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WALDEMAR WOŁCZYŃSKI*, WŁADYSŁAW GĄSIOR*, ZBIGNIEW MOSER*

INTERPRETATION AND MEANING OF THE DIFFUSION COEFFICIENT IN THE SOLID AL-3.5LI ALLOY BY MEASUREMENT OF THE LI-SOLUTE REDISTRIBUTION

INTERPRETACJA I ZNACZENIE WSPÓŁCZYNNIKA DYFUZJI NA PODSTAWIE POMIARÓW REDYSTRYBUCJI LITU W ZAKRZEPŁYM STOPIE AL-3.5LI

The galvanostatic method used in previous measurements of the chemical diffusion coefficient in the Al-rich aluminium-lithium alloys has given a numerical values of the above coefficient at four imposed temperatures. This directly measured values of diffusion coefficient is compared with the value obtained indirectly from the measurement of the Li-solute redistribution within the Al-3.5Li alloy solidified directionally in the *Bridgman* system. The adequate theoretical considerations dealing with the description of solute redistribution in eutectic system has been made to calculate the value of back-diffusion parameter for the performed 2D experiment. The definition of back-diffusion parameter has been rearranged to calculate the numerical value of the diffusion coefficient in the solid. It has been shown that back-diffusion parameter plays essential role in the model of solute redistribution which is discussed from the viewpoint of the application of current model for redistribution to calculation of the solidification path.

Metoda ogniw stężeniowych wykorzystana w poprzednich pomiarach chemicznego współczynnika dyfuzji dla stopów aluminium-lit pozwoliła na określenie wartości liczbowej tego współczynnika dla czterech zadanych temperatur. Ta bezpośrednio mierzona wartość współczynnika dyfuzji jest porównana z wartością liczbową tego współczynnika określoną pośrednio z pomiarów redystrybucji litu dla stopu Al-3.5Li poddanego krystalizacji w układzie *Bridgmana*. Opracowano odpowiednie równania dotyczące opisu redystrybucji w systemach eutektycznych celem obliczeń parametru dyfuzji wstecznej dla dwuwymiarowego (2D) eksperymentu krystalizacji. Definicja parametru dyfuzji wstecznej została przekształcona do postaci umożliwiającej obliczenia wartości liczbowej współczynnika dyfuzji w fazie stałej. Pokazano, że parametr dyfuzji wstecznej odgrywa zasadniczą rolę w modelu redystrybucji, co przedyskutowano z punktu widzenia wyznaczania ścieżek krystalizacji.

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

Notation

a – activity of a given solute in solid solution,
D^0_{Al} – self-diffusion coefficient of aluminium, m^2/s,
D^0_{Li} – self-diffusion coefficient of lithium, m^2/s,
D_C – volume diffusion coefficient of solute in the solid for galvanostatic experiment, m^2/s,
D_S – volume diffusion coefficient of solute in the solid solution for solidification experiment, m^2/s
G – temperature gradient at the solid/liquid interface, K/m,
H – heigth of columnar dendrite or cell, m,
k – equilibrium partition coefficient, mole fr./mole fr.,
L – half the dendrite/cell spacing, m,
N_E – eutectic concentration of solute, mole fr.,
N_0 – nominal alloying element concentration in a given alloy, mole fr.,
$N_L(x;\alpha)$ – solute concentration in the liquid, mole fr.,
$N_S(x;\alpha)$ – solute concentration at solid/liquid interface, mole fr.,
N^{β}_i – measured values of solute redistribution, mole fr.,
$N^{\beta}_S(x;x_0,\alpha)$ – solute redistribution within the solid, mole fr.,
p – pressure, Pa,
t_f – local solidification time, s,
T – temperature, K,
v – solidification rate, cm/s,
x – amount of growing crystal, mole,
x_0 – amount of crystal at a given stage of solidification, mole,
$x_K(\alpha, N_0)$ – total amount of crystal at the end of solidification, mole,
α – parameter of back-diffusion into the solid across s/l interface,
$\alpha_\varepsilon(N_0)$ – parameter of back-diffusion for crystal growth ended at N_ε,
β_{ex} – coefficient of extent of solute redistribution within the solid,
β_{in} – coefficient of intensity of solute redistribution within the solid,
γ – activity coefficient of a given solute in solid.

1. Introduction

Diffusion which plays an important role in the heat treatment of the Al-Li alloys seems to be one of the important factor deciding on solidification paths. So, the measured diffusion coefficient is a fundamental information in calculation of the so-called back-diffusion parameter and finally in determination of solute microsegregation as well as solute redistribution. On the other hand the diffusion coefficient can also be calculated if the numerical value of back-diffusion parameter is known.

The diffusion coefficient was recently measured by means of the galvanostatic method then compared to available published data, Gąsior and Moser, [1]. This direct measurement of the diffusion coefficient was made in Al-rich aluminium-lithium alloys at four different temperatures. The results of measurement are gathered in Table 1.

The diffusion coefficient can also be obtained indirectly from the measurement of solute redistribution when the appropriate model is available. This kind of model has recently been worked out, Wołczyński, [2] on the basis of previous analysis, Wołczyński and Kloch, [12]. It gives possibility to describe the solute microseg-

TABLE 1

Chemical diffusion coefficients obtained from the galvanostatic method at 568K, 638K, 783K and 868K, [1]

568K		783K		868K	
N_0 [mole fr.]	D_C*10^{11} [cm^2/s]	N_0 [mole fr.]	D_C*10^9 [cm^2/s]	N_0 [mole fr.]	D_C*10^8 [cm^2/s]
0.0079	4.999	0.0147	3.340	0.0139	1.490
0.0105	5.150	0.0186	2.972	0.0207	1.612
0.0131	3.224	0.0225	3.590	0.0274	1.608
683K		0.0264	3.959	0.0340	1.629
		0.0303	3.415	0.0406	1.653
N_0 [mole fr.]	D_C*109 [cm^2/s]	0.0490	3.837	0.0470	1.612
		0.0527	3.363	0.0534	1.712
		0.0563	3.199	0.0596	1.527
0.0049	1.546	0.0599	5.341	0.0658	1.508
0.0073	1.307	0.0706	4.622	0.0719	1.556
0.0097	1.333	0.0844	1.929	0.0779	1.463
0.0122	1.183	0.0878	1.620	0.0839	1.469
0.0145	1.158	0.0912	3.072	0.0898	1.302
0.0169	0.943			0.0956	1.245
0.0193	0.979			0.1013	1.072
0.0217	0.907			0.1070	1.064
0.0240	0.861			0.1125	0.932
0.0263	0.737			0.1181	1.225
0.0287	0.677			0.1235	0.777
0.0310	0.694			0.1289	1.361
0.0333	0.617			0.1342	0.797

regation, solute redistribution as well as estimate the numerical values of both back-diffusion parameter and diffusion coefficient in the solid solution.

2. Fundamentals of solute microsegregation

The differential equation for microsegregation related to the back-diffusion can be formulated according to mentioned analysis, Wołczyński and Kloch, [12] and Wołczyński, [2]:

$$\frac{d \ln N_L(x;\alpha)}{dx} = \frac{1-k}{1-(1-\alpha k)k}, \tag{1}$$

where α back-diffusion parameter is assumed to be constant during solidification process under investigation.

Applying the initial condition: $N_L(0;\alpha) = N_0$, the solution of equation (2) is obtained:

$$N_L(x;\alpha) = N_0(1+\alpha kx - x)^{\frac{k-1}{1-\alpha k}}, \qquad x \in [0; x_K]. \tag{2}$$

Finally, the description of solute concentration at formerly existing solid/liquid interfaces appearing in the sequence during crystal growth can also be formulated taking into account equation (2) and the partition ratio:

$$k = \frac{N_S(x;\ \alpha)}{N_L(x;\ \alpha)}. \qquad (3)$$

It yields:

$$N_S(x;\ \alpha) = kN_0(1+\alpha kx-x)^{\frac{k-1}{1-\alpha k}}, \qquad x\in[0;\ x_K]. \qquad (4)$$

The first step in the development of the microsegregation theory has been done by Scheil, [3]. Scheil, [3] was able to formulate the equation for the liquid behaviour during non-equilibrium solidification which leads to extreme microsegregation:

$$N_L(x;\ 0) = N_0(1-x)^{k-1}. \qquad (5)$$

Equation (5) can be rewritten in order to define solute microsegregation within the solid. In reality, it is description of solute concentration at formerly existing solid/liquid interfaces appearing in the sequence during crystal growth, analogously to equation (4):

$$N_S(x;\ 0) = kN_0(1-x)^{k-1}. \qquad (6)$$

In the case of Scheil [3] theory, where no diffusion in the solid is assumed, equation (6) describes simultaneously both solute concentration at the solid/liquid interface and solute redistribution within the solid. However, more practical prediction sometimes requires consideration of finite diffusion in the solid. This requirement is fulfilled by equations (2) and (4) from the view point of microsegregation.

The α-back-diffusion parameter has been originally defined by Brody and Flemings, [4].

However, contrary to the theory given by Brody and Flemings, [4], it was proved, in [2], that the definition of the back-diffusion parameter satisfies the following limitation: $0\le\alpha\le 1$.

It is evident that equation (2) is reducible to the Scheil approach, where $\alpha = 0$, that is to equation (5) as well as equation (4) is reducible to equation (6).

3. Theory of solute redistribution

The equation formulated for the description of solute redistribution is given independently of equation describing the microsegregation. It is:

$$N_S^{\beta}(x;x_0,\ \alpha) = [k+\beta_{ex}(x;x_0)\beta_{in}(x_0;\alpha)]N_L(x;\alpha), \qquad x\in[0,\ x_0], \qquad x_0\in[0,\ x_K]. \qquad (7)$$

Finally, the solute redistribution can be written in function of the layer (solid/liquid interface) concentration, N_S and liquid concentration, N_L:

$$N_S^{\beta}(x;x_0,\ \alpha) = N_S(x;\alpha)\beta_{ex}(x;x_0)]\beta_{in}(x_0;\alpha)N_L(x;\alpha), \qquad x\in[0,\ x_0], \qquad x_0\in[0,\ x_K]. \ (8)$$

The coefficient of the extent of the solute redistribution, β_{ex} and the coefficient of the intensity of the solute redistribution, β_{in} are precisely defined by means of lever rule and mass balance:

$$\beta_{ex}(x;\ x_0) = \frac{k(1-k)(x_0-x)}{1+kx_0-x_0} \tag{9}$$

and

$$\beta_{in}(x_0;\ \alpha) = \frac{\alpha(1+k-2\alpha k)(1+kx_0-x_0)[(1-kx_0-x_0)N_L(x_0;\alpha)-N_0]}{(1-k)[N_0(x_0+kx_0-1-2\alpha kx_0)+(1+\alpha kx_0-x_0)^2 N_L(x_0;\ \alpha)}. \tag{10}$$

The equation (8) formulated to describe the solute redistribution together with accompanying definitions (9) and (10) were used to determine the numerical value of back-diffusion parameter α.

4. Evaluation of diffusion coefficient from a measurement of the Li-solute redistribution

The cellular growth of the Al-3.5Li alloy has been performed by the Bridgman system with freezing by Drevet *et al.*, [5]. The only effective techniques in determination of Li-solute redistribution were Neutron Radiography with a cold neutron beam as well as Neutron Induced Autoradiography, Bayon *et al.*, [6]. The influence of convection on the back-diffusion phenomenon in the explored alloy has also been studied, Wołczyński, [2], Nguyen-Thi, *et al.*, [7]. According to mentioned investigations the back-diffusion parameter has been calculated using equation (10) and is equal to 0.21 for the experiment in which the following conditions v = μm/s and G = K/cm, were applied, Fig. 1.

It is to be emphasised that detailed definition of the back-diffusion parameter is given by Brody and Flemings, [4] and applied in the current model.

$$\alpha = \frac{D_S t_f}{L^2}. \tag{11}$$

The definition of back-diffusion parameter given by equation (11) can be rearranged in order to remove the t_f – parameter, with $t_f = \frac{H}{v}$ and to obtain a formula for D_S – parameter, which finally is as follows:

$$D_S = \frac{\alpha L^2 v}{H}. \tag{12}$$

The formula (12) is useful for the estimation of the D_S – value.

The estimated value of the D_S – diffusion coefficient, equation (12) is about 10^{-8} cm^2/s for the experiment carried out by Drevet *et al.*, [5] in the Bridgman system.

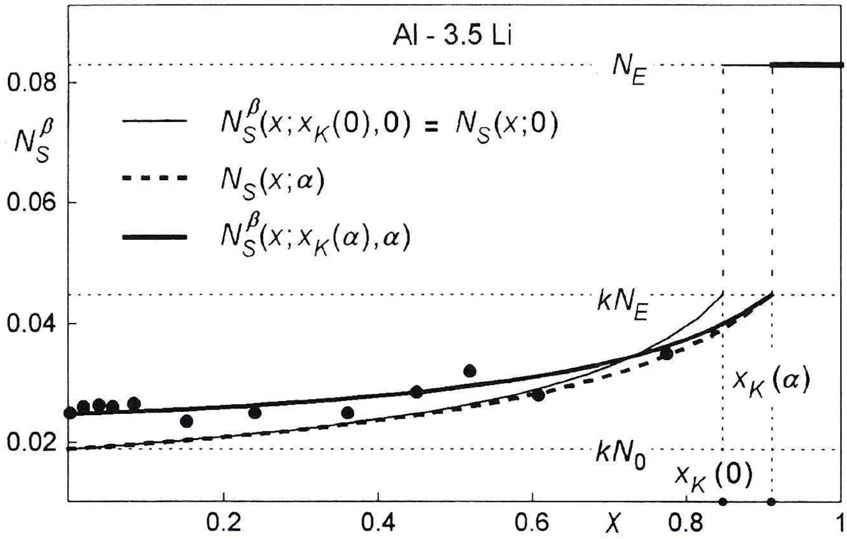

Fig. 1. Li-solute redistribution within cells of Al-3.5Li alloy solidified in *Bridgman system*; $\alpha = 0.21$, $x_K(0.21) = 0.91$, ● – N_i^β points, the dashed line determines the solute concentration at solid/liquid interfaces appearing consequently during the crystal growth, [2]

5. Concluding remarks

The estimated value of diffusion coefficient in the solid can also be discussed from the viewpoint of the influence of temperature on the obtained result. So, the experiment were carried in the Bridgman system and the morphology was frozen from the range of temperatures situated between liquidus and solidus lines. Therefore, it can be assumed that not only the solute redistribution, Fig. 1 but the values of back-diffusion parameter and diffusion coefficient can be estimated for this range of temperatures as well. Eventually, the determined value of diffusion coefficient can be compared to the analogous value of chemical diffusion coefficient, D_C shown in Table 1. The highest temperature explored in experiment carried out by Gąsior and Moser, [1] is equal to 868 K, D_C and diffusion coefficient at this temperature is described by following equation:

$$D_C \cdot 10^8 = 1.57 + 3.24 N_0 - 64 (N_0)^2, \qquad T = 868, \text{ K}. \tag{14}$$

The equation (14) is only the formal formula applied to fit the experimental data. However, it should be noticed that according to equation (14), $D_C = D_{Li}^0 = 1.57 \cdot 10^{-8}$ cm^2/s for $N_0 = 0$.

The D_C – value calculated from the equation (14) is equal to 0.99 10^{-8} cm^2/s and can be approximately compared to that obtained from the experiment carried out in the Bridgman system, Fig. 1 and estimated using equation (12). However, it should be noticed that the average temperature between liquidus-solidus range, estimated for the Al-3.5Li alloy (0.124 Li mole fr.) is about 913 K. This temperature assumed as temperature at which crystal growth was carried out in the Bridgman system is higher than temperature applied in the experiment carried out by Gąsior and Moser, [1].

Thus, the exact value of the D_C diffusion coefficient, which can be finally compared to that calculated from equation (12) is to be obtained by extrapolation. So, it is necessary to extrapolate the value of the diffusion coefficient D_C from 868 K to 913 K using Darken's equation

$$D_C = (D^0_{Li}(1-N_0)+D^0_{Al}N_0)\varepsilon \tag{15}$$

where

$$\varepsilon = \left.\frac{d\ln\alpha_{Li}}{d\ln N_0}\right|_{T.p} = 1+\left.\frac{d\ln\gamma_{Li}}{dN_0}\right|_{T.p}.$$

The value of the ε-thermodynamic factor tends to unity for the Al-rich alloys and the self-diffusion coefficient of aluminium is over one order greater than the self-diffusion coefficient of lithium, (at the temperature about 900 K). Thus, the value of D_C is practically equal to the self-diffusion coefficient of lithium, D^0_{Li}, multiplied by the Al concentration. So, the main increase of D_C diffusion coefficient with temperature is connected with the increase of the self-diffusion coefficient of lithium. Adequate equation describing the relation between D^0_{Li} and temperature is of the following form, Gąsior and Moser, [1]:

$$D^0_{Li} = 1.09\cdot 10^{-4}\exp\left(\frac{66.37}{RT}\right),\ [\mathrm{cm}^2/\mathrm{s}], \tag{16}$$

It yields from eqn (16) that $D^0_{Li} = 1.74\cdot 10^{-8}$ cm^2/s for 913 K while D_C diffusion coefficient for $N_0 = 0.124$ mole fr. riches the value of $1.53\cdot 10^{-8}$ cm^2/s.

The above value of diffusion coefficient can be compared directly to that estimated from the experiment carried out by Bridgman system, according which $D_S = 2.5\cdot 10^{-8}$ cm^2/s. Good agreement between both compared coefficients is visible. The comparison of both diffusion coefficient is justified because from the thermodynamic viewpoint the physical meaning of diffusion coefficient in both experiments is the same. It is because the chemical potential is the electromotive force for diffusion phenomenon in both compared situations. Thus, it may be concluded that

$$D_S \cong D_C. \tag{17}$$

It should be noticed that the self-diffusion coefficient calculated from the relation obtained by Minamino *et al.*, [8] is equal to $2.16\cdot 10^{-8}$ cm^2/s and is also close to both coefficients that obtained by Gąsior and Moser, [1] and that obtained in experiment explained by Nguyen-Thi, *et al.*, [7].

It should be emphasised that values of diffusion coefficients measured by Wen *et al.*, [10] and Costas, [11] are equal to $2.35 \cdot 10^{-8}$ cm^2/s and $5.01 \cdot 10^{-8}$ cm^2/s, respectively.

Such kind of model, like the current description of solute redistribution seems to be very useful in calculation of solidification path as discussed by Chen and Chang, [9]. Chen and Chang, [9] are able to calculate the solidification path taking into account the phenomenon of diffusion. It is to be however noticed that it is necessary to know local solidification time in their calculation. This parameter can be estimated due to proper experiment of crystal growth and morphological analysis, but the estimation is very erroneous. Thus, the current mode of calculation based on the measurement of solute redistribution seems to be more useful because such kind of measurement is very precise and give proper value of calculated back-diffusion parameter. This quite new idea to replace the estimation of local solidification time by measurement of solute redistribution can be additionally developed to new method of solute measurement together with the development of new techniques of electron microscopy, if any appears.

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REFERENCES

[1] W. Gąsior, Z. Moser, Scandinavian Journal of Metallurgy, 2001 (to be published).

[2] W. Wołczyński, Modelling of Transport Phenomena in Crystal Growth, p. 19–59. ed. WIT Press, Southampton – Boston, 2000, eds. J. Szmyd & K. Suzuki.

[3] E. Scheil, Zeitschrift für Metallkunde, **34**, 70–80 (1942).

[4] H. Brody, M.C. Flemings, Transactions of AIME **236**, 615–624 (1996).

[5] B. Drevet, D. Camel, C. Malmejac, Favier J.J., Nguyen-Thi H, Li Q, B. Billia, Advance Space Research **16**, 173–176 (1995).

[6] G. Bayon, B. Drevet, R. Ilic, M. Humar, J.J. Rant, H. Nguyen-Thi, Proceedings of the Fifth World Conference on Neutron Radiography, eds. Fischer CO, Stade J., Bock W., Deutsche Gesellschaft für Zerstörrungsfreie Prüfung E.V., Berlin, 417–424 (1996).

[7] H. Nguyen-Thi, B. Drevet, W. Wołczyński, Archives of Metallurgy, **44**, 365–373 (1999).

[8] Y. Minamino, T. Yamane, H. Araki, Metallurgical Transactions, **18A**, 1536–1538 (1987).

[9] S.W. Chen, Y.A. Chang, Metallurgical Transactions, **22A**, 267–271 (1991).

[10] L.P. Costas, USA EC Report TID-16676, 1–7 (1963).

[11] C.J. Wen, W. Weppner, B.A. Boukamp, R.A. Huggins, Metallurgical Transactions **11B**, 131–137 (1980).

[12] W. Wołczyński, J. Kloch, Bulletin of the Polish Academy of Sciences, Technical Sciences, **46**, 277–288 (1998).

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