A method for the determination of the concentration dependence of the chemical diffusion coefficient

Quite frequently needed information on the diffusivity of an element in a matrix at given temperature and concentration is not available. Experimental measurement of diffusivities can be done with reasonable accuracy using electron probe microanalysis. Very often, however, access to an electron microprobe is not easy. A compromise must then be made between accuracy and use of ordinary equipment.

A method is reported herein for the determination of the concentration dependence of the chemical diffusion coefficient of an element in an alloy, using solution treatments and quantitative metallography. A furnace and a microscope is all the equipment required for this determination.

In a study of solution kinetics of interdendritic nonequilibrium secondary phase in a cast 7075 aluminium alloy it was shown by Singh *et al* [1] that the extent of dissolution depends exclusively on the dimensionless parameter Dt/l^2, where D is the chemical diffusion coefficient of solute (copper) in the primary phase (cm²/sec), t is time of solution treatment (sec) and l is half the dendrite arm spacing (cm). This conclusion may be represented by:

$$\frac{g}{g_0} = f(Dt/l^2)$$

where f = function, g = volume fraction of secondary phase at time t, and g_0 = initial volume fraction of secondary phase. In their analysis Singh *et al* [1] developed a simple plate-like dendritic model [2] which assumed that dendrite arms are plates separated by plates of secondary phase.

Similar conclusions were formulated by other authors for various alloys and dendritic structures [3-5]. Thus, Bhambri *et al* [3] and Swartzbeck *et al* [4] analysed the solution kinetics of nonequilibrium Mg_7Zn_3 surrounding non-dendritic spherical grains of Mg-rich primary phase in a grain-refined Mg-5.1 wt % Zn-0.5 wt % Zr alloy. Using a spherical diffusion model it was shown that (g/g_0) was again a certain function, more complex than with the plate-like model, of (Dt/l^2), where l is the sphere radius. Finally, Swartzbeck *et al* [4] developed a cylindrical diffusion model to describe solution kinetics of non-equilibrium interdendritic Mg_7Zn_3 in a dendritic Mg-5.1 wt % Zn alloy. Again (g/g_0) was found to be a certain function of (Dt/l^2), where l is the cylinder radius. Similar conclusions were reached by Kattamis [5] with respect to solution kinetics of $CuAl_2$ in a dendritic cast aluminium alloy.

In a binary eutectic alloy a relationship can be derived between values of the chemical diffusion coefficient corresponding to various solute concentrations, using the exclusive dependence of (g/g^0) on (Dt/l^2). It is, of course, necessary that the interdendritic eutectic or secondary phase be, at least partly, nonequilibrium. To illustrate the procedure, assume n binary alloy specimens A $-$ c_i wt % B, with $0 < c_i < C_E$, where C_E is the eutectic composition and $i = 1 \ldots n$. Let D_i be the chemical diffusion coefficient in the ith alloy, l_i half the corresponding dendrite arm spacing in this alloy and t_i the solutionizing time necessary to achieve a given reduction in the volume fraction secondary phase, hence a given (g/g_0) the same for all alloys. The volume fraction secondary phase will be increasing with increasing c_i and the dendritic structure will become finer for a given cooling rate [6]. However, the general dendritic morphology will not be affected. Hence, the same diffusion model can be used independently of c_i and the same function f will be valid for all cases. Thus:

$$\frac{g}{g_0} = f\left(\frac{D_1t_1}{l_1^2}\right) = \ldots f\left(\frac{D_it_i}{l_i^2}\right) = \ldots f\left(\frac{D_nt_n}{l_n^2}\right) \quad \ldots\ldots (2)$$

For all three dendritic morphologies plate-like, cylindrical and spherical, f is a monotonous function. Hence:

$$\frac{D_1t_1}{l_1^2} = \ldots \frac{D_it_i}{l_i^2} = \ldots \frac{D_nt_n}{l_n^2} \quad (3)$$

TABLE I Volume fraction of interdendritic secondary phase versus time of solution treatment at 504°C

Alloy	i	Half dendrite arm spacing l_i(cm)	g_0	g (t = 5 h)	g (t = 10 h)	g (t = 20 h)
Al-1 wt % Cu	1	$l_1 = 39.7 \times 10^{-4}$	2.81	2.16	1.52	0.9
Al-3 wt % Cu	2	$l_2 = 26.2 \times 10^{-4}$	3.93	2.84	1.81	0.905
Al-5 wt % Cu	3	$l_3 = 11.72 \times 10^{-4}$	5.57	3.68	2.22	0.669

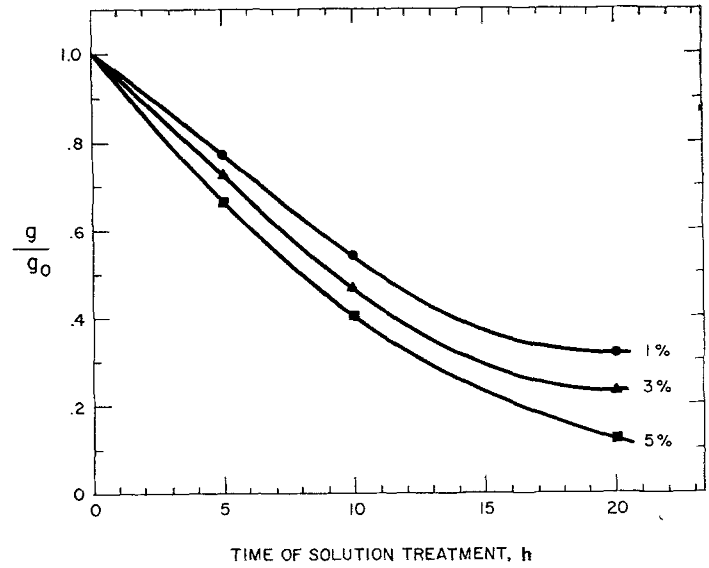

Figure 1 Variation of g/g_0 with time of solution treatment. Al-1 wt % Cu, Al-3 wt % Cu and Al-5 wt % Cu alloys.

As an example of application of this method three Al-Cu alloy ingots (cylinders, ¼ in. diameter × 3 in. high) were cast and dendrite arm spacings measured. These alloys were: Al-1 wt % Cu, Al-3 wt % Cu and Al-5 wt % Cu. The solution treatment was carried out at 504°C for various lengths of time. This temperature was chosen because the chemical diffusion coefficient in Al-Cu alloys at 504°C is known [7] and the accuracy of this method could then be tested. Measurement of volume fraction of interdendritic secondary phase ($CuAl_2$) in the as-cast (g_0) and solutionized conditions (g) was conducted by quantitative metallography using a two-dimensional systematic point count following the procedure of Hilliard *et al* [8]. Details of application of this method were reported elsewhere [1]. Volume fraction measurements are summarized in Table I.

TABLE II Relationship between chemical diffusion coefficient in Al-1 wt % Cu (D_1), Al-3 wt % Cu (D_2) and Al-5 wt % Cu (D_3), calculated for different values of (g/g_0).

g/g_0	$D_1' = D_1/D_3$	$D_2' = D_2/D_3$
0.8	7.30	4.05
0.7	7.90	4.15
0.6	8.10	4.18
0.5	8.15	4.22
0.4	6.90	4.00
Average values	$D_1' = 7.67$	$D_2' = 4.12$

Fig. 1 was plotted using information included in Table I. For a given (g/g_0) times t_i were taken from Fig. 1, half spacings l_i were taken from Table I and were introduced in equation 3. Finally, D_1 and D_2 were expressed in terms of D_3. Results are summarized in Table II.

Assuming $D_3 = 1.3 \times 10^{-10}$ cm²/sec, which has been determined by extrapolating data by Mehl *et al* [7], the values of D_1 and D_2 are found to be 9.97×10^{-10} cm²/sec and 5.35×10^{-10} cm²/sec, respectively. These values do not differ substantially from those determined by Mehl *et al* [7], using the Boltzmann-Matano analysis, namely: $D_1 = 5.8 \times 10^{-10}$ cm²/sec and $D_2 = 4.0 \times 10^{-10}$ cm²/sec. It can be seen that the chemical diffusion coefficient decreases with increasing Cu concentration within the primary Al-rich phase. This conclusion supports also the findings of Bückle [9] for 515 and 550°C. This method could be applied to more complex systems.

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