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THE KIRKENDALL EFFECT AND PHASE FORMATION KINETICS DURING SOLID STATE REACTIONS

PhD in Physics and Mathematics, associate professor,
M. V. Yarmolenko
Kyiv National University of Technologies and Design, Ukraine, Cherkasy

In the article it was proved theoretically and experimentally that the interface curvature can either accelerate or slow down the Kirkendall shift and the diffusion phase layer growth in cylindrical and spherical samples when compared with a planar sample depending on the average phase concentration only. It is shown that internal stress, arising due to dilatation during phase growth, can either accelerate or slow down the growth in addition to the above-mentioned effect, depending on the difference in mobilities of different atoms within each phase and independently on the sign of dilatation.

Key words: Kirkendall shift, Matano plane, reactive diffusion, vacancies, interfaces, intermetallic compounds, kinetics.

Кандидат фізико-математичних наук, доцент Ярмоленко М. В. Кінетика ефекту Кіркендалла та фазоутворення у процесі твердофазних реакцій / Київський національний університет технологій та дизайну, Україна, Черкаси.

У статті доведено теоретично та підтверджено експериментально, що кривизна міжфазної границі може як пришвидшувати, так і уповільнювати дифузійне утворення шарів фаз у циліндричних та сферичних зразках та зміщення Кіркендалла в залежності лише від середньої концентрації однієї з речовин. Додатково впливати на кінетику можуть також внутрішні механічні напруги, які виникають у процесі фазоутворення.

Ключові слова: зміщення Кіркендалла, площина Матано, реакційна дифузія, вакансії, міжфазні границі, інтерметаліди, кінетика.

кандидат физико-математичних наук, доцент Ярмоленко М. В. Кинетика еффекта Киркендалла и фазообразования в процессе твердофазных реакций / Киевский национальный университет технологий и дизайна, Украина, Черкассы.

В статье доказано теоретически и подтверждено экспериментально, что кривизна межфазной границы может как ускорять, так и замедлять диффузионное образование слоев фаз в цилиндрических и сферических образцах и смещение Киркендалла в зависимости только от средней концентрации одного из веществ. Дополнительно влиять на кинетику могут тоже внутренние механические напряжения, которые возникают в процессе фазообразования.

Ключевые слова: смещение Киркендалла, плоскость Матано, реакционная диффузия, вакансии, межфазные границы, интерметаллиды, кинетика.

Introduction. The shift of the crystal lattice during mutual diffusion in solids was first discovered by Kirkendall [1] and theoretically described by Darken [2]. There are a lot of experimental data of the Kirkendall effect for different binary systems. But still not all peculiarities of the process have been found. Treatments of diffusion in metallic solid solutions require an accurate, convenient analysis that takes account of the actual variations of atomic size with concentration. There are reference systems of two types: conventional reference systems (Fick and molecular), and the lattice (Kirkendall) reference system [3]. The Kirkendall effect is now considered as excellent evidence for the validity of a vacancy mechanism of diffusion in metals. For this reason, was solved a random-walk vacancy

problem with appropriate boundary conditions. The results of computer modeling and the analytical solution of the Kirkendall effect agree with the real experimental data [4]. Describing the growth of intermediate phase layers during chemical diffusion in cylindrical and spherical samples offers some difficulty, since the change in interface area S(R) should be taken into account. In addition, there is a considerable concentration dependence of the interdiffusion coefficient D(C) and an exact knowledge of D(C) is needed for each phase of a binary system. Moreover, if a phase grows with volume change, internal stress arises, influencing growth kinetics of the phases. Therefore, the problem can not be solved in a general form, no matter how modern the computer systems are.

Purpose. Solid state reactions (SSRs) are governed by two magic powers – thermodynamics and kinetics. Common understanding is that kinetics determines only the rate of fulfilment (implementation) of thermodynamic laws. Actually, the only concept, which had been taken from the nucleation theory, is the existence of critical nuclei [5]. The prevalent erroneous concept of an "invariant" for diffusion demonstrates the need for a clearer understanding of the role of reference planes in treatments of diffusion. The diffusion velocity, v, of a given component is used as the basis for defining the diffusion flux. Absolute values of v can be determined from data on the Kirkendall shift, but only relative values ($v - \Omega$) can be employed if only a conventional reference system is used in the analysis [3, 6].

Methods. For describing the growth kinetics of the phases and the Kirkendall shift kinetics, an approximation of constant diffusion flux along the diffusion direction within the width of each phase is used (so-called constant flux method) which is theoretically grounded in [7, 8]. This technique necessitates no allowance for the concentration dependence of

D(C). The relative change of the diffusion flux within the width of each phase is approximately equal to dC«1, where dC is the range of phase homogeneity, while the interdiffusion coefficient may vary by more than a factor of 10 over the region of homoheneity dC.

Originality. Computer simulation can not describe fairly well interface curvature influence on intermediate phase layers kinetics during chemical diffusion and the Kirkendall shift kinetics. So we have to use the mathematical equations [9, 10, 11].

Results.

1. The Kirkendall shift kinetics.

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 Kīrkendall plane shift, X0, versus time usually is given as:

$$X0 = 2(\sqrt{D_B} - \sqrt{D_A})\sqrt{t}/\pi \qquad (1)$$

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.

One can find another result [4]:

$$X0 = (D_B - D_A)\sqrt{t}/(\sqrt{\pi}\sqrt{D_B}) \qquad (2)$$

To compare these results a random-walk vacancy problem was solved with appropriate boundary conditions. The main assumption is:

$$pB/pA = const > 1. \qquad (3)$$

Here pA (pB) is the probability that an A-atom (a B-atom) will jump into any given neighboring vacant site.

The average number of jumps. Γ, a vacancy make per second in an A-B alloy is given by the following way:

$$\Gamma = C_a \Gamma_a + C_b \Gamma_b. \tag{4}$$

Here Γ_a and Γ_b are the numbers of jumps a vacancy make per second in pure A and in pure B correspondingly.

Monte Carlo modeling shows that the net vacancy flux is directed into substance B; the shift of an inert marker is directed in the same direction and is proportional to the square root of time of diffusion, and the time rate of change of the Kirkendall shift decreases with distance increasing from the Matano plane (see Fig.1). We can see that the graph slope is decreasing during diffusion. Besides, the graph slope on the left side from the Matano plane is greater than that on the right side from the Matano plane.
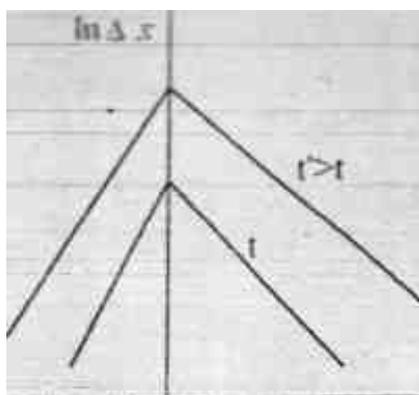

Figure 1. Results of Monte Carlo modeling of the Kirkendall shift dependence upon distance from the Matano plane.

2. **Interface curvature influence on intermediate phase layers kinetics during chemical diffusion.**

If an intermediate phase grows between substances A and B in planar sample, the rate of change of the phase layer width, $X = X_R - X_L$

(X_L *and* X_R are the coordinates relative to the Matano plane), with respect to time is given by [7, 8]

$$dX/dt=(I-dC)DdC/(XC_L(I-C_R)) \qquad (5)$$

Here C_L and C_R are the volume fractions of B on the left-hand and right-hand phase interfaces, $dC = C_R - C_L$, DdC is the diffusion penetrability of the phase ($DdC=\int D(C)dC$).

The solution of (1) is a well-known parabolic law

$$X^2 = 2(I-dC)DdCt/(C_L(I-C_R))=K^2t \qquad (6)$$

(K is the growth rate constant).

This constant can be obtained experimentally and it is possible to calculate DdC:

$$DdC=K^2C_L(I-C_R)/(2(I-dC)) \qquad (7)$$

If the phase grows in a spherical or cylindrical sample (substance A is in the centre of the sample), the rate of change the phase layer width, R, with respect to time is given by [7]

$$dR/dt=(C_Lr_L/r_R+(I-C_R)r_R/r_L)DdC/(RC_L(I-C_R)) \qquad (8)$$

for a spherical sample and by

$$dR/dt=(C_L+(I-C_R)r_R/r_L)DdC/(C_L(I-C_R)r_Rln(r_R/r_L)) \qquad (9)$$
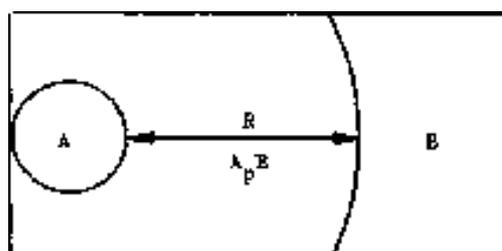
for a cylindrical sample (see fig.2).

Figure 2. The phase grows in a spherical or cylindrical sample.

Here r_L and r_R are the radii of the inner and outer interfaces, $R=r_R - r_L$. A comparison of (8), (9) and (5) shows that $dR/dt>dX/dt$ for the case $R=X$ and $(C_L +CR)/2=C<0.5$.

Therefore, R(t)>X(t) for the same t's. But if C>0.5, the spherical or cylindrical layer first grows more slowly than the planar layer, and then, for R/r_R =2-(1-dC)/C_L , it starts to grow more rapidly.

This method was applied for describing the growth kinetics of thin γ-brass and ε-brass layers in a cylindrical sample at 400°C (Cu=A and Zn=B). The γ-brass layer grew slower and the ε-brass layer grew more rapidly than in the planar sample (see fig.3).
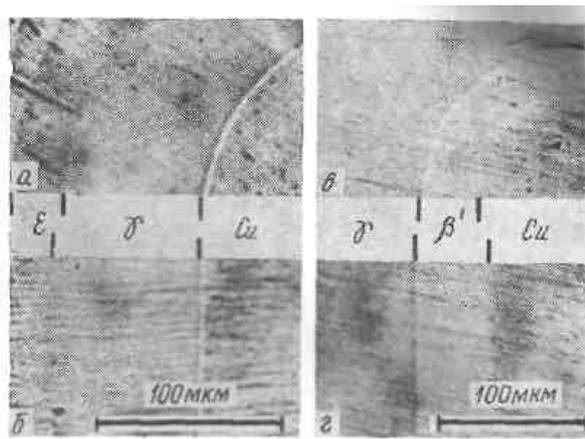

Figure 3. The γ-brass, ε-brass and β-brass are formed in the cylindrical sample.

Experimental results had confirmed the theoretical calculation both qualitatively and quantitatively.

3. Stress influence on intermediate phase layers kinetics during chemical diffusion.

If phase 1 grows with dilatation, it produces the internal stress. This stress influences the vacancy flux inside phase by means of the modulus effect. The stress influences diffusion penetrability of phase 2 since the phase is under pressure

$$P_A=-(l/3)tr\sigma_A \qquad (10)$$

created by phase 1 growing with dilatation. The diffusion penetrability of phase 2 decreases by a factor of exp(P_A). This fact was experimentally obtained during β-brass growth between Cu and γ-brass after Zn has

disappeared at 400°C in cylindrical sample and in a planar sample. The β-brass begins to grow under high pressure created by growing the γ-brass layer in the cylindrical sample (see fig.3).

Conclusions.

1. 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. The analytical solution and computer modeling can be applied for finding another peculiarities of the Kirkendall effect, especially under an external stress gradient.

2. Interface curvature can either accelerate or slow down diffusion phase layer growth. It depends on average phase concentration, C, of the external substance, B, only. Phase growth is accelerated toward the centre of the sample if C<0,5 and is slowed down if C>0,5.

3. For the second phase, growing without dilatation, the change in interdiffusion coefficient due to hydrostatic pressure created by the growing first phase should be taken into account.

4. The constant-flux approximation permits a fairly simple description of diffusion phase growth in planar, cylindrical, and spherical samples without any distinction for the various binary systems (only c_L, c_R, and radii should be taken into account).

5. There are several cases for two-phase binary systems. A slowly growing phase 2 in both cylindrical and spherical cases grows more rapidly than in the planar case; this is so if this phase surrounds a rapidly growing phase 1. Conversely, a slowly growing phase 2 in both cylindrical and spherical cases grows more slowly than in the planar case, if this phase is surrounded by a rapidly growing phase 1. A rapidly growing phase 1 can grow in both cylindrical and spherical cases, either more rapidly or more slowly than in the planar case

6. Attention is also drawn to the result, that the growth rates in convex and

concave surfaces, is such that the interface boundary is liable to smoothing during phase growth. The smoothing rate is the more pronounced, the smaller the roughness radius. Therefore, we consider the "ideal" surfaces (plane, cylinder, and sphere) instrumental in describing phase growth.

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