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# SOLID-PHASE REACTIONS IN POWDER MIXTURES – A DIVIDED-COUPLE MODEL

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*A new model of solid-phase reactions in binary powder mixtures is developed, namely, the model of a divided diffusion couple with different free surface areas $S_A$ and $S_B$. Numerical modeling based on ideas of the theory of diffusion competition of phases leads to the conclusion that the ratio $S_A/S_B$ is a controlling parameter of the process, affecting the kinetics and phase composition of the system.*

In the present work the kinetics of diffusion-controlled solid-phase reactions in powder systems is modeled. For these processes the Yander, Ginstling and Bronstein, and Carter models are best known [1, 2]. Below a new model of diffusion in powders is proposed for consideration - a divided diffusion couple model. Here by numerical methods we investigate the development of a diffusion process according to the new model and factors that affect its kinetics and result.

The model in question reflects the situation in the initial stage of sintering of powder mixtures, when the particles still preserve individuality and each initial component has a branched system of surfaces that are in "good" diffusion contact through surface or gas diffusion [3, 4]. This is possible when both components are high-melting and the sintering temperature is substantially lower than the melting temperature for each of them; therefore particles of one component are not enveloped by the other.

Semiinfinite bars $A$ and $B$ with different cross sections $S_A$ and $S_B$ are connected by a vacuum interlayer. We consider the time of transfer through the interlayer to be much smaller than the characteristic time of diffusion in the bars.

Let the existence of three intermediate phases be possible between mutually insoluble $A$ and $B$ on the phase diagram (the program for the given model enables us to consider the situation for $N$ of intermediate phases). In the process of diffusion the formation of intermediate phases on the surfaces of $A$ and $B$ begins in accordance with the concentration preparation. By writing the balance equations and solving this system we obtained the equations of thickness growth for each intermediate phase. Here, for the example, are these equations for regime $a$ (see Fig. 1):

$$\frac{d\Delta X_1}{dt}=\frac{1}{C_2-C_1}\left(D_1\frac{\Delta C_1}{\Delta X_1}\frac{C_2}{C_1}-D_2\frac{\Delta C_2}{\Delta X_2}\right);$$

$$\frac{d\Delta X_2}{dt}=\frac{1}{C_3-C_2}\left(-\frac{S_A}{S_B}D_3\frac{\Delta C_3}{\Delta X_3}+D_2\frac{\Delta C_2}{\Delta X_2}\frac{C_3-C_1}{C_2-C_1}-D_1\frac{\Delta C_1}{\Delta X_1}\frac{C_3-C_2}{C_2-C_1}\right);$$

$$\frac{d\Delta X_3}{dt}=\frac{1}{C_3-C_1}\left(D_3\frac{\Delta C_3}{\Delta X_3}\frac{1-C_2}{1-C_3}-\frac{S_A}{S_B}D_2\frac{\Delta C_2}{\Delta X_2}\right).$$

One of the problems arising in computer modeling of this process is the choice of the regime for which we write the equations of growth, i.e., in the initial stage of emergence of nuclei of the intermediate phases not only is regime $a$ possible but also regimes $b$, $c$, and $d$ (see Fig. 1). There are seven possible regimeds for three intermediate phases. (As the number of intermediate phases increases, the number of possible regimes grows.)

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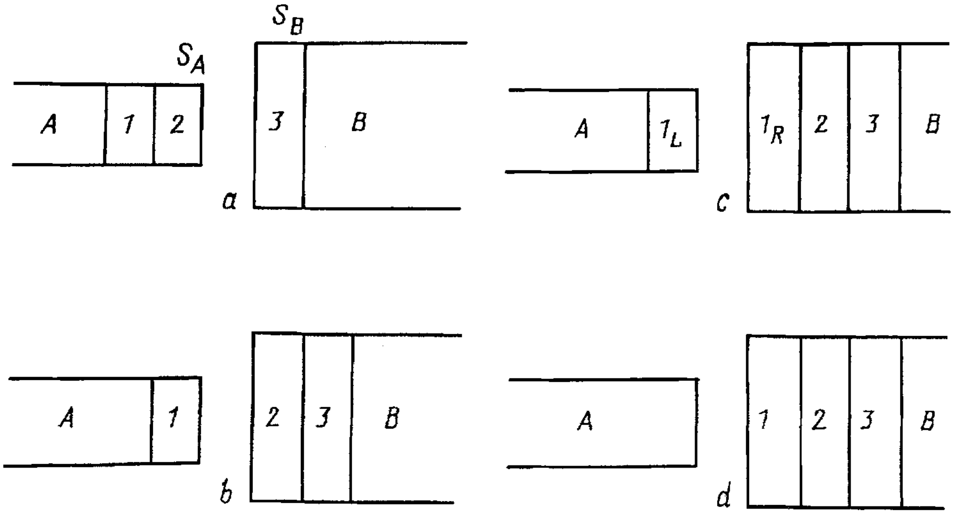

Fig. 1. Possible variants of growth of intermediate phases 1, 2, and 3 on the surfaces of $A$ and $B$, which are in ideal diffusion contact.

We propose the following approach to choosing the regime in the initial stage. If mass transfer between $S_A$ and $S_B$ proceeds much faster than volume diffusion it can be assumed that in the initial period there is the redistribution only between surface layers, and an equilibrium is established between them that is characterized by the surface concentrations $C' = C_B(A)$ and $C'' = C_B(B)$. For surfaces on the same footing the components are distributed uniformly: $C' = S_B/(S_A + S_B) = C''$. If $C'$ is located in the homogeneity region of one of the intermediate phases, say, phase 1, we start to consider the system's development with regime $c$.

If $C'$ is located in the concentration interval between the second and third phases, the process starts with regime $a$.

If $C' < C_1$, the situation corresponding to regime $d$ occurs. Subsequently, in accordance with the diffusion, $C'$ is located in the homogeneity region of the first phase, and therefore in these cases we start the investigation with regime $c$. We proceed similarly in situations where $C' > C_3$.

Now, when the rules of choosing the regime are stipulated, we dwell on some aspects of the algorithm of the program itself. Once $C'$ is determined and the regime is chosen, say, for example, regime $b$, all the phases have a dimension equal to the critical nucleus. And the subsequent "fate" of the nucleus is determined from the results of solving the system of equations for the given case:

$$\frac{d\Delta X_1}{dt} = \frac{1}{C_2 - C_1}\left(D_1 \frac{\Delta C_1}{\Delta X_1}\frac{C_2}{C_1} - \frac{S_B}{S_A} D_2 \frac{\Delta C_2}{\Delta X_2}\right);$$

$$\frac{d\Delta X_2}{dt} = \frac{1}{C_2 - C_1}\left(-\frac{S_A}{S_B} D_1 \frac{\Delta C_1}{\Delta X_1} + D_2 \frac{\Delta C_2}{\Delta X_2}\frac{C_3 - C_1}{C_3 - C_2} - D_3 \frac{\Delta C_3}{\Delta X_3}\frac{C_2 - C_1}{C_3 - C_2}\right);$$

$$\frac{d\Delta X_3}{dt} = \frac{1}{C_3 - C_2}\left(D_3 \frac{\Delta C_3}{\Delta X_3}\frac{1 - C_2}{1 - C_3} - D_2 \frac{\Delta C_2}{\Delta X_2}\right).$$

If the dimensions of phase 3 become smaller than the critical nucleus, i.e., this phase disintegrates, we assume that in place of the disintegrated phase the critical nucleus of the given phase 3 forms again. Therefore we also subsequently continue the calculation in regime $b$. Phase 3 will be in a suppressed state.

If phase 2 disintegrates, it will be "forced back" from the interface of specimens $A$ and $B$ by the nucleus of phase 1 but will not disappear but will exist, as in the case with phase 3, in the form of a layer of critical nuclei (i.e., it will be in a suppressed state). In this case the system switches to regime $c$, for which the calculation is performed by this time by new equations:

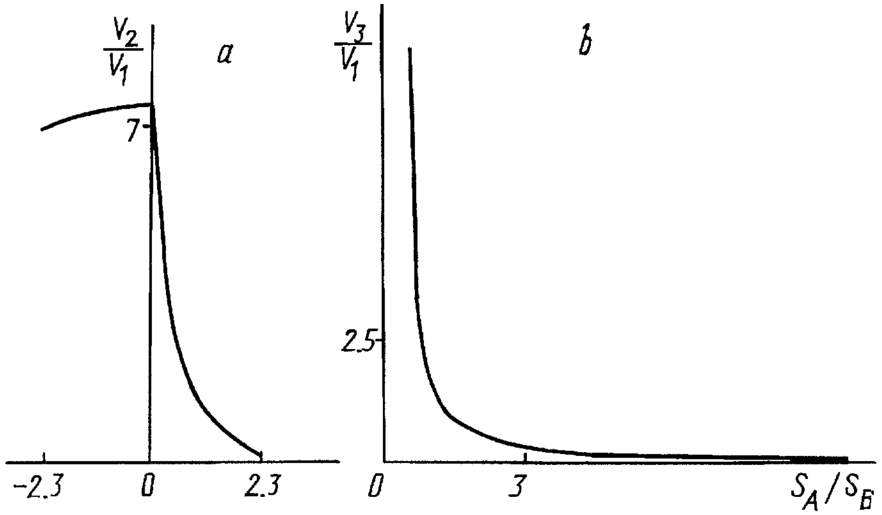

Fig. 2. Ratio of the volume of the second phase $V_2$ to the volume of the first phase $V_1$ (a) and of the volume of the third phase $V_3$ to the volume of the first phase $V_1$ (b) vs. the ratio between the areas of components $A$ and $B$ $S_A/S_B$.

$$\frac{d\Delta X_{1A}}{dt} = \frac{C' - C_1^L}{\Delta X_{1A}} \left( D_{B1}^L - D_{A1}^L + \frac{\widetilde{D}_1^L}{C_1} \right);$$

$$\frac{d\Delta X_{1B}}{dt} = \frac{1}{C_2 - C_1} \left( \frac{C_1^R - C'}{\Delta X_{1B}} (\widetilde{D}_1^R - (C_2 - C_1)(D_{B1}^R - D_{A1}^R)) - D_2 \frac{\Delta C_2}{\Delta X_2} \right);$$

$$\frac{d\Delta X_2}{dt} = \frac{1}{C_3 - C_2} \left( D_2 \frac{\Delta C_2}{\Delta X_2} \frac{C_3 - C_1}{C_2 - C_1} - D_3 \frac{\Delta C_3}{\Delta X_3} - \widetilde{D}_1^R \frac{C_3 - C_2}{C_2 - C_1} \frac{C_1^R - C'}{\Delta X_{1B}} \right);$$

$$\frac{d\Delta X_3}{dt} = \frac{1}{1 - C_3} \left( D_3 \frac{\Delta C_3}{\Delta X_3} \frac{1 - C_2}{C_3 - C_2} - D_2 \frac{\Delta C_2}{\Delta X_2} \frac{1 - C_2}{C_3 - C_2} \right).$$

**Results.** The phase with the largest value of D$\Delta$C is the most competitive one. After a lapse of time the system comes to a stable regime, where growth of all the intermediate phases permitted by the phase diagram is observed.

By varying the ratio $S_A/S_B$ we changed the value of $C'$ from 0.25 to 0.8 in the initial stage. Observation of the system for each value of $C'$ was performed until it reached the stable regime. The calculations were performed on an IBMPC/AT computer for the following values of the parameters: $C_0 = 0$; $C_1 = 0.35$; $C_2 = 0.5$; $C_3 = 0.6$; $C_4 = 1$; $\Delta C_1 = 0.01$; $\Delta C_2 = 0.03$; $\Delta C_3 = 0.06$; $D_1 = 3 \cdot 10^{-13}$ m$^2$/sec; $D_2 = 10^{-12}$ m$^2$/sec; $D_3 = 10^{-13}$ m$^2$/sec; $\Delta X_1 = 25 \cdot 10^{-10}$ m; $\Delta X_2 = 25 \cdot 10^{-10}$ m; $\Delta X_3 = 25 \cdot 10^{-10}$ m; $\Delta X_{1A} = 25 \cdot 10^{-10}$ m; $\Delta X_{1B} = 25 \cdot 10^{-10}$ m; $D_{A1}^L = 5.8 \cdot 10^{-13}$ m$^2$/s; $D_{B1}^R = 5.7 \cdot 10^{-13}$ m$^2$/sec; $D_{B1}^L = 1.5 \cdot 10^{-13}$ m$^2$/sec; $\widetilde{D}_{B1}^R = 1.5 \cdot 10^{-13}$ m$^2$/sec; $\widetilde{D}_1^L = 3 \cdot 10^{-13}$ m$^2$/sec; $\widetilde{D}_1^R = 3 \cdot 10^{-13}$ m$^2$/sec; $C_1^L = 0.345$, and $C_1^R = 0.355$ ($\Delta X_i$ is the size of the critical nuclei of the $i$-th phase).

It turned out that if the value of $S_A/S_B$ was located in the interval from 10 to 1.5 the system reached stable growth of all the phases permitted in the phase diagram in regime *b*. When $S_A/S_B$ was located in the interval 1.5-0.1, this occurred in regime *a*.

By varying the ratio $S_A/S_B$ it is possible in many cases to control the suppression time for the phase of interest (provided this phase is not the most competitive one).

The ratios of phase volumes in the regime of asymptotic growth $V_2/V_1$ and $V_3/V_1$ changed within wide limits with change in $S_A/S_B$ (see Fig. 2). Of interest is the nonmonotonic dependence for $V_2/V_1$, which reaches a maximum at $S_A \approx S_B$. This is apparently associated with the fact that when the regime changes from *a* to *b* phase 2, growing on specimen *A*, grows on *B* (see Fig. 1a and b). This is not observed with phases 3 and 1, as a computer experiment has shown, and the dependence of $V_3/V_1$ is monotonic. Thus, $S_A/S_B$ is a factor that can be used to affect the course and result of a solid-state reaction.

## NOTATION

$S_A$, $S_B$, surface areas of components $A$ and $B$; $\Delta X_i$, width of the $i$-th phase; $\Delta C_i$, concentration interval of the $i$-th phase; $D_i$, mutual diffusion coefficient of the $i$-th phase; $C_i$, concentration of the $i$-th phase; $C''$, total concentration on surfaces that are in ideal diffusion contact; $\Delta X_{1A}$, $\Delta X_{1B}$, thicknesses of subphases of the first phase on bars $A$ and $B$; $D_{A1}^L$, $D_{B1}^L$, $D_{A1}^R$, $D_{B1}^R$, partial coefficients of diffusion of components $A$ and $B$ in the subphases; $D_1^L$, $D_1^R$, coefficients of mutual diffusion of the subphases; $L$, $R$, indexes of the left and right subphases of phase 1.

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