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Relation between self diffusion and interdiffusion in Al-Cu melts

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Abstract

We compare the experimental interdiffusion constants D_{AlCu} in liquid $Al_{81.3}Cu_{18.7}$ at% to the experimental Cu self diffusion constants D_{Cu} in a similar $Al_{80}Cu_{20}$ at% melt. D_{AlCu} are measured by an X-ray radiography technique and D_{Cu} are measured by the quasi-elastic neutron scattering method. It was found that D_{AlCu} is enhanced by a factor of 3 with respect to D_{Cu}. The relation between D_{AlCu} and D_{Cu} is investigated in the context of Darken's equation where the interdiffusion constant D_{AB} in a binary A-B system is approximated by a simple linear combination of the self diffusion constants D_A and D_B, $D_{AB} = (D_A X_B + D_B X_A)\Phi$ (with X_A and X_B the mole fractions of A and B particles, respectively, and Φ the thermodynamic factor representing the thermodynamic driving force for interdiffusion). We also present a calculation of Φ from the Gibbs free energy data in molten Al-Cu. With these calculated Φ and the D_{Cu} data, interdiffusion coefficients in liquid Al-Cu have been calculated. However, the experimental D_{AlCu} are larger than the calculated ones by a factor of 2. These results suggest that the enhancement of interdiffusion in Al-Cu liquids can not be only attributed to the thermodynamic driving force. Here we propose that the missing factor of about 2 in the Darken equation comes from the contribution of cross correlations to interdiffusion in Al-Cu liquids.

Key words: Interdiffusion, self diffusion, Darken equation, thermodynamic factor, thermodynamic driving force, cross correlation

1. Introduction

Atomic transport properties, described by the diffusion coefficients, are important in many physical processes such as the nucleation, crystallization and glass-formation [1-3]. From a point view of engineering, the diffusion coefficients are also among the basic parameters for materials design from the melt. In a multi-component system, there exists both, self diffusion and interdiffusion. Whereas self diffusion describes the motion of a tagged particle at long times, interdiffusion originates from collective concentration fluctuations among different species [4]. Previous works have shown that Darken's equation is widely used to estimate the relation between self diffusion and interdiffusion in solid metals [5-8]. However, in liquid alloys, due to the difficulties in obtaining reliable diffusion coefficients and thermodynamic data, little is known about the relation between self diffusion and interdiffusion [9, 10].

Diffusion coefficients in liquid metals are usually measured by different long capillary techniques where one sets up a small concentration gradient and determines the diffusion constants based on phenomenological laws [11]. However, under terrestrial experimental conditions, these diffusion measurements might be disturbed by gravity-driven convection [12]. To better examine the disturbance in capillary experiments and thus to improve the accuracy of diffusion measurements, a time-resolved X-ray radiography (XRR) technique has been used to *in-situ* observe the diffusion process in capillaries [13, 14]. With this XRR method, the evolution of the concentration profiles inside the diffusion sample can be monitored and the liquid diffusion coefficient can be directly measured in the molten state. This is a real improvement compared to the *ex-situ* capillary method, where the liquid diffusion coefficient can only be deduced from the concentration profiles of the solidified sample after the diffusion experiment [15].

A convection-independent method for diffusion measurement is the quasi-elastic neutron scattering (QNS) [16]. QNS can detect the microscopic dynamics on atomic length scales and on a picosecond time scale, short enough to neglect convective flow. Thus, self diffusion coefficient of single elements can be deduced from these measured QNS signals in the equilibrium liquid accurately [16, 17].

In this report, the XRR method was used to measure interdiffusion coefficients in liquid Al-Cu [18]. The Cu self diffusion coefficients in Al-Cu liquid were measured by QNS [19]. The thermodynamic factors Φ in Al-Cu liquids were also calculated from Gibbs free energy data [20, 21]. Based on these experimental and calculated results, the relationship between self diffusion and interdiffusion in Al-Cu melts has been investigated in the context of the Darken equation.

2. Experimentals

XRR. Fig.1 schematically shows the XRR instrument for the interdiffusion measurement in liquid metals. A commercial X-ray radiography set-up was used to take pictures of the diffusion sample during the whole diffusion experiment from the heating

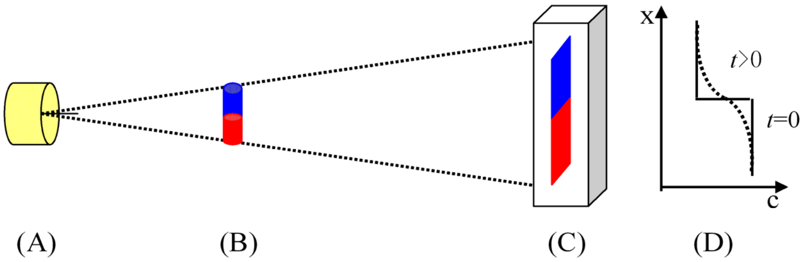

Fig. 1. Sketch of the X-ray radiography technique for interdiffusion measurements in liquid alloys. (A), (B) and (C) show the X-ray source, diffusion couple and flat panel detector, respectively. (D) represents the concentration profiles calculated from the images at times t = 0 (solid line) and t > 0 (dashed line).

phase, isothermal diffusion phase and cooling phase. The X-ray transmission tube is a product from the Phoenix | X-Ray company with a maximum voltage of 160 KV. For the detector (Hamamatsu Company), a time interval of about 4 seconds between two successive images is used to acquire X-ray pictures. In each diffusion experiment, a diffusion couple, i.e. two rods with 1.5 mm in diameter and 15 mm in length, with about 6 at % composition difference is used (see Fig.2). The mean composition of the diffusion couple is $Al_{81.3}Cu_{18.7}$ at% in this work. The diffusion couple was installed vertically inside a graphite tube furnace in order to avoid buoyancy-driven convection by solutal density layering [22]. Based on Beer's law, the concentration profile of the diffusion couple in each image can be calculated from the corresponding axial X-ray intensity profile of the diffusion couple by using references for calibration. An error function as a solution of the diffusion equation was utilized to determine the interdiffusion coefficient by fitting each concentration profile [14]. Because the concentration profiles are measured *in-situ* in the liquid, solidification effects like shrinkage pores, segregation and thermal expansion play no role. The technical details of the XRR method can be found in [14, 18].

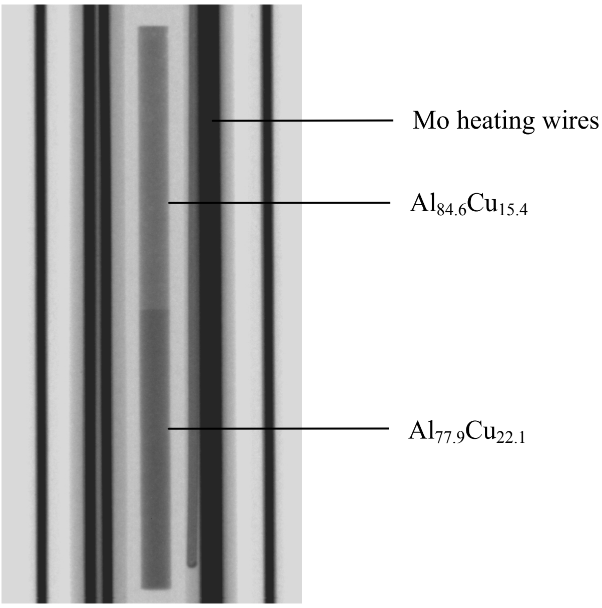

Fig. 2. A typical X-ray absorption image of the diffusion couple. The diffusion couple is installed inside a graphite tube, which will be heated by Mo electrical resistance wires.

QNS. The QNS experiments in $Al_{80}Cu_{20}$ at% were carried out at the time-of-flight spectrometer IN6 at the Institute of Laue-Langevin in Grenoble. The used wave numbers

q at the zero energy transfer are from 0.7 to 1.3 Å^{-1}. In this q range, the signal of $Al_{80}Cu_{20}$ liquid is controlled by the incoherent scattering of Cu. This is the theoretical base for deriving the self diffusion constant of Cu. At this low q range (the hydrodynamic regime), a q^2 dependence of the quasielastic line width can be observed. The self diffusion coefficient can be deduced via [16, 19]

$$D = \frac{\Gamma_q}{2\hbar q^2}. \tag{1}$$

Here, Γ_q is the full width at half maximum of the measured quasi-elastic line and $\hbar$ is the reduced Planck constant. The $Al_{80}Cu_{20}$ alloy was prepared by arc melting and was then held in an Al_2O_3 crucible for QNS measurements. More details can be found in [19].

3. Results and Discussion

Figure.3 shows interdiffusion coefficients D_{AlCu} in liquid $Al_{81.3}Cu_{18.7}$ measured by the XRR method and the QNS Cu self diffusion coefficients D_{Cu} of a similar composition $Al_{80}Cu_{20}$ as a function of inverse temperature, $1/T$, in a semi-logarithmic plot. As indicated in Fig.3, the statistical error bars of the measured D_{AlCu} and D_{Cu} are within 10%. Assuming that interdiffusion and self diffusion coefficients obey an Arrhenius relation, both D_{AlCu} and D_{Cu} are fitted by the function $D = D_0 \exp(-\Delta Q/\kappa_B T)$ with D_0 the pre-exponential factor, ΔQ the activation energy and κ_B the Boltzmann constant (see Fig.3).

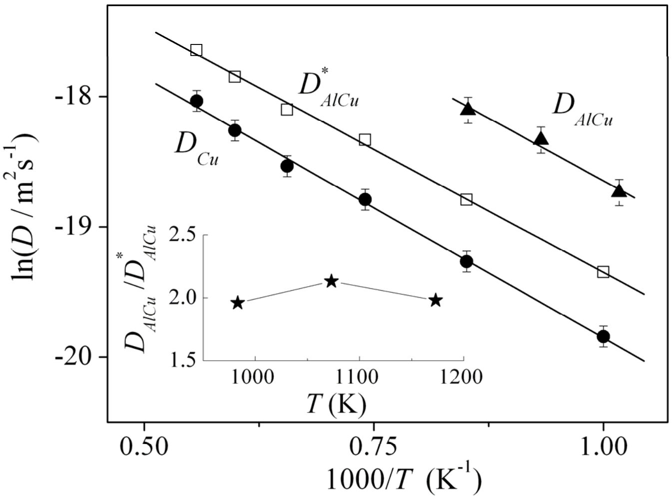

Fig. 3. Arrhenius plots of the interdiffusion constants D_{AlCu} (▲) in $Al_{81.3}Cu_{18.7}$ measured by XRR, self diffusion constants D_{Cu} (●) in $Al_{80}Cu_{20}$ by QNS and calculated interdiffusion constants D^*_{AlCu} (□) from Darken's equation in $Al_{80}Cu_{20}$. The solid straight lines show the corresponding Arrhenius fits to D_{AlCu}, D_{Cu} and D^*_{AlCu}. The inset presents the ratios D_{AlCu}/D^*_{AlCu} as a function of temperature T.

The fitted value ΔQ (0.33 eV) for D_{AlCu} in $Al_{81.3}Cu_{18.7}$ is close to that (0.34 eV) for D_{Cu} in $Al_{80}Cu_{20}$. The fitted factors D_0 are 3.7×10^{-7} m^2/s and 1.3×10^{-7} m^2/s for D_{AlCu} and D_{Cu}, respectively. However, the absolute value of D_{AlCu} ((13.7±1.3) $\times10^{-9}$ m^2/s) in $Al_{81.3}Cu_{18.7}$ at 1173 K is approximately 3 times as large as the value of D_{Cu} ((4.3±0.3) $\times10^{-9}$ m^2/s) in $Al_{80}Cu_{20}$ at 1175 K. Similarly, D_{AlCu} of $Al_{81.3}Cu_{18.7}$ at 983 K is 3 times as large as D_{Cu} of $Al_{80}Cu_{20}$ at 1000 K. Generally, in the measured T range of 983 K to 1173 K, liquid interdiffusion constants D_{AlCu} are larger than the self diffusion constants D_{Cu} by a factor of 3 in a nearly identical composition of $Al_{80}Cu_{20}$.

In the binary A-B alloy system, D_{AB} can be related to the self diffusion constants D_A and D_B as [4]

$$D_{AB} = (D_A X_B + D_B X_A)\Phi S, \tag{2}$$

where S is a kinetic factor measuring the contribution of cross correlations to D_{AB}. In crystals, S is also called the Manning factor [23]. In the case that all the cross correlation contributions are negligible (S = 1), Equation (2) reduces to the so-called Darken equation [5].

For the self diffusion constant D_{Al} of Al, we do not have the experimental data due to the lack of a second isotope of Al. In Al-Ni, the molecular dynamics simulations (MD) results show that the self diffusivities of Al and Ni are nearly the same [9]. Based on this result, we treat $D_{Al} = D_{Cu}$ in the present Al-Cu liquid.

To better understand the thermodynamic driving force for interdiffusion, we try to determine Φ alternatively from the Gibbs free energy G of the Al-Cu binary solution. Here Φ can be regarded as the second composition derivative of G for the Al-Cu solutions [2]:

$$\Phi = X_{Al} X_{Cu} \frac{\partial^2 G}{\partial X^2}, \tag{3}$$

where X_{Al} and X_{Cu} are the mole fractions of Al and Cu, respectively, X means X_{Al} or X_{Cu}, and G is given in [20] as

$$G = (X_{Al}{}^0G_{Al} + X_{Cu}{}^0G_{Cu}) + RT(X_{Al}\ln X_{Al} + X_{Cu}\ln X_{Cu}) + {}^EG. \tag{4}$$

Here, the first term represents the molar Gibbs energies of pure Al and Cu before mixing, which are composition independent. The second term comes from the free energy of mixing for an ideal solution. The third term ${}^EG$ means the excess Gibbs energy of the real liquid and is written in the Redlich-Kister form with temperature dependent parameters ${}^vL_{A,B}(T)$ [20]:

$${}^{\mathrm{E}}G(X_A, X_B, T) = X_A X_B \sum_{v=0}^{2} {}^vL_{A,B}(X_A - X_B)^v. \tag{5}$$

Using the parameters ${}^vL_{A,B}(T)$ in Al-Cu liquids taken from the literature [21], thermodynamic factors Φ for $Al_{80}Cu_{20}$ were calculated from equations (3)-(5) and are shown in Fig.4 as a function of 1000/T in the range between 1000 K and 1795 K. Φ decreases from 1.64 at 1000 K to 1.48 at 1795 K and the total variation is about 10 %, which means that at low temperatures the thermodynamic driving force is slightly stronger than at higher temperatures in this temperature regime.

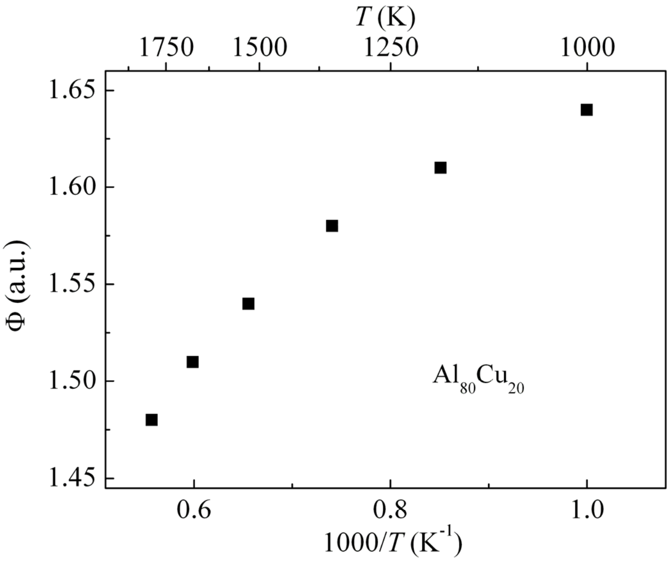

Fig. 4. T dependent Φ calculated from the second derivative of Gibbs free energy.

If we use these calculated Φ and also assume that $D_{Al} = D_{Cu}$, we can deduce the interdiffusion constants from the measured D_{Cu} data by Darken's equation and the calculated interdiffusion constants D^*_{AlCu} for $Al_{80}Cu_{20}$ liquid as a function of $1000/T$ were also plotted in Fig.3. Analogous to D_{AlCu} and D_{Cu}, D^*_{AlCu} also follows an Arrhenius relation with ΔQ of 0.33 eV and D_0 of 3.7×10^{-7} m^2/s. It is interesting that this ΔQ is identical to that for D_{AlCu}, implying that the calculated D^*_{AlCu} at least correctly reflects the temperature dependent tendency for interdiffusion. However, the values of D^*_{AlCu} are only half of the experimental values of D_{AlCu} in the T range from 983 to 1173 K. As inserted in the left corner of Fig.3, the ratios D_{AlCu}/D^*_{AlCu} at three temperatures, corresponding to the three measured D_{AlCu}, are nearly equal to a constant value of 2. These results demonstrate in the present Al-Cu liquids, that Darken's equation cannot satisfactorily describe the relationship between interdiffusion coefficients and self diffusion coefficients if the cross correlation term is not taken into account. Namely, the enhancement of interdiffusion with respect to self diffusion in the Al-Cu liquids is not only attributed to the thermodynamic factor Φ of ~1.5 but also attributed to the cross correlation factor S of ~2. Considering that it is difficult to obtain the accurate Gibbs free energy data and that the experimental values of D_{Al} are not present, the obtained values of Φ and S may have considerable errors. But the comparable values between Φ and S clearly state that the cross correlation contribution to interdiffusion in the Al-Cu liquid is important.

3. Conclusion

The interplay between self diffusion and interdiffusion has been investigated in the context of Darken's equation. We measured interdiffusion and Cu self diffusion in similar compositions of liquid $Al_{80}Cu_{20}$ and calculated the thermodynamic factor from Gibbs free energy data. , Interdiffusion is experimentally discovered 3 times as fast as the Cu self diffusion in the liquid Al-Cu. This enhancement of interdiffusion can be explained by a combination of the thermodynamic driving force by a factor of ~1.5 and the collective cross correlation contribution by a factor of ~2 in the liquid Al-Cu.

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