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.
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.

Purpose. Solid state reactions (SSRs) are obviously the most interesting topic in the world since they mean birth, competition, and growth of new “worlds” (phases) as a result of interactions between parent phases. SSRs are governed by two magic powers – thermodynamics and kinetics. Common understanding is that kinetics determines only the rate of fulfillment (implementation) of thermodynamic laws. Actually, the only concept, which had been taken from the nucleation theory, is the existence of critical nuclei. They appear due to some miracle called heterophase fluctuations, which are stochastic events and cannot be described by some deterministic model. The initial idea was just that each phase cannot start from zero thickness – it should start from a critical size particle (about a nanometer). Contrary to standard nucleation theory, the critical nuclei of intermediate phases during reactive diffusion are formed in a strongly inhomogeneous region – the interface between other phases. Therefore, from the very beginning they have to allow the diffusion fluxes pass through themselves. Evidently, fluxes change abruptly when passing across each new-formed boundary of the newly formed nucleus, and thus drive the boundary movement. This picture of interface movement due to flux steps is well known for diffusion couples under the name of “Stephan problem” and refers to diffusive interactions between neighboring phases. Yet, the initial width of each phase is taken to be the critical nucleus size (instead of zero). The peculiarity of the initial stage is just the possibility that the width of some phase nucleus (distance between left and right boundaries) can decrease as well as increase. If it decreases, the nucleus becomes subcritical and should disappear. Usually it happens if the neighboring phases have larger diffusivity and comparative thickness.

Methods. 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 $dC$.

**Originality.** Computer simulation can not describe fairly well interface curvature influence on intermediate phase layers kinetics during chemical diffusion [3, 4, 7]. 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, $X$, with respect to time is given by [2]

$$\frac{dX}{dt}=(l-dC)DdC/(XC_L(l-C_R)) \tag{1}$$

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

$$X^2 = 2(l-dC)Ddt/(C_L(l-C_R))=K^2 t \tag{2}$$

($K$ is the growth rate constant).

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

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

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]

$$\frac{dR}{dt}=(C_LrL/r_R+(l-C_R)r_R/r_L)DdC/(RC_L(l-C_R)) \tag{4}$$

for a spherical sample and by

$$\frac{dR}{dt}=(C_L+(l-C_R)r_R/r_L)DdC/(C_L(l-C_R)r_Rln(r_R/r_L)) \tag{5}$$

for a cylindrical sample (see fig.1).

![Fig.1. The phase grows in a spherical or cylindrical sample.](image)

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 (see fig.2).
Experimen results had confirmed the theoretical calculation both qualitatively and quantitatively [1, 3, 5, 7].

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

\[ P_A = -\frac{1}{3} tr \sigma_A \]  \( \text{(6)} \)

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 \( \beta \)-brass growth between Cu and \( \gamma \)-brass after Zn has disappeared at 400°C in cylindrical sample and in a planar sample. The \( \beta \)-brass begins to grow under high pressure created by growing the \( \gamma \)-brass layer in the cylindrical sample (see fig.2) [1, 3, 6, 7].

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 \( d_c \), 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.

References:

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