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IMPURITY DIFFUSION IN LIQUID ALUMINUM AND COPPER

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1. Introduction

Theoretical analysis of chemical diffusion can hardly be made because numerous factors are comprised in the process. The studies of impurity diffusion, that is, the diffusion of solute into pure solvent from the solvent liquid containing an extremely small amount of solute, would enable to evaluate the effects of various factors on diffusion and permit some insight into chemical diffusion. In order to obtain valuable information on the mechanism of chemical diffusion and the relative importance of such factors as valence, mass and size, the experiments on impurity diffusion have been carried out by using a modified capillary reservoir method. As the solvent metal monovalent copper and trivalent aluminum were chosen. Solute elements were systematically chosen on the basis of periodic table.

2. Experimental

For the measurements of diffusion coefficients of liquid metals, many methods, such as, capillary reservoir method, long capillary method and shear cell method have been proposed and modified. In the present study, the capillary reservoir method originally proposed by Anderson and Saddinog(1) was used because the source of errors had been well elucidated. The details of the experimental procedure were described in the papers previously published by one of the authors. Capillaries of 17 mm long and 1.1 mm diameter were used for the experiments. The compositions of the tracers in the reservoir liquid were mostly not more than atomic percent. The precision of the diffusion coefficients determined were about 6.5% or less.

3. Results and Discussion

3.1 Effect Arising from Difference in valence

In order to evaluate the effects of the valence of solute elements on diffusion, fourth period elements 59Fe, 60Co, 61Ni, 64Cu, and 72Ga which are of nearly the same size and mass with one another, were chosen as solutes. A linear relation was found between the logarithmic value of diffusion coefficient and the reciprocal value of temperature in K within the limits of experimental error. Assuming the following equation (1),

\[ D = D_0 \exp\left(-\frac{E}{RT}\right) \]  

the pre-exponential term \( D_0 \) and the apparent activation energy \( E \) were calculated by means of the least square method. Although an atom in solid state diffuses by several well defined mechanisms, mechanism for the diffusion in liquid state has not been well founded. Thus, it is still remained uncertain what the apparent activation energy means. For example, as the temperature increases not only kinetic energy of the system increases but also the structure of the liquid changes. In such a case the apparent activation energy would change continuously with increasing temperature. As mentioned above, however, the plots of Arrhenius type show a linear relation in the temperature range of melting point of aluminum to 200 C above it wherein the measurements were carried out. Since there is a clear correlation between the apparent activation energy and the position of a solute in the periodic table, the apparent activation energy seems to be a significant parameter for clarifying the relative importance of the factors which might control the diffusivity of impurity in liquid metal in limited range of temperature.

The most significant difference found among the elements belonging to the fourth period is
that of the valence. The relation between the apparent activation energy for diffusion of impurity and valence of the solute element relative to the solvent is shown in Fig. 1. Here, the relative valence of Fe, Co, Ni, Cu, Ga and As were defined as -5, -4, -3, -2, 0, and 1. As shown in Fig. 1, the apparent activation energy increases linearly with increasing relative valence. As also shown in Fig. 1, the same trend can be found for the impurity diffusion in liquid copper and silver. The trend observed can be explained by considering the electrostatic interaction between solute and solvent atoms. In order to induce the diffusive motion of impurity atoms in liquid, it is required that a kind of cavity or a low density region is formed in the vicinity of the impurity atom by the density fluctuation in the solvent. By the electrostatic field of the impurity atom, an additional repulsive (attractive) force is acted on the impurity atom with positive (negative) excess charge. Therefore, the energy which is necessary for the formation of low density region adjacent to the impurity atom with positive relative valence would be smaller than that of the impurity atom with negative valence. This agreed well with the observed results mentioned above.

On the other hand, in the cases of fifth and sixth period solutes, this correlation could not be found. This suggests that not only valence but also the other factors are important for the diffusion of fifth and sixth period solutes.

3.2 Correlation between Thermodynamic Properties and Diffusivity

As mentioned in the previous section, local bonding between solute and solvent atoms is important for the diffusion of solute. It is, however, difficult to evaluate the local bonding accurately. Therefore, thermodynamical properties which reflect the chemical bonding between solute and solvent were compared with the diffusion coefficients measured in the present study. In Fig. 2, impurity diffusion coefficients are plotted against the excess molar free energy of mixing between solute and solvent at infinite dilution of solute. As shown in Fig. 2, the impurity diffusion coefficient increases with increasing excess free energy of mixing. The trend observed may well be understood if the following concept is accepted: The diffusive displacement takes place if there is some kind of cavity or density fluctuation at the nearest neighbours of the impurity atom, that is, diffusion occurs when the bonding between solute and solvent atoms is stretched more than the mean distance.

For a solute having a negatively large excess molar free energy of mixing, the diffusive displacement would be small because the defects around it are small, that is, the more the excess free energy of mixing is, the larger the diffusion coefficient is.

3.3 Effects Arising from Difference in Size and Mass of Solute and Solvent Atoms

To evaluate the effects arising from the differences in size and mass of solute and solvent atoms, the diffusion experiments were carried out by using liquid aluminum as solvent and homovalent elements as solutes such as gallium, indium and thallium. The diffusion coefficients of these solutes are compared with the self-diffusion coefficient of aluminum which was calculated according to the corresponding states theory. As shown in Fig. 3, the diffusion coefficients are in the order $D_{Ga} > D_{In} > D_{Tl}$ over the temperature range where the experiments were carried out. These elements differ significantly in size and mass while they have similar physico-chemical properties. The relation between diffusion coefficient $D$ and the particle radius $r$ can be represented by the well known
Stokes–Einstein equation (2),
\[ D = \frac{kT}{\eta a} \]  
where \( \eta \) is the viscosity of solvent and \( a \) is a constant. The radii of these elements in liquid aluminum is not known, but the ionic and the atomic radii in solid state are in the order \( r_{\text{Ga}}^{\text{In}} > r_{\text{Ga}}^{\text{In}} \)

The observed results mentioned above agreed well with the prediction of the Stokes–Einstein equation. The same result has been obtained for the case of impurity diffusion in liquid copper. These facts indicate that size is an important factor which controls the impurity diffusion in liquid metals and should be taken into consideration in the prediction of the impurity diffusion coefficient.

Although only the repulsive force among the particles comprising a fluid is taken into consideration in the hard sphere theory, it has been successfully applied to the prediction of the transport properties of noble gas liquids, liquid metals and molten salts. From the results obtained by the molecular dynamics for the hard sphere systems, Dymond proposed that the self-diffusion coefficient in a liquid can be represented in terms of molar volume \( V_m \) by the following equation (3),
\[ D = c V_0^{3/2} \left( \frac{T}{\mu_1} \right)^{1/2} \left( V_m - bV_0 \right) \]  
where \( c \) and \( b \) are constants, \( V_m \) is the molar weight, and \( V_0 \) is the molar volume at close packing. Eq.(3) can be applied to impurity diffusion by substituting \( V_m \) for the reduced mass of solute and solvent. In Figs. 4 and 5, the values of \( D/\left( T/\mu_1 \right)^{1/2} \) are plotted against molar volume of aluminum for fourth and fifth period solutes, respectively, where \( \eta \) is the viscosity of aluminum, and \( \mu_1 \) is the reduced mass of solute and aluminum. As shown in Figs. 4 and 5, the values of \( D/\left( T/\mu_1 \right)^{1/2} \) and \( T^{1/2}/\eta \) increase proportionally with increasing molar volume of solvent for most of fourth and fifth period solutes in liquid aluminum. In addition, the lines showing the correlations between \( T^{1/2}/\eta \) or \( D/\left( T/\mu_1 \right)^{1/2} \) and molar volume of solvent intersect the axis of molar volume at the points extremely close with one another. The same plot was done for sixth period solutes in liquid aluminum and shown in Fig.6. The behaviour of iridium is the same as that of fourth and fifth period solutes. The values of \( D/\left( T/\mu_1 \right)^{1/2} \) for thallium, lead and bismuth deviate from the linear relation with increasing molar volume or temperature, and furthermore, the coordinates at which the lines intersect the axis of molar volume of solvent are much larger than those of fourth and fifth period solutes. Assuming the following equation (4), the values of intercept \( V_0 \) was calculated by means of the least square method.
\[ \frac{D}{\left( T/\mu_1 \right)^{1/2}} = k(V - V_0) \]  
As shown in Table 1, the values of \( V_0 \) are approximately equal to the molar volume of solid aluminum 10.6x10^{-5} m^3/mol at melting point within 3%. In Table 1, the values of \( V_0 \) for the solvent copper are also shown and nearly equal to the molar volume of solid copper at melting point in the similar manner as that for aluminum as the solvent. These results suggest that the free volume which...
Molar Volume, V / 10^{-6} m{^3}mol^{-1} 

Table 1 The parameter $V_0$ for aluminum and copper solvents.

<table>
<thead>
<tr>
<th>Solute</th>
<th>$V_0/10^{-6}$ m^{3}mol^{-1}</th>
<th>Solvent: Aluminum</th>
<th>Solvent: Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>11.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>10.91</td>
<td>7.51</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>10.85</td>
<td>7.65</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>10.36</td>
<td>7.62</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>10.80</td>
<td>7.53</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>7.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>-</td>
<td>7.77</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>-</td>
<td>7.70</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>10.79</td>
<td>7.15</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>10.92</td>
<td>7.54</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>10.76</td>
<td>7.65</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>10.80</td>
<td>7.31</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>10.88</td>
<td>7.73</td>
<td></td>
</tr>
<tr>
<td>Te</td>
<td>-</td>
<td>7.77</td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>10.94</td>
<td>7.55</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>10.83</td>
<td>7.22</td>
<td></td>
</tr>
<tr>
<td>Tl</td>
<td>11.22</td>
<td>7.92</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>11.30</td>
<td>7.90</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>11.34</td>
<td>7.84</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>10.82</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

The apparent activation energy for diffusion obtained decreases with increasing the valence of the solute for fourth period solute both in liquid aluminum and copper. This results indicate that the electrostatic interaction caused by the excess charge located at solute atom is important for impurity diffusion.

(2) Correlations between thermodynamic properties and diffusivity were found. The impurity diffusion coefficient increases with decreasing the excess free energy of mixing between solute and solvent.

(3) The diffusion coefficient increases with increasing size of diffusing particle for homovalent solutes both in liquid aluminum and copper. There was a linear relation between $D/(T/u)^{1/2}$ and molar volume of the solvent, where $u$ is the reduced mass of solute and solvent atoms.

References
(2) T. Ejima, N. Inagaki and M. Kameda: Trans. JIM, 7(1966), 133.

The molar volume of solute and solvent atoms. Therefore, the plots of $D/(T/u)^{1/2}$ and molar volume might be reduced to a definite line if the interaction between solute and solvent atoms were taken into consideration.

4. Summary

Impurity diffusion coefficients in liquid aluminum and copper for the solute elements systematically chosen were measured by using a modified capillary reservoir methods. The results obtained are summarized as follows:

(1) Temperature dependence of diffusion coefficients can be represented by an Arrhenius type equation.

The electrostatic interaction between solute and solvent atoms. This is the reason why the slope of the line which correlates $D/(T/u)^{1/2}$ and molar volume of solvent is characteristic of

contribute to the diffusive movement of solute atom is distributed to each atom at close packing when the metal is fused. However, solute atom shares in the amount of the free volume which is corresponding to the strength of interaction between solute and solvent atoms. This is the reason why the slope of the line which correlates $D/(T/u)^{1/2}$ and molar volume of solvent is characteristic of