{iPb} (i = Cu, Ga, Ag, and Sn) as a function of the predicted formula at 773 K.

4. Discussion

From the position data via MD simulations, the partial pair distribution functions were calculated for the Pb alloys. The solute atomic radius in the solvent was defined by subtracting the atomic radius of the solvent from the first peak position of the partial pair distribution function between the solute and the solvent. The atomic radii defined by the partial pair distribution function were Cu, Ag, Ga, Sn, and Pb in order of smallest to largest, which did not correspond to Ag and Ga in order of largest to smallest diffusion coefficients in **Fig. 2**. These solute atomic radii and the solvent atomic radius adopted to the proposed prediction formula[1] of impurity diffusion coefficient D_{is} (s: solvent and i: impurity) as following;

$$D_{is} = D_s^* \left(\frac{r_s}{r_i}\right) \phi_{is}. \quad (1)$$

Here, the self-diffusion coefficient D^*_s is the proportional constant for liquid Pb. The symbols r_i and ϕ_{is} are an atomic radius and a thermodynamic factor, respectively. In **Fig. 2**, incorporating this definition of the solute atomic radius into **Eq. (1)** yielded impurity diffusion coefficients in liquid Pb that aligned with MD-derived values. The maximum absolute value of the error from the prediction was within 4.5%. This error range is smaller than that of 6.1% which is incorporated as the Gold–Schmidt radii in **Eq. (1)**. This suggests that the contribution of atomic radius ratios is more important than the predicted values in order of atomic radius in predicting impurity diffusion coefficients.

5. Conclusions

The predicted values of the prediction formula adapted to the definition of a solute atomic radius from partial pair distribution functions reproduced the impurity diffusion coefficients in liquid Pb.

Acknowledgments

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Conflicts of Interest

The authors declare no conflict of interest.

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