



The transport of the components is almost absent in such compositions in the initial stage of evolution of the system, but this still does not mean that the chemical reaction in these compositions will always be fast. When there is no structural similarity between the starting composition and the reaction product, the nucleation can occur so slowly that the system relaxes to one or simultaneously to several intermediate states. In such a system metastable states, glassy or crystalline phases among them, can form. These states have the same chemical composition as the target product, but another crystal structure. Also, phases of the starting reagents and (or) phases differing in their composition from the target product can form (see, for example, [8, 9]).

One or another type of the system evolution depends on the presence of corresponding nucleation centers. In the listed alternatives of the evolution, along with formation of phases with a chemical composition identical to that of the product, the advantage of the starting composition is lost, because the mean distances between particles of reagents increase, relationship (1) ceases to be true, and transport processes become necessary to yield the product. A similar situation can occur also in the case of formation of phases with the chemical formula of the end product, but another structure, if these phases transform into the end product via intermediate compounds with a composition differing from the composition of the target compound.

Therefore the possibility of a fast solid-phase chemical reaction in a starting composition with the atomic degree of mixing of the reagents is determined by the structural similarity of the starting composition and the target product. In this case the very chemical reaction can be considered as a phase transition. According to Buerger's classification, it will be fast if no changes in the type of chemical bonds, no rearrangements in the first and second coordination spheres, and (or) no ordering (or disordering) processes by the interchange of atoms are required. Otherwise corresponding nucleation centers must be introduced into the system for the process to be fast.

Systems with atomic (or molecular) degree of mixing of reagents are commonly obtained by coprecipitating the reagents from liquid solutions or from gas mixtures, by quenching melts, by cryochemical technology, etc. However, within the framework of these methods it is often difficult to control the structure of the resulting composition [8, 10]. This problem is responsible for the fact that in some cases it is advantageous to sacrifice the spatial proximity of reagents, i.e., a short relaxation time of transport processes, for

creating compositions with a developed network of nucleation centers and, consequently, with a high nucleation rate. In this case the starting composition represents a heterogeneous system in which one or several reagents have a structure similar to the structure of the product, i.e., they are nucleation centers. In spite of the fact that in such systems the transport of components begins to affect significantly the solid-phase reaction, there are cases when the relaxation time of transport processes is rather short. Among these compositions are the systems with mean distances between centers of the particles of reagents comparable to the thickness of a two-dimensional nonautonomous phase  $h_{2n}$ , i.e., meeting relationship (2):

$$d \approx h_{2n}. \quad (2)$$

We will set off such systems into the second group. It was shown in [6, 11] that all the processes in solid-phase systems, limited by the transport of components, are initiated only upon attaining a particular critical temperature equal to the melting point of two-dimensional nonautonomous phases [6]:

$$T_{m2n} = \gamma T_{m(e)}. \quad (3)$$

Here  $T_{m(e)}$  is the melting point of an autonomous phase (the eutectic temperature in the case of multiphase systems);  $\gamma$  is a parameter having close values for similar compounds (Table 1). Therefore, in heterogeneous systems in which condition (2) is met at  $T > T_{m2n}$ , mass transfer of reagents occurs mostly via liquid two-dimensional nonautonomous phases. In general, reagents in such systems are transported by two mechanisms: (1) the flow of liquid two-dimensional nonautonomous phases based on lower-melting reagents  $i$  ( $T > T_{m2n(i)}$ ) across the surface of comparatively high-melting reagents  $j$  ( $T_{m2n(j)} > T$ ) and (2) mass transfer of reagents through liquid two-dimensional nonautonomous phases.

It was shown in [13] that the relaxation time of the first process can be estimated by expression (4):

$$\tau_{so} = k \varphi_{j-i} \mu_{2n(i)} h_{2n(i)} / f. \quad (4)$$

Here  $\varphi_{j-i} = (S_{sp(j)} - S_{cont.(j-i)}) / S_{cont.(j-i)}$ ;  $S_{sp(j)}$  is the specific surface area of the  $j$ th (relatively high-melting) reagent;  $S_{cont.(j-i)}$  is the mean surface area of the particle contact of the  $j$ th and  $i$ th reagents;  $\mu_{2n(i)}$  is the dynamic viscosity of a two-dimensional nonautonomous phase based on the  $i$ th component;  $f$  is the force initiating the flow of the liquid two-dimensional nonautonomous phase across the surface of the  $j$ th

**Table 1.** Experimental and calculated parameters  $\gamma$  [formula (3)] for certain oxides<sup>a</sup>

Compound	$\gamma_{\text{calc}}$	$\gamma_{\text{exp}}$
H <sub>2</sub> O	0.68	0.66 [12]
BO <sub>1.5</sub>	0.78	0.74 [6]
AlO <sub>1.5</sub>	0.65 ± 0.15	0.69 [6]
SiO <sub>2</sub>	0.75 ± 0.05	0.70 [6]
FeO <sub>1.5</sub>	0.54	0.62 [6]

<sup>a</sup> The values are calculated on the assumption that  $\Delta S_{\text{m vib}} \gg \Delta S_{\text{m conf}}$ , where  $\Delta S_{\text{m vib(conf)}}$  is the vibration (configuration) component of the entropy of melting.

**Table 2.** Time of spill-over ( $\tau_{\text{so}}$ ) a liquid two-dimensional nonautonomous phase based on  $A_i$  component over the surface of  $A_j$  component

System $A_j-A_i$	Parameters <sup>a</sup>		$\tau_{\text{so}}$ , s	
	$\varphi_{j-i}$	$\varepsilon_{j-i}$	calculation	experiment <sup>b</sup>
BeO-FeO <sub>1.5</sub>	22	0.9	$1.8 \times 10^2$	$2 \times 10^2$
BeAl <sub>2</sub> O <sub>4</sub> -FeO <sub>1.5</sub>	25	0.8	$1.4 \times 10^2$	$1.5 \times 10^2$
MgO-FeO <sub>1.5</sub>	23	0.9	$1.8 \times 10^2$	$1 \times 10^3$
MgO-MgFe <sub>2</sub> O <sub>4</sub>	12	3.1	$1.5 \times 10^4$	$1 \times 10^4$
AlO <sub>1.5</sub> -FeO <sub>1.5</sub>	23	1.6	$0.9 \times 10^3$	$1.5 \times 10^3$
AlO <sub>1.5</sub> -TiO <sub>2</sub>	22	1.5	$0.7 \times 10^3$	$1 \times 10^3$
SiO <sub>2</sub> -FeO <sub>1.5</sub>	80	7.5	$2.6 \times 10^9$	$4.5 \times 10^4$

<sup>a</sup> Starting data for the calculation of the parameters were taken from [6, 14]. <sup>b</sup> Experimental data of [14–16].

component. Its value is determined by the difference in the surface energies of the  $j$ th and  $i$ th reagents ( $\Delta\sigma_{(j-i)}$ );  $k$  is a constant close to unity.

An examination of relaxation times  $\tau_{\text{T}}$  obtained under the conditions when  $\mu_{2n(i)}$  and  $f$  are variables (Table 2) shows that if the condition  $\varepsilon_{j-i} = \log \Psi_{j-i} \leq 1$  [where  $\Psi_{j-i} = \mu_{2n(i)} h_{2n(i)} / (f 1c)$ ] is met, the contact factor  $\varphi_{j-i}$  only slightly affects the total rate of a solid-phase reaction, because in this case the maximal relaxation time of the reagent transport into the reaction zone is no longer than 2–3 min, i.e., it is much shorter than the time required for a solid-phase reaction to occur (Table 3). Otherwise the reaction can be expected to be fast only in starting compositions with minimal  $\varphi_{j-i}$ , i.e., with a maximal degree of spatial conjugation of reagents ( $\chi_{j-i} = 1 - \varphi_{j-i}$ ). This examination was carried out for temperatures close to the melting point of the two-dimensional nonautonomous phase, when  $h_{2n(i)}$  only slightly varies with

temperature, remaining at almost the same level of  $h_{2n(i)} \sim 1\text{--}10$  nm for all the systems [6, 19, 20].

The relaxation time of the mass transfer of reagents through liquid two-dimensional nonautonomous phases depends on  $d$  and on the effective rate of diffusion of the reagents in a liquid two-dimensional nonautonomous phase  $D_{\text{eff}}$  [equation (5)]:

$$\tau_{\text{d}} \approx d^2/D_{\text{eff}} \quad (5)$$

When a synthesis is carried out at  $T \sim T_{\text{m}2n}$  and, consequently, in systems with  $d \sim 1\text{--}10$  nm, this process can be neglected even for reasonably viscous two-dimensional nonautonomous phases (with small  $D_{\text{eff}}$ ) owing to relatively small values of  $\tau_{\text{d}}$ . At high homologous temperatures  $t = T/T_{\text{m}} = 0.95\text{--}1$  the value of  $h_{2n}$  and, consequently, the values of  $d$  sharply increase (Fig. 2). This results in the increased relaxation time  $\tau_{\text{d}}$ . In this case the mass transfer through a liquid two-dimensional nonautonomous phase can become the limiting stage of the solid-phase reaction, and low values of  $D_{\text{eff}}$  will result in a considerable deceleration of the chemical reaction. In such a situation the reaction can be accelerated only by decreasing the viscosity (increasing  $D_{\text{eff}}$ ) of the two-dimensional nonautonomous phase, for example, by introducing small additions of appropriate compounds.

Compositions meeting condition (2) can generally consist of solid domains of autonomous phases having various shapes: filamentary, lamellar, or isometric. However, the systems currently realized in technology consist of particles of one reagent of any shape, covered with a layer of another reagent, or of mixtures of isometric particles regularly distributed over the space. In the latter case it is almost impossible to achieve high degrees of spatial conjugation of reagents. Hence such compositions will ensure a high rate of chemical reaction only if  $\varepsilon_{j-i} \leq 1$ .

To the third group we will assign the starting compositions in which the mean distances between the centers of the particles of reagents meet relationship (6):

$$d \gg h_{2n} \quad (6)$$

If temperatures of the synthesis are close to melting points of two-dimensional nonautonomous phases, relationship (6), as follows from [20], is met for the  $d$  values of the order of 0.1  $\mu\text{m}$  and greater. Solid-phase reactions in such compositions involve fairly distant transport of the components. At the same time, if a pathway for a fast mass transfer is organized in the reaction system, the rate of a chemical reaction can be sufficiently high even in this group of systems.

**Table 3.** Effect of the history of the starting composition on the rate of solid-phase chemical reactions, by the example of  $\text{AlO}_{1.5}\text{-MeO}_n$  systems (Me is Be, Si, Ti)

System	Method for preparing the starting composition	Distances $d$ between centers of reagent particles, nm	Relaxation time of the synthesis at $T \sim T_{m2n}$ , s
$\text{AlO}_{1.5}\text{-SiO}_2$	Controlled hydrolysis of solutions of metal alcoholates	$\sim N \times 10^{-1}$	$\sim 10^2$
$\text{AlO}_{1.5}\text{-TiO}_2$	"	$\sim N \times 10^{-1}$	$\sim 10^2$
$\gamma\text{-AlO}_{1.5}\text{-SiO}_2$	Molecular layering of the silicon oxide component	$\sim N \times 10^0$	$\sim 10^2$
$\gamma\text{-AlO}_{1.5}\text{-TiO}_2$	Molecular layering of the titanium oxide component	$\sim N \times 10^0$	$\sim 10^2$
$\alpha\text{-AlO}_{1.5}\text{-BeO}$	Mechanical mixing of the components	$\geq 10^4$	$\sim 10^3$
$\alpha\text{-AlO}_{1.5}\text{-SiO}_2$	"	$\geq 10^4$	$\sim 10^5$
$\gamma\text{-AlO}_{1.5}\text{-SiO}_2$	"	$\geq 10^3$	$\sim 10^4$
$\alpha\text{-AlO}_{1.5}\text{-TiO}_2$	"	$\geq 10^3$	$\sim 10^5$
$\gamma\text{-AlO}_{1.5}\text{-TiO}_2$	"	$\geq 10^3$	$\sim 10^4$

<sup>a</sup> The data of [3, 4, 9, 16–18] were used;  $N$  is a number from the (1, 10) interval.

Since the diffusion coefficients in solid phases are by four orders of magnitude lower than the diffusion coefficients in liquid two-dimensional nonautonomous phases [21], a fast transport of reagents to the reaction zone can be expected if a large volume fraction of two-dimensional nonautonomous phases is maintained in the system. A high rate of mass transfer of reagents through the liquid two-dimensional nonautonomous phases is associated not only with relatively high diffusion coefficients and, consequently, with a fast diffusion transfer, but also with a cooperative motion (flow) of the two-dimensional nonautonomous phase under the action of force  $f$  resulting from the difference between the surface energies of reagents and from the gradient of the chemical potential along the surface of particles [22].

Solid reagents can be transported rapidly also through the gas phase if they are highly volatile. The condition of a high reaction rate in this case is similar to the preceding condition, namely, a large specific surface area of reagents and a product (minimal values of  $\chi$ ) must be maintained in the course of the reaction. Since chemical reactions of the latter type, strictly speaking, are not among pure solid-phase reactions (Fig. 1), they are not discussed in this work.

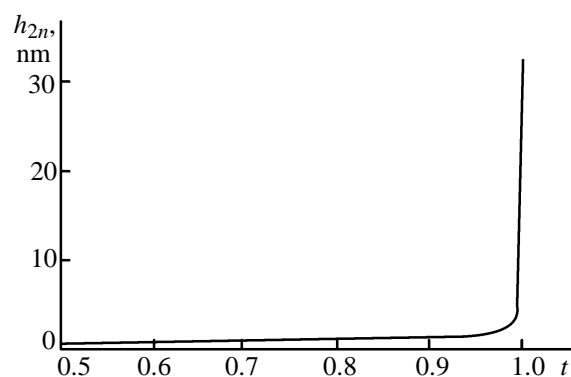
A mechanism providing an increase and maintenance of large volume fractions of two-dimensional nonautonomous phases in the course of the reaction has been described in [3, 4]. Such a mechanism is realized in a solid-phase reaction if a number of conditions are met: (1) the relaxation time of the transfer of components through the two-dimensional nonautonomous phases and the time of nucleation are small and comparable to each other, and (2) the rates

of the growth of nuclei and of the grains of starting components are much lower than the rate of nucleation. In this case the volume fractions of the two-dimensional nonautonomous phases  $V_{2n}$  and of the product phase  $V_a$  increase exponentially with time [equations (7), (8)] [3]:

$$V_a = V_{2n}(0) k_1^{-1} \exp[E/(RT)] \times (\exp\{k k_1 \exp[-(W + E)/(RT)] \tau\} - 1), \quad (7)$$

$$V_{2n} = V_{2n}(0) \exp\{k k_1 \exp[-(W + E)/(RT)] \tau\}. \quad (8)$$

Here  $W$  is the work of nucleation;  $E$  is the activation energy of the transfer of the components from the autonomous phase to the two-dimensional nonautonomous phase;  $k$  and  $k_1$  are coefficients slightly varying with time;  $V_{2n}(0)$  is the volume fraction of the



**Fig. 2.** Thickness of two-dimensional nonautonomous phase  $h_{2n}$  as a function of homologous temperature  $t = T/T_m$ . Calculation was carried out for  $t_{m2n} = T_{m2n}/T_m = 0.65$  by a formula given in [20].

two-dimensional nonautonomous phases in the starting composition;  $T$  is temperature, K;  $\tau$  is time;  $R$  is the universal gas constant. Such a pattern of increasing volume fractions of the product and of the two-dimensional nonautonomous phases in the system is accounted for by the fact that the processes of nucleation and transport of reagents are related by a positive feedback. The nucleation under the conditions when the rate of the growth of nuclei can be neglected increases the fraction of the liquid two-dimensional nonautonomous phases in the system at  $T > T_{m2n}$  and, consequently, facilitates the transport of reagents to the reaction zone. An increase in the rate of transport processes increases the number of the resulting nuclei, because it increases the surface area of the contact of reagents. Following this cycle, the process proceeds in an avalanche-like way until either the reagents are exhausted, or the transport pathway is increased to the limiting values for such a mechanism, or the product particles grow together to form a layer separating the reagents.

Similar mechanisms of self-accelerating heterogeneous chemical reactions were put forward recently to describe the nitriding of liquid aluminum and gallium with dry ammonia [23] and the hydrogenation of some intermetallic compounds in the La-Ni-Cu system [24]. Thus, the mechanism, advanced in [3, 4], of self-acceleration of solid-phase chemical reactions due to the increase in the fraction of two-dimensional nonautonomous phases and, consequently, in the surface of the contact of reagents is applicable to a wider scope of heterogeneous reactions. A similar self-acceleration process seems to be first observed in 1916 by Morgan, who studied the decomposition of formic acid in the presence of sulfuric acid at 40°C (the data are cited by [25]). This reaction resulted in an avalanche-like frothing of solution (exponential increase in the fraction of two-dimensional nonautonomous phases), because the decomposition of formic acid occurred faster in the froth than in the bulk (autonomous) phase.

The above-listed possibilities for occurrence of fast solid-phase chemical reactions in compositions with various  $d$  are confirmed by numerous experimental data. Some of them, descriptively illustrating the efficiency of the described approach to choosing the methods of increasing the rate of solid phase reactions, are given in Table 3.

In this work we did not examine methods for reaction acceleration by various intense energy impacts on a system, for example, laser radiation, neutron flux, high-energy electrons,  $\gamma$ -radiation, blast waves, etc. The mechanism of their influence on solid-phase re-

actions has been considered in detail in [26–31]. Activation of the reactions during so-called non-gaseous combustion (self-propagating high-temperature synthesis [32]) also was not considered here.

High rates of solid-phase chemical reactions in the systems considered in this work were achieved by the proper preparation of a starting composition and by the choice of appropriate temperature. The decisive condition for a high rate of solid-phase chemical reactions in all the cases under consideration is the transfer of a two-dimensional nonautonomous phase into a liquid-like state. Therefore, in spite of the fact that these chemical reactions are solid-phase according to the classification given in Fig. 1, they also can be considered to some extent as liquid-phase processes. Such a situation is typical for any solid-phase processes involving mass transfer: they are activated and begin to occur at a detectable rate only after a particular critical temperature is attained, coinciding with the melting point of a two-dimensional nonautonomous phase.

## REFERENCES

1. Tret'yakov, Yu.D., *Tverdogaznye reaktsii* (Solid-Phase Reactions), Moscow: Khimiya, 1978.
2. Buerger, M.J., *Fortschr. Miner.*, 1961, vol. 39, pp. 9–24.
3. Gusarov, V.V. and Suvorov, S.A., *Zh. Prikl. Khim.*, 1987, vol. 60, no. 9, pp. 1953–1956.
4. Gusarov, V.V. and Suvorov, S.A., *Zh. Obshch. Khim.*, 1988, vol. 58, no. 4, pp. 932–934.
5. Gusarov, V.V., Malkov, A.A., Malygin, A.A., and Suvorov, S.A., Abstracts of Papers, *Int. Conf. on Metallic Coatings and Thin Films*, San Diego, 1994, p. 21.
6. Gusarov, V.V., *Doctoral (Chem.) Dissertation*, St. Petersburg, 1996.
7. Shimiza, A. and Hao, Y.-J., *J. Am. Ceram. Soc.*, 1997, vol. 80, no. 3, pp. 557–568.
8. Kay, B.D. and Assink, R.A., *J. Non-Cryst. Solids*, 1988, vol. 104, no. 1, pp. 112–122.
9. Feltz, A. and Schmidt, F., *J. Eur. Ceram. Soc.*, 1990, vol. 6, pp. 107–110.
10. Jaymes, J. and Dony, A., *J. Am. Ceram. Soc.*, 1992, vol. 75, no. 11, pp. 3154–3156.
11. Gusarov V.V. and Suvorov, S.A., Available from ONIITEKhim, Cherkassy, 1988, no. 787-KhP.
12. Barer, S.S., Kvlividze, V.I., Kurzaev, A.B., Sobolev, V.D., and Churaev, N.V., *Dokl. Akad. Nauk SSSR*, 1977, vol. 235, no. 3, pp. 601–603.
13. Gusarov, V.V., Abstracts of Papers, *Vserossiiskoe*

- soveshchanie "Nauka i tekhnologiya silikatnykh materialov v sovremennykh usloviyakh rynochnoi ekonomiki"* (All-Russian Conf. "Silicate Materials Science and Technology under Modern Conditions of Market Economy"), Moscow, 1995, p. 86.
14. Gusarov, V.V., Malkov, A.A., Malygin, A.A., and Suvorov, S.A., *Zh. Prikl. Khim.*, 1994, vol. 67, no. 6, pp. 935–941.
  15. Gusarov, V.V., Malkov, A.A., Malygin, A.A., and Suvorov, S.A., *Izv. Ross. Akad. Nauk, Neorg. Mater.*, 1995, vol. 31, no. 3, pp. 346–350.
  16. Smirnova, Zh.N., Gusarov, V.V., Malkov, A.A., Firsanova, T.V., Malygin, A.A., and Suvorov, S.A., *Zh. Obshch. Khim.*, 1995, vol. 65, no. 2, pp. 199–204.
  17. Gusarov, V.V., Malkov, A.A., Malygin, A.A., and Suvorov, S.A., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 4, pp. 554–557.
  18. Huling, J.S. and Messing, G.L., *J. Am. Ceram. Soc.*, 1989, vol. 72, no. 9, pp. 1725–1729.
  19. Dash, J.G., *Contemp. Phys.*, 1989, vol. 30, no. 2, pp. 89–100.
  20. Gusarov, V.V. and Suvorov, S.A., *Zh. Prikl. Khim.*, 1993, vol. 66, no. 7, pp. 1529–1534.
  21. Kaur, I. and Gust, W., *Fundamentals of Grain and Interphase Boundary Diffusion*, Stuttgart, 1989.
  22. Deryagin, B., Sidorenkov, G., Zubashchenko, E., and Kiseleva, E., *Kolloidn. Zh.*, 1947, vol. 9, no. 5, pp. 335–347.
  23. Grekov, F.F., *Zh. Prikl. Khim.*, 1994, vol. 67, no. 2, pp. 230–234.
  24. Semenenko, K.N., Yakovleva, N.A., and Burnasheva, V.V., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 4, pp. 529–534.
  25. Tret'yakov, Yu.D., Oleinikov, N.N., Gudilin, E.A., Vetegel, A.A., and Baranov, A.N., *Izv. Akad. Nauk, Neorg. Mater.*, 1994, vol. 30, no. 3, pp. 291–305.
  26. Heinicke, G., *Tribochemistry*, Berlin: Akademie, 1984.
  27. Bugaenko, L.T., Kuz'min, M.G., and Polak, L.S., *Khimiya vysokikh energii* (High Energy Chemistry), Moscow: Khimiya, 1988.
  28. Horie, Y. and Kipp, M.E., *J. Appl. Phys.*, 1988, vol. 63, no. 12, pp. 5718–5727.
  29. Kardashov, G.A., *Fizicheskie metody intensivatsii protsessov khimicheskoi tekhnologii* (Physical Methods of Intensification of the Processes of Chemical Technology), Moscow: Khimiya, 1990.
  30. Boldyrev, V.V., Voronin, A.P., Lyakhov, N.Z., and Kanimov, B.K., *Zh. Vses. Khim. O-va*, 1990, vol. 35, no. 5, pp. 540–545.
  31. Batsanov, S.S., Gavrilkin, S.M., Markis, F.D., and Meiers, M.A., *Zh. Neorg. Khim.*, 1997, vol. 42, no. 1, pp. 110–117.
  32. Merzhanov, A.G., *Fizicheskaya khimiya. Sovremennye problemy* (Physical Chemistry. Modern Problems), Moscow: Khimiya, 1983, pp. 6–45.