

PHASE FORMATION KINETICS DURING BINARY DIFFUSION IN SOLID STATE

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Abstract. 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 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: reactive diffusion, vacancies, interfaces, intermetallic compounds, kinetics.

Аннотация. 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 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: реакционная диффузия, вакансии, межфазные границы, интерметаллиды, кинетика.

Introduction. 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. For describing the growth kinetics of the phases, 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 [1, 2]. 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 . Computer simulation can not describe fairly well interface curvature influence on intermediate phase layers kinetics during chemical diffusion [3, 4]. So we have to use the mathematical equations.

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 , with respect to time is given by [2]

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

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 ($DdC=\int D(C)dC$).

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

$$X^2 = 2(1-dC)DdCt/(C_L(1-C_R))=K^2t \quad (2)$$

(K is the growth rate constant).

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

$$DdC=K^2C_L(1-C_R)/(2(1-dC)) \quad (3)$$

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 [2]

$$dR/dt=(C_Lr_L/r_R+(1-C_R)r_R/r_L)DdC/(RC_L(1-C_R)) \quad (4)$$

for a spherical sample and by

$$dR/dt=(C_L+(1-C_R)r_R/r_L)DdC/(C_L(1-C_R)r_R\ln(r_R/r_L)) \quad (5)$$

for a 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 ($Cu=A$ and $Zn=B$). The γ -brass layer grew slower and the ϵ -brass layer grew more rapidly than in the planar sample. Experimental results had confirmed the theoretical calculation both qualitatively and quantitatively [1,3].

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 the phase by means of the modulus effect. The

stress influences diffusion penetrability of phase 2 since the phase is under pressure

$$P_A = -(1/3)\text{tr}\sigma_A \quad (6)$$

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 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[1,3].

Conclusions. 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 $C > 0,5$. For the second phase, growing without dilatation, the change in interdiffusion coefficient due to hydrostatic pressure created by a growing first phase should be taken into account.

References:

1. Yarmolenko M.V. Grain Boundary Diffusion Parameters Determination using A-Kinetics of Intermetallic Layer Formation // Solid State Phenomena. - 2000. - Vol.72, pp. 251-254.
2. 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.
3. Yarmolenko M.V. Principles of interactive learning fundamentals of Physics based on virtual laboratories // Scientific review . – 2016. – №9(30). – P. 139–149.
4. Andriy M. Gusak, Fiqiri Hodaj, Guido Schmitz, “Flux-driven nucleation at interfaces during reactive diffusion” // Philosophical Magazine Letters, (2011), v.91, №10, pp. 610-620.