

**Grain Boundary Diffusion Parameters Determination using A-Kinetics  
of Intermetallic Layer Formation**

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**Abstract**

A method of GB Diffusion Parameters Determination during A-regime of Intermetallic Layer Formation is suggested. Experimental data on Cu<sub>5</sub>Zn<sub>8</sub> Diffusion growth Kinetics are used for separate Determination of the volume Diffusion Activation Enthalpy and the GB Activation Enthalpy.

**Introduction**

The shift of the crystal lattice during mutual diffusion in solids was first discovered by Kirkendal [1] and theoretically described by Darken [2]. There are a lot of experimental data of the Kirkendali effect for different binary systems. But still not all peculiarities of the process have been found.

**Model**

It is very difficult to find precisely the dependence of the concentration profile upon time of diffusion for an A-B binary system. Van Loo, Bastin and Vrolijk [3] modelled the concentration profile as two error functions that meet with the same slope at the Kirkendali plane. With such an approximation the Kirkendali plane shift,  $x_0$ , versus time is given as:

$$x_0 = 2(\sqrt{D_B} - \sqrt{D_A}) / \pi \sqrt{t} \quad (1)$$

Here  $D_A$  and  $D_B$  are intrinsic diffusion coefficients, substance A is on the left side of the couple, and substance B is on the right side of the couple. Morral, Son and Thompson [4] assumed that the concentration gradient at the Kirkendal plane can be approximated by an analytical expression for the concentration gradient at the Matano plane. They obtained:

$$x_0 = (D_B - D_A) / \sqrt{(\pi D_{11})} \sqrt{t} \quad (2)$$

Here  $D_{11} = (DB+DA)/2$ .

We can see that Eqs (1) and (2) are the same for the case  $DA = DB$ . We should expect to obtain an analogous expression for  $x_0$ .

We wish to find the Kirkendali shift,  $X$ , depending upon the coordinate,  $xK$ , relative to the Kirkendali plane ( $x_0 = x(XK=0)$ ).

The analytical solution for the case  $DA=DB=D$  is well-known [5]:

$$C(z) = 1/2 + 1/2 * \text{erf}(z/2), \quad \text{erf}(z) = 2/\sqrt{\pi} * \int_0^z e^{-u^2} du \quad (3)$$

Here  $z = X/\sqrt{Dt}$ ,  $X$  is the coordinate relative to the Matano plane,  $C$  is the atomic concentration of substance B (substance B is on the right side of the couple). This exact solution can be approximated by the following expression (it has a deviation from the exact solution of less than 1.9%)

$$c_1(z) = 1/(1 + e^{-(2z/\sqrt{\pi})}) \quad (4)$$

It is a precise solution for the main part of the diffusion zone (the deviation is less than 0,1% if  $z < 0,5$ ).

We can see that  $C(Z=0) = C_1\{Z=0\} = 1/2$  and

$$dc/dz(z=0) = dc_1/dz(z=0) = 1/(2*\sqrt{\pi}). \quad (5)$$

#### Solution for the case $DA \neq DB$ ( $DB(c=0) < DB(c=1)$ )

In such a case [5-7] there is substantial "asymmetry" in  $C(x)$  with much deeper penetration on the substance B side, and  $c(x=0) > 0.5$ . One can find an analogous expression for the case  $DA \neq DB$ :

$$C_2(z) = 1/(1 + B * e^{-(2zn/\sqrt{\pi})}) \quad (6)$$

Here  $B = (DB-DA)/DB$ ,

$C_2$  is the atomic concentration of substance B.

We assume the ratio  $DB/DA$  does not depend upon concentration and  $B = \text{const}$

(it is not important, but the term  $(DB - DA)$  should not change sign).

We can estimate  $n$  using the following conditions: a) the diffusion flux,  $J_2$ , through the Matano plane must be less than  $J(DA=DB)$ , b) the concentration profile slope at the Matano plane,  $dc_2/dx$ , must be greater than  $dc/dx$ , and c) the area on the left side from the Matano plane must be equal to the area on the right side from the Matano plane.

We assume [2]

$$D = c_A DB + c_B DA = DB(1 - c_2 B) \quad (8)$$

### Computer modeling

■ To compare this result with experimental data a computer program was worked out to model the Kirkendall effect by Monte Carlo calculations. It takes into account the random vacancy jumps in a cubic lattice, appearance and disappearance of vacancies due to climbing of dislocations to be parallel to the Kirkendall plane, vacancy quasi-equilibrium in all points of each substance, different frequency of exchange of vacancy and the atoms of different kinds, and external stress gradient.

The Kirkendall effect is now considered as excellent evidence for the validity of a vacancy mechanism of diffusion in metals [9]. For this reason, we solved a random-walk vacancy problem with appropriate boundary conditions. The main assumption is:

$$p_B/p_A = \text{const} > 1. \quad (9)$$

Here  $p_A$  ( $p_B$ ) is the probability that an A-atom (a B-atom) will jump into any ---give n-neigh h bo ring vacan t site.

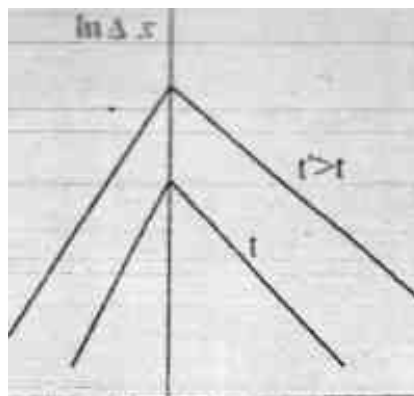
The average number of jumps,  $\Gamma$ , a vacancy make per second in an A-B alloy is given by the following way [10]:

$$\Gamma = C_A \Gamma_A + C_B \Gamma_B. \quad (10)$$

Here  $\Gamma_A$  and  $\Gamma_B$  are the numbers of jumps a vacancy make *per* second in pure A and in pure B correspondingly.

Monte Carlo modeling shows that a) the assumption (9) leads to Eq.(10) automatically; b) the equilibrium vacancy concentration in substance B is greater than that in substance A ; c) the net vacancy flux is directed into substance B ; d) the shift of an inert marker is directed in the same direction and is proportional to the square root of time of diffusion: and e) the time rate of change of the shift decreases with distance increasing from the Kirkendall plane (see Fig.1).

Fig.1 Results of Monte Carlo modeling of the Kirkendall shift dependence upon  $XK$ .



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We can see that the graph slope is decreasing during diffusion. Besides, the graph slope on the left side from the Kirkendall plane is greater than that on the right side from the Kirkendall plane. The same results were obtained in [8] experimentally. These results agree with Eq.(8) since  $D_b$  on the right side of the couple is greater than  $D_b$  on the left side of the couple.

Consequently, the validity... of the theoretically obtained dependence of the Kirkendall shift upon time and coordinate is verified by computer modeling and by the real experimental data. This program can be applied for finding another peculiarities of the Kirkendall effect, especially under an external stress gradient.

### Conclusion

The results of computer modeling and the analytical solution of the Kirkendall effect agree with the real experimental data, and we can conclude that the theory and the modeling describe correctly this very interesting phenomenon.

- [1] A.Smigelskas and E.KirkendaH, Trans. A.I.M.E. **171**, 130 (1947).
- [2] L.Darken, Trans. A.I.M.E. **174**, 84 (1948).
- [3] F.J.J.van Loo. G.F.Bastin and .f.YV.G.A.Vrolijk. Metall.Trans. **18A**. 80I (1987).
- [4] J.E.Morrall, Yoon-Ho Son and M.S.Thompson. Acta Metal!. 36, No.8. 1971 (1988).
- [5] P.G.Shewmon. Diffusion in Solids. Second edition. -Warrendale. Pennsylvania (1989).
- [6] J.Crank, The Mathematics of Diffusion, 2nd edn. - Clarendon Press, Oxford (1975).
- [7] U.E.Ugaste and V.f.Neverov. Fiz. i him. obrab. mater. No.1.107 (1993).
- [S] VJ.Neverov and U.E.Ugaste. Fiz. i him. obrab. mater. No.6,116 (1992).
- {9} D.Lazarus. Materials Science Forum 1. 1 (1984).
- fIOJ J.R.Manning. Acta Metall. 15. S17 (1967).