

Diffusion in Al-Cu Melts Studied by Time-Resolved X-Ray Radiography

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We use time-resolved x-ray radiography in order to monitor interdiffusion processes *in situ* in liquid alloys. We measure temperature and composition dependent interdiffusion coefficients (D_{AlCu}) in Al-rich Al-Cu melts. At constant temperature, D_{AlCu} only exhibits a weak dependence of the alloy composition. As compared to self-diffusion, interdiffusion is enhanced by a factor of about 3. Our results demonstrate that it is not possible to express interdiffusion in terms of self-diffusion and thermodynamic driving forces.

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Driven by density and concentration fluctuations, diffusion of mass is a fundamental property of liquids [1–3]. Upon undercooling below the melting point the diffusion behavior in the liquid affects the formation of crystal nuclei and limits the growth rate of the crystal phase. In general, the self-diffusion coefficients of the particular components in a multicomponent liquid are related to the mean square displacement of the tagged atoms or molecules, respectively, whereas the interdiffusion coefficients are related to collective transport of mass driven by concentration gradients. Up to date little is known in liquid alloys about the interplay of self-diffusion and interdiffusion, due to a lack of accurate experimental data.

A common method to measure diffusion coefficients in liquid alloys is the long capillary technique and its variations [4–6]. There a diffusion couple of different composition, in the case of interdiffusion, or containing a different amount of isotopes, in the case of self-diffusion, is annealed in the liquid state and subsequently quenched to ambient temperature. The diffusion profiles are analyzed *post mortem* applying Fick's law of diffusion. However, in most cases, the temperature quench induces crystallization, and the thus evolving microstructures alter the concentration profiles to an *a priori unknown* extent. Here, we apply a technique that allows for an *in situ* monitoring of liquid interdiffusion processes in diffusion couples that exhibit a x-ray radiographic contrast. Diffusion profiles along the liquid sample are also time resolved, thus allowing us to detect influences of convective flow on the diffusion process.

Self-diffusion coefficients in liquid alloys can also be measured *in situ* with quasielastic neutron scattering (QNS). QNS probes the dynamics on atomic length scales and on a picosecond time scale, short enough to be undisturbed by the presence of convective flow. In the case of an incoherent scattering contribution, e.g., from a liquid containing Ni, Ti, or Cu, the low- q signal is dominated by the incoherent contributions to the scattering signal. From the resulting intermediate scattering function the self-diffusion coefficient can be obtained on an absolute scale [7,8]. The

self-diffusion of Cu in liquid $\text{Al}_{80}\text{Cu}_{20}$ has recently been investigated with QNS [9].

For the measurement of interdiffusion coefficients we use a commercial Phoenix x-ray source that is continuously operated at 150 kV. After penetration through sample, holder and furnace, absorption images are recorded in an Hamamatsu flat panel detector (Fig. 1). The x-ray intensity profile along the length direction of the diffusion couple is transformed to a concentration profile via a normalization to the intensity values of two reservoirs containing two standard reference compositions placed just above and below the sample. The detector is readout and reset in intervals of about 4 seconds, thus resulting in a series of diffusion profiles that allow us to monitor the interdiffusion process as a function of time from melting the sample to its solidification [Fig. 2(a)].

The sample holder is made of high purity graphite. Its cylindrical shape, with a diameter of 10 mm and a length of 90 mm, provides a bore of 1.5 mm in diameter and 25–30 mm in length in its center. Over its entire length the graphite holder is heated by Mo electrical resistance wires, resulting in a temperature homogeneity along the sample of better than 0.5 K. The sample holder is mounted in an evacuated quartz tube and aligned along the axis of gravity placing the composition with the higher density on the bottom of the capillary. More technical information on

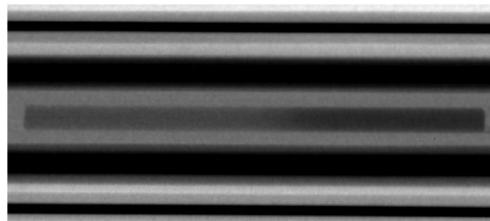


FIG. 1. X-ray image of the sample during diffusion annealing. Dark lines represent absorption by the Mo heating wires. Cu concentration profiles [Fig. 2(a)] are derived from the gray values along the sample in the center of the graphite holder. For a better representation the image is rotated by 90°.

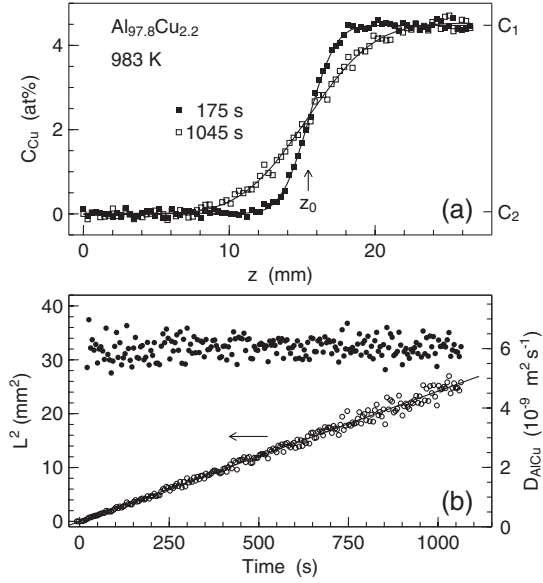


FIG. 2. (a) Concentration profiles for the Al-AlCu_{4.5} diffusion couple at two different annealing times. Lines are fits with Eq. (1). (b) Diffusion length square, $L^2 = 4D_{\text{AlCu}}t$ (open circles), as a function of annealing time at 983 K and resulting interdiffusion coefficients D_{AlCu} (closed circles).

the setup including a detailed discussion concerning the error analysis will be published elsewhere [10].

Al-Cu alloys were prepared from pure Al and Cu metals by induction melting in compositions of 4.5 at %, 9.6 at %, 15.4 at %, and 22.1 at % (atomic percent) Cu content (10, 20, 30, and 40 weight percent Cu, respectively). For the diffusion experiments rods of 1.5 mm in diameter and 10 or 15 mm in length were manufactured on a lathe from large size ingots and pure Al. The chemical composition and its homogeneity was checked along the sample with energy dispersive x-ray spectroscopy (EDX) and x-ray radiography (XRR). Interdiffusion experiments were done on 4 different diffusion couples, 0 at % Cu–4.5 at % Cu, 4.5 at %–9.6 at %, 9.6 at %–15.4 at %, 15.4 at %–22.1 at %, giving alloys with mean compositions of Al_{97.8}Cu_{2.2}, Al₉₃Cu₇, Al_{87.5}Cu_{12.5}, and Al_{81.3}Cu_{18.7}, respectively. All samples were annealed at 983 K—the Al_{81.3}Cu_{18.7} samples in addition at 1073 and 1173 K.

Figure 2(a) shows two concentration profiles at different annealing times. Starting with a concentration step in the solid, in the liquid interdiffusion causes mass transport through the initial interface resulting in a broadening of the diffusion zone. All liquid concentration profiles are well described by the following error function formula which represents a solution of Fick's second law of diffusion for a long capillary experiment [3]

$$C(z, t) = \frac{C_1 + C_2}{2} + \frac{C_1 - C_2}{2} \operatorname{erf}\left(\frac{z - z_0}{\sqrt{4D_{\text{AlCu}}t}}\right) \quad (1)$$

with $L^2 = 4D_{\text{AlCu}}t$ for a diffusion length L . C_1 and C_2

represent the Cu content (in at %) of the two alloys of the diffusion pair, z_0 the position of their interface and t the annealing time. For all diffusion runs the position of the interface z_0 did not change measurably.

Resulting L^2 are shown in Fig. 2(b). Already ≈ 20 seconds after the time at which first traces of liquid diffusion can be detected, the L^2 exhibits a linear increase in time as expected for a purely diffusive process. Subsequently, $D_{\text{AlCu}}(t)$ remained constant within statistical errors for about 1050 s, before the sample is quenched to the solid state. The resulting interdiffusion coefficient is obtained from a fit with a linear function to L^2 .

Convective flow during diffusion annealing is recognized to be a severe problem in capillary experiments. As has been shown by comparison of LC diffusion experiments on ground with experiments under microgravity conditions in space on liquid Sn [5,11], or with QNS measurements on liquid Cu [12], resulting LC values on ground are systematically larger by several 10% to 100%. The concentration profiles obtained on the Al-Cu systems measured here *in situ* do not show obvious influences of convective flow. During the entire diffusion annealing the fit parameters for the end concentrations C_1 and C_2 remained constant within error bars [Fig. 2(a)]. In addition, the *in situ* monitoring of diffusion processes with a flat panel detector allows us to integrate intensities along the fringes of the sample and the center axis separately. Resulting diffusion coefficients are equal within error bars. Systematic differences cannot be detected. Apparently, the small capillary diameter in combination with the diffusion couples used here, that provide a sufficiently large difference in density, results in a stable density layering that in turn suppresses convective flow.

Relying on a post mortem analysis one does not only not know how convective flow altered the diffusion profiles, the solidification of the sample itself poses a problem. In general, in alloys a more or less coarse grained microstructure is forming during crystallization that depends on the alloy composition, quench rates and resulting temperature gradients. E.g. in the Al-Cu system only minor concentrations of Cu can be stably dissolved in crystalline Al. With increasing Cu content Al-rich dendrites form and Cu is enriched in eutectic and nonequilibrium Al-Cu phases [13]. This alters the resulting concentration profiles on mm length scales and in many cases renders a post mortem analysis impossible.

In conventional LC diffusion experiments, the uncertainty in the knowledge of the absolute value of the annealing time t and the required correction for the thermal expansion of the sample pose additional sources of errors. For a post mortem analysis, one has to retransform the z coordinate of the determined concentration profile from the crystalline state to the liquid state, which requires the knowledge of thermal expansions or absolute values of densities. Using XRR the interdiffusion coefficient is di-

rectly read off from the slope of L^2 . A length correction is not required.

Another approach to estimate interdiffusion coefficients is the analysis of the concentration profile of the solute boundary layer in a quenched directionally solidified alloy [14]. Also in this case, a post mortem analysis inherits similar problems on the data accuracy like mentioned above for the direct measurement via Fick's law. In addition, a model free analysis can only be realized under the assumption of a steadily growing planar solid-liquid interface under isothermal conditions, which is difficult to maintain in experiments.

Figure 3 shows the interdiffusion coefficients measured here at a constant temperature of 983 K for the different alloy compositions. As compared to Cu self-diffusion coefficients in liquid $\text{Al}_{80}\text{Cu}_{20}$ interdiffusion coefficients are about a factor of 3 larger (Fig. 4).

A simple ansatz to relate self and interdiffusion goes back to Darken [15]. He expresses the kinetic contributions to the interdiffusion coefficient by the self-diffusion coefficients, however, neglecting the dynamic cross correlations. A thermodynamic factor Φ represents the contribution from a thermodynamic driving force. In Darken's equation the interdiffusion coefficient reads:

$$D_{\text{AlCu}}^* = (C_{\text{Cu}}D_{\text{Al}} + C_{\text{Al}}D_{\text{Cu}})\Phi, \quad (2)$$

where D_{Al} and D_{Cu} are the self-diffusion coefficients in the alloy of Al and Cu, respectively, and C_{Al} and C_{Cu} represent the alloy composition in at %. Φ is the 2nd derivative of the Gibbs free energy with respect to concentration of the binary Al-Cu solution. For the calculation of Φ thermodynamic data from Ref. [16] have been used. The dependence of Φ from the alloy composition is shown in Fig. 3. In $\text{Al}_{80}\text{Cu}_{20}$ Φ is decreasing by about 13% on increasing the temperature from 1000 to 1800 K. Note that Φ values derived from thermodynamic data from Ref. [17] are about 8% smaller and Φ values calculated from heats of mixing [18] under the assumption of a regular solution are about 12% larger than the data used here.

For an exact expression of interdiffusion coefficients, Darken's equation has to be extended by an additional

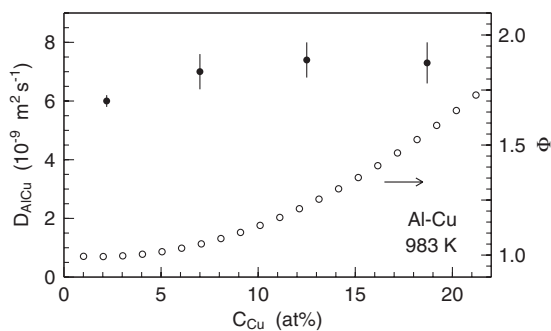


FIG. 3. Interdiffusion coefficients D_{AlCu} (closed circles) and thermodynamic factor Φ (open circles) as a function of mean alloy composition of the diffusion couple at 983 K.

factor S that takes dynamic cross correlations into account [19]. In order to calculate S the knowledge of distinct velocity correlation functions of center of mass motions are required. As will be shown in the following, the influence of dynamic cross correlations can be large, and therefore, it is in general not possible to describe interdiffusion in terms of self-diffusion of the atoms and thermodynamic driving forces.

In Al based alloys, the measurement of Al self-diffusion coefficients is challenging due to a lack of a second stable isotope or a significant incoherent neutron scattering cross section. Figure 4 shows calculated D_{AlCu}^* under the assumption that $D_{\text{Al}} = D_{\text{Cu}}$. Interdiffusion coefficients calculated via Eq. (2) are underestimating our experimental values by about a factor of 2. The estimated D_{AlCu}^* can match experimental values only if $D_{\text{Al}} \approx 6D_{\text{Cu}}$. Such a difference in the self-diffusion coefficients is not supported by our QNS results [9]. There coherent correlations decay in a single exponential manner, supporting also the assumption that $D_{\text{Al}} \approx D_{\text{Cu}}$.

The thermodynamic factor Φ is increasing from a Cu content of 7 at % to 18.7 at % by about 50% whereas over this range in composition the D_{AlCu} are equal within error bars (Fig. 3). Apparently, the kinetic contributions to interdiffusion are roughly decreasing to the extent at which the thermodynamic contributions to interdiffusion increase. This is supported by QNS measurements on liquid alloys $\text{Al}_{90}\text{Cu}_{10}$, $\text{Al}_{83}\text{Cu}_{17}$, and $\text{Al}_{75}\text{Cu}_{25}$ alloys [20]. Although the data analysis in terms of a jump diffusion model is not appropriate, the widths of the quasielastic signals indicate, that at 973 K in these alloys the Cu self-diffusion is decreasing by about 25% with increasing Cu content.

This is in line with recent molecular dynamics (MD) simulations on liquid Al-Ni [21]. On the Al-rich side, the values of the Al and Ni self-diffusion coefficients are decreasing with increasing Ni content. Ni self-diffusion

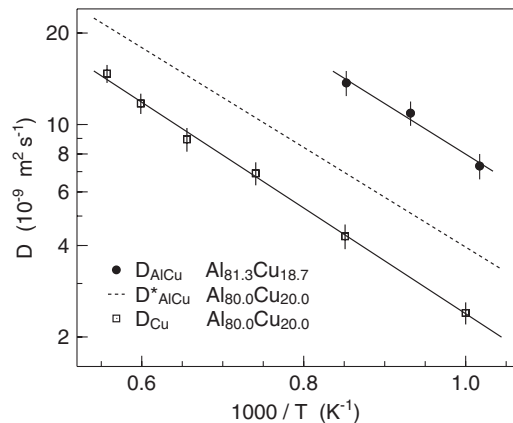


FIG. 4. Temperature dependent diffusion coefficients in Al-Cu melts determined by XRR and QNS. The dashed line represents interdiffusion coefficients derived via the Darken equation [Eq. (2)] under the assumption that $D_{\text{Al}} = D_{\text{Cu}}$. The solid lines are guides to the eye.

coefficients measured with QNS [22] exhibit a similar behavior. In the MD simulation S is decreasing as well with increasing Ni content; however, in MD Al-Ni reported S remain smaller than 1 over the entire composition range.

MD simulations on liquid Al₈₀Ni₂₀ [19] also result in $D_{\text{Al}} = D_{\text{Ni}}$ within error bars. At 1500 K the interdiffusion coefficient is about 1.7 times larger than the self-diffusion coefficients. With a thermodynamic factor of about 2.1, the MD simulations on liquid Al₈₀Ni₂₀ indicate that the Darken equation is a good approximation, in contrast to our findings in Al-Cu. With a factor S that is close to 2, apparently, in Al-Cu, dynamic cross correlations play a more important role and enhance interdiffusion coefficients even more than expected by the thermodynamic factor in Darken's equation. These findings are also in contrast to results of a theoretical mode coupling analysis using experimental partial static structure factors of liquid Zr₆₄Ni₃₆ as input [23]. Resulting Zr and Ni self-diffusion coefficients and the interdiffusion coefficient are similar, although the thermodynamic factor is about 5. Here, dynamic cross correlations strongly reduce the kinetic contribution to interdiffusion.

In conclusion, we present an advanced technique to measure interdiffusion coefficients applying a combination of LC diffusion experiments with *in situ* monitoring via x-ray radiography. In Al-Cu alloys diffusion profiles exhibit no evident features caused by convective flow during the annealing in the liquid phase. As compared to Cu self-diffusion measured with quasielastic neutron scattering in Al₈₀Cu₂₀ resulting interdiffusion coefficients are about a factor of 3 larger. The thermodynamic driving force giving a thermodynamic factor of about 1.6, is in Darken's ansatz not large enough to account for this difference. In Al-Cu dynamic cross correlations further enhance interdiffusion with respect to the self-diffusion of the atoms by about a factor of 2. This shows that, interdiffusion coefficients have to be measured and cannot be obtained from the knowledge of self-diffusion coefficients and the thermodynamic factor alone.

Accurate diffusion coefficients pose a key to the understanding of liquid dynamics and of mass transport mechanisms, and are vital for a comprehensive approach to the modeling of solidification. *In situ* monitoring of interdiffusion processes in liquid alloys with radiography paves the way for accurate measurements of transport coefficients, where one can rule out, or eventually even correct for, convective contributions to the resulting concentration profiles, and where the experiment is not altered by the microstructure evolution during solidification. X-ray radiography is currently extended to the use on synchrotron radiation facilities, where the radiographic contrast of different components in an alloy depends on the selected

wavelength of the monochromatic beam. Our capillary and furnace setup can also be used on neutron sources. There, the radiographic contrast is in most cases complementary to that of x rays and can even be changed by the use of proper isotopes. In combination the use of radiographic techniques will allow not only for the measurement of the interdiffusion coefficient in binary alloys, but also for the determination of the four different interdiffusion coefficients in a ternary alloy.

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