

3. Slyusar I.T. *Kormi z osushenogo gektara // I.T. Slyusar, M.I. Shtakal, M.K. Tsarenko. - K: Agrarna nauka, 1998. - 164 s.*
4. *Silskogospodarske vikoristannya osushenih zemel gumidnoyi zoni Ukraini // V.R. Gimbarazhevskiy, T.M. Kovalenko, I.T. Slyusar ta inshi. / Metodichni rekomendatsiyi. - K: Agrarna nauka, 2000. - 76 s.*
5. *Slyusar I.T. Lukivnitstvo z osnovami nasinnitstva // I.T. Slyusar, V.A. Vergunov, M.M. Gavrilyuk. - K.: Agrarna nauka, 2001. - 196 s.*
6. *Slyusar I.T. Osoblivosti sistemi zemlerobstva na osushenih zemlyah gumidnoyi zoni Ukraini: problem', shlyahi virishennya //I.T Slyusar, O.P. Solyanik / Zb. Ekologiya: problem' adaptivno-landshaftnogo zemlerobstva. - Zhitomir: Derzhavniy ekologichniy universitet. 2005. - S. 38-42.*
7. *Pethchenko V.F. Luchne kormovirobnitstvo i nasinnitstvo trav // V.F. Petrchenko, P.S. Makarenko. - Vinnitsya «Dilo», 2005.-338 s.*
8. *Slyusar I.T. Sinokosi i pasovishcha na osushuvanih zemlyah / I.T. Slyusar, O.P. Solyanik, V.O. Serbenyuk, O.M. Gera, V.M.Virovka. - K: TsP "Komprint", 2017. - 258 s.*

УДК 539.219.3**PHASE FORMATION AND THE KIRKENDALL EFFECT KINETICS DURING SOLID STATE REACTIONS****PhD in Physics and Mathematics, Associate professor,****Yarmolenko M.V.** 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 diffusion phase layer growth in cylindrical and spherical samples and the Kirkendall shift 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 фазоутворення та ефекту Кіркендалла 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-математических наук, доцент Ярмоленко М.В. Кинетика фазообразования и эффекта Киркендалла 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 влияют 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 [4]. 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 [5,6]. 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 [8]. 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 ($v - Q$) can be employed if only a conventional reference system is used in the analysis [3].

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]. 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 $dC \ll 1$, 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 homogeneity 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 [5, 6, 8]. So we have to use the mathematical equations.

Results.

1. 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]

$$dX/dt = (1-dC)DdC/(X_C(L-C_R)) \quad (1)$$

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 ($DdC = ID(C)dC$).

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

$$X^2 = 2(l-dC)DdCt / (C_L(l-C_R)) = K^2t \quad (2)$$

(K is the growth rate constant).

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

$$DdC = K^2 C_L (l - C_R) / (2(l - dC)) \quad (3)$$

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]

$$dR/dt = (C_L r_L / r_R + (l - C_R) r_R / r_L) DdC / (R C_L (l - C_R)) \quad (4)$$

for a spherical sample and by

$$dR/dt = (C_L + (l - C_R) r_R / r_L) DdC / (C_L (l - C_R) r_R \ln(r_R / r_L)) \quad (5)$$

for a cylindrical sample (see fig.1).

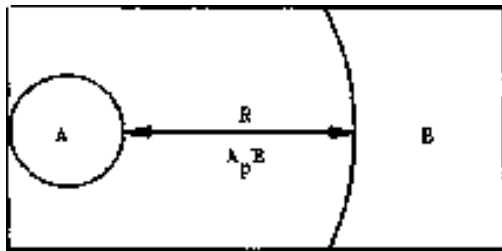


Fig.1. The phase grows in a spherical or cylindrical sample.

Here r_L and r_R are the radii of the inner and outer interfaces, $R = r_R - r_L$. A comparison of (4), (5) and (1) shows that $dR/dt > dX/dt$ for the case $R = X$ and $(C_L + C_R) / 2 = C < 0.5$. 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 ($\text{Cu} = \text{A}$ and $\text{Zn} = \text{B}$). The γ -brass layer grew slower and the ϵ -brass layer grew more rapidly than in the planar sample (see fig.2).

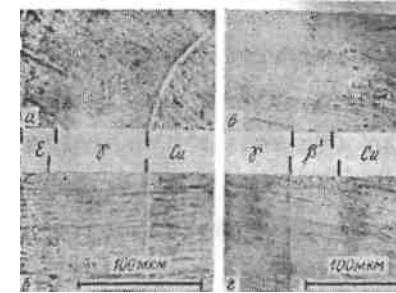


Fig.2. The γ -brass, ϵ -brass and β -brass are formed in the cylindrical sample.

Experimental results had confirmed the theoretical calculation both qualitatively and quantitatively [7, 9 - 18].

2. 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

$$P_A = -(l/3) \text{tr} \sigma_A \quad (6)$$

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 p -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.2) [9, 15, 17].

3. The Kirkendall shift kinetics.

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 shift decreases with distance increasing from the Kirkendall plane (see Fig.3). 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.

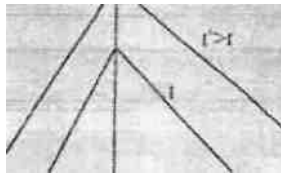


Fig.3 Results of Monte Carlo modeling of the Kirkendall shift dependence upon distance from the Kirkendall plane.

Conclusions.

1. 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 $C > 0,5$.
2. 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.
3. It is necessary to use the constant-flux approximation instead of the constant diffusion coefficient approximation in describing diffusion phase

growth in binary systems,. This is because the diffusion coefficient may vary by more than a factor of 10 within the range of phase homogeneity dc , while the diffusion flux may vary by only a few percent.

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. If the average phase concentration of the external substance is less than 0.5, the phase in both cylindrical and spherical cases grows more rapidly than in the planar case. By contrast, if $c > 0.5$, the phase in both cylindrical and spherical cases grows more slowly than in the planar case, but the growth accelerates towards the centre of the sample.

6. If $0.55 < C < 0.7$, the phase growth in cylindrical and spherical samples may be described by a parabolic dependence similar to the planar case.

7. 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 (see conclusion 5; the value 0.5 is replaced by $0.5c_2$).

8. 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.

9. 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.

References:

1. A.Smigelskas and E.Kirkendall, *Trans. A.I.M.E.* 171, 130(1947).
2. L.Darken, *Trans. A.I.M.E.* 174, 84(1948).
3. A.Guy, *Reference planes for binary diffusion with variable molar volume // Journal of Materials Science.* - 1985, Volume 20, Issue 12, pp. 4317-4328.
4. D.Lazarus. *Materials Science Forum* 1. 1 (1984)
5. Yarmolenko M. V. *The Kirkendall Effect: Analytical Solution and Monte Carlo Modeling // Defect and Diffusion Forum.* - 1997. Vols. 143-147. p. 509-514.
6. Yarmolenko M. V. *Grain Boundary Diffusion Parameters Determination using A-Kinetics of Intermetallic Layer Formation // Solid State Phenomena.* - 2000. - Vol.72, pp. 251-254.
7. A.M. Gusak, M. V. Yarmolenko, "A simple way of describing the diffusion phase growth in cylindrical and spherical samples" // *Journal of Applied Physics.* -1993. - Vol.73,№10. -pp. 4881-4884.
8. M. V. Yarmolenko, *Interdiffusion in Binary Systems during Rapid Heating: Thermoelastic Stress Influence // Defect and Diffusion Forum.* – 1996. - Vols. 129-130, pp. 321-322.
- 9.Yarmolenko M.V. *Solid State Reactions during Diffusion: Phase Formation Kinetics // Scientific review.* - 2017. - №4 (36). - c.188 - 193.
- 10.M. V. Yarmolenko, "Describing the Diffusion Phase Growth in Polycrystals: Analytical Solution", *Defect and Diffusion Forum*, Vols. 143-147, pp. 1567-1572, 1997.
- 11.M. V. Yarmolenko, "Enhanced Diffusion and Other Phenomena during Rapid Heating of Bimetals: Theory and Experiments", *Defect and Diffusion Forum*, Vols. 143-147, pp. 1613-1618, 1997

12. M.V. Yarmolenko, A.M. Gusak, K.P. Gurov, *A model of growth of an intermediate phase in bi- and polycrystals // Journal of Engineering Physics and Thermophysics.* – 1993. – 65(3). – P. 876 – 881.
13. Gurov K. P., Gusak A. M., Yarmolenko M. V. *Constancy of the Flow in a Growing Intermetallic Layer Under Conditions of Interdiffusion // Metallofizika.* – 1988. – T. 10. – №. 5. – С. 91-92.
- 14.Yarmolenko M. V. *Kinetyka utvorenniya dyfuziynoyi zony pid chas shvydkogo nagrivu binarnykh zrazkiv // Visnyk Cherkaskogo inzhenerno-tehnologichnogo instytutu.* – 1996. – N1. – P. 34 – 40.
- 15.M. V. Yarmolenko, *Deviation from Parabolic Growth of Phase Layers in Cylindrical and Spherical Samples: Curvature and Internal Stress Influence // Proceedings of PTM'94 Conference Solid-Solid Phase Transformations: Minerals, Metals and Materials Society (USA).* – 1995. – pp. 1177 – 1182.
16. V.V. Bogdanov, A.M. Gusak, L.N. Paritskaya, M.V. Yarmolenko, *Characteristics of Diffusion Phase Growth in Cylindrical Specimens // Metallofizika.* – 1990. – 12(3). – P. 60 – 66.
17. V.V. Bogdanov, L.N. Paritskaya, M.V. Yarmolenko, *Effect of Internal Stresses on Diffusion Phase Growth in Cylindrical Specimens // Metallofizika.* – 1990. – 12(5). – P. 98 – 104.
18. M.V. Yarmolenko, K.P. Gurov, A.M. Gusak, *On the Effect of Surface Smoothing During Growth of Intermetallides Between Substrate and Coating // Fizika i Khimiya Obrabotki Materialov.* 1989. – №4. – P. 138 – 140.