International Journal of Heat and Mass Transfer 52 (2009) 6042–6049

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Diffusion measurements using the shear cell technique: Investigation of the role of Marangoni convection by pre-flight experiments on the ground and during the Foton M2 mission

Raluca Roşu-Pflumm [a,*], Wolfgang Wendl [b], German Müller-Vogt [b], Shinsuke Suzuki [c], K.-H. Kraatz [d], G. Frohberg [d]

[a] *Karl-Winnacker-Institut, Dechema e.V., Theodor-Heuss-Allee 25, 60486 Frankfurt am Main, Germany*
[b] *Kristall- und Materiallabor, University of Karlsruhe(TH), D-76131 Karlsruhe, Wolfgang-Gaede-Str. 1, Germany*
[c] *Institute of Scientific and Industrial Research, Osaka University, Osaka, Japan*
[d] *Institute for Materials Science and Technology, Technical University of Berlin, Berlin, Germany*

ARTICLE INFO

Article history:
Received 24 April 2008
Received in revised form 3 April 2009
Available online 6 September 2009

ABSTRACT

An experimental investigation on the disturbing influence of the solutal Marangoni convection during diffusion measurements is presented. We used the systems Sn–Bi, Pb–Ag and Sn–In with decreasing differences in surface tension. For all systems we measured surface tension and – under varying free surface conditions – diffusion coefficients. We succeeded in measuring diffusion coefficients on the ground under nearly non-free surface conditions. The results are compared with the results of the FOTON M2-satellite mission with similar µg-experiments. We show that temperatures from around 400 °C to about 800 °C and the degree of free surfaces influences strongly the measured value for the diffusion coefficient.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

The quality of crystals depends strongly on the uniform transport of matter through the nutrition phase to the growth front. The diffusion is one part of these transports which is in any case present in such systems. Therefore exact knowledge of the capability of the diffusional transport is essential for the crystal growth process as well as for any solidification process of high quality materials.

Diffusion measurements in liquids are difficult to perform on earth due to possible additional convective transports, especially for metallic and semiconductor melts which normally show low Prandtl-numbers. Convective contributions lead to the measurement of a higher effective diffusion coefficient rather than the real one. So reported data of diffusion coefficients may scatter about some orders of magnitude for example in the Ga–As system [1]. The shear cell method has been proved to be very well suited to measure diffusion coefficients in III–V and II–VI semiconductor melts and metals as well [1–3]. This is due to the fact that segregation and volume expansion effects do not affect the results gained with this technique. Convectional contributions have been shown to be small and can be eliminated by special techniques. Nevertheless the scattering of the measured data in numerous experiments also with this technique is still higher than the statistical error of about 5% for a single experiment and ranges from about 10% up to nearly one order of magnitude, depending on the investigated system (cf. [4]). This shows that the experiments may be disturbed by convective transports.

Even in the case of an almost isothermal environment and a stable density configuration (the heavier component is situated on the bottom of the vertical arranged one-dimensional diffusion-couple) there is still a remarkable scattering of data. This scattering of data was mainly attributed to buoyancy driven convection and almost no attention was given to solutal Marangoni convection even in the case of microgravity experiments [5,6]. The first mention about the possible influence of the Marangoni convection on a diffusion experiment has been done by Frohberg et al. [7]. They explained the failure of the first liquid diffusion experiments in space in the seventies by a “Residual Marangoni Effect” (RME). The occurrence of the full “Marangoni Effect” was believed to be prevented by solid oxide layers but it is still possible to develop the so called RME on cracks of oxide layers. Müller et al. [4] have found later an evidence of the occurrence of solutal Marangoni convection in shear cell experiments done both under laboratory conditions and under microgravity if intentional free surfaces are present. The latter could not be evaluated in the planned manner due to a malfunction of the thermal controlling of the AGAT furnace during the FOTON 12 mission.

---

* Corresponding author. Tel.: +771 608 6474; fax: +771 608 6103.
E-mail addresses: pflumm@dechema.de (R. Roşu-Pflumm), wwendl@phys.uni-karlsruhe.de (W. Wendl), gmuevo@phys.uni-karlsruhe.de (G. Müller-Vogt), suzuki@sanken.osaka-u.ac.jp (S. Suzuki), kraatz@physik.tu-berlin.de (K.-H. Kraatz), FrohbergProf@aol.com (G. Frohberg).

0017-9310/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2009.06.001

In the meantime the shear cell developed at TU Berlin [8] was further improved to a versatile tool for diffusion measurements which allows a great variety of experimental arrangements. Interdiffusion experiments could be performed either as diffusion from a thick layer into a 'semi infinite' space of a (here pure) component ("TLD") or as typical "interdiffusion-couple" experiments (symmetrical diffusion between two practically semi-infinite spaces "SID") in which about one half of the sample length is filled with an alloy and the other contains a pure component. Due to the fact that most of the metals and semiconductors do not wet the graphite surface of the capillary it is possible to change the fraction of free surfaces by means of specific surface treatments of the capillary walls and the variation of the pressure onto the liquid column.

The solutal Marangoni convection was estimated to have the potential to create an additional transport much higher than the diffusion [7]. But the lack of free surfaces either due to the assumed full contact of the liquid with the capillary wall or due to the occurrence of solid oxide layers on the surfaces of the liquid was believed to suppress such additional transports quantitatively up to the above cited work. Hence much more research seems to be necessary to know more about the occurrence of the Marangoni convection and the possibility to reveal and avoid such unknown contributions at the measurement of diffusion coefficients.

So we decided to use three systems which on the one hand could be filled into the shear cell arrangement by means of drawn wires and on the other hand show variations both in density and surface tension. Such systems are in order of increasing difference in density and surface tension: $Sn_{0.90}In_{0.10}$ versus pure Sn, $Pb_{0.95}Ag_{0.05}$ versus pure Pb, and $Sn_{0.985}Bi_{0.015}$ versus pure Sn. The surface tension was measured at the University of Karlsruhe for all three systems by means of the sessile drop method [9,10]. The density as a function of the composition is only well known for the system Sn–In [11]. For Pb–Ag there are literature data only for higher temperatures [12] which show the tendency of the alloy being denser. For Sn–Bi there are two publications [13,14] in which different densities for Sn-rich alloys are reported. As reliable quantitative density data at the adequate temperatures for the two systems were not available we used the shear cell itself with the unstable configuration (the heavier component is situated on the top of the vertical arranged one-dimensional diffusion-couple) to conclude from the concentration profile on the density.

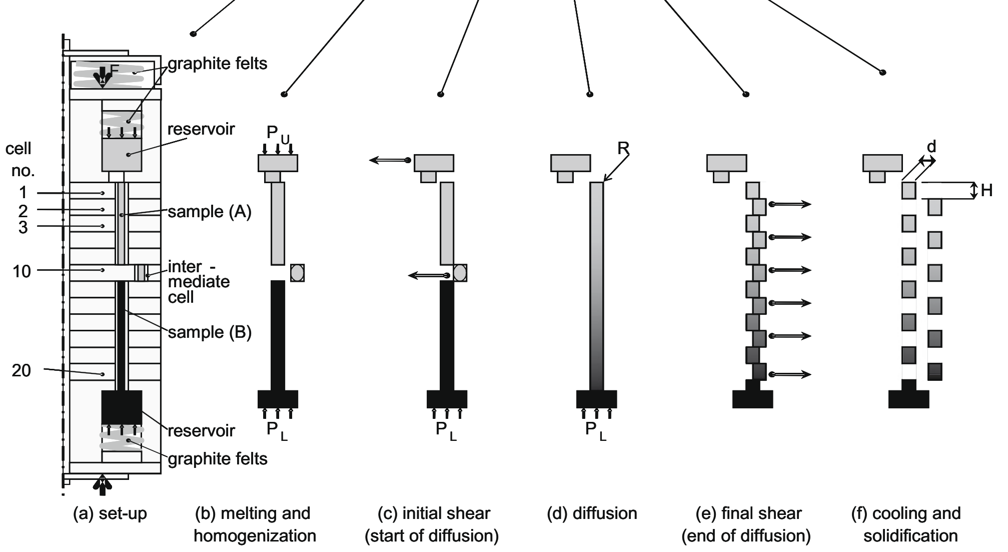
For comparison we performed diffusion measurements with different amounts of free surface both under 1 g and under µg conditions during the Foton M2 Mission:

(a) in capillaries with a high pressure (40 kPa at TU Berlin and 25 kPa at University of Karlsruhe) on the liquid column in order to avoid free surfaces,
(b) with reduced pressure (12.5 kPa, University of Karlsruhe) to extend the free surfaces stemming from menisci and the surface roughness of the graphite wall and
(c) with reduced pressure (as b)) and artificially created "additional" free surfaces by slits in the capillary wall.

2. Experimental

2.1. Diffusion measurements

The shear cell used for the ground experiments was the same as that specially developed at TU Berlin for the mission FOTON M2 (and M1) [8,16]. A Foton shear cell consists of 20 graphite discs of 3 mm thickness; each with 4 capillaries of 1.5 mm diameter. Fig. 1 shows a principal sketch of the used system. During heating



(a) set-up (b) melting and homogenization (c) initial shear (start of diffusion) (d) diffusion (e) final shear (end of diffusion) (f) cooling and solidification

Fig. 1. Diffusion experiment with the FOTON shear cell. A 1 g-experiment is illustrated as an example. p_L, p_U are lower and upper pressures ($p_L = p_U = p$ under µg), R the capillary radius, $d = 2R$.

up the diffusion samples remain separated and can homogenize (cf. Fig. 1a, b). The start of diffusion (cf. Fig. 1c) and the end (cf. Fig. 1d) is well defined and segregation is strictly limited to the separated parts of the capillary during cooling down (cf. Fig. 1e and f). We made efforts to get a high degree of operation reliability and of minimisation of the shear convection and of free surfaces. The Foton shear cell is designed for flexible set-ups. Every second disc of the shear cell can be used as the intermediate disc, which connects the two different parts of the diffusion partners at the beginning of diffusion. Thus we can arrange the discs for any type of diffusion experiment, e.g. such that a thick layer experiment (TLD) can be performed or a symmetric interdiffusion experiment between the two parts of the diffusion couple (SID). The complete operation and shearing sequence is demonstrated in [15]. The switching between the stable or unstable density layering can be done just by turning the cell arrangement upside-down. Thus the diffusion direction of the diffusing component can be set parallel or antiparallel to the g-vector. The experimental procedure in the present 1 g experiments was the same as for the μg experiments in the AGAT furnace (also developed at TU Berlin) in the FOTON M2 mission. The Foton shear cell was installed in a vacuum chamber with the same dimensions as in the AGAT furnace. The temperatures were measured by thermo-couples at three points along the axis of the cell (close to both ends of the capillary and the middle position) so that the axial temperature gradient can be checked, being smaller than 1 K/cm.

After the diffusion experiment, the alloys in the capillaries were pushed out of the disc, weighed and then dissolved in nitric acid in the case of Pb or aqua regia in the case of Sn, respectively. The amount of the diffusing metal (Ag, In and Bi) was determined by Flame AAS. Preliminary measurements had shown that the light absorption of these gaseous metal atoms was slightly influenced by the acid concentration. So we adjusted identical acid concentrations in the sample solutions and the working solutions used for calibration to avoid these chemical interferences. The accuracy of the method was tested with alloys of about the same composition as in our diffusion samples and was about 0.5% for Ag and 3% for In and Bi, respectively.

In all cases of the thick layer diffusion (TLD) the measured data $c(x,t)$ were fitted with the thick layer solution of the diffusion equation:

$$c(x,t) = \frac{c_1}{2}\left(\operatorname{erf}\left(\frac{h+x}{2\sqrt{Dt_{Diff}}}\right) + \operatorname{erf}\left(\frac{h-x}{2\sqrt{Dt_{Diff}}}\right)\right)$$

where x is the distance from the end of the alloy part (Fig. 2), D is the diffusion coefficient and $t = t_{Diff}$ is the measured diffusion time. The fitting parameters were h (initial thickness of the thick layer), c_1 (final maximum concentration) and the product Dt_{Diff}. $2Dt_{Diff}$ can be interpreted as the measured mean square diffusion depth. Fitting was done using least squares with no weight for all concentrations above the lower working limit of the AAS.

The fitting of the measured symmetrical interdiffusion (SID) data were done with the function (see [16])

$$c(x,t) = \frac{c_0 + c_1}{2} + \frac{c_1 - c_0}{2} \cdot \operatorname{erf}\left(\frac{x - x_0}{2\sqrt{Dt_{diff}}}\right)$$

Here x is the distance from the original interface between the two parts of the diffusion couple (Fig. 3) and x_0 is accounting for a possible shift of the diffusion centre due to the filling process at the insertion of the intermediate disc. c_0 and c_1 describe the initial concentration step. c_0, x_0 and Dt_{Diff} are the fitting parameters.

All data analysis is done under the assumption of a practically concentration independent diffusion coefficient (all experimental data proved this assumption to be valid in the investigated systems cf. Table 1). The influence of the shearing process and others on the diffusion coefficients has been corrected according to [17].

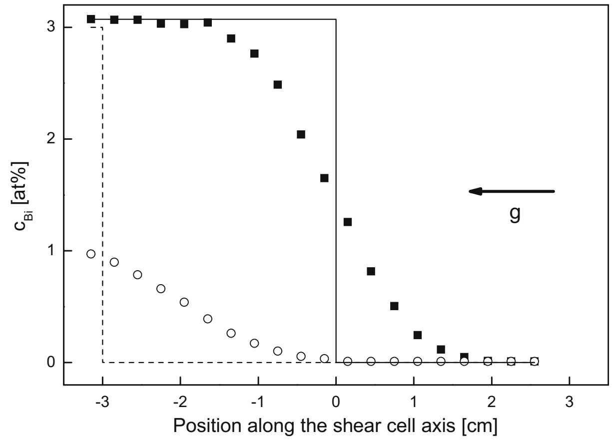


Fig. 2. Diffusion profiles obtained in the system Sn–Bi by a symmetrical interdiffusion experiment (SID, $T = 300$ °C, diffusion time = 12600 s, squares) and by a thick layer diffusion experiment (TLD, $T = 300$ °C, diffusion time = 28,800 s, circles), with Sn–Bi on the bottom, the stable arrangement. g represents the gravitation vector. The full black line shows the initial concentration step for the symmetrical interdiffusion. The dashed black line shows the initial concentration step for the thick layer diffusion.

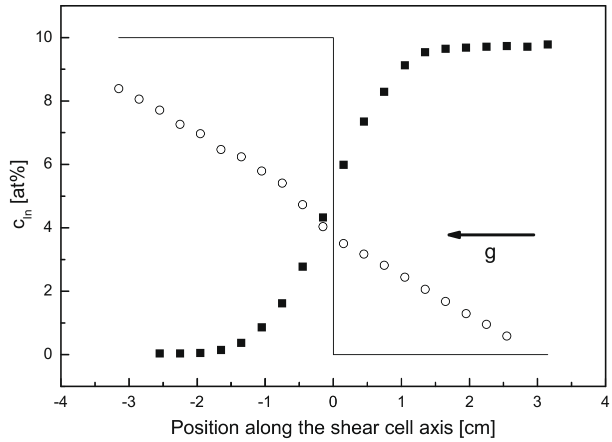


Fig. 3. Concentration profile from stable (squares) and unstable (circles) arrangements for Sn–In at 400 °C; the initial concentration step for the unstable arrangement (full line) is also included. g represents the gravitation vector.

2.2. Surface tension measurements

The measurement of the surface tension has been done at University of Karlsruhe using the sessile drop method [9]. A quartz tube closed at both ends with vacuum tight flanges containing quartz windows is situated in a furnace for temperatures up to about 800 °C. A syringe is mounted within this argon flushed chamber and allows to fill up a crucible from the bottom with drops of liquid metal. The contour of the drop above the crucible is viewed against a lighted background by an electronic camera through the quartz windows. Its contour is transferred to the computer and the surface tension is evaluated using the Laplace–Young equation in a standard procedure [10].

The vacuum level achieved inside the furnace is the same as in our diffusion experiments. The oxidation of the surface is not avoidable under these circumstances but it should be similar to

Table 1
Reference data for the measured systems.

System	Type of experiment	T (°C)	D (10^{-5}cm^2/s)	$\frac{D}{\Delta D}$ (%)	Experiments No. versus capillary No.	Source
SnBi1.5–Sn	TLD[a]	300	2.35	2.5		TU Berlin-1 g [8]
SnBi3–Sn	TLD	300	2.41	2.3		TU Berlin-1 g [8]
SnBi3–Sn	SID[b]	300	2.31	3.4	1/4	TH Karlsruhe-1 g
SnBi3–Sn	TLD	300	2.4	4.4	1/4	TH Karlsruhe-1 g
SnBi1.5–Sn	SID	300	2.36	4.2	3/9	TH Karlsruhe-1 g
SnBi1.5–Sn	SID	300	2.4	10[g]		μg [22,26]
SnBi0.5–Sn	SID	300	2.21[c]	5		Magnet.field [23]
SnBi3–Sn	TLD	400	3.09[d]	2.3		TU Berlin-1 g [8]
SnBi1.5–Sn	SID	400	3.14	5.2	3/7	TH Karlsruhe-1 g
SnBi1.5–Sn	SID	400	3.22[d]	10[g]		μg [22,26]
SnBi0.5–Sn	SID	400	2.99[c]	5		Magnetfield [23]
SnIn10–Sn	TLD	400	3.73	3.0		TU Berlin-1 g [8]
SnIn10–Sn	SID	400	3.60	2.7	3/8	TH Karlsruhe-1 g
SnIn1–Sn	SID	400	3.58[e]	10[g]		μg [22,26]
SnIn1–Sn	SID	400	3.78[e]	4		Magnetfield [23]
PbAg5–Pb	TLD	450	2.93[f]	2.3		TU Berlin-1 g [16]
PbAg5–Pb	SID	450	2.73	3.5	3/9	TH Karlsruhe-1 g [16]

[a] Thick layer diffusion.
[b] Symmetrical interdiffusion.
[c] Extrapolated by $D = A\,T^{1.84}$ cm^2/s, $T = T$ (K) [8], from $D = 2.04 \cdot 10^{-5}$ cm^2/s at 275 °C (548 K) [23].
[d] Extrapolated by $D = A\,T^{1.84}$ cm^2/s, $T = T$ (K) [8], from $D = 2.4 \cdot 10^{-5}$ cm^2/s at 301 °C (574 K) [22,26].
[e] Extrapolated by $D = A\,T^{1.92}$ cm^2/s, $T = T$ (K) [8], from $D = 2.6 \cdot 10^{-5}$ cm^2/s at 301 °C (574 K) [22,23,26].
[f] $D = 1.367 \times 10^{-11}\,T^{2.215}$ cm^2/s, $T = T$ (K) [16].
[g] Sum of maximum errors (no standard deviation) [23].

the degree reached in the diffusion experiments. A fresh produced metallic drop needs some hours to reach a stationary state of its contour. Values of the surface tension are only measured in that state.

The measurement of the surface tension from the contour of a sessile drop needs the knowledge of the density as well. The literature data for the system Pb–Ag are given only for higher temperatures than we used in our experiments [12]. In the case of Sn–Bi there are two reported values [13,14] So we had to evaluate the density by own measurements. The surface tension is an important input into the solutal Marangoni number:

$$Ma_S = \frac{\left(\frac{\delta\sigma}{\delta c}\Delta c\right)h}{D\upsilon}$$

with σ the surface tension, Δc the concentration difference along h, the characteristic length, D the diffusion coefficient, and υ the kinematic viscosity. The strength of the solutal Marangoni convection is proportional to the value of the solutal Marangoni number at constant temperature.

3. Results

3.1. Reference values for diffusion

First of all we made for all systems experiments with high pressure on the liquid column in the stable density arrangement. The temperature range reached from 300 °C to 450 °C. We did experiments in different laboratories (TU Berlin with a pressure estimated to about 40 kPa and University of Karlsruhe with a pressure estimated to about 25 kPa) and with different arrangements (thick layer diffusion TLD and symmetrical interdiffusion SID). Fig. 2 shows concentration profiles of two shear cell experiments for the system $Sn_{0.985}Bi_{0.015}$ versus pure Sn with TLD and SID arrangement, respectively. Details for the system $Pb_{0.95}Ag_{0.05}$–Pb are given in [16]. All possible (low) reference data together with the results for the system $Sn_{0.9}In_{0.1}$–Sn are compiled in Table 1. From that compilation it can be seen that for the system Sn–Bi the values obtained under microgravity and under high magnetic fields, which are believed to serve as reference values, are reached even under laboratory conditions with a deviation and a scattering lower than 5%. In [16] we reported that the 1g-values for the system Pb–Ag are remarkable lower than reported values gained from microgravity experiments [24]. Therefore we take the lowest values (1g) given in Table 1 for that system as reference values.

3.2. Surface tension

3.2.1. Measurements of the alloys density

At the University of Karlsruhe we used the shear cell itself at 300–400 °C in the unstable arrangement to get semi-quantitative data about the density of Sn–Bi and Pb–Ag alloys. The influence of the unstable arrangement with the heavier component in the upper half of the diffusion-couple on the resulting diffusion profiles has been reported in [16]. The symmetric interdiffusion, SID, was proven to be very sensitive to differentiate between the stable and the unstable arrangement in particular for very little differences in the specific weight of the original parts of the diffusion couple. Fig. 3 shows two concentration profiles of experiments with stable and unstable arrangement, respectively, for the system Sn–In. Stable and unstable arrangements were used in different capillaries during the same run. This type of measurements have been done for three concentration steps of In in Sn (5, 10 and 20 at%). The same measurements have been done for concentration steps of 2, 5 and 10 at% in the Pb–Ag system.

If we treat the profiles of Sn–In and Pb–Ag in the unstable arrangement as if they would have been produced by pure diffusion we can estimate an effective diffusion coefficient D^*. This coefficient may be conventionally described as the sum of the undisturbed diffusion coefficient D and an additional transport D_{add}, due to the unstable layering. For simplicity we suppose here that this additional transport is only a function of the two alloy densities, neglecting differences in viscosity, diffusion or any other convective influences. This relation was measured for the system Sn–In where we used the density data of [11]. Using this as calibration curve for D_{add} with respect to the density difference $\Delta\rho$, we correlated each D_{add} value in the Pb–Ag system with a corresponding $\Delta\rho$. So we have deduced $\Delta\rho = 0.021$ g/cm^3 between Pb and 5 at% Ag in Pb which is in a very good agreement with the results reported for higher temperatures [12].

While the systems Sn–In and Pb–Ag showed for the unstable arrangements increasing D_{add} in the developed concentration profile with increasing density difference (similar to Fig. 3), the system Sn–Bi reacted even for an initial concentration step of 1 at% in the unstable arrangement with somewhat like an overturn of the concentration step with subsequent diffusion. Therefore we can only say that $\Delta\rho$ for Sn–Bi must be remarkable higher in that case than for the other two systems. As the data of [14] fulfil that condition better than those of [13] we used these values for the density.

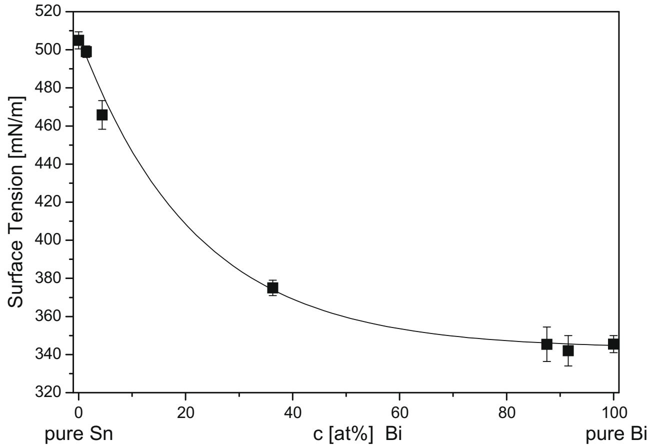


Fig. 4. Surface tension in the Sn–Bi system, from pure Sn to pure Bi at 400 °C. A surface tension gradient of 4 mN/(m at%) was calculated on the Sn-rich side by linear regression. This means a solutal Marangoni number of 2.06×10^6 for an initial concentration step of 1.43 at%.

Table 2
Marangoni numbers and the density difference for the investigated systems and concentration steps.

System	Δc (at%)	T (°C)	$(\frac{\partial\sigma}{\partial c})\cdot\Delta c$ (mN/m)	Ma_S (10^6)	$\Delta\rho$ (g/cm^3)
Sn–Bi	1.43	400	6.00	2.06	0.079
		600	7.00	2.08	
		800	10.00	2.77	
Pb–Ag	5	450	5.00	1.32	0.023
		600	10.00	1.94	
		800	14.00	2.56	
Sn–In	10	400	0.50	0.15	0.016
		600	1.18	0.32	
		800	0.80	0.15	

3.2.2. Measurements of surface tension

3.2.2.1. Surface tension of Sn–Bi. Fig. 4 shows the surface tension in the system Sn–Bi at 400 °C as function of the composition. We calculated a surface tension variation of 4 mN/(m·at%) by means of a linear interpolation between 0 and 4 at% Bi in Sn. Table 2 contains the calculated Ma_S.

3.2.2.2. Surface tension of Sn–In. The same measurements have been done for the system Sn–In at 400 °C. The surface tension values for pure Sn and pure In are very close to each other. We did not observe any remarkable change of the measured surface tension by varying the amount of In in Sn. If we fit the values by a linear regression we obtain a surface tension variation of 0.05 mN/(m·at%) which seems to be an upper limit. The corresponding Ma_S is shown in Table 2 as well.

3.2.2.3. Surface tension of Pb–Ag. Using the density difference mentioned before, we measured a surface tension variation of 1 mN/(m·at%) between pure Pb and 5 at% Ag in Pb at 450 °C. The calculated Ma_S is presented in Table 2 as well.

The same hierarchy of the solutal Marangoni numbers has been confirmed by surface tension and diffusion measurements at 600 and 800 °C, respectively (see Table 2) for the three above mentioned systems. The diffusion coefficients needed for the calculation of the Ma_S at each temperature are the corresponding $D^{1g}_{\text{Reference}}$ from Tables 1 and 3. All these data show that the strength of the solutal Marangoni convection for each investigated system does not change significantly with temperature.

Measurements of the diffusion coefficient using the shear cell on earth have to be done using the stable layering arrangement with the heavier component lying beneath the lighter one while the shear cell axis is parallel to the gravitation vector. Such a stabilising solute gradient during the diffusion process could reduce the convection related transport.

The clear result of the surface tension and density measurements is that there is an increase of the solutal Marangoni number and the density difference as well between the diffusion partners when going from Sn–In to Pb–Ag and to Sn–Bi (see Table 2).

3.3. Diffusion in capillaries with additional free surfaces

Provided with values for the diffusion coefficient, which we believe to be reference values due to the reasons mentioned above, we varied at University of Karlsruhe a lot of experimental parameters and investigated their influence on the measured diffusion

Table 3
Reference diffusion coefficients and the increase in diffusion coefficient values due to the solutal Marangoni convection from 1 g measurements. $D^{1g}_{\text{Reference}}$ represents the considered reference value of the diffusion coefficient. D^{HP} was measured under a pressure of 25 kPa, D^{LP} and D^{LPS} under a pressure of 12.5 kPa in unslitted and slitted capillaries, in the SID arrangement.

System	T (°C)	$D^{1g}_{\text{Reference}}$ (10^{-5}cm^2/s)	$\frac{D^{\text{HP}}}{D^{1g}_{\text{Reference}}}$	$\frac{D^{\text{LP}}}{D^{1g}_{\text{Reference}}}$	$\frac{D^{\text{LPS}}}{D^{1g}_{\text{Reference}}}$
Sn–In	400	3.72[a]	0.95	1.02	No results due to a diffusion barrier that has obviously arisen
	600	5.90[a]	1.00	1.12	1.23
	800	8.62[b]	1.24	2.14	3.68
Pb–Ag	450	2.73[a]	1.07	0.93	1.00
	635	4.87[a]	1.04	1.33	1.54
	800	7.06[b]	1.56	2.44	3.24
Sn–Bi	400	3.09[a]	0.96	0.89	0.99
	600	5.12[a]	1.00	1.52	1.56
	800	7.66[b]	1.95	3.63	7.25

[a] Measured under a pressure of both 25 and 40 kPa. No dependence on the experimental arrangement (SID or TLD) has been shown.

[b] Measured under a pressure of 40 kPa and with TLD experimental arrangement.

coefficients. For each investigated system diffusion experiments have been performed simultaneously in a capillary with high pressure (about 25 kPa) on the melt, a capillary with low pressure (about 12.5 kPa) on the melt and finally a capillary with low pressure together with additional free surfaces, which were introduced by slits sawed into the capillary wall of 4 discs around the initial concentration step. Each slit is 0.1 mm wide and 1 mm deep. The amount of additional free surfaces introduced by six slits represents about 13% from the entire surface of the capillary wall in the active diffusion zone.

We performed identical experiments under 1 g and μg at temperatures of 400 °C (Sn–Bi and Sn–In systems) and 450 °C (Pb–Ag system) to separate the effects due to buoyancy from that ones generated by solutal Marangoni convection. Additionally experiments at higher temperatures of 600 (Sn–Bi, Sn–In), 635 (Pb–Ag) and 800 °C (all investigated systems) were carried out on the ground. Measurements at higher temperatures were not possible under μg because of limited time and energy economics during the space flight.

The results obtained at University of Karlsruhe for a temperature of 400 °C for the systems containing Sn and 450 °C for Pb–Ag are given in Fig. 5a–c. According to our surface tension measurements we calculated solutal Marangoni numbers $0.15{\cdot}10^6$ for Sn–In, 1.3×10^6 for Pb–Ag, and 2×10^6 for Sn–Bi, respectively. The high Marangoni numbers of the latter two systems indicate that here Marangoni convection should initiate a strong additional transport which is not observed for 1 g experiments. There is a slight increase under μg, being larger for Sn–Bi with slits. Our new measurements on FOTON M2 lay in all cases over the ground measurements and some over previous values measured in space. The slightly enhanced values measured under μg conditions during the FOTON M2 mission in the case of Sn–In and Pb–Ag are not much above the error due to normal scattering of our experiments. For the system Sn–Bi these values are clearly beyond that error. The lower values on earth may be due to density stabilization.

The measurements at lower temperature have been followed by similar ground experiments at higher temperatures of about 600 °C and 800 °C. The results of the diffusion experiments under different pressures on the melt (which means a different amount of available free surfaces) and with slits are shown in Fig. 6a–c. We have measured a significant increase in the value of the diffusion coefficient with increasing free surfaces for a temperature of 800 °C, even in the case of Sn–In. Much lower diffusion coefficients were measured under a high pressure of about 40 kPa on the melt using a TLD arrangement at TU Berlin than with a pressure of 25 kPa on the melt and the SID arrangement at University of Karlsruhe. TLD introduces lower concentration gradients compared to SID, which means lower level of contamination of the diffusion coefficient by solutal Marangoni convection.

That's why the group of Berlin focused on experiments with high pressure on the melt (estimated pressure of 40 kPa) and TLD arrangement. The results from their experiments have been taken as reference $D^{1g}_{\text{Reference}}$ at higher temperatures, since no other data about a reference diffusion coefficient measured under the same conditions over the investigated concentration and temperature range has been available at the moment and the TU Berlin method has been shown the ability to reproduce μg values in other cases. The goal at University of Karlsruhe was to investigate the influence of the solutal Marangoni convection by decreasing the pressure on the melt from an estimated starting pressure of 25–12.5 kPa and adding different amounts of free surfaces. The lower starting pressure compared to the 40 kPa at TU Berlin results in a stronger scattering and higher diffusion coefficients at these temperatures. The enhancement of the diffusion coefficient under the described experimental conditions with respect to $D^{1g}_{\text{Reference}}$ are summarised in Table 3 for the investigated temperature range.

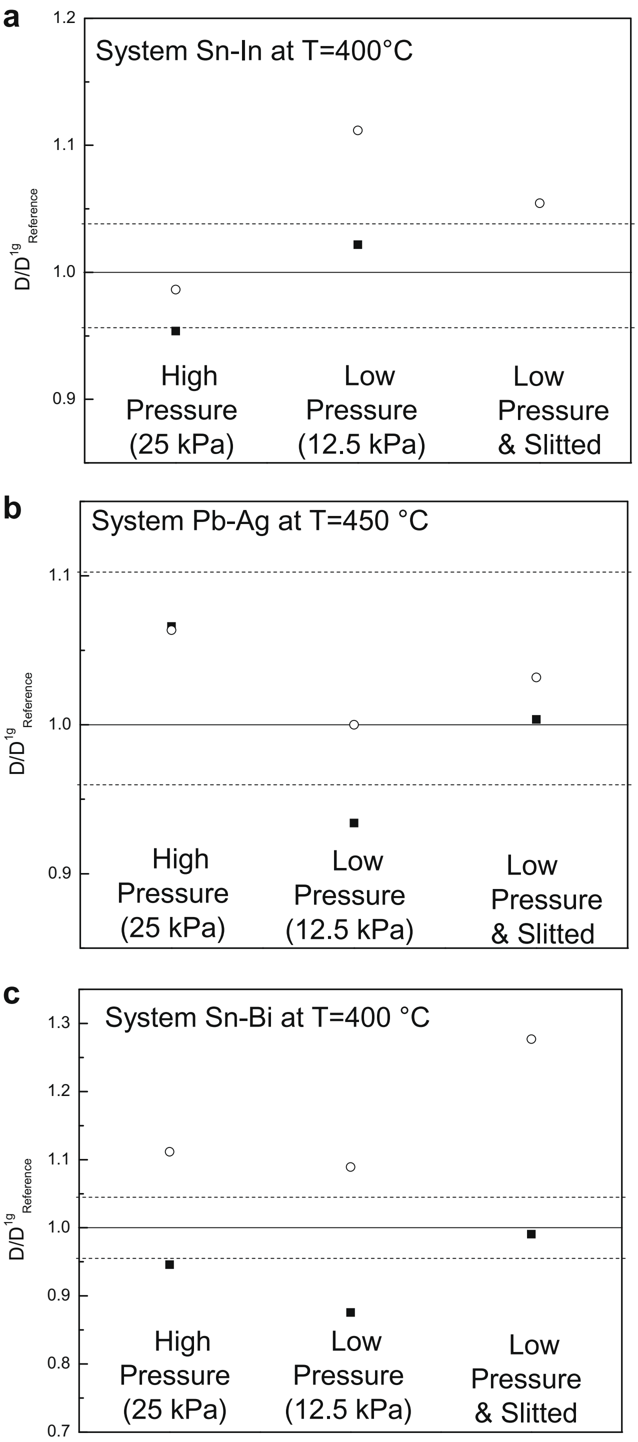


Fig. 5. (a–c) Ratio between the diffusion coefficients measured under 1 g (black squares) and μg (open circles) conditions in capillaries with high pressure (25 kPa) and low pressure (12.5 kPa) on the melt and the corresponding reference values of the diffusion coefficient cf. Table 3. The available amount on free surfaces increases from "high pressure" to "low pressure and slitted". The full line corresponds to the reference diffusion coefficient. The dotted lines show the maximum scattering of 1 g results.

4. Discussion

If we consider the results of our measurements (Fig. 6) over the whole temperature range we can state that the dramatic effects are to be seen at elevated temperatures comparable to those measured in [4]. We have to find explanations for the relatively high stability

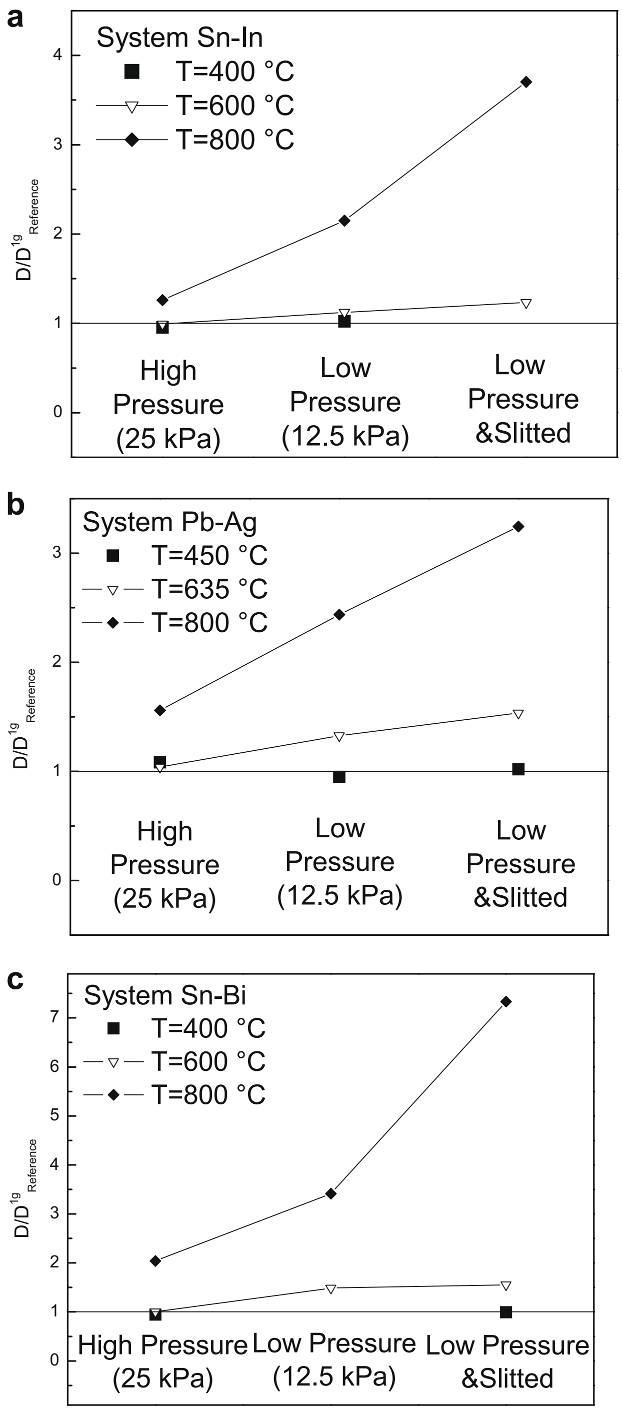


Fig. 6. (a–c) Ratio between the diffusion coefficients measured under 1 g conditions in capillaries with high pressure (25 kPa) and low pressure (12.5 kPa) on the melt and the corresponding reference values of the diffusion coefficient cf. Table 3. The available amount on free surfaces increases from "high pressure" to "low pressure and slitted".

of the low temperature experiments against additional transports and the nature of the fairly low stability of the high temperature experiments.

The buoyancy driven convection due to radial gradients and the damping effect of the stable layering are effects which operate within the volume of the liquid column. In the temperature range from 400 °C to 800 °C the radial temperature field does not change significantly according to our experience. Therefore buoyancy should not be mainly responsible for the increasing instability. The relatively small contribution of the stable layering may be seen from the fact that an increase of the diffusion coefficient in the case of Sn–Bi at 400 °C measured in space of about 25% (Fig. 5c) may be damped away. But much higher contributions of convection as for the temperatures at 600 and 800 °C could not be avoided. Further a decrease of viscosity or other material properties inherent in the volume of the liquid cannot explain the experimental finding of the significant increase with temperature of the additional transports and their dependence on the amount of free surfaces.

The solutal Marangoni convection depends on the changing of the surface tension within the concentration gradient which for a concentration step is fairly high within an initially very narrow region. If really free surfaces are present on the liquid, this difference in surface tension leads to strong convection in the melt as estimated for instance in [18]. The capillary wall shows micro pores and scratches due to machining. The metallic liquid does not wet graphite and if the pressure on the liquid column is lower than the corresponding capillary pressure free surfaces remain. The influence of the solutal Marangoni convection in a diffusion couple changes with time due the changing of the concentration gradient during the run of an experiment. The decreasing and broadening of the concentration gradients is different for the both methods TLD and SID, respectively, used during our project. Due to the limited amount of diffusion species in the case of TLD the gradients slow down much faster and are flattening stronger than in the case of SID for which the concentration difference remains constant and only the broadening is responsible for the flattening of the concentration. By the way the different behaviour of the concentration gradient is responsible for the different damping effect of the stable layering in both cases too. That the amount of the free surfaces plays an essential role is to be seen from the result shown in all three figures a–c of Fig. 6.

Due to the reduction of the pressure and the roughness of the capillary wall we introduce free surfaces of an unknown amount which are distributed over the whole wall. The artificial free surfaces due to the slits around the initial concentration step represent a locally limited area. Without the artificial surfaces the Marangoni convection acts within the concentration gradient similar as the diffusion itself. So there is no possibility to distinguish between both contributions by deviations from the ideal error function form of the concentration profiles even if the diffusion coefficient is enhanced with a factor of 3.6 in the case of Sn–Bi at 800 °C. If in that case artificial free surfaces (slits) are present the enhancement in the diffusion coefficient is nearly a factor of eight and the concentration profile is deformed around the initial concentration step.

The fact that the solutal Marangoni convection at temperatures of about 400 °C does not work as efficient as at higher temperatures may be explained by oxide layers existing on the liquid surface, because earlier estimations have shown, that a really free surface would create a much stronger Marangoni convection, increasing our measured D_{add} by more than a factor of 1000 [7]. Naturally, the processing of the feed material (wire drawing and filling handling) is done in normal atmosphere. So oxide layers on the surface of the liquid develop. This is to be seen on the surface of the reservoirs after the experiment. From other experiments on the chemical behaviour of metal oxides on graphite surfaces [19] or influence of oxygen on the oxidation of graphite [20] it is known that the reduction of some metal oxides like for instance SnO_2 starts at temperatures of about 600 °C upwards. Hence the inert behaviour against additional transports at lower temperatures seems to be due to the prevention of nearly all Marangoni convection through an effective oxide layer. A residual Marangoni effect may be additionally damped by density stabilization. At higher temperatures that damping effect is reduced by the reduction of the oxide layers through the graphite of the capillary walls of the shear cell and perhaps also by the dissolution of the oxides in the liquid metal [21]. One of the central problems is that there is no quantitative information on the degree of oxidation or solubility. Therefore it can only be stated that the potential of the solutal Marangoni convection under the existence of so-called "free" but partly oxidized surfaces is really able to create additional velocities inside the liquid volume much greater then the velocity due to diffusion.

With which perfection solutal Marangoni convection may be suppressed is still not exactly proven. The experiments at TU Berlin concentrated on the prevention of Marangoni convection by the use of the maximum available pressure on the liquid column of about 40 kPa. At University of Karlsruhe have been used a high pressure of about 25 kPa. For the system Sn–Bi at 800 °C we get in Berlin the lowest values for the diffusion coefficient but still with a scattering of about ±5%, which is higher than the expected inaccuracy due to the chemical analysis. Our experiments nearly reach the Berlin values but with a much higher scattering of about ±20%. Remarkable is that a system like Sn–In which has a low Marangoni number compared to the other two systems shows a great influence of the free surfaces, which could be due to the very low density stabilization. Perhaps also inhomogeneities in the oxide coverage of the free surfaces during the reduction process are important, since the surface tension is very sensitive with respect to the oxide coverage of the melt [25].

5. Conclusions

The solutal Marangoni convection has been shown to have a great disturbing potential in the measurements of diffusion coefficients for the used three systems. Under unfavourable conditions the material transport due to Marangoni convection may reach eight times that one by diffusion alone. On the other hand we have found two possibilities to suppress these additional transports. First a pressure high enough to avoid free surfaces allows no surface tension driven convection. Second the systems we used show a strong affinity to oxygen. At lower temperatures these oxygen layers reduce the influence of Marangoni convection with high efficiency as well. Hence at low temperatures pressures of some kPa together with a buoyancy stabilization are sufficient to measure pure diffusion under laboratory conditions. At temperatures higher than about 600 °C the thickness of the oxide layer is reduced and a pressure of at least 40 kP has to be applied on the liquid column to barely suppress the Marangoni effect. With the knowledge of these results diffusion coefficients measured in earlier experiments should be critically re-evaluated.

Acknowledgment

The authors gratefully acknowledge the financial support by the German DLR under Contract Nos. 50 WM 0049 and 50 WM 0349.

References

[1] G. Müller-Vogt, P. Bräuer, R. Kößler, Z. Peranic, J. Schlegelmilch, T. Strasser, W. Trillsam, in: L. Ratke (Ed.), Immiscible Alloys and Organics, DGM-Informationsgesellschaft, Oberursel, 1992, p. 125, 12th General Conference of Condensed Matter Division EPS and Arbeitskreis Festkörperphysik DPG März/April, 1993.
[2] G. Müller-Vogt, R. Kößler, Application of the shear cell technique to diffusivity measurements in melts of semiconducting compounds: Ga–Sb, J. Cryst. Growth 186 (1998) 511.
[3] P. Bräuer, G. Müller-Vogt, Measurements of aluminium diffusion in molten gallium and indium, J. Cryst. Growth 186 (1998) 520.
[4] H. Müller, G. Müller-Vogt, Investigation of additional convective transports in liquid metals and semiconductors during diffusion measurements by means of shear cell technique, Cryst. Res. Technol. 38 (2003) 707.
[5] T. Hibiya, I. Egry, Thermophysical property measurements of high temperature melts: results from the development and utilization in space, Meas. Sci. Technol. 16 (2005) 317.
[6] T. Masaki, T. Fukazawa, S. Matsumoto, T. Itami, S. Yoda, Measurements of diffusion coefficients of metallic melt under microgravity – current status of the development of shear cell technique towards JEM on ISS, Meas. Sci. Technol. 16 (2005) 327.
[7] G. Frohberg, K.-H. Kraatz, H. Wever, Diffusion and transport phenomena in liquids under microgravity, in: Proceedings 6th European Symposium on Material Sciences under Microgravity Conditions, Bordeaux (France) (1986), ESA SP-256, February 1987, pp. 585–591.
[8] S. Suzuki, K.-H. Kraatz, G. Frohberg, Diffusion measurements on liquid metallic materials and development of shear cell (preparation for Russian satellite mission Foton-M2), J. Jpn. Soc. Microgravity Appl. 22 (3) (2005) 165–174.
[9] N. Eustathopoulos, M.G. Nicholas, B. Drevet, Wettabillity at high temperatures, Ed. Pergamon Mat. Sci. (1999) 106.
[10] Data Physics Instruments GmbH, Filderstadt, Germany: Manual der OCA Serie.
[11] P.-E. Berthou, R. Tougas, The densities of liquid In–Bi, Sn–In, Bi–Sb, and Bi–Cd–Tl alloys, Metal. Trans. 2978, vol. 1, October 1970.
[12] F. Sauerwald, The densities of molten alloys with segregation tendencies, Adv. Phys. 16 (1967) 545.
[13] Landolt-Börnstein, 6th Edition, Zahlenwerte und Funktionen, II. Band, 1. Teil, Mechanisch-Thermische Zustandsgrössen, p. 779.
[14] Z. Moser, W. Gasior, J. Pstrus, Surface tension measurements of the Bi–Sn and Sn–Bi–Ag liquid alloys, J. Electron. Mat. 30 (9) (2001) 1104.
[15] S. Suzuki, K.H. Kraatz, G. Frohberg, R. Rosu, G. Müller-Vogt, Vortrag: impurity diffusion measurements of Bi in liquid Sn using stable density layering and the shear cell technique, in: 12th International Conference on Liquid and Amorphous Metals 2004, Metz, Frankreich, J. Non-Cryst. Solids, accepted for publication.
[16] S. Suzuki, K.-H. Kraatz, G. Frohberg, R. Rosu, W. Wendl, G. Müller-Vogt, Pre-flight diffusion measurements on liquid metals under 1G-conditions for the Foton-M2 mission, Ann. N.Y. Acad. Sci 1077 (2006) 380.
[17] S. Suzuki, K.-H. Kraatz, A. Griesche, G. Frohberg, Shear cell development for diffusion experiments in Foton-satellite mission and on the ground with consideration of shear-induced convection, Microgravity Sci. Technol. XVI–I (2005) 127.
[18] Y. Malmejac, G. Frohberg, in: H.U. Walter (Ed.), Chapter V in Fluid Sciences and Material Science in Space, Springer-Verlag, Berlin, 1987, p. 159.
[19] S.R. Kelemen, H. Freund, O_2 oxidation studies of the edge surface of graphite, Carbon 23 (6) (1985) 619.
[20] G. Müller-Vogt, W. Wendl, Chemical reactions in the graphite tube for some carbide and oxide forming elements, Spectrochimica Acta 39B (Nos 2/3) (1984) 237.
[21] N. Eustathopoulos, M.G. Nicholas, B. Drevet, Wettabillity at high temperatures, Ed. Pergamon Mat. Sci. (1999) 238.
[22] J.-P. Garandet, G. Mathiak, V. Botton, P. Lehmann, A. Griesche, Reference microgravity measurements of liquid phase solute diffusivities in Sn- and Al-based alloys, Int. J. Thermophys. 25 (1) (2004) 249.
[23] V. Botton, PhD thesis (in French), National Institute of Polytechnics Grenoble, France, 2001, pp. 84–87.
[24] R.W. Smith, Xiaohe Zhu, M.C. Tunnicliffe, T.J.N. Smith, L. Misener, J. Adamson, The influence of gravity on the precise measurement of solute diffusion coefficients in dilute liquid metals and metalloids, Ann. N.Y. Acad. Sci. 974 (2002) 57.
[25] E. Ricci, L. Nanni, A. Passerone, Oxygen transport and dynamic surface tension of liquid metals, Phil. Trans. R. Soc. Lond. A 356 (1998) 857–870.
[26] J.P. Praizey, J.P. Garandet, G. Frohberg, A.Griesche, K.H. Kraatz, Diffusionsexperiments in liquid metals, Preliminary results (AGAT-Module, Foton 12), in: Proc. 1. Symp. Microgravity Research & Appl. Phys. & Biol. Sci., Sorrento, Italy, ESA SP-454, 2000, p. 481.