Shinsuke Suzuki, Kurt-Helmut Kraatz, Günter Frohberg

The Effect of Shear Convection on Diffusion Measurements in Liquid Metals using the Foton Shear Cell

The shear convection in the Foton shear cell was investigated quantitatively and interpreted as an additional diffusion-like mixing. Diffusion experiments were done under 1g and µg (Foton-M2 mission June 2005). Since the measured mean square diffusion depth *(MSDD) is a linear function of time, the offset represents the additional mass transport (and the averaging effect due to the analysis by Atom Absorption Spectroscopy, AAS). The offset is 1-3% of the MSDD and can be used to eliminate this systematic error. The influence of the liquid's viscosity on the shear convection is discussed, using a simple fluid dynamical model. The absence of buoyancy convection in 1g-experiments was shown by comparison with the µg-result.*

Authors

Shinsuke Suzuki, Kurt-Helmut Kraatz, Günter Frohberg
Institute for Material Science and Technology,Technical University of Berlin

Shinsuke Suzuki
Present: The Institute of Science and Industrial Research
Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan.

Correspondence

Shinsuke Suzuki
Tel:+81-6-6879-8436, Fax: +81-6-6879-8439
e-mail:suzuki@sanken.osaka-u.ac.jp

Introduction

The shear cell method is a standard tool for liquid diffusion measurements under space [1-2] and 1g [3-5] conditions (Fig.1). At the beginning the two different samples are kept separate (Fig. 1(i)), get molten and homogenized. By the initial shearing (at diffusion temperature) the diffusion starts (ii) and is finished by dividing the sample into a lot of cells (here 20) by the final shearing Fig.1 (iii). After cooling down (iv), the concentration in each cell is analyzed. Thus no temperature and thermal liquid expansion corrections are necessary for the heat-up and cool-down phases as with the long capillary technique. The only systematic error is due to shear convection [6], averaging effect [7] and thermal expansion of the crucible (which for graphite is smaller (max.0.9%) than the standard deviation (2-3%) of our diffusion coefficients D). Anyway, also other systematic and statistical errors can result from buoyancy and/or Marangoni convection. The present shear cell was designed for µg-diffusion experiments on-board the Russian satellite Foton-M2 in June 2005 [7], but was also used for 1g experiments, as

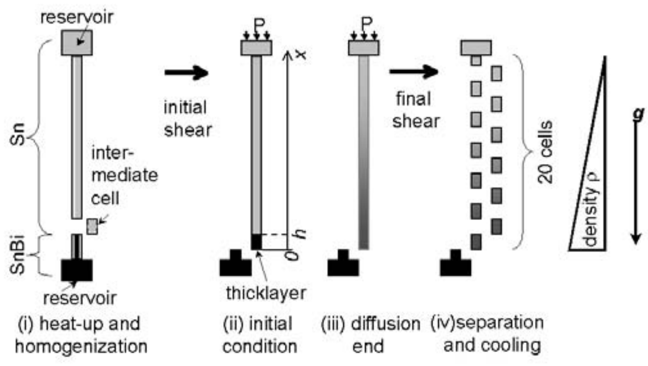

Fig.1: The Foton shear cell experiment.

it offers two reservoirs with adjustable pressures at both ends of a capillary to reduce free surfaces, i.e. Marangoni convection. The stable density layering is applied to reduce buoyancy convection in 1g-experiments. Meanwhile the combination of both techniques has been shown to give reliable D-values under 1g, comparable with µg results or even better. A few papers [8,9] have reported about a dependence of D-values on diffusion time from initial additional transport, but there was no detailed discussion. We investigated already the shear convection in the Foton shear cell by short time diffusion experiments, both in low-g (parabolic flight PFC31) and in 1g [7], which gave similar results. In the present investigation, systems Sn-Bi and Sn-In from the Foton-M2 program were used.

Experimental

1g-experiments

The shear cell (graphite) and the experimental procedure (see Fig.1) were the same as in the AGAT facility in the Foton-M2 satellite. From numerical simulations [6] and model experiments [10] the cell size (H=3mm, d=ϕ1.5mm) and the shear velocity v_o=0.5mm/s were chosen. The axial temperature gradient was <10K/mm. The samples gave sufficient density gradients to check the reduction of buoyancy convection. Diffusion was from a thick layer (H=3mm) of SnBi3at% or SnIn10at% into pure Sn (57mm), where the diffusion axis was vertical. All 4 capillaries of a shear cell were filled with the same samples allowing to discuss the reproducibility. At a vacuum of 0.8Pa the furnace was heated-up to the diffusion temperature for 1h of homogenization. After diffusion the samples were cooled down and analyzed by AAS. The data are shown in Table 1.

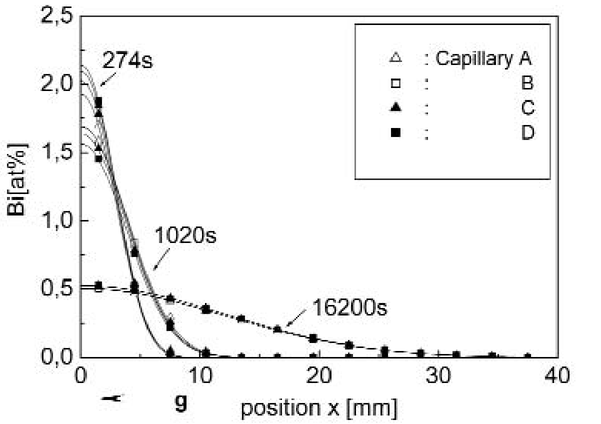

Fig. 2: Bi profiles at 500°C for diffusion times 274s, 1020s, and 16200s with 4 profiles each.

µg-experiment

In the Foton-M2 mission 24 diffusion experiments were performed in 6 shear cells in the AGAT facility, one was for diffusion of SnBi5at% into Sn at 500°C for 5h (same experimental procedure as in the 1g-experiments). The values are shown in Table 1.

Results and Discussion

Mean square diffusion depth

Fig.2 shows the concentration profiles of Bi at 500°C for diffusion times 274s, 1020s and 16200s from 4 parallel experiments each. For In (see Table 1) similar profiles were obtained. The concentration curves were fitted with the thick layer solution (c_o concentration in the first layer)

$$c(x,t) = \frac{c_0}{2}\left(erf\left(\frac{h+x}{\sqrt{2\overline{X^2}_{meas}}}\right) + erf\left(\frac{h-x}{\sqrt{2\overline{X^2}_{meas}}}\right)\right) \quad (1).$$

The fitting parameter was 2Dt, i.e. the *measured* MSDD, cor-

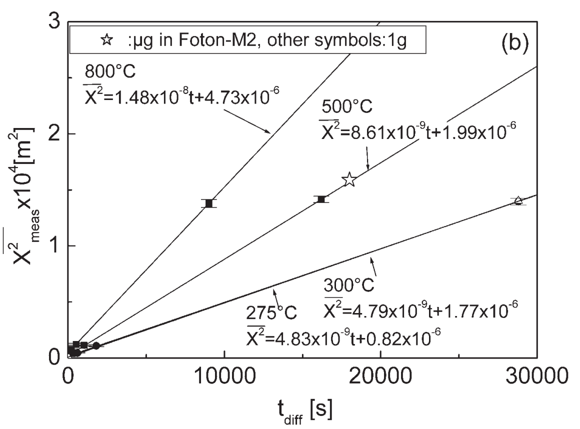

Fig. 3: $\overline{x^2}_{meas}$ for different times and temperatures. The slope gives D, offset is from convection and averaging effect.

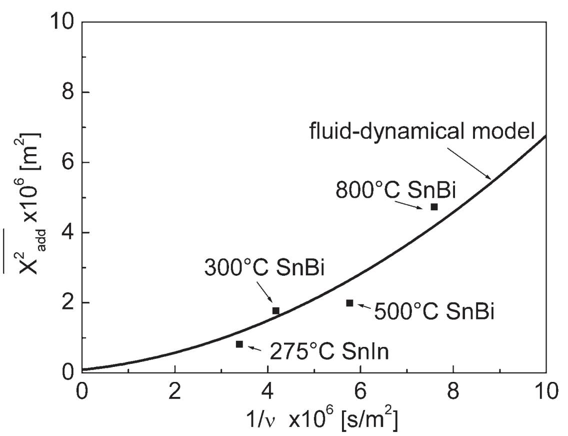

Fig. 4: Influence of viscosity depending on temperature[11] on offset from shear convection. Line : fluid dynamical model.

rected for the expansion of the capillary.

$$\overline{X^2}_{\mathrm{meas}} = 2Dt = 2Dt_{diff} + \overline{X^2}_{\mathrm{add}}$$
$$\text{with } t = t_{\mathrm{diff}} + t_{\mathrm{add}},$$
$$\overline{X^2}_{\mathrm{add}} = 2Dt_{add} \text{ and } D = \frac{d\overline{X^2}_{\mathrm{meas}}}{2dt_{diff}} \qquad (2).$$

The offset $\overline{x^2}_{add}$ is equivalent to an additional (pseudo) diffusion time $t_{add.}$ $\overline{x^2}_{meas}$ and the error from the 4 capillaries is shown in Table 1. In Fig.3 $\overline{x^2}_{meas}$ values from 1g-experiments were fitted by eq.(2), with offset $\overline{x^2}_{add} = \overline{x^2}_{shear} + \overline{x^2}_{aver}$ from shearing and averaging ($\overline{x^2}_{aver} = H^2/12 = 0.75 mm^2$, depending on H only [7] for $\overline{x^2}_{meas} > 1mm^2$). In Fig.5 the µg-value drops on the line fitted to the 1g-values at 500°C, showing the absence of buoyancy-convection in the 1g-experiments. Values $\overline{x^2}_{shear}$ are shown in Table 1.

Simple fluid-dynamical model

To understand the influence of geometry, shear velocity and viscosity/density [11] on $\overline{x^2}_{shear}$, the flow pattern of the initial shearing is sketched in Fig.6. Since the exchange of matter between neighboring cells is small, a rough estimation will be done. The velocity distribution of matter at the interface (e.g. A, B) is assumed to be sinus-like, amplitude v_o. Then the volume exchange can be calculated by a numerical integration over time and area for volumes from cell A to B is $\Delta V = 0.0511 * d^3$. With $V_c = \pi d^2 H/4$ the initial relative volume exchange fraction is $f_i = \Delta V/V_c = 0.065 d/H$ (does not depend on kinematic viscosity ν and on v_o). The volume V of mass m in B, moving with an average velocity of $v_o/2$ (as in a tube, diameter d/2, here bent by 180°), is estimated as $V = \pi d^3/8$, i.e. $m = V\rho$, ρ density. The retarding force on the liquid then is $F = 4\pi L\rho\nu v_o$ (Hagen-Poiseuille (HP) law, tube length $L = \pi d/4$). But this tube has a smaller damping wall area A_r, estimated by 1/4 of the cell's girth and d/4 in x-direction, while for the tube $A = \pi d\, L/2$. Hence we add a correction factor $\alpha = \pi\beta d^2/16A = 0.080$ to the HP-force, with β = 1/2, because there is only rotation (no internal friction)

Table 1: Measured mean square diffusion depth, errors and shear contribution

Sample material	diffusion temperature T[°C]	diffusion time t_{diff}[s]	$\overline{x^2}_{meas}$ (± $\Delta\overline{x^2}_{meas}$)[1] [m²]	$\Delta\overline{x^2}_{meas}/\overline{x^2}_{meas}$ [%][7]	$\overline{x^2}_{add}$ x 10^6 [m²]	$\overline{x^2}_{shear}$ x 10^6 [m²]	D x 10^9 [m²/s] (slope)
SnBi-Sn	300 (1g)	600	4.55(±0.41) x 10^{-6}	9.0			
		1800	1.08(±0.09) x 10^{-5}	7.9	1.77	1.02	2.39
		28800	1.39(±0.03) x 10^{-4}	2.1			
	500(1g)	274	3.94(±0.20) x 10^{-6}	5.0			
		1020	1.12(±0.04) x 10^{-5}	3.8	1.99	1.24	4.31
		16200	1.42(±0.03) x 10^{-4}	2.0			
	500 (µg, Foton-M2)	18000	1.58(±0.005[2]) x 10^{-4}	0.3[3]	-----[4]	-----[4]	4.36[5]
	800 (1g)	206	7.72(±0.43) x 10^{-6}	5.6			
		525	1.22(±0.08) x 10^{-5}	6.4	4.73	3.98	7.40
		9000	1.38(±0.04) x 10^{-4}	2.6			
SnIn-Sn	275 (1g)	14	8.88(±1.69[6])) x10^{-7}	19.1	0.82	-----[8]	2.42
		28800	1.42(±0.04) x 10^{-4}	2.7			

1) average and statistical error from 4 capillaries.
2) fitting error.
3) only 1 capillary; no reproduction error.
4) only 1 long diffusion time.
5) correction by eq.(2).
6) as 1) but from 3 capillaries.
7) average error of (long time) 1g experiments : 2.8% of D (including 1% temperature error).
8) averaging contribution can not be represented by $H^2/12$ because of the too short diffusion time.

for about half of the tube. From F=8πLρνvα=-m(dv/dt) we get a relaxation time t_r=m/8πLρνα. Then the volume into B is given by $\Delta V_r=\pi d^2 v_o t_r/16$ and $f_r=\Delta V_r/(\pi d^2 H/4)$. Since the final shearing is the inversion of the initial one, we assume $f_f = f_i$. Thus the total relative exchange is $f= f_i + f_r + f_f$. Now, the concentration change is $\Delta C=\Delta n/V_c$ (n=CV_c mole number of diffusing substance). For the exchange at both cell sides (-/+) within a depth h=4fH we find with $A_c=\pi d^2/4$ and Fick's second law

$$\Delta n = \Delta CV_c = ((dC_-/dx) - (dC_+/dx))h^2Ac/2 =$$
$$(d^2C/dx^2)h^2HA_c/2 = (dC/dt)h^2V_c/2D$$

and thus

$$\overline{x^2}_{shear} = 2D\Delta t = 4H^2f^2 \quad \text{with} \quad f = \kappa d/2H + d^2v_o/64\pi\alpha H\nu \quad (3)$$

and

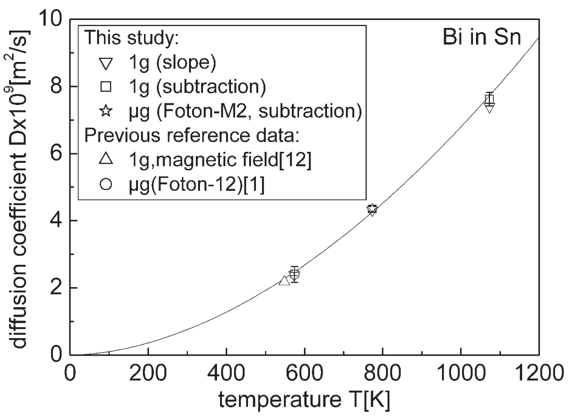

Fig. 5: Corrected D(T) for the diffusion of Bi in Sn. Line fitted to 1g results : D=2.87 10^{-14} $T^{1.79}$ (m²/s).

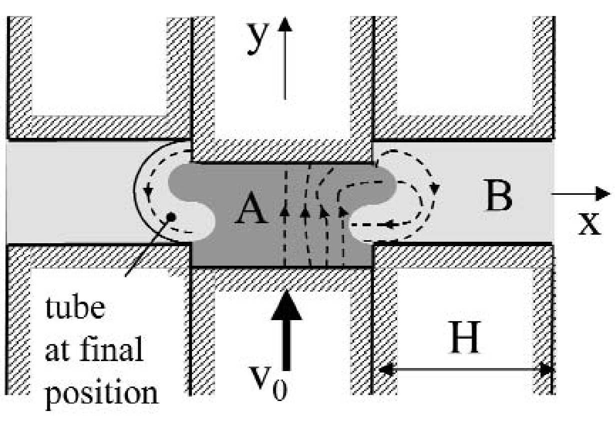

Fig. 6: Flow pattern of the initial & relaxation shearing. "Tube" for the relaxation process indicated left of A.

κ=0.26 , α=0.080.

Relation (3) (line in Fig.4) is close to the measured values within their low accuracy of about 50%. The advantage of eq.(3) is that it shows the dependence on ν, v_o, d and H. Note that eq.(3) has been derived without including stabilization, buoyancy and Marangoni effects. Hence deviations in Fig.4 may be also due to that. Nevertheless it seems that the model gives a somewhat reliable tool to describe the MSDD $\overline{x^2}_{shear}$ also for other materials, temperatures and other v_0, H and d values. Here we investigated experimentally the dependence only on the viscosity.

Diffusion coefficients

From eq.(2) we can now suggest a correction method to eliminate the systematic errors from shear convection and the averaging effect. With a) one long time (-l) or b) at least one short (-s) *and* one long time experiment we get two different possibilities to correct the diffusion coefficient:

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

or (4 a, b).

$$D = \frac{\overline{X^2}_{\text{meas-l}} - \overline{X^2}_{\text{meas-s}}}{2\left(t_{diff-l} - t_{diff-s}\right)}$$

In the first case $\overline{x^2}_{shear}$ has to be taken from eq.(3) while in the second case, which should give always good results, an additional short time experiment under the same conditions has to be made. If both procedures are used, a check for the equivalence can be made. Fig. 5 demonstrates the consistency of both equations and with the reference-values from Foton-M2, Foton-12 [1] and 1g-experiments in a magnetic field [12].

Conclusions

From pairs of short and long time shear cell diffusion experiments under 1g (for SnBi and SnIn) and from μg experiments we have shown that the contributions from shearing to the D-value is 1-3% (see Table 1). The MSDD from shearing and averaging is $\overline{x^2}_{meas}=2Dt_{diff}+\overline{x^2}_{add}$, $\overline{x^2}_{add}=\overline{x^2}_{shear}+\overline{x^2}_{aver}$, $\overline{x^2}_{aver}$ = H²/12 (AAS analysis). $\overline{x^2}_{add}$ is from $\overline{x^2}_{meas}$ at t_{diff}=0 from short ($\overline{x^2}_{meas}$ >1mm²) and long time experiments and the correct D value from the slope (eq.(4b)). A simple fluid-dynamical model (eq.(3)) for $\overline{x^2}_{shear}$ was derived and compared with measurements. *Two ways are possible to eliminate the shearing and averaging contributions*

a) by a pair of short and long time experiments (eq.(4b)), which should always work;

b) by relying on eq.(3). With known kinematic viscosity the correction is possible by eq.(4a) without short time experiments. Both procedures a), b) were used to eliminate the systematic shearing and averaging error.

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