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原子量の影響を考慮した液体 Sn 中における不純物拡散係数の予測式

Predicted Equation with Effect of Atomic Weight for Impurity Diffusion Coefficients in Liquid Sn

椎木政人 [1], 登林兼丸 [1], 西村友希 [1], 山中亜里紗 [1], 鈴木進補 [1]
Masato SHIINOKI[1], Kanemaru NOBORIBAYASHI[1], Yuki NISHIMURA[1], Arisa YAMANAKA[1], and Shinsuke SUZUKI[1]
[1] 早稲田大学, Waseda University

1. Introduction

Impurity diffusion coefficients in liquid metals are essential thermophysical properties for understanding solidification. Our research group proposed a prediction method[1)] of impurity diffusion coefficient as deviated values from the self-diffusion coefficient of the solvent based on the reliable data under the microgravity condition and on the ground. However, it is necessary to include the effect of atomic weight in the predicted equation[1)] to improve the predictive accuracy. The objective of this study is to establish predicting methods empirically for impurity diffusion coefficients including the effect of atomic weight in liquid Sn. The impurity diffusion coefficients of Al, Au, and Cu in liquid Sn at 573 K were measured with high accuracy using the shear cell technique and stable density layering. Al and Au were selected as solute elements under the conditions that their atomic diameters are similar to that of Ag used in our previous experiment[1)], and their atomic weights are smaller and larger than that of Ag, respectively. Cu was selected as the solute element under the condition that its atomic diameter was sufficiently smaller than that of Sn.

2. Experimental procedure

A shear cell device[2)] with four capillaries was used. The detail design and procedure of the diffusion experiments can be referred to previous expertiments[1)]. The diffusion samples of Sn, Sn-Cu, Sn-Au, and Sn-Al were prepared. The contents of the impurity elements were 1 and 3 at.% for Cu, 3 at.% for Au, and 2 at.% for Al. The diffusion temperature was 573 K and diffusion times t_{diff} were 28800 s for Cu and Au and 21600 s for Al. When the samples were set into the shear cell device, the higher density samples were placed on the lower side to obtain stable density layering.[2)] That is, Sn-Cu and Sn-Au alloys were set on the lower side, whereas Sn-Al alloys were placed on the upper side. The diffusion axis was set parallel to the direction of gravity, and the zero position of the x-axis was defined at the edge of the alloy sample. After homogenization, the diffusion process started. At the end of the diffusion time, each capillary sample was mechanically separated into 20 cell samples and was cooled down. The concentrations of Cu, Au, and Al in the cell samples were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES).

3. Results

Each concentration curve was obtained by fitting thick layer solution in Eq. (1) to 20 plots in each capillary.

$$c_i(x) = \frac{c_0}{2}\left\{\mathrm{erf}\left(\frac{h_0+x}{\sqrt{2\langle X^2_{\mathrm{meas}}\rangle}}\right)+\mathrm{erf}\left(\frac{h_0-x}{\sqrt{2\langle X^2_{\mathrm{meas}}\rangle}}\right)\right\} \quad (1)$$

Here, c_i is the concentration of impurity solute i, x is the position in the capillary, c_0 is the initial concentration of impurity solute i, h_0 is the initial thickness of the alloy cell, and $\langle X^2_{\mathrm{meas}}\rangle$ is the measured mean-square diffusion depth obtained from the diffusion experiments including systematic errors. In the fitting process, c_0 and $\langle X^2_{\mathrm{meas}}\rangle$ were varied as fitting parameters and h_0 was set at a constant value of 3 mm as the thickness of the cell of the shear cell device. Diffusion coefficient was calculated by correcting the additional mass transport as following equation;

$$D = \frac{\langle X^2_{\mathrm{meas}}\rangle - \langle X^2_{\mathrm{add}}\rangle}{2t_{\mathrm{diff}}} \quad (2)$$

Here $\langle X^2_{\mathrm{add}}\rangle$ indicates the systematic error sources depended on the shear cell technique[2]. **Figure 1** shows the concentration profiles of Au at 573 K, which indicates that each obtained profile agrees with a thick layer solution in Eq. (1). The other concentration profiles of Cu and Al also agreed with the thick layer solution in Eq. (1). The averages of four measured impurity diffusion coefficients of Cu D_{CuSn}, of Au D_{AuSn}, and of Al D_{AlSn} were 2.88×10^{-9}, 2.71×10^{-9}, and 3.70×10^{-9} m^{2}s^{-1}, respectively.

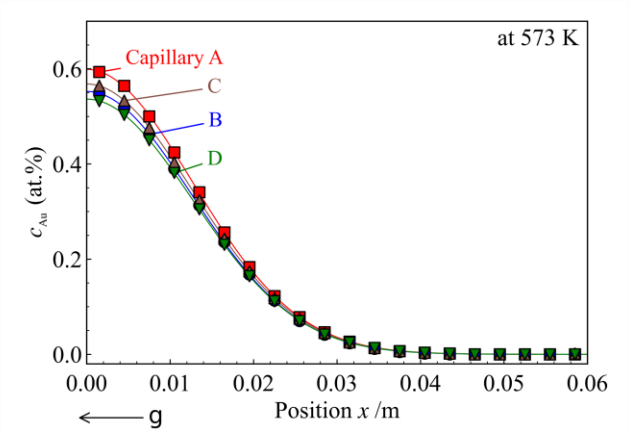

Figure 1. Measured concentration profiles of Au at 573 K. The symbol "←g" indicates the direction of gravity.

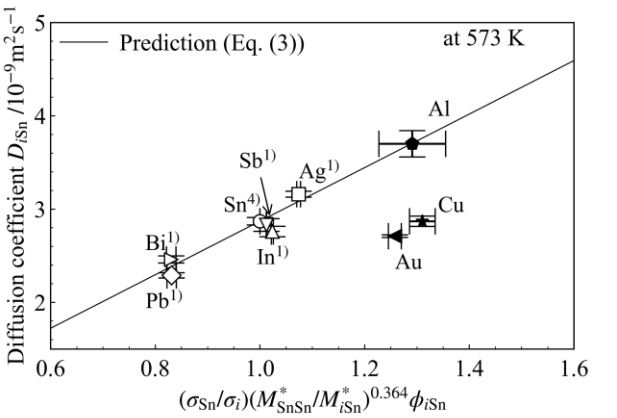

Figure 2. Measured impurity diffusion coefficient in liquid Sn $D_{i\mathrm{Sn}}$ (i = Al, Sb, Bi, Cu, Au, In, Pb, Ag, and Sn) as a function of the predicted equation corrected for the effect of atomic weight at 573 K.

4. Discussion

The concentration profiles of Au in **Figure 1** showed that the experiment was highly reproducible. The other concentration profiles of Cu and Au also showed these experiments were reproducible. In addition, the relative standard deviations in all experiments of Cu, Au and Al were much smaller than 6%: this value includes the factors of uncertainty from temperature, duration, convection, and composition measurements, in the microgravity experiment estimated by Garandet et al.[3)] The reproducibility of all experiments at 573 K was higher than the estimated measurement error range of the microgravity experiment mentioned above. It was therefore determined that all experiments at 573 K were performed with suppressed natural convection.

The values of D_{CuSn} and D_{AuSn} were close to the value of the self-diffusion coefficient of Sn[4)] $D^*_{\mathrm{Sn}} = 2.88 \times 10^{-9}$ m^{2}s^{-1}. Therefore, the condition for a discontinuity point in impurity diffusion coefficients in liquid Sn is that $(\sigma_{\mathrm{Sn}}/\sigma_i)\phi_{is}$ is approximately 1.2 or larger. In the range of $(\sigma_{\mathrm{Sn}}/\sigma_i)\phi_{is} < 1.2$, the effect of atomic weight is corrected by the reduced mass ratio in predicted equation[1)]: Predicted equation of impurity diffusion coefficient D_{is} (s: solvent, i: impurity) is proposed to $D_{is} = D^*_s(\sigma_s/\sigma_i)(M^*_{ss}/M^*_{is})^n\phi_{is}$ with the effect of atomic weight

M^*_{ss}/M^*_{is}. Here, the self-diffusion coefficient D^*_s is the proportional constant, σ_i and ϕ_{is} are an atomic diameter and a thermodynamic factor, respectively. M^*_{is}(= $(M_iM_s)/(M_i+M_s)$) is a reduced mass, and M_i is an atomic weight. The obtained values of the exponent n were 0.364 by fitting the proposed equation to D_{is} measured in Sn-Al and precious studies[1)] as following;

$$D_{is} = D^*_s \left(\frac{\sigma_s}{\sigma_i}\right) \left(\frac{M^*_{ss}}{M^*_{is}}\right)^{0.364} \phi_{is}. \quad (3)$$

Figure 2 shows the relationship between the proposed equation in n = 0.364 and the measured impurity diffusion coefficients in liquid Sn at 573 K. The proposed equation was in good agreement with the D_{is} of reference values with Al within 6 %.

5. Conclusions

The following different prediction methods for impurity diffusion coefficients of elements can be proposed based on $(\sigma_{Sn}/\sigma_i)\phi_{is}$.

(1) When $(\sigma_{Sn}/\sigma_i)\phi_{is}$ is approximately 1.2 or small:
The impurity diffusion coefficients in liquid Sn near the melting point can be estimated to be proportional to the product of the following three factors with the self-diffusion coefficient of the Sn as the slope: (i) the atomic diameter ratio of the Sn to the solute element σ_{Sn}/σ_i, (ii) 0.364 power of the reduced mass ratio of the Sn to the solute element $(M^*_{SnSn}/M^*_{iSn})^{0.364}$, and (iii) thermodynamic factor ϕ_{is}.

(2) When $(\sigma_{Sn}/\sigma_i)\phi_{is}$ is approximately 1.2 or large:
The impurity diffusion coefficients of elements in liquid Sn are close to the self-diffusion coefficient of Sn.

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References

1) N. Yamada, S. Suzuki, K. Suzuki, A. Tanaka, R. Morita, C. Chenglin and G. Frohberg: Investigation of the Influence of Different Solute on Impurity Diffusion in Liquid Sn using the Shear Cell Technique. Int. J. Microgravity Sci. Appl., **35** (2018) 350402, DOI:https://doi.org/10.15011/jasma.35.4.350402.
2) S. Suzuki, K.-H. Kraatz and G. Frohberg: Ground-based diffusion experiments on liquid Sn-In systems using the shear cell technique of the satellite mission Foton-M1. Ann. N. Y. Acad. Sci., **1027** (2004) 169, DOI:https://doi.org/10.1196/annals.1324.016.
3) J. P. Garandet, G. Mathiak, V. Botton, P. Lehmann and A. Griesche: Reference Microgravity Measurements of Liquid Phase Solute Diffusivities in Tin- and Aluminum-Based Alloys. Int. J. Thermophys., **25** (2004) 249, DOI:https://doi.org/10.1023/B:IJOT.0000022338.21866.f9.
4) M. Shiinoki, N. Hashimoto, H. Fukuda, Y. Ando and S. Suzuki: Self-diffusion measurements of liquid Sn using the shear cell technique and stable density layering. Metall. Mater. Trans. B, **49** (2018) 3357, DOI:https://doi.org/10.1007/s11663-018-1416-3.