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Determination of the diffusion coefficients of iron and chromium in Pb17Li

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Abstract—A method with controlled forced convection using a cylindrical rotating sample has been devised to determine the diffusion coefficients of iron and chromium dissolved in Pb17Li liquid metal at 500°C. The following values have been obtained:

$$D(\mathrm{Fe/Pb17Li})_{500^\circ\mathrm{C}} = 4 \pm 2 \times 10^{-14}\ \mathrm{m^2\,s^{-1}}$$

$$D(\mathrm{Cr/Pb17Li})_{500^\circ\mathrm{C}} = 8 \pm 2.5 \times 10^{-11}\ \mathrm{m^2\,s^{-1}}.$$

A value of chromium solubility in Pb17Li at 500°C has also been deduced, $C_s = 90.9\ \mathrm{g\,m^{-3}}$ (10 wppm), which is compatible with the existing data at lower temperatures.

1. INTRODUCTION

Liquid eutectic Pb17Li is a prime candidate as a tritium breeder material for application in a future fusion reactor. Its compatibility with structural materials is the subject of a significant research programme in the EEC, and the present work is included in this project.

The convective diffusion of dissolved metallic species in a liquid metal in boundary layer conditions is one of the elementary steps of the overall mass transfer process induced by a thermal gradient. In particular, previous studies [1] have shown that dissolution of martensitic Fe–Cr steels contacting Pb17Li liquid metal, is very probably limited by this step. An experiment for determining the iron and chromium diffusion coefficients in liquid lithium–lead eutectic was thus developed [2]. The results are reported and discussed below.

2. EXPERIMENTAL

2.1. *Experimental method*

Among the different existing experimental methods which allow diffusion coefficients in liquid metals [3] to be measured, we chose a method with well-defined forced convection, which gives a better control of mass transfer.

Indeed, when mass transfer is controlled by convective diffusion of dissolved species in boundary layer and is the rate determining step, the first Fick law with the Nernst hypothesis yields:

$$J = D(C_s - C)/e \qquad (1)$$

where J is the diffusion flux, D the diffusion coefficient, C the bulk concentration of the dissolved species in liquid metal and C_s its saturation value corresponding to the solubility of the relevant species in liquid metal, e the thickness of the diffusion boundary layer. Equation (1) implies that C_s is the concentration at the solid metal–liquid metal interface.

In forced convection systems, when the thickness of the laminar boundary layer can be expressed either by an empirical formula or mathematically calculated, weight loss measurements lead to the determination of diffusion coefficients. Moreover, if the periods of time are sufficiently short, the bulk concentration C can be neglected as compared to the solubility C_s and the mass flux becomes:

$$J = DC_s/e. \qquad (2)$$

There are at least two simple ways for controlling the hydrodynamic conditions, either the rotating disk system or the rotating cylinder. For the first geometry, the thickness e is known from the Levich theory [4]:

$$e = 1.61 D^{1/3} \Omega^{-1/2} \nu^{1/6} \qquad (3)$$

where Ω is the rotation speed (rad $\mathrm{s^{-1}}$) and ν the kinematic viscosity ($\mathrm{m^2\,s^{-1}}$).

When the bulk concentration of the dissolved spec-

NOMENCLATURE

A	atomic weight of the element [g]
C	bulk concentration of the dissolved species in liquid metal [μg m^{-3}]
C_s	saturation value corresponding to the solubility of the relevant species in liquid metal [μg m^{-3}]
D	diffusion coefficient of the dissolved species in liquid metal [m^2 s^{-1}]
d	specimen diameter [m]
e	thickness of the diffusion boundary layer [m]
f	specimen rotation speed [rad s^{-1}]
J	diffusion flux of the dissolved species in liquid metal [μg m^2 s^{-1}]
Re	Reynolds number
S	sample surface [m^2]
Sc	Schmidt number
t	time duration of the experiment [s]
V	Pb17Li volume [m^3].

Greek symbols

ν	kinematic viscosity [m^2 s^{-1}]
Ω	rotation speed [rad s^{-1}].

ies can be neglected as compared to the solubility and for high Schmidt number values ($Sc = \nu/D$ must be higher than 10^3), the dissolution flux is given by:

$$J_d = 0.62\, C_s D^{2/3} \nu^{-1/6} \Omega^{1/2}. \qquad (4)$$

M. Eisenberg *et al.* [5] have deduced for the rotating cylinder system, an empirical correlation which expresses the thickness of the boundary layer in turbulent flow:

$$e = 5.67\, d^{-0.4} \nu^{0.344} D^{0.356} f^{-0.7} \qquad (5)$$

where d is the cylinder diameter (cm) and f the specimen rotation speed (Hz).

In turbulent flow conditions and for $C \ll C_s$, the dissolution flux is given by the following equation:

$$J_c = 0.176\, C_s d^{0.4} \nu^{-0.344} D^{0.644} f^{0.7}. \qquad (6)$$

The flow regime depends on the Reynolds number Re which is defined by the same expression for both the cylinder or the disk systems:

$$Re = \Omega d^2 / 4\nu.$$

However, the laminar to turbulent transition takes place for $Re \approx 200$ for the cylinder, whereas for the disk it occurs around 2×10^5. This is why, due to our experimental conditions, equations (4) and (6) correspond to the laminar and turbulent flows, respectively. In the present work, the cylinder geometry was chosen because for a given rotation speed, a more important weight loss on the cylindrical surface can be obtained as compared to that due to the cross-section cylinder (the disk).

The weight loss is defined for either system as:

$$\Delta m = JSAt$$

where S is the active surface, A the atomic weight of the element and t the time duration of the experiment. Therefore, the ratio of the weight loss for the cylinder to that for the disk can be expressed as:

$$\Delta m_c / \Delta m_d = 7.86 \times 10^{-2} d^{0.4} \nu^{-0.178} f^{0.2} (S_c/S_d).$$

In our operating conditions:

$$d = 10^{-2}\ \text{m}$$

$$\nu = 1.25 \times 10^{-7}\ \text{m}^2\ \text{s}^{-1}$$

$$f = 52.33\ \text{rad s}^{-1}$$

$$h = \text{height of the cylinder} = 3 \times 10^{-2}\ \text{m}.$$

Eisenberg's correlation has been established for ratios h/d between 0.3 and 3. This provides $\Delta m_c/\Delta m_d = 4.65$.

Therefore, though the weight loss on the cylinder was significantly greater than that on the disk, it was not possible *a priori* to ignore the latter one.

2.2. *The apparatus*

The apparatus, represented in Fig. 1, consisted of a molybdenum crucible of 5 cm diameter containing 3.6 kg of Pb17Li. It was placed in a airtight container with a magnetic device, allowing the cylindrical specimen to rotate with no mechanical transmission. Two different heating resistances induced a thermal gradient between a hot isothermal zone (corresponding to the vicinity of the cylinder and, therefore, where equations (4) or (6) derived for isothermal conditions were valid) and a cold one located at the top and at the bottom of the crucible, respectively. The cold zone was not essential but allowed a decrease in the concentration of dissolved species C, equal to the solubility at cold temperature.

2.3. *The materials*

The studied materials were: iron with impurities less than 0.01%; chromium with impurities less than 0.5%; martensitic 1.4914 steel (86 Fe, 10.6 Cr wt%) and eutectic Pb17Li were provided by "Métaux spéciaux" Company.

The specimens were cylindrical: 1 cm diameter, 3 cm height, 9.3 cm^2 cylindrical area. The mean roughness of the surface was about 1 μm. Just before testing, the cylinder was cleaned in alcohol–acetone mixture and the cylindrical surface was lightly polished with a grinding paper (1200 grade) in order to eliminate the superficial oxide layer. Indeed, in liquid metals, the

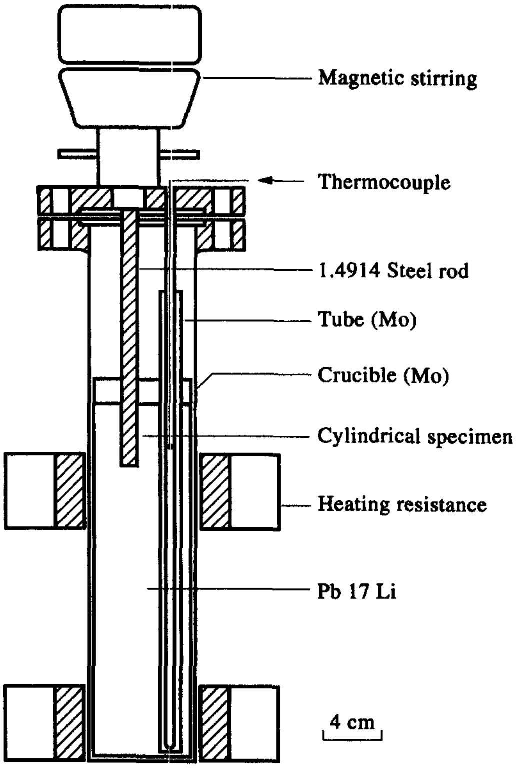

Fig. 1.

wetting of the solid metal can be strongly decreased by the presence of the superficial oxide layer covering the solid material.

After test, weight-losses of specimens were determined by weighting after successive immersions in acetic acid–hydrogen peroxide–alcohol mixture until the specimen weight remained constant.

2.4. *Operating conditions*

The velocities of the rotating cylinder are high enough to maintain a turbulent flow. Indeed, the Reynolds number Re is:

$$Re = rV/v$$

with

$$r = d/2$$

$$V = 2\pi rf.$$

In our operating conditions, the minimal rotational speed of the specimen is 21 rad s^{-1} which corresponds to $Re = 4500$. This number is higher than the critical value for a turbulent flow: $Re = 200$, in the case of the cylindrical rotating specimen [6].

The temperatures of the hot and cold isothermal zones were respectively 500°C and 440°C. The rotational speeds of the samples were between 21 and 105 rad s^{-1}, where the flow is turbulent.

All the operating conditions are summed up in Table 1.

3. RESULTS AND DISCUSSION

3.1. *Results*

After testing, in spite of the polishing pretreatment made on the cylindrical surface, the specimens appeared to be incompletely wetted, as shown by micrographic observations. Indeed the cylinder was corroded on 23–64% of the surface, according to the experiments (Table 1). Moreover, the disk surface which had not been repolished was practically unwetted. This fact justifies, *a posteriori*, neglecting the influence of the disk contribution to the weight loss.

So, from the weight loss of the specimen measured after complete elimination of Pb17Li at the specimen surface, a default value of the dissolution flux can be obtained by considering the total cylindrical surface of the specimen and by taking into account only equation (6) (uncorrected value of Table 2).

Moreover, a corrected value has been calculated by taking into account only the wetted fraction of the specimen surface. Indeed, electrochemical studies have been performed with electrodes having alternately active and inactive zones, in order to show up the influence of inactive zones upon the diffusion current [7]. This work shows that, when the active zones are large and not numerous, the diffusion currents is a linear function of the surface of the active zones. So, as such is the case in our experiments, the following correction (corrected value of Table 2) was performed:

$$J_{\text{corrected}} = J_{\text{measured}} S_{\text{cylinder}} / S_{\text{wetted}}.$$

Figures 2 and 3 show that the kinetics of martensitic 1.4914 steel and pure chromium obtained from the corrected and uncorrected weight losses are linear in the rotational speed range studied. These results agree with the assumption that the bulk concentration C of dissolved species in the liquid metal is low compared to the solubility in the hot zone.

For each material and each rotational speed, two limiting values are calculated by linear regression upon the corrected and uncorrected weight losses, to estimate the dissolution flux. It was found that:

For 1.4914 steel:

$$J(21\ \text{rad s}^{-1}) = 7\text{–}25\ \mu\text{g m}^{-2}\,\text{s}^{-1}$$

$$J(105\ \text{rad s}^{-1}) = 30\text{–}60\ \mu\text{g m}^{-2}\,\text{s}^{-1}.$$

For pure Cr:

$$J(21\ \text{rad s}^{-1}) = 100\text{–}200\ \mu\text{g m}^{-2}\,\text{s}^{-1}$$

$$J(52\ \text{rad s}^{-1}) = 175\text{–}350\ \mu\text{g m}^{-2}\,\text{s}^{-1}.$$

These values reveal a much larger dissolution flux for chromium than for martensitic steel.

Table 1. Operating conditions and weight loss of the rotating specimen

Material test	Rotational speed [rad s^{-1}]	Duration [h]	Weight loss [mg]	Wetted fraction of the surface [%]	Corrected weight loss (*) [mg]
1.4914					
1	21	69	2.5	64	3.9
2	21	95	2	23	8.7
3	21	103	2.1	23	9.1
4	105	77	7.4	56	13.2
5	105	143	15.1	51	29.6
Fe	105	143	15.8	50	31.6
Cr					
1	21	7	3.4	50	6.8
2	21	26	9.7	43	22.6
3	52	4	2.2	26	8.5
4	52	6	3.4	30	11.3

(*) Weight loss corrected with the wetted fraction of the surface.

Table 2. Dissolution flux of 1.4914 steel and chromium

Material test	Rotational speed [rad s^{-1}]	Dissolution flux uncorrected value [$\mu g\ m^{-2}\ s^{-1}$]	Dissolution flux corrected value [$\mu g\ m^{-2}\ s^{-1}$]
1.4914	21	7	25
	105	30	60
Cr	21	100	200
	52	175	350

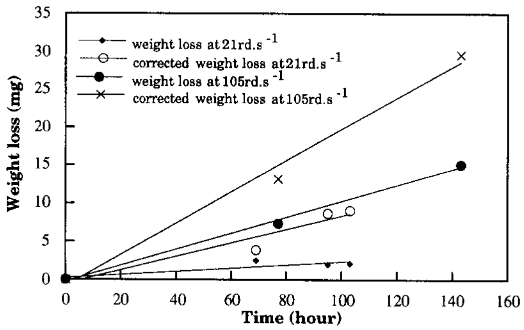

Fig. 2.

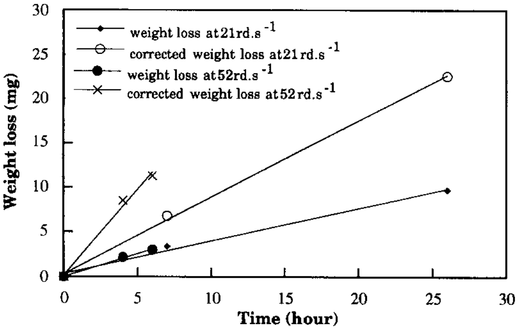

Fig. 3.

3.2. *Discussion*

According to equation (6), it was first verified that the curve representing the dissolution flux values as function of the rotational speed at 0.7 power is linear, and then the slope allows determination of the diffusion coefficient when v and S are known.

3.2.1. *Determination of the iron diffusion coefficient.* Figure 4 shows that the dissolution flux of the martensitic steel is actually a linear function of the rotational speed of the specimen at 0.7 power. These curves confirm the rate control of the material dissolution by diffusion in liquid Pb17Li.

Now from Table 1, it can be seen that the weight losses and the wetted fractions of the specimen's surface, obtained at 105 rad s^{-1} over a 143-h duration, are similar for 1.4914 steel and pure iron. This indicates that the corrosion of 1.4914 steel is controlled by the iron dissolution in the liquid metal. So, iron diffusion coefficient in Pb17Li can be estimated from the data for 1.4914 steel.

The slopes of the two straight lines yield two limiting values for the iron diffusion coefficient in Pb17Li at 500°C:

$$\text{slopes} = 4\times10^{-6}\ \text{to}\ 9\times10^{-6}\ \text{g}\,\text{m}^{-2}\,\text{s}^{-1}$$

with

$$d = 10^{-2}\ \text{m}$$

$$C_s(\text{Fe})_{500^\circ\text{C}} = 427\ \text{g}\,\text{m}^{-3} \quad [8]$$

$$v(\text{Pb17Li})_{500^\circ\text{C}} = 1.25\times10^{-7}\ \text{m}^2\,\text{s}^{-1} \quad [9].$$

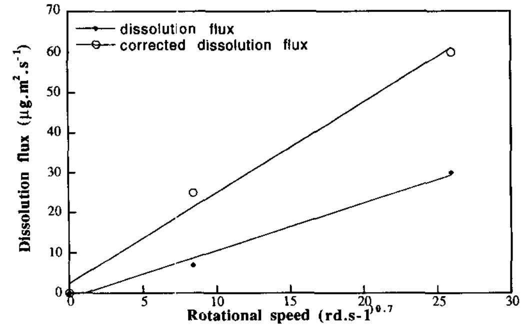

Fig. 4.

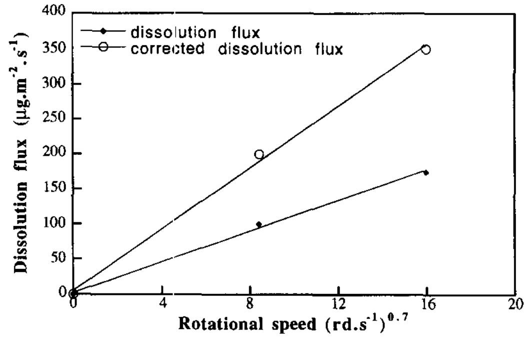

Fig. 5.

It can be found that $D(\mathrm{Fe/Pb17Li})_{500^\circ\mathrm{C}} = 4 \pm 2 \times 10^{-14}$ $\mathrm{m^2\,s^{-1}}$.

This diffusion coefficient value agrees with that deduced from calculations of the corrosion rate of martensitic steel tubes with flowing Pb17Li [1]. This value can be obtained with the same assumptions as above:

$$D(\mathrm{Fe/Pb17Li})_{500^\circ\mathrm{C}} = 4 \times 10^{-14}\,\mathrm{m^2\,s^{-1}}.$$

Nevertheless, it is 10^{-4} times lower than that corresponding to the diffusion coefficient in liquid lead [10]:

$$D(\mathrm{Fe/Pb})_{500^\circ\mathrm{C}} = 5 \times 10^{-10}\mathrm{m^2\,s^{-1}}.$$

3.2.2. *Determination of the chromium diffusion coefficient.* Figure 5 presents the uncorrected and corrected values of the chromium dissolution flux as a function of the rotational speed at 0.7 power. The curves are linear, which proves that the chromium dissolution is limited by diffusion in the liquid metal.

The range for the slope is between: 40 and $130 \times 10^{-6}\,\mathrm{g\,m^{-2}\,s^{-1}}$.

But as chromium solubility is not well defined at 500°C from the only data in ref. [7], a rough estimate can be found:

$$6 \times 10^{-6} < C_s \cdot D^{0.644} < 2 \times 10^{-5}. \qquad (7)$$

In order to estimate C_s at 500°C, long duration tests with chromium specimens rotating at 52 rad $\mathrm{s^{-1}}$ have been carried out.

The C_s and D values were determined by considering that the diffusion in the liquid metal is the limiting step. From the Fick's law:

$$J = (C_s - C) \cdot D/e = (V/S)\,\mathrm{d}C/\mathrm{d}t \qquad (8)$$

with V, Pb17Li volume and S, surface area of the rotating specimen.

The bulk concentration C is therefore not zero and must not be disregarded with respect to C_s

Solution of equation (8) gives:

$$C(t) = C_s\{1 - \exp(-DSe^{-1}V^{-1}t)\}$$

and the weight loss $M(t)$ can be deduced as

$$M(t) = VC_s\{1 - \exp(-DSe^{-1}V^{-1}t)\} \qquad (9)$$

with

$$S = 3\pi \cdot 10^{-4}\mathrm{m^2}$$

$$V = 3.52 \times 10^{-4}\,\mathrm{m^3}.$$

Equation (9) was regressed to the data with a Simplexe procedure by considering two parameters, the amplitude factor "VC_s" and the time constant "DSe^{-1} V^{-1}". The best fit for the corrected values are obtained with:

$$\text{"}VC_s\text{"} = 26 \pm 7 \times 10^{-3}[\mathrm{g}]$$

and

$$\text{"}DSe^{-1}V^{-1}\text{"} = 2.5 \pm 1.2 \times 10^{-5}[\mathrm{s^{-1}}]$$

which corresponds to:

$$C_s = 8 \pm 2\,\mathrm{ppm} \quad \text{and} \quad D = 8 \pm 2.5 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}.$$

Results are summarized in Table 3 and the corrected

Table 3. Weight loss of chromium specimens rotating at 52 rad $\mathrm{s^{-1}}$

Test	Rotational speed [rad $\mathrm{s^{-1}}$]	Duration [h]	Weight loss [mg]	Wetted fraction of the surface [%]	Corrected weight loss (*) [mg]
3	52	4	2.2	26	8.5
4	52	6	3.4	30	11.3
5	52	24	18.6	100	18.7
6	52	48	21.8	60	36.3

(*) Weight loss corrected with the wetted fraction of the surface.

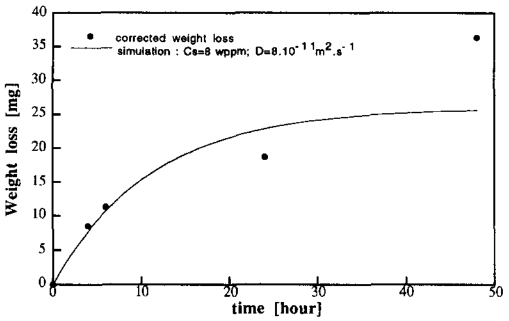

Fig. 6.

weight loss curve as a function of time is presented in Fig. 6. The coarse fit and the large confidence intervals on the parameters are partly due to the experimental error (estimated here as a relative constant value of about 25%) and to the small number of data.

However, the values of solubility obtained in this way are similar to those measured by M. G. Barker between 260 and 460°C [8].

And $D(\text{Cr/Pb17Li})_{500^\circ\text{C}} = 8 \pm 2.5 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$, is a diffusion coefficient value in good agreement with those obtained for other metals like Co, Ni and Fe in liquid lead [10].

Finally, the following condition: $10^{-5} < C_s D^{0.644} < 3.5 \times 10^{-5}$, which is not far from inequation (7), can be deduced.

4. CONCLUSION

In this study, a method with controlled forced convection using a cylindrical rotating sample has been adapted to determine diffusion coefficients of dissolved species in a liquid metal.

Iron and chromium diffusion coefficients in Pb17Li at 500°C have been estimated:

$$D(\text{Fe/Pb17Li})_{500^\circ\text{C}} = 4 \pm 2 \times 10^{-14}\,\text{m}^2\,\text{s}^{-1}$$

$$D(\text{Cr/Pb17Li})_{500^\circ\text{C}} = 8 \pm 2.5 \times 10^{-11}\,\text{m}^2\,\text{s}^{-1}.$$

The value of the chromium diffusion coefficient in liquid lithium–lead at 500°C is in good agreement with the values obtained for other metals in liquid lead. Then, for the iron diffusion coefficient at the same temperature, a value (3 orders of magnitude lower) has been obtained, which is not expected considering the similarity of the physical properties of iron and chromium. Still, this diffusion coefficient value agrees with that deduced from the expression of the corrosion rate of martensitic steel tubes in flowing Pb17Li [1]. So one should wonder whether the diffusing species is really a lone iron atom. Nevertheless, this assumption is not inconsistent with the fact that the mass transfer of the martensitic steel is controlled by the diffusion of a dissolved element associated with the iron atom and having a diffusion coefficient of about $4 \pm 2 \times 10^{-14}\ \text{m}^2\ \text{s}^{-1}$ at 500°C.

This study will be carried on with the determinations of the iron and chromium diffusion coefficients in Pb17Li as a function of temperature.

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