CONVECTIVE EFFECTS IN THE MEASUREMENT OF DIFFUSIVITIES AND THERMOTRANSPORT COEFFICIENTS. LIQUID METAL ALLOYS AND THE USE OF A MAGNETIC FIELD

T. Alboussière
Department of Engineering
University of Cambridge
Trumpington Street, Cambridge CB2 1PZ
J.P. Garandet
Commissariat à l'Energie Atomique, DTA/CEREM/DEM
LRBS au CENG, 38054 Grenoble Cedex 9
P. Lehmann, R. Moreau
Laboratoire EPM-Madylam, CNRS UPR A 9033
ENSHMG BP 95, 38402 Saint Martin d'Hères

In long capillary experiments, thermodiffusivity measurements may be deeply disturbed by convective mass transfer. These convective transfers can be accounted for by the use of an effective diffusivity and are shown, both analytically and experimentally, to vary as B^{-4} in the presence of a magnetic field B.

Effets convectifs en mesures de coefficients de diffusion et de thermodiffusion. Alliages métalliques liquides et utilisation d'un champ magnétique

La mesure de coefficients de thermodiffusion en capillaire long peut être profondément influencée par la contribution convective au transport de masse. Celle-ci accroît la diffusivité apparente et nous montrons analytiquement et expérimentalement qu'en présence d'un champ magnétique B, cette contribution suit une loi en B^{-4}.

Nomenclature	
CEA	Commissariat à l'énergie Atomique
CEREM	Centre d'études et de Recheche sur les Matériaux
CNES	Centre National d'Études Spatiales
D_{eff}	effective diffusivity
D_{Teff}	effective thermotransport coefficient
Δ_S	two-dimensional Laplacian operator in a cross-section
erf	error function
EPM	Electromagnetic Processing of Materials
EPSRC	Engineering and Physical Sciences Research Council
G_D	axial solute composition gradient
Gr	Grashof number
G_T	axial thermal gradient
Ha	Hartmann number
Madylam	Magnetodynamique des liquides - Application à la métallurgie
Sc	Schmidt number
< >	average on a cross-section

1. INTRODUCTION

The measurement of thermophysical properties in liquid metal alloys is of great importance for crystal growth and metallurgy. Digital models for the relevant processes become more and more coefficient with the development of computer speed and memory : however, these models still rely on measured thermophysical data. Despite the difficulty of measuring diffusivities and thermodiffusivities in liquid metals, some teams are involved in such programs [1, 2, 3].

Our objective in this paper is to show how buoyancy driven convection can affect the measurement of solute diffusivities and thermotransport coefficients and how the use of a steady magnetic field can reduce these convective effects in liquid metal alloys.

In a long capillary setup, an axial temperature gradient G_T is imposed. In the final steady state, the mass transport due to thermodiffusion must be balanced by solute diffusion; hence an axial solute composition gradient G_D must develop. Denoting D and D_T the diffusivity and thermotransport coefficient, the equilibrium is reached when :

$$D_T G_T + D G_D = 0 \qquad (1)$$

As we shall see in section 3, convective effects will be modelled by replacing D by an effective diffusivity D_{eff}. If the thermodiffusion results are analyzed assuming that pure diffusion takes place, an effective thermotransport coefficient D_{Teff} is obtained, related to the real thermotransport coefficient by the following relationship :

MOTS-CLÉS énergétique / thermodiffusion / champ magnétique / alliages métalliques liquides
KEYWORDS energetics / thermal diffusion / use of a magnetic field / liquid metal alloys

$$D_{Teff} = D_T \frac{D}{D_{eff}}. \quad (2)$$

The effect of convection on the measurement of thermodiffusion coefficients is thus directly related to that of convection on diffusivities measurements and the paper will be devoted to obtaining D_{eff}

The buoyancy forces can be of thermal or of solute origin. In the case of thermal buoyancy forces, there is a decoupling between the hydrodynamical problem and the solute transport, whereas there is a complex coupling when solute buoyancy forces are significant. In both cases, we shall consider the application of a steady uniform magnetic field that will exert a braking effect on convection.

After a presentation of the experimental technique in section (2), the model of effective diffusivity aiming at modelling the mass transport induced by convection will be recalled (section 3). How a magnetic field damps the convective contribution to mass transport is analyzed in (4) in the framework of the effective diffusivity. In the following section (5), experimental results of diffusivity measurements under magnetic field are presented and compared to our model. Section (6) is devoted to a discussion of the use of magnetic fields in the measurement of solute diffusivities and thermotransport coefficients.

2. THE SHEAR CELL TECHNIQUE

In a purely diffusive transfer, the mass transfer density field **J** is modelled by the phenomenological Fick's law in the limiting case of dilute alloys : $\mathbf{J} = -\rho D \nabla c$, where ρ, D, c denote the constant and uniform density, solute diffusivity and solute concentration expressed in mass fraction respectively. A configuration is settled in such that a one dimensional diffusion is expected.

The initial state is a step function of concentration along the axis where diffusion will proceed, which we denote the x-axis. The conservation of solute mass ρc along with the expression of the diffusion flux **J** leads to a local equation of conservation in the x direction :

$$\frac{\rho \partial c}{\partial t} + \frac{\partial J_x}{\partial x} = 0,$$

where J_x is the single non zero component of **J**. The solution of this local equation, well known since the 19th century results in heat transfer, is an *erf* function

$$c(x,t) = \frac{\delta c}{2}\left[1 + erf\left(\frac{x}{2\sqrt{Dt}}\right)\right], \quad (3)$$

when the initial condition is $c = 0$ for $x < 0$ and $c = \delta c$ for $x > 0$. The knowledge of the composition at a time T enables to derive the diffusivity.

The originality of the shear cell technique (see figure 1) initially proposed at the CEREM by Praizey [4], creates the conditions of one-dimensional diffusion from a step function and provides the possibility of «freezing» the composition function at a time T, determined by the operator. A thin capillary of diameter of order 1 mm is formed by the alignment of a number of discs where an eccentric circular hole has been drilled. All the discs can be rotated around a common central axis. Three configurations are needed during a measurement experiment. Firstly, the long capillary is split in two half capillaries, allowing their filling with the alloy at different compositions. Secondly, the full capillary is formed, creating the initial step function. Thirdly, after a duration T of diffusion prescribed by the operator, all fractions of the capillary can be isolated, e.g. by rotating every other disk. How these steps can be performed is a matter of subtle technology. After the last step, the temperature is decreased to room temperature and the solid elementary alloy samples contained in each disk are globally analyzed. The mean value of the axial solute distribution on each disc length after a diffusion duration T is obtained. By comparison with the solution (3), an experimental value of the diffusivity D is derived.

3. CONVECTION AND EFFECTIVE DIFFUSIVITY

The previous section describes the ideal purely diffusive case. In this section, the effect of a weak convection on mass transport is addressed. A steady divergence free velocity field **v** is supposed to take place in the capillary with a zero normal component at the boundaries. In comparison with earlier works in the field, it is not necessary to suppose that the flow is one-dimensional. Nevertheless its variations in the direction of the x axis are assumed to take place on a larger length scale than the capillary diameter.

Fick's law for solute transfer holds in the reference system where matter is at rest. When expressed in the laboratory system of reference, in the presence of convection, it becomes $\mathbf{J} = -\rho D \nabla c + \rho c \mathbf{v}$. It remains possible and enlightening to express a local solute conservation equation along x. The basic experimental observable is the mean value of the concentration in the

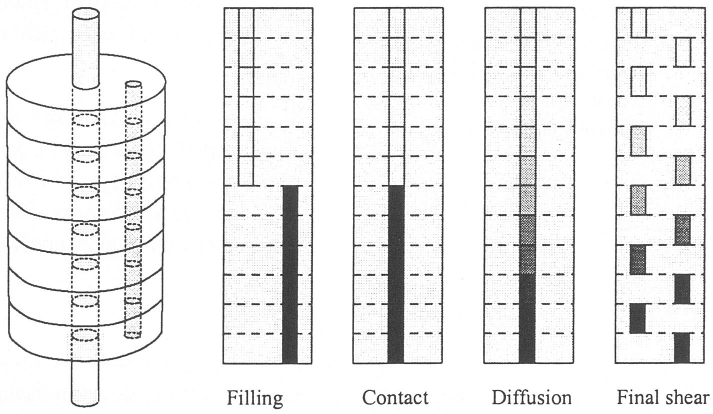

Fig. 1 Shear cell sketch and principle

plane orthogonal to the x-axis at a given coordinate x, denoted $c_0(x, t)$, while the variations of concentration within this plane are represented by $c_1(x,y,z,t) = c(x,y,z,t) - c_0(x,t)$. The conservation of species along x takes the form $\rho\partial c_0/\partial t + \partial <J_x>/\partial x = 0$, where $<>$ denotes the average in the plane perpendicular to the x axis. A zero net global mass flux being assumed in the x direction, because the fluid is confined in a closed cavity, it is not difficult to derive the following form $<J_x> = -\rho D(\partial c_0/\partial x) + \rho <v_x c_1>$, where v_x is the x component of the velocity field. The solute equation along x can now be written

$$\frac{\partial c_0}{\partial t} = D\frac{\partial^2 c_0}{\partial x^2} - \frac{\partial \langle v_x c_1 \rangle}{\partial x}. \quad (4)$$

It is clear from equation (4) that the field c_1 has to be considered in order to obtain a proper equation for c_0. The local point-wise solute conservation equation is $\rho\partial c/\partial t + div\,\mathbf{J} = 0$, which can be expanded as $\partial c/\partial t + \mathbf{v}\cdot\nabla c = D\Delta c$. The difference between this isotropic equation and the x equation (4) is written here without approximation :

$$\frac{\partial c_1}{\partial t} + \mathbf{v}\cdot\nabla c_0 + \mathbf{v}\cdot\nabla c_1 - \frac{\partial}{\partial x}<v_x c_1> - D\Delta c_1 = 0\,. \quad (5)$$

Our primary goal being the analysis of the departure of species transfer from the purely diffusive case, we will treat convection as a small parameter. We can anticipate that the perturbation $\mathbf{v}$ is at the origin of a field c_1 of the same order, and both $\mathbf{v}\cdot\nabla c$ and $(\partial/\partial x)<v_x c_1>$ are second order terms in (5) compared to $\mathbf{v}\cdot\nabla c_0$. For a weak convection, it is also safe to neglect the first term $\partial c_1/\partial t$ in comparison with $D\Delta c_1$: these terms should be comparable if only axial variation was looked at, but by definition of c_1, and due to the aspect ratio of the cell, its variations in the cross-section are very large compared to its axial variation[1]. The first order disturbance form of (5) is

$$\Delta_S c_1 = D^{-1} v_x \frac{\partial c_0}{\partial x}, \quad (6)$$

where Δ_S denotes the Laplacian operator in the cross section and where ∇c_0 was replaced by its single non zero component $\partial c_0/\partial x$. The field c_1 must satisfy a zero normal gradient at the circular boundary. The solution of equation (6) is $f D^{-1}\partial c_0/\partial x$, where f is solution of $\Delta_S f = v_x$ and admits a zero normal gradient on the boundary. Using that result, the term $<v_x c_1>$ takes the form $<v_x f> D^{-1}\partial c_0/\partial x$ and the basic equation for c_0 (4) can be written

$$\frac{\partial c_0}{\partial t} = \frac{\partial}{\partial x}\left[\left(D - \frac{<v_x f>}{D}\right)\frac{\partial c_0}{\partial x}\right]. \quad (7)$$

The term in brackets can be regarded as an effective diffusivity [5], $D_{eff} = D - <v_x f>/D$, by analogy of (7) with a diffusion equation. The convective part in the effective diffusivity is quadratic in the convective disturbance. In the case of a fully-established convection along the axis, the effective diffusivity is independent of x and the equation governing c_0 becomes strictly identical to that of pure diffusion : given an experimental measurement of a diffusivity, it is impossible to guess what part of it is due to convection (see [6]). In spirit, this effective diffusivity model is similar to that developed by Taylor [7] for solute dispersion in Poiseuille flows.

4 EFFECT OF A MAGNETIC FIELD

A simple configuration is now specified : the capillary of diameter H is assumed to be horizontal and an axial uniform temperature gradient G is applied. It has been shown in [8], that this configuration was analogous to a vertical capillary in a transverse temperature gradient, since only the curl of the buoyancy driving force is to be considered. Let us denote z the direction opposite to the gravity vector and y the orthogonal direction to the x and z axis. The problem of the viscous[2] buoyancy driven convective flow in the cylindrical cell has been given a solution by Bejan [9] :

$$v_x = \frac{Gr\,Sc}{32}\left[4Z^3 + 4ZY^2 - Z\right]\frac{D}{H}, \quad (8)$$

where $Z = z/H$, $Y = y/H$
and $Gr\,Sc = (\beta g G H^4)/(\nu D)$
can be considered as the product of a Grashof number and a Schmidt ν/D number (β, g and ν denote the volume expansion coefficient, gravity and the kinematic viscosity, respectively). Following the previous section analysis, the resulting effective diffusivity is determined analytically :

$$D_{eff} = D\left[1 + \frac{7(GrSc)^2}{11796480}\right]. \quad (9)$$

In the same configuration, a transverse uniform vertical magnetic field is applied. When its magnitude B is such that the Hartmann number $Ha = \sqrt{\sigma/(\rho\nu)}\,B\,H$ (where σ denotes the electrical conductivity) is very large compared to unity, the convective velocity profile for electrically insulating boundaries tends towards [10] :

$$v_x = -\frac{Gr\,Sc}{Ha^2}2Z\frac{D}{H}, \quad (10)$$

This damping is due to the Lorentz force $\mathbf{j} \times \mathbf{B}$ where $\mathbf{j}$ is the electrical current density and $\mathbf{B}$ the imposed magnetic field. The analytical derivation of D_{eff} yields :

$$D_{eff} = D\left[1 + \frac{7(GrSc)^2}{384\,Ha^4}\right]. \quad (11)$$

5. MEASUREMENT OF DIFFUSIVITY IN SnIn

In the laboratory EPM-Madylam, an experimental shear-cell setup was designed and built to study the influence of an applied magnetic field

[1] Here is also made use of the assumption that the axial scale of variation of convection is much larger than the diameter.

[2] The assumption of negligible inertia (small Reynolds number) is safe, the kinematic viscosity being much larger than the species diffusivity for liquid metals and semiconductors.

on the measured diffusivity. The 2 mm diameter capillary was horizontal and the applied magnetic field vertical. The SnIn alloy was chosen because its density depends weakly on its concentration : the concentration of indium was 1% on one side while pure tin was placed on the other side. An axial thermal gradient of 68 $K.m^{-1}$ was applied and was mainly responsible for the convection in the capillary. The diffusivity was measured for five different values of the magnetic field from 0.2 *T* to 0.75 *T* and the results are plotted in figure 2.

First, it can be noticed that the experimental values can be split into two sets, the circles and triangle points, each of them following a linear variation. They are corresponding respectively to the case when the small buoyancy forces of solute origin (dependence of density on concentration) add to the thermal buoyancy (circles) or oppose the thermal buoyancy (triangles). Two points (circle and triangle) at the same value of the magnetic field are obtained during the same experiment with two capillaries of opposite orientation.

Secondly, these two sets of points converge towards the same value at high magnetic field, $D = 2.3\ 10^{-9} m^2.s^{-1}$, in agreement with recent micro-gravity results [3].

Thirdly, the relationship (11) was plotted, to assess the validity of the effective diffusivity model. Given the accuracy of the measured diffusivities ($\pm\ 10^{-10} m^2.s^{-1}$), the model is relatively close to the upper experimental values. The discrepancy for the two smallest values of *B* (two highest values of B^{-4}) may result from a too low value of the Hartmann number (13.8 and 17.3) for which the asymptotic treatment is not valid.

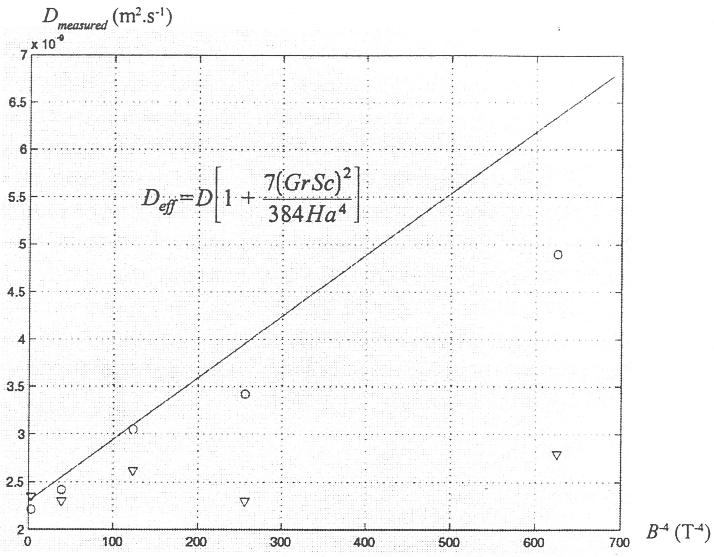

Fig. 2 Measured diffusivity of In into Sn for different values of the magnetic field applied

6. DISCUSSION

The influence of a magnetic field on the effective diffusivity is very important, with a Ha^{-4} term in the convective contribution, according to the effective diffusivity model presented here. This B^{-4} variation has been tested experimentally on the SnIn dilute alloy. As stated in the introduction, the use of a magnetic field in the measurement of thermo-diffusion coefficients might also be beneficial.

Despite the general agreement of the experimental results with our model, the question of the effect of an *a priori* negligible solute buoyancy force is raised (see figure 2) : when it is opposed to the dominant thermal buoyancy, it seems to reduce drastically the convective mass flux.

The question whether a strong magnetic field could have an influence on the value itself of the molecular diffusivity is also to be kept in mind, although the agreement of our model (based on the invariance of the diffusivity) with our experimental results does not suggest such a dependence for SnIn, in the range of magnetic field 0.2 - 0.75 *T*.

Acknowledgments

This work was conducted within the framework of the Gramme agreement between the CEA and the CNES for J.P. Garandet. It was supported by the grant GR/L84193 from EPSRC and the grant 97/CNES/071/6881 from the CNES. Thanks are due to the team of Professor Müller-Vogt at the Kristall und Materiallabor der Fakultät für Physik (Karlsruhe, Germany) for the careful chemical analysis of our samples.

Bibliographie

[1] Bräuer P., Müller-Vogt G., « *Measurement of aluminium diffusion in molten gallium and indium* », J. Crystal Growth, 186, 520-527, (1998).

[2] Müller-Vogt G., Kössler R., « *Application of the shear cell technique to diffusivity measurements in melts of semiconducting compounds* », Ga-Sb., J. Crystal Growth, 186, 511-519, (1998).

[3] Mathiak G., Griesche A., Kraatz K.H., « *Diffusion in liquid metals* », Journal of Non-crystalline Solids, 205-207, 412-416, (1996).

[4] Praizey J.P., « *Benefits of microgravity for measuring thermotransport coefficients in liquid metallic alloys* », Int. J. Heat Mass Transfer, 32 (12), 2385-2401, (1989).

[5] Garandet J.P., Barat C., Duffar T., « *The effect of natural convection in mass transport measurements in dilute liquid alloys* », Int. J. Heat Mass Transfer, 38 (12), 2169-2174, (1995).

[6] Garandet J.P., Praizey J.P., Van Vaerenberg S., Alboussière T., « *On the problem of natural convection in liquid phase thermotransport coefficients measurements* », Phys. Fluids, 9 (3), 510-518, (1997).

[7] Taylor G., « *Dispersion of soluble matter in solvent flowing slowly through a tube* », Proc. of the Roy. Soc. of London A., 219, 186-203, (1953).

[8] Garandet J.P., Alboussière T., Moreau R., « *Buoyancy driven convection in a rectangular enclosure with a transverse magnetic field* », Int. J. Heat and Mass Transfer, 35 (4), 741-748, (1992).

[9] Bejan A., « *Convection Heat Transfer* », Wiley and sons, (1994).

[10] Alboussière T., Garandet J.P., Moreau R., « *Buoyancy driven convection with a uniform magnetic field. Part I. Asymptotic analysis* », J. Fluid Mech., 253, 545-563, (1993).