Diffusion Measurements on Liquid Metallic Materials and Development of Shear Cell
(Preparation for Russian Satellite Mission Foton–M2)

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Abstract

For exact diffusion measurements of liquid metals we improved the shear cell technique which is available for both under μg-conditions (Foton–M2 satellite mission) and under 1 g-conditions. The main points of the design were minimization of the shear convection, minimization of the Marangoni convection, and improvement of reliable operation. The effect of the shear convection was investigated by short time diffusion experiments both under low-g (parabolic flight in a plane) and under 1 g. As the result the additional mean square diffusion depth caused by the shear convection turned out to be in the order of $10^{-7}$ m$^2$, which is smaller than 1% of the usual mean square diffusion depth. We found a correction method for the additional diffusion depth. Using the shear cell diffusion experiments in Sn–Bi, In–Sn, and Al–Ni alloys were performed, with a stable density layering under 1 g-conditions. The concentration profile at each experiment was obtained by the analysis of atom absorption spectroscopy (AAS) and yielded the diffusion coefficients by using the correction method. The diffusion coefficients were the same as the μg-reference data and those from the magnetic field under 1 g-conditions. The temperature dependence of the diffusion coefficient obeyed the power law. On the basis of these results the diffusion types were classified according to the reliability of 1 g-measurement.

1. Introduction

Exact diffusion measurements of liquid metals are very much in demand from both physical and metallurgical points of view. Until now most of the reliable diffusion data of liquid metals were obtained under μg conditions where the liquid metals are mostly free from buoyancy convection. The measurement tool for most of the diffusion experiments was the long capillary method. Recently, the shear cell method became a standard measurement tool. Fig. 1 shows an example of a diffusion experiment with the shear cell. Two kinds of samples are connected only during the diffusion phase. Due to this mechanism the shear cell technique has several advantages compared to the long capillary method:

1) no necessity to correct diffusion coefficients during the heating and the cooling phase,
2) no necessity to correct diffusion coefficients for the effect of volume expansion and shrinkage,
3) possibility of homogenization before the diffusion phase starts (e.g. in case of polyphasic alloys), and
4) no influence of segregation during solidification.

Especially the advantage 4) is the most important to expand the variation of sample selection into multi-component systems which show the segregation problem.

From these reasons we do diffusion experiments with the shear cell technique on the Russian satellite mission Foton–M2 planned to be launched in early 2005. The shear cell technique, however, has a complex structure and function. Thus we improved the shear cell technique (named Foton shear cell) based on that one developed for the Foton–12 mission aiming at a high reliability of operation, minimization of the shear convection and minimization of free surfaces.

At the same time, we are investigating the possibility of 1 g-shear cell-diffusion experiments using a stable density layering. The diffusion axis is set parallel to the gravity vector and the samples are set such that the density increases monotonously downwards during the whole diffusion time. In such a case, even if forces are generated by temperature gradients and try to start convection rolls, the force generated by the density gradient can cancel them mostly. For this purpose, binary alloys are favorable as diffusion samples. The shear cell technique is effective to solve the segregation problem of these alloys. The first purpose of 1 g-experiments is to check the Foton shear cell before the flight and to establish a highly completed shear cell technique. The second purpose is to classify the diffusion types according to the reliability of 1 g-measure-
Fig. 1 Operational diagram of the path of a diffusion experiment with the Foton shear cell. An interdiffusion experiment is illustrated as an example.

2. Development of Foton Shear cell

2.1 Minimization of shear convection

There are several reports about shear convection in a diffusion experiment using the shear cell technique. Arnold et al. investigated the effect of the shear convection by numerical simulations. It was concluded that the aspect ratio of the cell length H and the diameter d of a capillary is important; for H/d > 3 the measurement is unaffected by the shearing action, for 1 < H/d < 3 convective mixing exists but the disturbance is small enough to be corrected well, for H/d < 1 convective mixing is contributing strongly. If the cell length H is longer, the averaging effect of AAS (mentioned below) will be larger, but can be corrected. Considering the results and the restriction to minimize
the whole shear cell length and weight, we decided to use $H = 3\, \text{mm}$, $d = \phi 1.5\, \text{mm}$.

The shearing mode is also critical for the shear convection. Mathiak et al.\cite{13} investigated this problem by numerical simulations. Griesche et al.\cite{14} observed the shear convection of colored water in a transparent model shear cell made of Plexiglas\textsuperscript{TM} in parabolic flight experiments. They showed that the initial shearing mode with an intermediate cell has a smaller penetration depth than the mode with two half columns. There was no large difference between the comb shearing and the helical shearing for the final shearing process. Considering these results, the Foton shear cell employs the mode with an intermediate cell as the initial shearing and the comb shearing as the final shearing mode. If it is needed, the initial shear mode with two half columns is also possible by changing the set-up of the Foton shear cell.

The smoothness of the rotation is also critical to avoid vibration and convection. From this point of view a stepping motor, which causes vibration, is not preferable, although it is advantageous for the positioning of the cells. We employed a DC-motor with a specially designed amplifier circuit which controls the tachometer voltage (rotation speed). Positioning is done with a software which detects the rapid increase of the motor current at the end of a shear process and then switches off the motor. The discs are pressed together by elastically compressed graphite felts. The compression force $F$ in Fig. 1(a) was set to $2\, \text{N}$, which is large enough to avoid leakage of liquid sample as mentioned below. With this compression force the friction force between the discs is small enough to guarantee a smooth rotation of the discs/cells.

The intensity of the shear convection is proportional to the shear speed\cite{15}. On the other hand, this kind of motor regulation system has a low torque at a low speed. Thus the shearing speed of the discs was set between 0.5 and 1 mm/s.

### 2.2 Minimization of free surfaces

Free surfaces on the liquid diffusion samples can cause Marangoni convection, which also disturbs the concentration profile in diffusion experiments\cite{15}. Misalignment of cells causes e.g. free surfaces. To avoid this problem and a leakage of liquid sample materials, highly precise machining with a tolerance of about 10 $\mu\text{m}$ is required.

Another technique in this study for the minimization of free surfaces is setting reservoirs with sufficient high pressure on both ends of the capillary (Fig. 1(a)). At the set-up the volume of solid samples in the capillaries must be 20% smaller than the capillary capacity; otherwise the expanded sample material opens the gap between the discs and molten sample material leaks out through the gap. In the reservoir we use a sample material which is identical to the material in the capillary. Pressure on the material is created by elastically compressed graphite felts in the reservoir. At the liquidus temperature of the sample, the compressed elastic graphite felts press onto the molten metal and fill the capillary completely. To minimize free surfaces, it is required to keep a sufficient pressure $P_s$ (Fig. 1) on the liquid in the capillary during the diffusion phase. Hence, the diameter of the reservoir must be much larger than that of the capillary so that there is only a small reduction of the spring force of the felts. At the initial shearing one of the reservoirs is separated from the capillary, but the other remains in position. The curvature radius $R_c$ (Fig. 1(d)) of the free surface at the corner in the capillary can be estimated by $\gamma/P_L$, where $\gamma$ is the surface tension of the molten sample. On the other hand a too high pressure could cause leakage of the molten sample from the capillary. Considering also the requirement of the smooth rotation as mentioned above, we chose the reservoir pressures as $10 – 30\, \text{kPa}$. $R_c$ is estimated as $20 – 60\, \mu\text{m}$, for example, in case of Sn at $300\, ^\circ\text{C}$, $\gamma = 560\, \text{mN/m}$\cite{16}.

### 2.3 Construction of the Shear Cell

The photo embedded in Fig. 1 shows the construction of the Foton shear cell. The main parts of the shear cell are made of graphite and the weight is about $400\, \text{g}$. A shear cell unit has a set of four diffusion capillaries so that four parallel experiments can be performed simultaneously. The whole shear cell consists of an outer fixed tube, an inner rotatable tube, 20 discs, two reservoir units and an axle. Each capillary inside the discs has $60\, \text{mm}$ length and $1.5\, \text{mm}$ diameter. The shear cell is heated up by a Mo-wire isolated by ceramic tubes and mounted around the outer fixed tube. Ceramic fiber sheets (not shown in the photo) are wound around the outer fixed tube for thermal isolation and for damping of mechanical shocks at launching. Six shear cells can be operated in six separate chambers in the AGAT-furnace (Foton–M2 mission). The holders on both ends of the shear cell are fixing the shear cell inside the chamber. The motor rotates the inner tube and thereby every second disc (comb shearing).

### 3. Experimental procedure using the Foton shear cell

#### 3.1 Diffusion experiments

By varying the combination of the samples and the position of the intermediate cell, the Foton-shear cell can perform several types of diffusion experiments:

1. interdiffusion (diffusion between semi-infinite sources) (Fig. 2(a)),

2. thick layer diffusion (diffusion into double semi-infinite liquids from a planar source) (Fig. 2(b)), and

3. thick layer diffusion (diffusion into a single semi-infinite liquid from a planar source) (Fig. 2(c)).

Each sample part is weighed before insertion in ord-
er to check filling of the capillary after the experiment. If we discuss the reproducibility of measurements, all of the four capillaries (named A, B, C and D) are filled with samples with the same composition from the same charge and the experiments are simultaneously performed.

The experimental procedure follows that one shown in Fig. 1, which is the same as that foreseen for the experiments in the improved AGAT-furnace facility (Foton–M2 mission). The 1 g and low-g (parabolic flight) diffusion experiments are performed by using the Foton shear cell installed in a single vacuum chamber which has the same dimension as in the AGAT-furnace.

After evacuating the chamber the furnace is heated up to the diffusion temperature. The vacuum pressure is lower than 0.1 Pa (1 g-experiments), and about 50 Pa (low-g experiments). After a one-hour homogenization phase the initial shear process is performed at a shear speed $v_0$ of 0.5 mm/s (1 g) and 1 mm/s (low-g) to start the diffusion process. The axial temperature gradient is smaller than 100 K/m. At the end of the diffusion time the final shear was started at 0.5 mm/s (1 g) and 1 mm/s (low-g) and then the heater is switched off. After cooling down each sample piece is pressed out of the cell mechanically, weighed and dissolved in aqua regia for the analysis by atomic absorption spectroscopy (AAS). The concentration of the components in each cell is plotted with an error of ±2% at the center position of each cell.

3.2 Evaluation of mean square diffusion depth

By fitting the following functions to the concentration profiles obtained by AAS, the measured mean square diffusion depths $x_{\text{meas}}^2$ were determined. Here the cases of the diffusion of an impurity component in an alloy into a pure material are described.

The concentration profile for the interdiffusion is fitted with

$$c(x, t) = \frac{c_0}{2} \text{erfc} \left( \frac{x - x_0}{\sqrt{2Dt}} \right)$$

(1)

The concentration profile for the thick layer diffusion is fitted with the thick layer solution:

$$c(x, t) = \frac{c_0}{2} \left[ \text{erf} \left( \frac{h + x}{\sqrt{2Dt}} \right) + \text{erf} \left( \frac{h - x}{\sqrt{2Dt}} \right) \right]$$

(2)

Here $D$ is the diffusion coefficient, $t$ is the diffusion time, $c_0$ is the initial concentration of the impurity in the alloy side, $x$ is the distance from the edge of the diffusion sample in eq. (1) (Fig. 2(a)) and in eq. (2) (Fig. 2(c)) and the distance from the center of the intermediate cell in eq. (1) (Fig. 2(b)) and $x_0$ is the position of the interface. The initial thickness of the planar source is either 2 h in case of Fig. 2(b) or h in case of Fig. 2(c). The fitting parameters were $h$, $x_0$ and the product $Dt$, which can be described by a measured mean square diffusion depth:

$$\sqrt{x_{\text{meas}}^2} = 2Dt$$

(3)

Because $x_{\text{meas}}^2$ includes contributions from the shear convection and the averaging effect, as mentioned below, eq. (3) has to be dealt carefully. The details of the calculation of $D$ from $x_{\text{meas}}^2$ is described in 4.5.

4. Shear convection research

The effect of the shear convection in the Foton-shear cell was investigated in two kinds of experimental methods. One is short-time diffusion experiments both under low-g (parabolic flight) and under 1 g (with a stable density layering), where the contribution of the shear convection to the mass transport is larger than that of the diffusion process. The other is measurements of the time dependence of $x_{\text{meas}}^2$, where the contribution from the diffusion process is proportional to the diffusion time and the additional mass transport is independent from the diffusion time. Thus extrapolation to the initial time yields the contribution of the additional mass transport.

4.1 Short time diffusion experiments (low-g)

Using the Foton shear cell, short time diffusion experiments were performed on ESA’s parabolic flight campaign (PFC31) by Airbus A300. Two parallel experiments were performed simultaneously with two capillaries in the shear cell. One capillary was prepared for interdiffusion between Sn47In53 alloy (sample A) and Sn (sample B), the diffusion type shown in Fig. 2(a). The other capillary was prepared for diffusion of Sn47In53 (sample A) from a thick layer into Sn (sample B), the diffusion type shown in Fig. 2(b). Each shear process took 2.5 s and the completely overlapped position of the capillaries and the intermediate cell remained for 10 s. The diffusion time $t_{\text{diff}}$ was defined...
4.2 Short time diffusion experiments (1 g)

Similar short time diffusion experiments were performed also under 1 g conditions. But to avoid buoyancy convection, the experimental set-up was changed to achieve a stable density layering (described in 5.). The g-vector was parallel to the x-direction. The diffusion type was thick layer diffusion from Sn90In10 (sample A) into pure Sn (sample B), the diffusion type shown in Fig. 2(c). The density increases from Sn90In10 to Sn monotonically. The diffusion temperature was 275°C and the diffusion time \( \tau_{\text{diff}} \) was 14 s. The concentration profiles and the obtained values of \( \overline{x}^2_{\text{meas}} \) are shown in Fig. 3 and Table 1, respectively.

4.3 Time dependence of diffusion coefficient

If the diffusion time is longer than the relaxation time of the shear convection, the mean square diffusion depth caused by the shear convection is independent from the diffusion time. Thus the additional transport except the pure diffusion process can be determined by extrapolation of the measured mean square diffusion depth as a function of the diffusion time to \( \tau = 0 \). The Foton-shear cell was investigated by this method, using a stable density layering under 1 g conditions, as described in 5. The configuration was the thick layer diffusion (Fig. 2(c)) where sample A was SnBi3 at% and sample B was Sn. The g-vector was anti-parallel to the x-direction. The diffusion experiments were performed at 300°C for 600, 1800 and 28800 s. For each condition four parallel experiments were performed simultaneously. After the concentration measurements, \( \overline{x}^2_{\text{meas}} \) was determined (Fig. 4). The extrapolation from the measured values to the y-intercept gave \( \overline{x}^2_{\text{diff}} = 1.8 \times 10^{-6} \text{ m}^2 \). Half of the inclination of the line represents the diffusion coefficient at the temperature and is \( D = 2.43 \times 10^{-9} \text{ m}^2/\text{s} \), which corresponds to the result determined using another correction method (eq. (6)) shown in Table 3.

4.4 Influence of shear convection

The obtained \( \overline{x}^2_{\text{meas}} \) is theoretically the sum of the values of the mean square diffusion depths of different origins under the assumption that the additional mass transports can be also interpreted as additional diffusion processes:

\[
\overline{x}^2_{\text{meas}} = \overline{x}^2_{\text{diff}} + \overline{x}^2_{\text{add}} = \overline{x}^2_{\text{diff}} + \overline{x}^2_{\text{aver}} + \overline{x}^2_{\text{shear}}
\]  

(4)

Here \( \overline{x}^2_{\text{diff}} \) is the contribution from diffusion \( (= 2D\tau_{\text{diff}}) \) and \( \overline{x}^2_{\text{aver}} \) is the contribution from the mixing effect inside a single cell, which can be converted from \( \overline{x}^2_{\text{meas}} \) by using a diagram. This mixing is induced by the shear convection after the final shear process, by the segregation effects during the solidification and finally by the integrating analysis of AAS or ICP. \( \overline{x}^2_{\text{shear}} \) is the contribution from the initial and the final shear convection and can be calculated by subtraction of \( \overline{x}^2_{\text{diff}} \) and \( \overline{x}^2_{\text{aver}} \) from \( \overline{x}^2_{\text{meas}} \). If we consider \( \overline{x}^2_{\text{shear}} \) as a quasi-prolongation
Table 1  Measured mean square diffusion depths and the influence by the shear convection for each experiment

<table>
<thead>
<tr>
<th>diffusion type</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>gravity</td>
<td>Interdiffusion</td>
<td>thick layer diffusion</td>
<td>thick layer diffusion</td>
</tr>
<tr>
<td>In53Sn47–Sn</td>
<td>In53Sn47–Sn</td>
<td>Sn90In10–Sn</td>
<td></td>
</tr>
<tr>
<td>measured mean square diffusion depth $\overline{x_{\text{meas}}} \pm \Delta \overline{x_{\text{meas}}} \times 10^6 [m^2]$</td>
<td>$1.04 \pm 0.08$[1]</td>
<td>$1.00 \pm 0.03$[1]</td>
<td>$0.89 \pm 0.17$[1]</td>
</tr>
<tr>
<td>mean square diffusion depth caused by shear convection $\overline{x_{\text{shear}}} \pm \Delta \overline{x_{\text{shear}}} \times 10^6 [m^2]$</td>
<td>$0.23 \pm 0.07$[2]</td>
<td>$0.20 \pm 0.03$[2]</td>
<td>$0.12 \pm 0.10$[3]</td>
</tr>
<tr>
<td>quasi prolonged diffusion time caused by shear convection $t_{\text{shear}} \pm \Delta t_{\text{shear}} [s]$</td>
<td>$56 \pm 17$[2]</td>
<td>$49 \pm 7$[2]</td>
<td>$24 \pm 19$[3]</td>
</tr>
</tbody>
</table>


Fig. 4  Measured mean square diffusion depth $\overline{x_{\text{meas}}}$ as a function of the diffusion time in diffusion experiments of SnBi3–Sn at 300°C.

of a diffusion time, the extended time $t_{\text{shear}}$ is calculated by

$$t_{\text{shear}} = \frac{\overline{x_{\text{shear}}}}{2D}$$

(5)

The results of the evaluations are shown in Table 1. For the calculations we used $D = 2.1 \times 10^{-9} m^2/s$ (250°C), $2.3 \times 10^{-9} m^2/s$ (275°C) according to the µg-reference data in the D1-mission).

As a result, the shear convection turned out to be small. The mean square diffusion depths caused by the shear convection were in the order of $10^{-7} m^2$, which is much smaller than 1% of the typical value $x_{\text{diff}} \approx 10^{-4} m^2$ in a standard diffusion experiment using the Foton shear cell. Nevertheless this value can be used for the correction of diffusion experiments.

4.5 Correction Method for the Determination of Diffusion Coefficients

By using these results we can suggest a correction method of these influences for the determination of $D$-values in long time diffusion experiments using eq. (4):

$$D = \frac{1}{2t_{\text{diff}}} (\overline{x_{\text{meas}}} - \overline{x_{\text{shear}}} - \overline{x_{\text{aver}}})$$

$$= \frac{1}{2t_{\text{diff}}} \left( \overline{x_{\text{meas}}} - \overline{x_{\text{shear}}} - \frac{H^2}{12} \right)$$

(6)

where $\overline{x_{\text{meas}}}$ is the result of any long time diffusion experiment and $\overline{x_{\text{shear}}}$ is the result of the corresponding short time diffusion experiment, i.e. at the same temperature and in the same diffusion system under the same gravity conditions. Here $\overline{x_{\text{shear}}}$ was approximated as $H^2/12$ and depends only on the cell geometry under the assumption $t_{\text{diff}}$ is sufficiently long[1]. For the Foton shear cell, $H$ (the thickness of a disc) is 3 mm and is $7.5 \times 10^{-7} m^2$.

In the present investigation of a short time experiment, $\overline{x_{\text{shear}}}$ could be determined because $\overline{x_{\text{diff}}}$ could be calculated from $2D_{\text{diff}}$ and $D$ was known from $\mu g$-experiments. But nevertheless we can use eq. (6) in the following way: Let us denote the short time data with $\overline{x_{\text{shear}}}$. Then from eq. (4) we have

$$\overline{x_{\text{shear}}} = \overline{x_{\text{meas}}} - 2D_{\text{diff}}/0 - \frac{H^2}{12}$$

(7)

Inserting in eq. (6) results in the generally applicable form:

$$D = \frac{\overline{x_{\text{shear}}} - \overline{x_{\text{meas}}}}{2(t_{\text{diff}} - t_{\text{diff}}/0)}$$

(8)

This equation allows to eliminate the disturbing shear convection and the averaging effect of shear cell diffusion experiments by the additional performance of a short time diffusion experiment (zero-experiment). This is advisable if an accuracy of <2–3% is envisaged. If a higher deviation is accepted, it will be normally not necessary to use the correction with eq. (8). Then eq. (6) with $\overline{x_{\text{shear}}} \approx 0$ could be sufficient.

5. Reliability of 1 g-diffusion measurements

5.1 Experimental conditions

The sample materials were selected from the following points of view: 1) related to the Foton experiment...
Table 2  Measured mean square diffusion depths, diffusion coefficients, errors and reference data

<table>
<thead>
<tr>
<th>sample material</th>
<th>1 g-experiments in this study</th>
<th>reference data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capillary</td>
<td>$\Delta D^{[2]}$</td>
</tr>
<tr>
<td>T$_{diff}$ [°C]</td>
<td>$\Delta D^{[2]}$</td>
<td>$\Delta D^{[3]}$</td>
</tr>
<tr>
<td>300 (28800) SnBi1.5–Sn</td>
<td>2.35 ± 0.06</td>
<td>2.5</td>
</tr>
<tr>
<td>275 (28800) SnIn10–Sn</td>
<td>2.44 ± 0.07</td>
<td>2.8</td>
</tr>
<tr>
<td>730 (18000) AlNi1.6–Al</td>
<td>3.81 ± 0.12</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 3  Diffusion coefficients and errors in 1 g experiments

<table>
<thead>
<tr>
<th>sample materials</th>
<th>diffusion temperature T [°C]</th>
<th>$\Delta D^{[2]}$</th>
<th>$\Delta D^{[3]}$</th>
<th>$\Delta D^{[4]}$</th>
<th>$\Delta D^{[5]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnBi3–Sn</td>
<td>300</td>
<td>2.41 ± 0.05</td>
<td>2.1</td>
<td>a) 2.4 ± 0.14</td>
<td>b) 2.3 ± 0.014</td>
</tr>
<tr>
<td>500</td>
<td>4.35 ± 0.10</td>
<td>2.3</td>
<td>a) 2.74 ± 0.27</td>
<td>b) 2.6 ± 0.27</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>7.62 ± 0.20</td>
<td>2.7</td>
<td>a) 3.9 ± 0.29</td>
<td>b) 3.7 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>SnIn10–Sn</td>
<td>275</td>
<td>2.44 ± 0.07</td>
<td>2.8</td>
<td>a) 2.4 ± 0.14</td>
<td>b) 2.3 ± 0.014</td>
</tr>
<tr>
<td>600</td>
<td>5.82 ± 0.14</td>
<td>2.4</td>
<td>a) 2.6 ± 0.27</td>
<td>b) 2.6 ± 0.27</td>
<td></td>
</tr>
<tr>
<td>AlNi1.6–Al</td>
<td>400</td>
<td>4.51 ± 0.20</td>
<td>4.5</td>
<td>a) 3.9 ± 0.29</td>
<td>b) 3.7 ± 0.12</td>
</tr>
<tr>
<td>600</td>
<td>6.79 ± 0.28</td>
<td>4.2</td>
<td>a) 3.9 ± 0.29</td>
<td>b) 3.7 ± 0.12</td>
<td></td>
</tr>
</tbody>
</table>

5.2 Data analysis

It is generally known from the previous results, that if convection exists in the liquid sample, the measured concentration curve has wave-like deviations from the fitting function, the reproducibility of the diffusion measurements is low and the diffusion coefficient becomes larger than in the case without convection. To check the influence of the buoyancy-convection on the diffusion measurements, the obtained data were investigated from these three points of view.

5.2.1 Agreement with fitting function

As a typical example, Fig. 5 shows Bi-concentration profiles in four parallel experiments with SnBi3–Sn at 300°C. In the other experiments, the concentration profiles are similar as in Fig. 5. All data were well described by the fitting function (coefficient of determination $R^2 > 0.995$). This means that there was no indication of buoyancy-driven convection.

The profile can be also approximately described by a thin layer profile using

$$c(x, t) = \frac{c_0 h}{\sqrt{4D(t + t_0)}} \exp \left( -\frac{x^2}{4D(t + t_0)} \right)$$

where $t_0 = h^2/6D$ is the time offset at $t = 0$, which gives the same mean square diffusion depth as the real start profile. Because of the linearity of the relationship between $x^2$ and $\ln c$, eq. (9) can be used to show the absence of non-diffusion-like convection (Fig. 6).

5.2.2 Reproducibility of diffusion experiments

As shown in Fig. 5 and Fig. 6, the four concentration curves gave about the same diffusion coefficient.
The reproducibility can be investigated by the standard deviation $\Delta D'$ among the four parallel diffusion experiments. Since the $\Delta D'$-values only represent the reproducibility under nearly equal external conditions, all statistical errors should be included there except those from the temperature measurement. Hence for the total statistical error $\Delta D$ in Table 2 and Table 3 we have additionally included a standard temperature deviation on the basis of the relation $D=AT^2$ by the equation:

$$
\frac{\Delta D}{D} = \sqrt{\frac{1}{N-1} \sum_{n=1}^N \left( \frac{D_n - D}{D} \right)^2 + (2\sigma_{\text{temp}})^2} \tag{10}
$$

where the number of the capillaries $N$ is four in this case, $D_n$ is the diffusion coefficient individually measured for the $n$th capillary and $D$ is the average value among the $D_n$-values and the standard temperature deviation $\sigma_{\text{temp}}$ is estimated as 1%. Thus we arrive at relative total statistical errors of $\Delta D/D = 2 \sim 5\%$, which is indeed lower than in the Foton-12 mission, as described in 5.2.3.

Only the experiments of SnIn10–Sn at 800°C have a relative large total statistical error of 7.2%. This has not yet been explained clearly. There might have been a malfunction of the AAS procedure. This remains a future subject. In any case, 7.2% of total statistical error is still lower than in the Foton-12 mission.

### 5.2.3 Comparison with reference data

Now we compare the obtained diffusion coefficients with the reference data to check the quality of these 1 g-experiments. Reference $\mu g$-data on the diffusion of Bi in Sn, In in Sn, and Ni in Al were obtained in Foton-12(21). Garandet et al. analyzed all expected error sources in these diffusion measurements in Foton-12. They assumed a maximum error $\Delta D/\Delta \mu g$ of 6% for the SnBi1.5–Sn inter-diffusion experiment at 300°C, 10% for the SnIn1–Sn inter-diffusion experiment at 300°C, and 7.5% for the AlNi1.5–Al inter-diffusion experiment at 700°C. For the diffusion of Bi in Sn, and In in Sn, the results of 1 g-measurement in a magnetic field are available. The reference values are shown in Table 2. This comparison shows that the 1 g values in this study agree well with both the $\mu g$-reference data and the results of 1 g-measurements in a magnetic field. Furthermore it seems remarkable that the total statistic errors in our present 1 g-experiments are less than half of the error values of $\Delta D_{\mu g}$, also for the concentration measurements, as can be seen from the reproducibility. We think that the reduction of the total statistic errors in this study is the result of the upgrade of the shear cell from the Foton-12 model. From these new investigations, no evidence of disturbance of convective flow was detected in the 1 g-measurements.

### 5.3 Effect of density layering

The results of the present study indicate that buoyancy convection was largely suppressed in these 1 g-experiments by using the condition:

$$
\frac{dp}{dx} \hat{c} \cdot \hat{g} > 0 \tag{11}
$$

where $\hat{c}$ is the unit vector in the $x$-direction. Strong buoyancy convection is normally caused by a density gradient antiparallel to the $g$-vector i.e. the left side in eq. (11) is negative. Since

$$
\frac{dp}{dx} \hat{c} \cdot \hat{g} = \frac{\partial p}{\partial c} \frac{dc}{dx} \hat{c} \cdot \hat{g} + \frac{\partial p}{\partial T} \frac{dT}{dx} \hat{c} \cdot \hat{g} \tag{12}
$$

and $\partial p/\partial T$ is normally negative, the condition for $\partial p/\partial x$ can be met by an upwards temperature gradient $\partial T/\partial x$ and/or a positive contribution from the solutal term in eq. (12). Our liquid diffusion experiments are designed to meet both conditions.

Since it is difficult to arrange the temperature gradient exactly antiparallel to the $g$-vector, we have to consider horizontal temperature gradients, say $\partial T/\partial y$. Such gradients produce forces that try to start convection rolls, too. Then it can be shown that there are always convection rolls, but a sufficient negative solutal
density gradient can strongly reduce the velocity of the rolls so that the influence on the determination of the real atomic diffusion coefficient is below a certain wanted level. It depends on the material parameters in eq. (12) whether the condition can be fulfilled at least in the main part of the diffusion zone. We are presently working on that problem. It can normally not be met in the capillary parts away from the diffusion zone, since there c is constant and dT/dx should be small.

6. Temperature dependence of the diffusion coefficients

The temperature dependence of the diffusion coefficients in liquid metals has been discussed for a long time. One of the descriptions is the power law. The results of molecular dynamics simulations showed a temperature dependence of \( D = A T^n \) with \( n = 1.7 \sim 2.3 \). Several results of \( \mu \)-experiments (self-diffusion of Sn (FSLP\(^{1}\), MSL-1\(^{19}\)), In, Pb and Sb (D\(^{20}\)), interdiffusion of Sn–In (D\(^{21}\)), showed \( D = A T^2 \), which is considered as a special case of the power law.

The function \( D = A T^n \) was fitted to the measurement results of the experiment of In in Sn, Bi in Sn (Fig. 7) and Sn in In (Fig. 8) using weighted least squares according to \( \Delta D \). The results are summarized in Table 4. In every case, the temperature dependence is described better with a fitting parameter \( n \) between 1.5 and 2 than with a fixed \( n \) of 2. This suggests the possibility of the power law with a variable exponent according to the measured system. But the number of the fitting points is so small that this discussion does not exclude the possibility of the \( T^2 \)-law. In any case it was confirmed that the temperature dependence can be well described by the power law. The linearity of \( \ln D-\ln T \) plots (Fig. 9) demonstrates the validity of the power law.

![Fig. 7](image1.png)

**Fig. 7** Temperature dependence of diffusion coefficients of Bi in Sn, In in Sn, and Sn* in Sn\(^{3} \).

![Fig. 8](image2.png)

**Fig. 8** Temperature dependence of diffusion coefficients of Sn in In, and In* in In\(^{3} \).

![Fig. 9](image3.png)

**Fig. 9** "Linear plot" of \( \ln D-\ln T \) in the diffusion experiments of Bi in Sn, In in Sn, and Sn in In.

### Table 4

<table>
<thead>
<tr>
<th>systems</th>
<th>( A(\pm \Delta A)^{[1]} ) [m(^2)/s•K(^{1/2})]</th>
<th>( \Delta A/A ) [%]</th>
<th>( n(\pm \Delta n)^{[1]} )</th>
<th>( \Delta n/n ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>In in Sn</td>
<td>8.03(±0.12)\times10^{-15}</td>
<td>1.5</td>
<td>2.00±0.00</td>
<td>fixed</td>
</tr>
<tr>
<td></td>
<td>1.36(±0.60)\times10^{-14}</td>
<td>44.1</td>
<td>1.92±0.07</td>
<td>fit parameter</td>
</tr>
<tr>
<td>Bi in Sn</td>
<td>7.06(±0.09)\times10^{-15}</td>
<td>1.3</td>
<td>2.00±0.00</td>
<td>fixed</td>
</tr>
<tr>
<td></td>
<td>2.00(±0.67)\times10^{-14}</td>
<td>33.5</td>
<td>1.84±0.05</td>
<td>fit parameter</td>
</tr>
<tr>
<td>Sn in In</td>
<td>9.33(±0.29)\times10^{-15}</td>
<td>3.1</td>
<td>2.00±0.00</td>
<td>fixed</td>
</tr>
<tr>
<td></td>
<td>1.61(±0.003)\times10^{-13}</td>
<td></td>
<td>1.57±0.00</td>
<td>fit parameter</td>
</tr>
</tbody>
</table>

\(^{[1]}\)statistic error caused by the fitting process, \(^{[2]}\)only two fitting data
Table 5 Classification of diffusion types and possible conditions

<table>
<thead>
<tr>
<th>diffusion type</th>
<th>possibility of stabilization by density gradient</th>
<th>segregation (in general)</th>
<th>possible gravity conditions</th>
<th>possible techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-diffusion</td>
<td>in elements</td>
<td>no (or low)</td>
<td>no</td>
<td>(\mu g)</td>
</tr>
<tr>
<td></td>
<td>in alloys</td>
<td>no</td>
<td>yes</td>
<td>(\mu g)</td>
</tr>
<tr>
<td>Impurity diffusion</td>
<td>in elements</td>
<td>yes (at sufficient high concentrations)</td>
<td>if “no”</td>
<td>(\mu g, 1 \text{ g})</td>
</tr>
<tr>
<td></td>
<td>in alloys</td>
<td>no (at low concentration)</td>
<td>no</td>
<td>(\mu g)</td>
</tr>
<tr>
<td>Interdiffusion</td>
<td>in binary alloys</td>
<td>if “yes”</td>
<td>yes</td>
<td>(\mu g, 1 \text{ g})</td>
</tr>
<tr>
<td></td>
<td>in multi-component alloys (&gt;2 components)</td>
<td>no (because of drag effects)</td>
<td>yes</td>
<td>(\mu g)</td>
</tr>
<tr>
<td>Combination of inter and self-diffusion</td>
<td>in binary alloys</td>
<td>if “yes”</td>
<td>yes</td>
<td>(\mu g)</td>
</tr>
<tr>
<td></td>
<td>in multi-component alloys (&gt;2 components)</td>
<td>if “no”</td>
<td>yes</td>
<td>(\mu g)</td>
</tr>
</tbody>
</table>

\(\text{SC}\): shear cell. \(\text{LC}\): long capillary

law. But the power law has not yet been explained conclusively with a clear physical model. This is still under work.

7. Outlook

7.1 Classification of diffusion types and the reliability of 1 g-measurements

If exact diffusion measurements are required, the combination of \(\mu g\)-conditions and the shear cell is always helpful. But both the shear cell and \(\mu g\)-conditions are not always available and necessary. Here we classified the diffusion types in Table 5 that shows in which cases the shear cell can be substituted by the classical long capillary method or in which cases diffusion experiments can be performed also under \(1 \text{ g}\)-conditions. If a sufficient stabilization is possible by density gradients, there is the possibility to perform impurity diffusion, interdiffusion in binary alloys and the combination of inter and self-diffusion under \(1 \text{ g}\) conditions. Only in case of no segregation we can use the long capillary, but such a case is rare and the shear cell is usually needed.

But if no sufficient stabilization is possible, we need \(\mu g\)-conditions, for example, in the case of self-diffusion in elements or impurity diffusion at low concentration. In the case of interdiffusion with more than three components, because of drag effects it is not possible to obtain a stable density layering, and hence the shear cell and \(\mu g\)-conditions are necessary. Usual alloys for commercial use have more than three components. Also if reliable reference data are needed, this is up to now only by \(\mu g\)-diffusion data.

7.2 Open questions and further plans

A more exact quantitative discussion about the necessary density layering arrangement to avoid the buoyancy convection is a future subject. More exact thermodynamical data of the samples are required for the discussion.

For a more detailed discussion on the diffusion mechanism, more measurements are required. The influence of the atomic weight, the atomic radius and the electronic structure of the tracer element on the diffusion coefficients is significant. From these points of view, the next experiments will be planned.

Furthermore the stable density layering is expected to suppress also Marangoni convection. Hence in the case of Marangoni convection, a stable density layering on the ground can be more advantageous than \(\mu g\)-conditions. Müller-Vogt et al. at the Univ. Karlsruhe are investigating this topic about the influence of Marangoni convection.

8. Conclusions

For both \(\mu g\) and \(1 \text{ g}\)-experiments, the Foton shear cell was developed and optimized for considering the minimization of shear convection, minimization of free surfaces and a reliable operation. The short time diffusion experiments under low-\(g\) and \(1 \text{ g}\) conditions and the measurement of the time dependence of \(\overline{X}_{\text{meas}}\) showed that the mass transport caused by the shear convection is smaller than 1% of that caused by diffusion in a usual diffusion time. Nevertheless we
proposed a correction method for the determination of the
diffusion coefficient.

1 g-experiments of In in Sn, Bi in Sn, Sn in In, and
Ni in Al with the Foton shear cell using a stable density
layering showed a good agreement between the con-
centration profile and the fitting function, a high re-
producibility with a small deviation among parallel ex-
periments, and a good agreement with \( \mu g \)-reference
data. Thus the high reliability of our 1 g D-values is
demonstrated. On the basis of these results the diffusion
types were classified according to the reliability of
1 g-measurement. It is expected that the experimental
method in this study can deliver a large amount of ex-
act diffusion data.

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