ARCHIVES OF METALLURGY

Volume 46 2001 Issue 3

WŁADYSŁAW GĄSIOR*, ZBIGNIEW MOSER*

CHEMICAL DIFFUSION COEFFICIENTS IN SOLID Mg-RICH LITHIUM-MAGNESIUM ALLOYS

CHEMICZNE WSPÓŁCZYNNIKI DYFUZJI W STAŁYCH STOPACH LIT-MAGNEZ O DUŻEJ ZAWARTOŚCI MAGNEZU

The concentration galvanic cell method was used in measurements of the equilibrium electromotive forces and in the galvanostatic experiments of the interdiffusion coeficient in the solid Mg-rich Li-Mg alloys at 578 K, 783 K and 860 K. It has been found that the calculated excess Gibbs free energies of Li show negative deviations from the ideal solutions and that the minimal values do not exceed – 11 kJ/mol. The measured chemical diffusion coefficients were described by the Darken's relation, and the self-diffusion coefficient of Li was calculated. Next, the Arrhenius equation was worked out. The obtained value of the activation energy is equal to 69.09 kJ/mol. It is close to that predicted from the empirical relation describing the dependence of the activation energy on the melting temperature of metal.

Wykorzystując równowagowe pomiary metodą ogniw stężeniowych oraz pomiary galwanostatyczne zostały zmierzone równowagowe siły elektromotoryczne i chemiczne współczynniki dyfuzji dla stałych stopów lit-magnez, o dużych stężeniach magnezu, w temepraturach 578 K, 783 K oraz 860 K. Ustalono, że uzyskane z pomiarów równowagowych nadmiarowe energie swobodne magnezu wykazują ujemne odstępstwa od właściwości roztworów doskonałych a najniższe wartości nie przekraczają – 11 kJ/mol. Zmierzone chemiczne współczynniki dyfuzji zostały opracowane zależnością Darkena, a wyznaczone współczynniki samodyfuzji litu opisano równaniem Arrheniusa. Wyznaczona wartość energii aktywacji wynosi 69.09 kJ/mol i jest bliska wartości, którą można obliczyć z empirycznego równania opisującego zależność między energią aktywacji a tamperaturą topnienia metalu.

* INSTYTUT METALURGII I INŻYNIERII MATERIAŁOWEJ IM. A. KRUPKOWSKIEGO, PAN, 30-059 KRAKÓW, UL. REYMONTA 25

1. Introduction

Aluminium base alloys, with low amount of the other metals, especially Mg, Cu, and Si, have been used for years in several branches of industry as the construction materials. In the last two decades new Al-rich alloys with various amounts of lithium were intensively investigated. It was due to the fact that these alloys are characterised by good mechanical properties, by lower density in comparison with the other Al-rich group alloys which is especially important in air-craft, missiles and automotive industries.

In our Institute, under the frame of co-operation with Max-Planck Insitute in Stuttgard, calorimetrically measured enthalpies of mixing liquid alloys were presented in [1], and next, in 1993, lithium activities from emf studies were reported [2].

From 1996 till 1999 the chemical diffusion coefficients in Al-rich Al-Mg and Al-rich Al-Li, Mg-rich Mg-Li and Al-rich Al-Mg-Li alloys were measured using the galvanostatic method. The obtained results of the chemical diffusion coefficient for Al-Mg were presented during the Conference in Warsaw [3], and next published in the proceedings. Similar studies for Al-Li system were presented at the Conference in Sweden [4] and accepted for publication in the Scandinavian Journal of Metallurgy.

The main aim of this work is to report the results of the measurements of the chemical diffusion coefficient, using the galvanostatic method, at three temperatures (578 K, 783 K and 860 K), used for calculation of the self-diffusion coefficients of Li by means of the Darken relation. The Arrhenius' equation describing the temperature dependence of the self-diffusion coefficient of lithium was also worked out and compared with the other data available in literature.

2. Experimental method

The measurements of chemical diffusion coefficients were performed using the galvanostatic technique (constant current). It is the extension of the emf equilibrium studies based on coulometric titration technique by means of the following concentration cell:

$$(\text{Al-Li})_{\text{ref}}/\text{electrolyte with Li ions}/\text{Mg-Li}_{(S)}. \qquad (1)$$

Two kinds of the eutectic liquid salt mixtures – LiCl-LiF and LiCl-KCl-RbCl were used as electrolyte both in the equilibrium and the galvanostatic diffusion measurements. The two phase $(\alpha+\beta)$Al-Li solid alloy was applied as the lithium reference electrode. The electrode was prepared by the pirometallurgical method from Al 99.995 at.% and Li 99.5 at. % purity. The measured potential of the reference electrode $(\alpha+\beta)$Al-Li versus liquid lithium was in good agreement with the data of Wen et al. (5).

The chemical diffusion coefficient D and the self-diffusion coefficients D^0_{Li} and D^0_{Al} are related to each other through the thermodynamic factor Tf [6]:

$$D = (D^0{}_{Li}X_{Al} + D^0{}_{Al}X_{Li})^* Tf \tag{2}$$

$$Tf = (\mathrm{dln}(a_{Li})/\mathrm{dln}(X_{Li}))_T \tag{3}$$

$$\ln(a_{Li}) = -nFE/RT, \tag{4}$$

where: a_{Li} is the activity of Li, F is Faraday's constatnt, R is the gas constant, T is the temperature and E is the equilibrium electromotive force measured by cell (1).

Analysing Eq. 2, one can observe that in the case of measurement of D at the concentration range ($Tf \sim = 1$) and when the self-diffusion coefficient of one component is considerably greater than that of the second one ($D_{1(2)} > D_{2(1)}$), the chemical diffusion coefficient D is practically equal to the product $D_{1(2)}{}^* X_{2(1)}$. I such a case the self-diffusion coefficient $D_{1(2)}$ can be calculated with a negligible error from Eq. 2.

On the other hand, the chemical diffucion process in the solid is descibed by the Fick's second law:

$$\partial C/\partial t = D \cdot \partial^2 C/\partial x^2 \qquad D = \text{constant}, \tag{5}$$

where x is the distance between the electrolyte/electrode interface and the solid, C is the local concentration (in mol/cm^3), and D is the chemical diffusion coefficient.

In the galvanostatic measurements of D, that is, when the constant current I flows through the cell (1), the appropriate initial and boundary conditions are as follows:

$$C = C(0) \qquad 0 \le x \le L \qquad t = 0 \tag{6}$$

$$D \cdot \partial C/\partial x = I/zFs \qquad x = 0 \qquad t > 0 \tag{7}$$

$$\partial C/\partial x = 0 \qquad x = L \qquad t \ge 0, \tag{8}$$

where: z is the valence of Li ions, F is Faraday's constant, s is the surface of the electrode, I is the value of the constant current passing through the cell, L is the thickness of the sample (alloy electrode), t is time of the electrolysis.

For small values of time, i.e., $t \ll L^2/D$ and $x = 0$, the solution of Eq. 5 is given by the following relation:

$$C_{Li}(0,t) - C_{Li}(0) = [2I/zFs(\pi D)^{0.5}] \cdot t^{0.5}, \tag{9}$$

where: $C_{Li}(0)$ is the concentratrion of Li at the electrode/electrolyte interface at the time $t = 0$ (equilibrium state) and $C_{Li}(0,t)$ is the concentration of Li at any time t during the deposition of lithium at the electrode surface by the constant current I.

The values of $C_{Li}(0)$ and $C_{Li}(0,t)$ are calculated according to the equation:

$$C_{Li}(0,t) = X_{Li}(t)/V_m \tag{10}$$

in which: $X_{Li}(t)$ is the molar fraction of Li at the time t at the surface of the electrode, and it is calculated from the relation describing the dependence of the equilibrium emfs of cell (1) on concentration, and V_m is the molar volume of the Al-Li solid alloy.

Equatin 9 is a linear dependence verses the independent variable $t^{0.5}$:

$$C_{Li}(0,t) = C_{Li}(0) + bt^{0.5} \tag{11}$$

and the slope b is given of the equation:

$$b = 2I/zFs(\pi D)^{0.5} \tag{12}$$

Transforming Eq. (12), one obtains the final relation used for calculation of the chemical diffusion coefficient

$$D = 4I^2/z^2s^2F^2\pi^2b^2 \tag{13}$$

Because the solution of the Fick's equation (4) is given for D = constant, and from the Darken's equation (2) it is known that D is concentration dependent; the value of D calculated from the galvanostatic measurements is the middle value in the concentration region from $C(0)$ to $C(0,t)$. However, when in the course of the experiment, the difference in the concentrations $C(0)-C(0,t)$ is small, the difference between $D(0)$ and $D(0,t)$ is very small and it can be thought to be constant. It is obvious that the measurements of the chemical diffusion coefficient should be conducted in a such way as to satisfy the above remarks and this has been taken into account in this study.

It should be emphasised that the measurements of D using the galvanostatic technique were performed at the assumption that: 1) the charge-transfer reaction occuring at the electrode/electrolyte interface during the flow is so rapid that it can be assumed to be at or near equilibrium and, 2) that the ionic transport through the electrolyte phase is not rate-limited. Under these conditions the measured voltage of cell (Eq. 1) provides a direct measure of the activity of Li in the sample electrode at the electrode/electrolyte interface, and thus, the concentration of Li at this interface. By perturbing this concentration in an experimentally controllable manner (constant current), the chemical diffusion coefficient can be calculated from galvanostatic experimental data of emfs using Eqs (9–13).

Coulometric titration technique was used in the study of the Mg-Li solid alloys, when passing through the cell (1) a well known amount of charge (ions of Li). The equilibrium potential, as indicated by the time-independence of the cell open-circuit potential, was recorded as a function of electrode composition, and the chemical diffusion coefficients were calculated using the emf time-dependent dcharacteristics which were obtained when a constant current was passing through the cell (1).

3. Results and discussion

The results obtained from equilibrium emf measurements by means of cell (1) were used to calculate the excess Gibbs free energies of Li, which were next described by the polynomials dependent on lithium concentration. The obtained dependences at each temperature are as follows:

$$T = 578\ \mathrm{K} \qquad X = X_{\mathrm{Li}}$$

$$G^E_{\mathrm{Li}} = -10933 + 106292 \cdot X - 1314083 \cdot X^2 + 6370996 \cdot X^3\ [\mathrm{J/mole}] \tag{14}$$

$T = 783$ K

$$G^E_{Li} = -8189 - 23101 \cdot X + 101095 \cdot X^2 \text{ [J/mole]} \tag{15}$$

$T = 860$ K

$$G^E_{Li} = -8827 - 62649 \cdot X + 559819 \cdot X^2 - 1168788 \cdot X^3 \text{ [J/mole]}. \tag{16}$$

The equations [14–16] were next used in calculations of the chemical diffusion coefficients in the solid Mg-rich Li-Mg alloys from the galvanostatic characteristics of emf vs. time. The sequence of calculations was as follows;

1) from the emf vs. time relation mole fraction of Li (X_{Li}) for any alloy were calculated at the electrode surface using one of the polynomials (14–16), next

2) using Eq. (10) concentrations of Li ($C(0)$, $C(0,t)$ in mole/cm^3) were calculated. The data of the molar volumes V_m were calculated from equations reported in [7],

3) the slope of Eq. (11) was calculated by the least squares method, and finally

4) the chemical diffusion coefficient was calculated using Eq. (13).

The linear behaviour of C(0,t) on the square root of time $t^{1/2}$ for three different Li concentrations at 783 K are shown in Fig. 1, which confirms the assumption that the chemical diffusion coefficient can be assumed to be constant for the short time of the galvanostatic measurements.

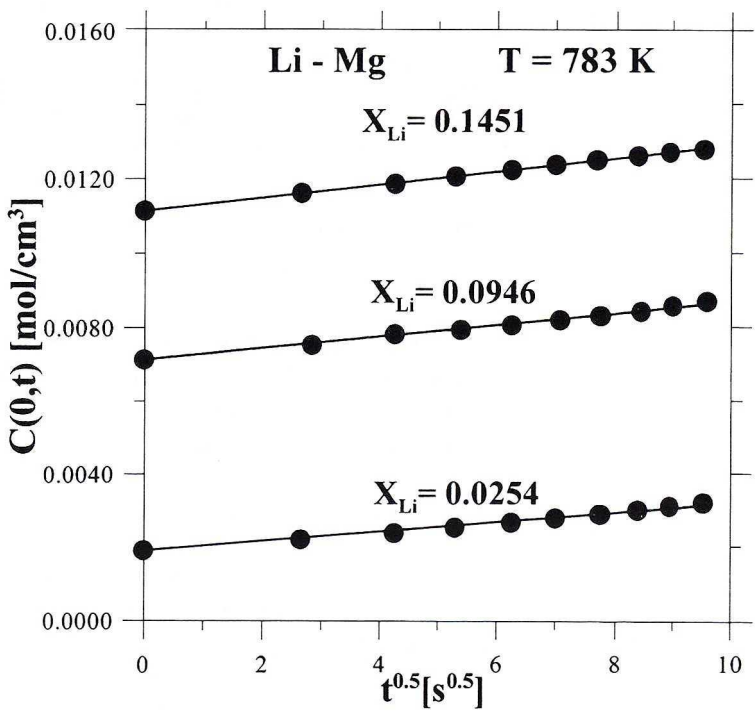

Fig. 1. Examples of the linear relation of the lithium concentration (mole/cm^3) at the surface of the electrode as the square root of time at 783 K. ● – experimental data, ____ – values calculated from the least squares line (Eq. 11)

The cylindrical alloy electrodes of the diameter equal to 10 mm and the height 0,2 mm were used. The constant current from 0.002 to 0.0005A was passed through the cell depending on temperature. The higher the temperature of the measurements the higher constant current was used. The chemical diffusion coefficients in Mg-rich Li-Mg solid alloys obtained using galvanostatic measurements are reported in Table. The results vary from the 10^{-10} cm^2/s at 578 K to 10^{-8} cm^2/s at 860 K.

TABLE

Chemical diffusion coefficients measured in the solid Mg-rich Li-Mg alloys using the galvanostatic measurements

T = 578 K		T = 783 K		T = 860 K	
X_{Li}	$D \cdot 10^{10}$ [cm^2/s]	X_{Li}	$D \cdot 10^{9}$ [cm^2/s]	X_{Li}	$D \cdot 10^{8}$ [cm^2/s]
0.0105	1.290	0.0254	9.620	0.0229	2.683
0.0157	0.533	0.0377	8.475	0.0386	2.163
0.0209	0.977	0.0496	6.722	0.0539	2.115
0.0310	2.477	0.0613	5.474	0.0686	1.333
0.0360	3.736	0.0727	5.801	0.0829	1.217
0.0506	1.799	0.0838	4.425	0.0968	1.100
		0.0946	6.195	0.1102	1.460
		0.1052	3.677	0.1233	1.955
		0.1155	4.305	0.1360	1.116
		0.1256	4.901	0.1483	2.296
		0.1355	6.643	0.1602	1.003
		0.1451	5.014	0.1719	1.237
		0.1638	6.380		
		0.1728	5.725		

In the next step the results of the chemical diffusion coefficients obtained in this study were used in calculations of the self-diffusion coefficient of lithium using Darken equation (2). The thermodynamic factor was calculated using the Eq. (14–16). The data of the self-diffusion coefficients of Mg were calculated from the following equation

$$D_{Mg} = 1.\exp(-134/RT)\ [cm^2/s] \tag{17}$$

presented by Adda and Philibert [8] from the radioactive tracer method. The values of D_{Li} of this study obtained from Eq. 2 together with the value of D_{Li} measured by Ivadate et al. [9] at 693 K were next used to work out the Arrhenius equation describing the temperature dependence of the self-diffusion coefficient of lithium on temperature. The correlation of the experimental values of D_{Li} with those calculated using Arrhenius equation is shown in Fig. 2 (logarithmic form). The logarithmic and the exponential forms of this equation are presented in Fig. 2. There should be emphasised

the good agreement between the self-diffusion coefficients of Li measured in this study and that obtained by Ivadate et al. [9] (Fig. 2) and the values of D_{Li} calculated from the beneath equation

$$D^0_{Li} = 1.09 \cdot 10^{-3} \exp(-66.37/RT), \tag{18}$$

which was obtained by [4] basing on data of the chemical diffusion coefficients measured for the Al-rich Al-Li solid alloys at the temperature range from 573 K to 860 K.

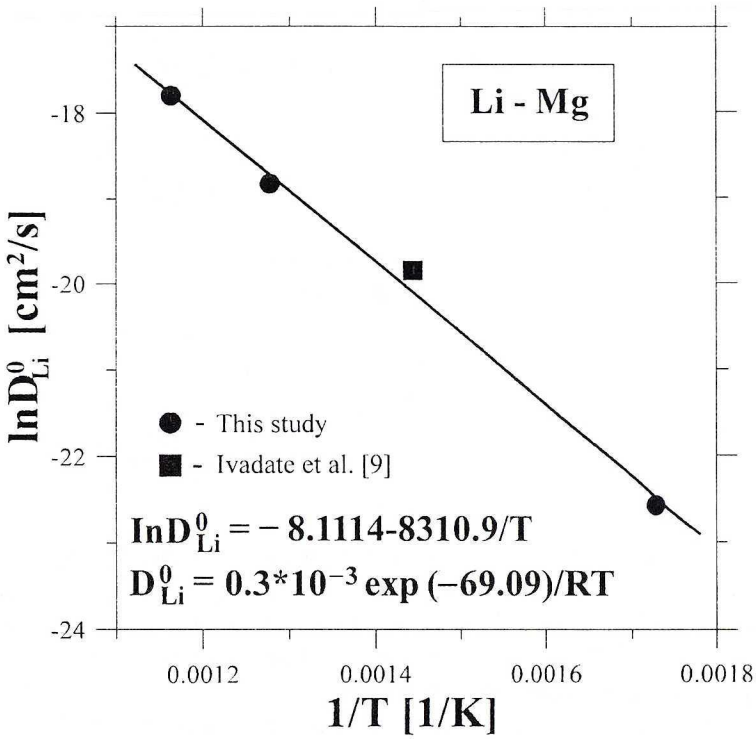

Fig. 2. Arrhenius relation of the Li self-diffusion coefficient in the Mg-rich Mg-Li solid alloys. ● – the present study, ■ – Ivadate et al. [9], ——— – values calculated from the logarithmic equation draw in Fig. 2

The values of the activation energy calculated in this and the earlier study [4] are close to each other (69.09 kJ/mole, 66.37 kJ/mole) and about 15% higher than those of Adda and Philibert [8] and Naumov and Ryskin [10] obtained from the radioactive tracer method (55÷56 kJ/mol). About twice higher values of the activation energy than those from this study were obtained by Wen and Huggins [5], Costas [11] and Minamino [12]. It should be noticed that the following empirical equation:

$$Q = 0.1423\ T_m \tag{19}$$

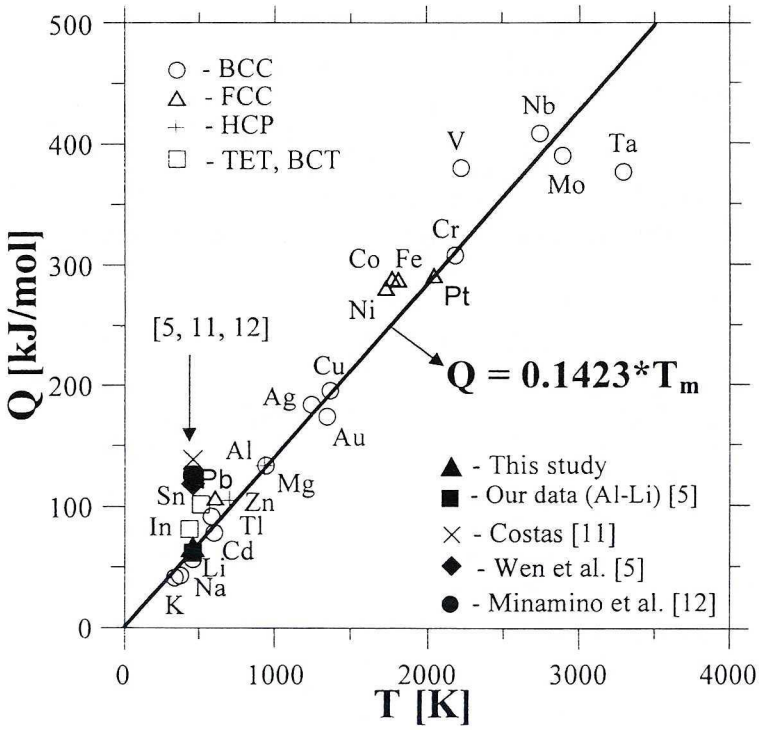

Fig. 3. Dependence of the activation energy on the melting temperature of metals

describing the dependence of the activation energy of metal on the melting temperature T_m (Fig. 3) is presented in literature [13] and that the value of Q for Li calculated from Eq. [19] is equal 64.46 kJ/mole. This value is in very good agreement with those from this and our earlier study [4] and about 20% higher than those reported by Adda and Philibert [8] and Naumov and Ryskin [10]. The other cited above values of the activation energy [5, 11, 12] are much higher than those calculated from Eq. (19).

4. Summarising

The measurements of excess Gibbs free energies of Li and the chemical diffusion coefficients conducted at the temperatures 578 K, 783 K and 860 K allowed the calculation of the self-diffusion coefficients of lithium employing Darken's equation.

The obtained values of the self-diffusion coefficient of Li at 578 K, 783 K and 860 K together with the data of Ivadate et al. [9] at 693 K were used in working out the Arrhenius equation describing the dependence of the self-diffusion coefficient of Li on the temperature.

The diffusion activation energy of Li calculated in this study is in good agreement with those reported in [4] and calculated from the empirical relation [Eq. 19] and about 20% higher than those obtained by Adda and Philibert [8] and Naumov and Ryskin [10] from the radioactive tracers method. The values of Q reported by Wen and Hughins [5], Costas [11] and Minamino [12] are twice as high as those obtained in this study.

REFERENCES

[1] Z. Moser, R. Agarwal, F. Sommer, B. Predel, Z. Metallkde **82**, 317 (1991).
[2] Z. Moser, W. Gąsior, F. Sommer, W. Zakulski, H.J. Seifert, H.L. Lukas, CALPHAD XIV. May 21–26, 1995 Kyoto, Program and Abstracts, p. 29.
[3] W. Gąsior, Z. Moser, Proceedings of the International Conference on Progress in Calculation of Physiochemical Properties, 11–13 November, 1999 Warszawa, Poland, p. 114–121.
[4] W. Gąsior, Z. Moser, Scandinavian J. Metall., (in pritn).
[5] C.J. Wen, W. Weppner, B.A. Boukamp, R.A. Huggins, Met. Trans. **11B**, 131 (1980).
[6] L.S. Darken, Trans AIME **175**, 184 (1948).
[7] W. Gąsior, Z. Moser, J. Pstruś, J. Phase Equilibria **19** 234 (1998).
[8] Y. Adda, J. Philibert, Presses Univ. de France, **12**, 1268 (1966).
[9] Y. Iwadate, M. Lassouani, F. Lantelme, M. Chemla, J. Appl. Electrochem. **17**, 385 (1987).
[10] A.I. Naumov, G.J. Ryskin, Journal Teoreticeskoj Phiziki, **29**, 188 (1959).
[11] L.P. Costas, U.S.A.EC Report TID-16676, 1 (1963).
[12] Y. Minamino, T. Yamane, H. Araki, Metall. Trans. **18A**, 1536 (1987).
[13] M.Z. Jarzębski, Dyfuzja w metalach, Katowice 1975.

REVIEWED BY: DOC. DR HAB. INŻ. WALDEMAR WOŁCZYŃSKI

Received: 10 May 2001.