The role of non-autonomous phases in the formation and transformation of solid-phase oxide systems

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ABSTRACT It is shown that the nature of processes in oxide solid-phase systems, primarily in nanosized ones, is determined by the behavior of the substance in a non-autonomous state. The composition of non-autonomous phases, the temperature of transition of non-autonomous phases to a liquid-like state, the equilibrium (locally equilibrium) and metastable thickness of non-autonomous phases, and the viscosity of the liquid-like non-autonomous phase are considered as the main parameters of non-autonomous phases.

1. Introduction

According to the definition given in the works of Defay and Prigogine [1, 2], surface phases, as well as phase and grain boundaries in polycrystalline systems are considered in a number of works as non-autonomous phases [4–46]. Such a definition has a number of advantages due to its more general nature. In this regard, the present paper employs this particular terminology.

A large number of both original works and reviews have been and are devoted to the formation and transformation of solid-phase oxides [46–66]. It should be noted that in the majority of the works on this topic, which have become classic, the main attention is paid to the influence, which the diffusion of components in bulk (autonomous) phases has on the processes occurring in the systems based on solid phases [61–66]. However, recent decades have shown an increased interest in studying the features of phase formation processes in nanopowders [47–61]. The volume fraction of non-autonomous phases in nanocrystalline systems, including those based on oxide nanocrystals, can be very significant [9]. This, apparently, should be taken into account in experimental studies, when determining the mechanisms and kinetics of the processes of phase formation and transformation, and when constructing physicochemical models of chemical and structural transformations in nanocrystalline systems. By now, there are no works that would analyze studies on the influence of the composition, structure, and properties of the non-autonomous phases on processes in solid-phase systems and, in the first place, in nanocrystalline systems. Of particular interest is the study of phase formation and phase transformation processes in materials based on oxide systems, since this is apparently the class of materials most widely represented in nature and in technology [65–73].

In relation to the listed reasons, this work is aimed at analyzing the results available in the literature, which are related to the determination of the properties and behavior of non-autonomous phases in polycrystalline systems and their influence on the course of phase formation processes and structural transformations, mainly in oxide phases.

2. Non-autonomous phases in polycrystals: composition, structure, properties

Conclusions that the composition, structure and surface properties of solid substances differ from their bulk properties were made on the basis of empirical data already in the works of 19th century scientists [74–76]. The works of Gibbs [77] theoretically consider some features of the behavior and properties of the surface of substances (interphase regions) from a thermodynamic standpoint. A detailed thermodynamic description of the regions between bulk (autonomous) phases as non-autonomous phases was given in [1–3]. These works considered the non-autonomous phases as regions between the coexisting (bordering on each other) autonomous phases, having a finite thickness, composition and structure, and changing from one autonomous phase to another.

It was shown in [4, 78–80] that such a description of non-autonomous phases is equivalent from the thermodynamic point of view to such a consideration of surface phases, in which all their 'excessive' properties are attributed to some

two-dimensional surface, as was proposed in [1–3]. This statement is absolutely true when the volume fraction of non-autonomous phases is negligibly small compared to the volume fraction of autonomous phases, i.e. for the case of macrocrystalline systems. When the particle (crystallite) sizes decrease to nanometer values, the volume fraction of non-autonomous phases increases sharply [11, 15]. In this case, it is no longer possible to ignore the thickness of non-autonomous phases. It is especially important to know the sizes and behavioral features of non-autonomous phases when considering the kinetics of processes in solid-phase systems [15].

The work [81] shows a certain similarity in the behavior of substance at the boundaries of different autonomous phases and at the boundaries of grains of one phase. That is why further on, as is shown in [81], non-autonomous phases can be understood as layers of finite thickness also in the autonomous phases contact area and at the boundaries of grains of the same phase, if these layers have not formed their own autonomous phase.

A detailed analysis of experimental data and the construction of calculation models, carried out in [81], showed that in the case of high-angle boundaries of grains of the same autonomous phase of variable composition, components redistribution between the autonomous and non-autonomous phases can be described in the first approximation by a dependency shown in Fig. 1. This result was obtained assuming that the non-autonomous phases formed at high-angle boundaries of the autonomous phase grains contain a thin layer of amorphous substance (Fig. 2). Naturally, a dependency similar to that shown in Fig. 1 cannot be expected in cases with low-angle and special boundaries of grains.
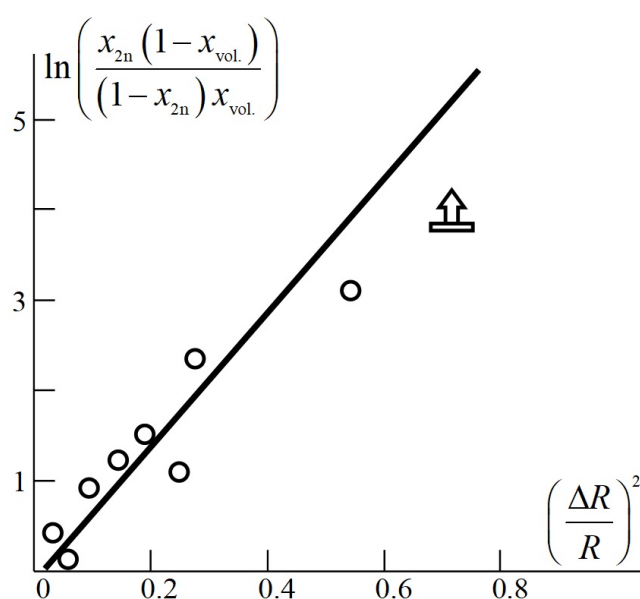

FIG. 1. Dependence of the impurity component distribution between the autonomous and non-autonomous phases [81]

It should be noted that the described effect of components redistribution between the autonomous and non-autonomous phases in particles based on crystalline autonomous phases can lead to the formation of structures of the core-shell type. In these structures, the shell appears due to the segregation of some components located on the particles surface in the non-autonomous phase. This effect is most noticeable when obtaining nanocrystalline particles. To date, a large number of examples of such structures formation are known [82–87]. A variant of the mechanism for the core-shell nanoparticles formation is described in [87]. However, apparently, this is only a special case of such nanostructures formation, and this area will be expanded subsequently.

When different solid autonomous phases are in contact, then the composition of the corresponding non-autonomous phase at temperatures not much different from the eutectic temperature will be close to the eutectic composition [81]. It should be noted that this result allows for describing the phenomenon of eutectic melting from positions different from the traditional ones [88].

Another case where it is convenient to use the term 'non-autonomous phase', or more precisely, the 'non-autonomous state of substance', is the state of substance under conditions of spatial limitations, when the amount of substance is insufficient for the formation of an autonomous phase with a composition and structure characteristic of the specified temperature and pressure. Such states may be exemplified by nanoparticles of certain sizes, thin surface layers, as well as the substance in micropores, in nanochannels, and in the matrices of composites with inclusions of nanoparticles at a certain placement density [89–106]. In this case, when the spatial restrictions are chemically inert, a substance, being in a non-autonomous state, will be unable to change the initially specified composition, but will have a structure different from that of the autonomous phase of the same composition at the same temperature and pressure.
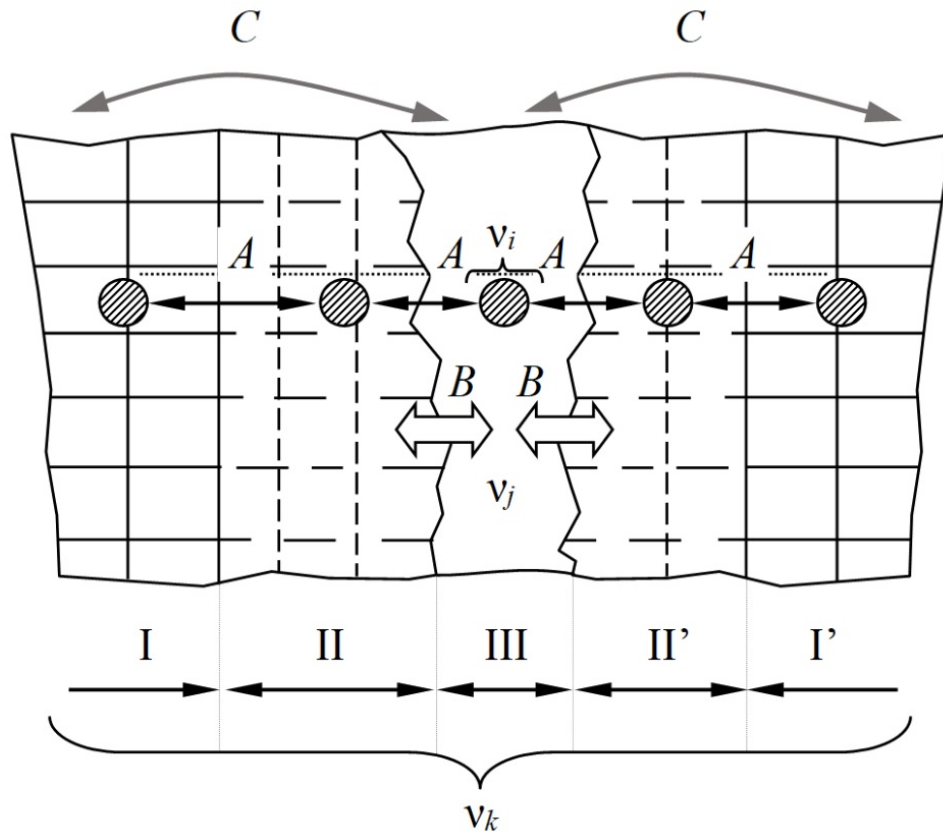
FIG. 2. Schematic representation of a 2-D non-autonomous phase (regions II, II', III) and relaxation processes in a polycrystalline system [81]. **Regions**: ν_i – inside autonomous (I, I'), structured (II,II') and amorphized (III) zones of the non-autonomous phase; ν_j – region coinciding with the amorphized zone of the 2-D non-autonomous phase; ν_k – two grains in contact with each other together with the intergranular formation. **Processes**: A – establishment of the locally equilibrium state in regions ν_i by introducing corresponding changes in the structure and composition; B – establishment of the locally equilibrium thickness of region III without mutual turning of grains; C – turning and shift of grains until the crystal sublattices completely coincide – for polycrystals based on one autonomous phase, or until the energy of translational mismatch is minimized – for systems consisting of different phases

The possibility of a liquid phase appearance at the boundary of solids at a temperature below their melting point was exemplified by ice already in [74, 75], but the quantitative relationship between the melting temperatures of the surface and bulk of solids was revealed only after an of experimental series by Tammann et al. [107]. It should be noted that despite the establishment of a quantitative relationship between the solid phase melting point and the so-called Tammann temperature (T_T) in these works (Table 1), the discovered phenomenon was interpreted incorrectly. For instance, the authors of [107] believed that volume diffusion processes are activated at the Tammann temperature. Only after a series of similar experiments, it was concluded in [108] that the T_T value in processes described in [107] determines the temperature, above which mass transfer is activated at the boundaries of solid phase particles.

TABLE 1. Tammann temperature for different materials

Materials	Tammann temperature	References
Metals	$\sim 0.33\,\mathrm{T}_m$	[107]
Oxide	$\sim 0.57\,\mathrm{T}_m$	
Metals	$\sim 0.3\,\mathrm{T}_m$	[108]

Based on the analysis of [109], the work [110–112] presents the generalized data on the temperature dependency of the diffusion in the crystalline (autonomous) phase, on the surface, and at the boundaries of grains, i.e. in non-autonomous phases. Taking into account the results of [107, 108], as well as the dependency of the surface phase thickness

on temperature [11], these results can be illustrated by Fig. 3. The data presented in Fig. 3 allow concluding that the substance in the non-autonomous phase is found in the liquid (liquid-like) state at temperatures above T_T.
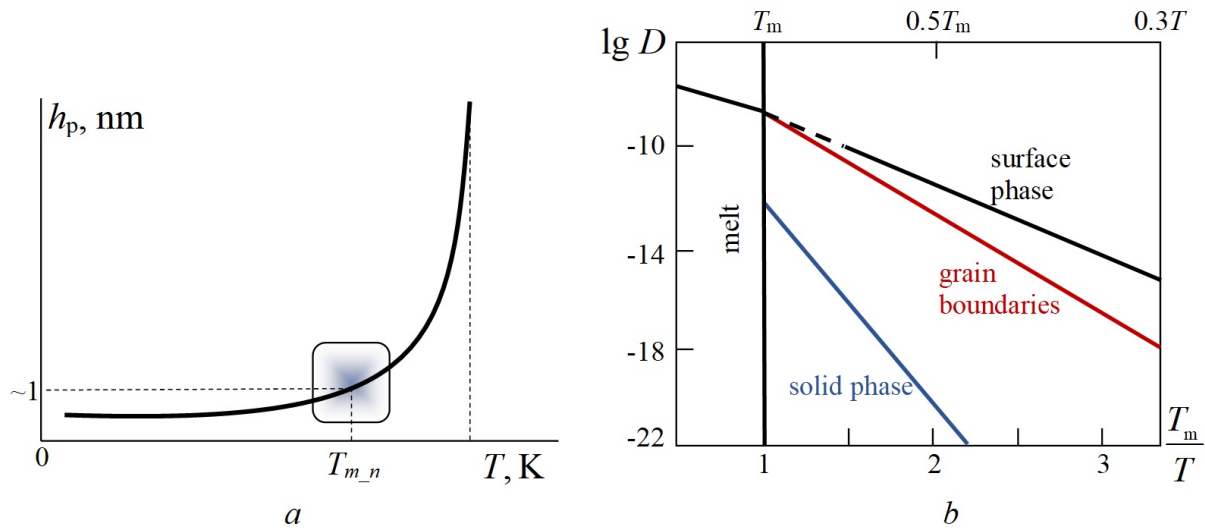

FIG. 3. Temperature dependences of the surface phase thickness (a) and the diffusion coefficients of the substance (b). For case (b), the solid lines are from [81], the dashed line is an extrapolation of the dependence presented in [81]

By now, a significant number of experimental and theoretical works analyze the transition of non-autonomous phases to the liquid (liquid-like) state [113–131]. A detailed thermodynamic analysis of the relationship between the melting temperatures of autonomous and non-autonomous phases was made in [81]. It was shown in [11] that in cases when non-autonomous phases contain a thin amorphous layer of substance, the dependency between the melting temperatures of the autonomous and non-autonomous phases can be represented by the expression

$$T_{m\_n} \approx \frac{1 - \alpha_H}{1 - \alpha_S} T_m, \qquad (1)$$

where $\alpha_H = \Delta H_{am}/\Delta H_m$; $\alpha_S = \Delta S_{am}/\Delta S_m$; T_m – is the autonomous phase melting temperature, K; T_{m_n} – is the melting temperature of the non-autonomous phase of the same composition, K; ΔH_{am} – is the amorphization enthalpy; ΔH_m – is the melting enthalpy; ΔS_{am} – is the amorphization entropy; ΔS_m – is the melting entropy.

Further on, expression (1) was analyzed in [18] for a number of oxide substances, and the limits of variation of the non-autonomous phase melting temperature were determined as a function of the autonomous phase melting temperature for this class of compounds:

$$T_{m\_n} = \gamma T_m, \qquad (2)$$

where γ – is a dimensionless parameter that takes values from 0.55 to 0.75, but most often 0.65.

A comparison of expression (2) with that for the Tammann temperature given in Table 1 shows their good agreement. This result once again confirms that in physical sense the empirical dependency of the Tammann temperature on the substances melting point reflects the dependency of the temperature of the non-autonomous phase transition into the liquid (liquid-like) state on the melting point of the autonomous phase of the corresponding composition. It should be noted that, as was analyzed in [81], the temperature of the non-autonomous phase transition into the liquid-like state depends on the phase structure. For example, in cases of the coherent grain intergrowth, this temperature approaches the autonomous phase melting point [81].

Another important parameter for the analysis of high-temperature processes in polycrystalline systems is the thickness of non-autonomous phases. From the mid-20th century to the present, a large number of experimental, theoretical papers and reviews have been devoted to the problem of determining the thickness and structure of non-autonomous phases. The works [2,115,116,122,126–132] can be cited as an example. An important component of these works is the determination of the dependency of the non-autonomous phase thickness on temperature. The most well-known expressions for the non-autonomous phase thickness as a function of temperature are presented in Table 2. Among the expressions given in this Table, it is possible to single out the dependency described in [81], which differs from the others by two factors. First, this dependency changes at the non-autonomous phase melting point, which was not reflected in other formulas (Table 2). Second, when approaching the melting point of the solid phase, its thickness does not tend to infinity, as in other expressions, but remains a finite (albeit large) value. In this case, the crystal sizes decrease, apparently, to nanometer values. Physically, this means, as was indicated in [81], that the melting of solids can be considered as the

autonomization of the liquid non-autonomous phase with the transition of the crystalline (autonomous) phase to non-autonomous nanoclusters in the melt. To confirm the possibility of such a consideration of the melting process, the work [81] cited [135–144], in which various experimental data and theoretical calculations allowed making conclusions that solid (crystalline) clusters are observed in the melt near the melting point. The existence of nanosized solid clusters above the melting point of the substance, demonstrated in these works, allowed constructing in [145–154] a model of nanofluid flow in nanochannels, which under certain conditions predicts an unusually high flow rate due to the effect of solid clusters slipping along the nanochannel walls. Along with that, the cases where the channel dimensions were smaller than those of the nanoclusters, the effect of sharp deceleration of such liquids flow was described [146].

TABLE 2. Dependence of the thickness of the non-autonomous phase on temperature

Formula	References
$h_p = \alpha \ln(\dfrac{\beta}{T_m - T} + \delta)$	[113]
$h_p = \dfrac{C}{(T_k - T)^{\frac{1}{6}}}$	[4]
$h_p = \dfrac{a}{(T_m - T)^{\frac{1}{24}}}$	[115]
$h_p = \xi \ln(\gamma T)$	[116]
$h_p = \dfrac{a}{(T_m - T)^{\frac{1}{3}}}$	[119]
$h_p = \dfrac{\alpha}{(T_m - T + (T_{m2n} - T)H(T_{m2n} - T)\beta + \delta)^{\frac{1}{3}}}$	[11]

The dependencies of the non-autonomous phase thickness on temperature given in Table 2 describe the equilibrium (locally equilibrium) value of its thickness. However, the dimensional parameters of the particles of a substance in the non-autonomous state may turn out to be larger than those described by these expressions. In such cases, this non-autonomous state can be regarded as metastable, associated with the existence of some spatial or other limitations for mass transfer, described, for instance, in [155]. These limitations on the amount of substance in the system do not allow the formation of an autonomous phase, i.e. a solid phase with a structure that it would have at the given temperature and pressure if the said limitations did not exist. A substance in the metastable non-autonomous state can stably exist in the amorphous or crystalline state, but its crystalline structure will differ from that of the equilibrium (autonomous) phase. Similar cases of metastable non-autonomous states of substance have been experimentally discovered and theoretically described for a large number of oxide compounds and some other substances [94–106]. It should be noted that the thermodynamic estimate of the particle sizes of a substance in some metastable non-autonomous state may differ from the actually observed sizes [89, 156]. This is connected not only with the evaluative nature of the calculated data, but also with the role of kinetic factors, which can play a decisive role at temperatures below the melting point of non-autonomous phases [156].

Another important characteristic of non-autonomous phases for the analysis of interaction processes in solid polycrystalline systems is the viscosity of the liquid (liquid-like) non-autonomous phase. It was shown in [157] that by assuming that the viscosity of a liquid non-autonomous phase at a certain temperature can be calculated by extrapolating the dependency of the viscosity of the molten autonomous phase of the same composition on a given temperature, it is possible to obtain a quantitative match between the experimental and calculated data for the rate of particles migration through ice. Such an approach to predicting the non-autonomous phase viscosity is also corroborated by the temperature dependency of the diffusion coefficients of the substance in it (Fig. 3), since these values are closely related to each other [158]. Based on the above-mentioned nature of the dependency of the non-autonomous phase viscosity on temperature, some phenomena that can be observed during the liquid non-autonomous phase flow in polycrystalline systems were theoretically predicted in [12, 81, 159, 160].

Of considerable interest from the point of view of understanding the structural features of non-autonomous phases are the results of an experimental study of the nature of the viscous behavior of the surface layer (surface – non-autonomous phase) of the crystalline phase, given in [126]. It was experimentally shown in this work that the nature of the viscous behavior of the surface layer at relatively high values of the homologous temperature can only be described if this layer is imagined as inhomogeneous, consisting of a liquid phase with inclusions of solid particles of very small size. It can be noted that essentially this result is close to the conclusions made in [81, 138, 139], in which melting was considered as developing in a rather narrow, but still certain temperature range, as a transition of solid autonomous phase particles to a non-autonomous state, and of the non-autonomous liquid phase to the autonomous one. Another conclusion, apparently very important for understanding the features of the liquid-like non-autonomous phase behavior at high temperatures, is

an experimentally derived conclusion that the thickness of these phases is several times greater compared to the values presented in conclusions of works [161–164].

So to date many basic questions related to the structure and properties of non-autonomous phases remain open. Moreover, this applies both to the region of high values of the homologous temperature, and to the region of temperatures below the melting point of the non-autonomous phase. In the latter case, this is due to the 'frozen' state of the non-autonomous phase, which complicates studies of the processes of approaching this state to equilibrium.

3. Solid-phase reactions and sintering of materials

The experimental works of Tammann and co-authors [107] were aimed at determining the temperature of the onset of active sintering of particles of different composition (T_T). The further studies, which interpreted the effect discovered in these works as associated with the transition of phase boundaries and grains (non-autonomous phases) into the liquid-like state [119], began considering the Tammann temperature (T_T) as a boundary temperature, upon reaching or exceeding which any processes of solid particles interaction, including solid-phase reactions, start [61]. Along with that, the mechanisms and models of solid-phase chemical reactions, the rate of which was determined by the mass transfer between components, were described as those limited by the rate of diffusion in the solid phase [61, 65]. This situation was apparently due to the fact that the volume fraction of non-autonomous phases in these works was significantly smaller than the fraction of solid (autonomous) phases. The transition of a non-autonomous phase to the liquid-like state could increase only the rate of reagent particles agglomeration. This led to a noticeable increase in the contact area of the interacting particles. In addition, point contacts of solid particles were replaced by areas with a liquid-like interlayer. An increase in the rate of components diffusion through the liquid-like non-autonomous phase in the case of interaction of relatively large particles of micron and even submicron sizes could not significantly affect the total mass transfer rate due to the extremely small proportion of non-autonomous phases in such reaction systems.

The situation changed dramatically when chemical reactions began to take place between nanosized reagent particles. For example, it was shown in [166–169] that in nanosized layers obtained by molecular layering [169–173], no interaction between reagents resulting in formation of solid-phase compounds is observed at temperatures below the non-autonomous phase melting point, and upon reaching this temperature, the synthesis proceeds at such a high rate, which cannot be described as that limited by solid-phase diffusion. A similar situation is observed in the case of synthesizing solid-phase compounds from nanosized reagent powders [174–178]. An analysis of the processes of solid-phase compounds synthesis in oxide compositions consisting of nanosized reagent particles in [179] yields a somewhat paradoxical conclusion that all solid-phase chemical reactions occurring at a high or simply noticeable rate are liquid-phase to some extent, i.e. a liquid-like non-autonomous phase must first form in the reaction system for such reactions to start. The role of non-autonomous phases in the processes of solid particles interaction was considered in more detail in [15]. Numerous examples of the influence of liquid-like non-autonomous phases on mass transfer in solid-phase systems and on the synthesis of solid-phase compounds are given in [28–34, 36, 180].

Other processes in solid-phase systems that start only after the transition of the non-autonomous phases to the liquid-like state, as was shown, e.g. in [81, 107, 108], are the processes of sintering and inelastic deformation of ceramics by the mechanism of high-temperature creep. It should be noted that the role of liquid-like non-autonomous phases can consist not only in increasing the rate of particles agglomeration due to the facilitation of their sliding relative to each other due to the appearance of a liquid-like non-autonomous phase, but, as was shown in [9, 10, 12, 81], also by the transformation-transport mechanism of solid-phase particles interaction. Such interactions are schematically illustrated in Fig. 4a,b. It was shown in [81] that proceeding from a more general model relationship and variation of the expressions for the non-autonomous phase viscosity, the transformation-transport mechanism makes it possible to obtain practically the same dependencies as a set of known models of sintering and inelastic deformation of materials obtained by applying different mechanisms. The corresponding comparison of models is given in Table 3.

An important role in solid-phase chemical reactions, in the processes of sintering and inelastic deformation of ceramics, can be played by small additives of relatively fusible solid-phase substances, even in cases where they are chemically inert to other components of the solid-phase system. It was shown in [5, 81, 182] that such additives get quickly distributed over the surface of other components at a temperature equal to or higher than the melting point of the non-autonomous phase based on such additives. This, in turn, promotes agglomeration of particles of the solid-phase system and, as a consequence, an increase in the rate of solid-phase synthesis and sintering of ceramics.

Another area for which the transition of non-autonomous phases to the liquid-like state is important is the construction of phase equilibrium diagrams in solid-phase systems. For instance, while the approach to the equilibrium state in oxide solid-phase systems at high temperatures requires hours, tens or hundreds of hours [185], the process of approaching equilibrium in the low-temperature region can take a year or more [185], or even geological epochs. In this regard, the analysis of characteristic values of the diffusion rate in solid phases in [185] resulted in proposing the time criterion as a criterion for dividing into high-temperature and low-temperature processes. When the time of approaching the equilibrium state in a solid-phase system is a year and more, then it is proposed to define such systems as low-temperature ones [185]. However, the above analysis of the role of non-autonomous phases in the behavior of solid-phase systems allows proposing another criterion for dividing solid-phase processes into high-temperature and low-temperature ones.

TABLE 3. Parametric dependence of shrinkage during sintering and hot pressing of materials

| Model	Time, t	Average particle radius $\hat{R} = \dfrac{d}{2}$	Mechanical force per square of the average particle radius, $f = \dfrac{F}{\hat{R}}$
Transformation-transport mechanism (approximation without taking into account the contribution of dislocation tubes to transport processes)			
Asymptotic equation of the initial stage of sintering [81]	t^1	$\hat{R}^{-1}$	–
Equation of sintering limited by mass transfer of a substance through a liquid non-autonomous phase [81]	$t^{\frac{2}{3}\cdot\frac{n}{1+n}}$	$\hat{R}^{-\frac{2}{3}\cdot\frac{1+2n}{1+n}}$	$f^{\frac{2}{3}\cdot\frac{1}{1+n}}$
n=0.5	$t^{\frac{1}{2}}$	$\hat{R}^{-\frac{8}{9}}$	$f^{\frac{4}{9}}$
n=1 (Newtonian fluid)	$t^{\frac{1}{3}}$	$\hat{R}^{-1}$	$f^{\frac{1}{3}}$
n=2	$t^{\frac{4}{9}}$	$\hat{R}^{-\frac{10}{9}}$	$f^{\frac{2}{9}}$
n=3	$t^{\frac{1}{2}}$	$\hat{R}^{-\frac{7}{6}}$	$f^{\frac{1}{6}}$
n→ ∞	$t^{\frac{2}{3}}$	$\hat{R}^{-\frac{4}{3}}$	f^0
Compaction due to redistribution of particles in the liquid phase [183]	t^{1+x}	$\hat{R}^0$	f^1
Volume diffusion			
[182]	$t^{0.49}$	$\hat{R}^{-0.98}$	$f^{0.49}$
[183]	$t^{0.4}$	$\hat{R}^{-0.8}$	$f^{0.40}$
[184]	$t^{\frac{1}{2}}$	$\hat{R}^{-1}$	$f^{\frac{1}{2}}$
[182]	$t^{0.46}$	$\hat{R}^{-0.92}$	$f^{0.46}$
[116]	$t^{0.48}$	$\hat{R}^{-0.96}$	$f^{0.48}$
Volume diffusion to grain boundaries and spherical surface of particles [184]	$t^{0.53}$	$\hat{R}^{-1.06}$	$f^{0.53}$
Grain boundaries diffusion			
[182]	$t^{\frac{1}{3}}$	$\hat{R}^{-1}$	$f^{\frac{1}{3}}$
[184]	$t^{\frac{1}{3}}$	$\hat{R}^{-1}$	$f^{\frac{1}{3}}$
[184]	$t^{0.31}$	$\hat{R}^{-0.93}$	$f^{0.32}$
[116]	$t^{0.32}$	$\hat{R}^{-0.96}$	$f^{0.31}$
Limited dissolution of the solid phase in the liquid and diffusion-viscous flow of the liquid phase [183]	$t^{\frac{1}{3}}$	$\hat{R}^{-1}$	$f^{\frac{1}{3}}$
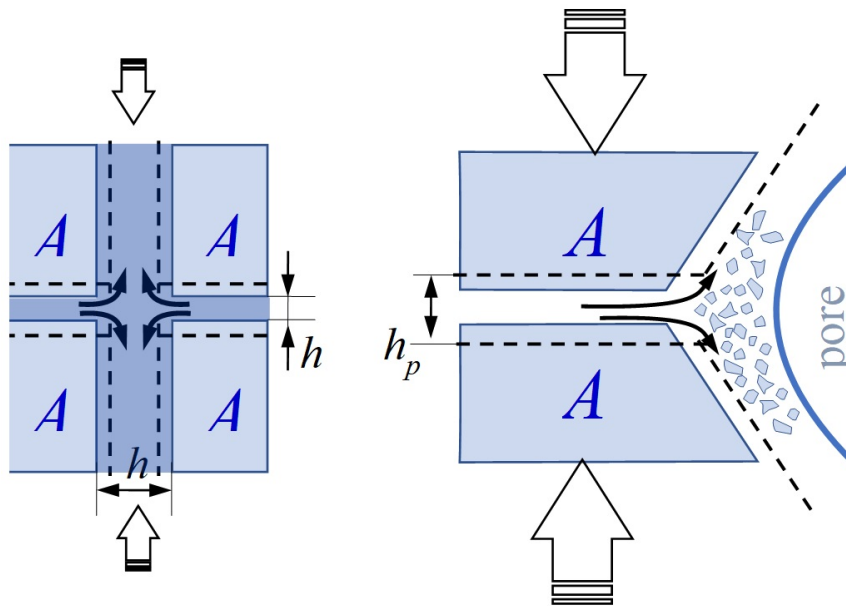
FIG. 4. Schematic representation of the transformation-transport mechanism of solid phase particles interaction

Apparently, it makes more physical sense to use the temperature of the non-autonomous phases transition to the liquid-like state as such a criterion. The corresponding division of processes in solid-phase systems into high-temperature and low-temperature ones is schematically shown in Fig. 5. It should be noted that in terms of the real division of solid-phase systems, the proposed boundary does not differ much from that proposed in [185], but is more justified in physical sense.
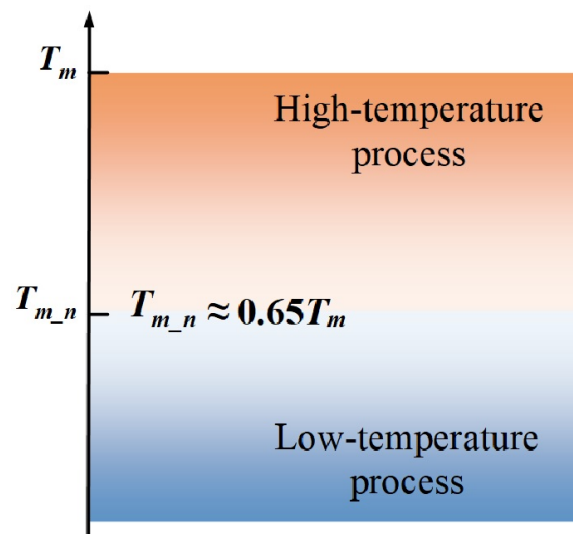

FIG. 5. Scheme of processes division in solid-phase systems into high-temperature and low-temperature

4. Conclusion

An analysis of the literature data on the nature of processes in oxide solid-phase systems demonstrated that the decisive role in them is played by the behavior of the substance in the non-autonomous state. A particularly great influence the non-autonomous phases have on the behavior of nanosized systems. The main parameters of the non-autonomous phases that determine the properties and behavior of the solid-phase, especially nanocrystalline ones, are the composition of the non-autonomous phases, the temperature of the non-autonomous phase transition to the liquid-like state, the equilibrium (locally-equilibrium) and metastable thickness of non-autonomous phases, and the viscosity of the liquid-like non-autonomous phase.

The data available in the literature show that there are still a large number of open questions both on the structure and properties of the substance in the non-autonomous state, and on the influence of the non-autonomous state on the behavior and properties of solid-phase systems, which indicates the prospects for further research in this area.

References

[1] Defay R. *Etude thermodinamique de la tension superficielle*. Gauntier-Vellarg and Cie, Paris, 1934, 372 p.

[2] Defay R., Prigogin I. *Tension superficielle et adsorption*. Edition Desoer., Liege, 1951, 295 p.

[3] Defay R. Prigogin I. Sanfelg A Surface Termodynamics. *J. Colloid Interface Sci*, 1977, **58**(3), P. 498–510.

[4] Rusanov A.I. *Phase equilibria and surface phenomena*. Chemistry, Leningrad, 1967, 234 p. (in Russian)

[5] Gusarov V.V., Egorov F.K., Ekimov S.P., Suvorov S.A. Mössbauer study of the kinetics of formation of film states during the interaction of magnesium and iron oxides. *Rus. J. Phys. Chem. of the USSR*, 1987, **61**(6), P. 1652–1654.

[6] Gusarov V.V., Suvorov S.A. Autocatalytic solid-phase reaction of chrysoberyl formation. *J. General Chem. of the USSR*, 1988, **58**(4), P. 932–934.

[7] Gusarov V.V., Suvorov S.A. Melting-point of locally equilibrium surface phases in polycrystallibe systems based on a single volume phase. *J. Appl. Chem. of the USSR*, 1990, **63**(8), P. 1560–1565.

[8] Gusarov V.V., Suvorov S.A. Self-accelerating processes of development of solid-phase systems (synthesis and functioning). Promising directions of chemistry and chemical technology. *Chemistry, Leningrad*. 1991, P. 153–158.

[9] Gusarov V.V., Suvorov S.A. Transformation of non-autonomous phases and compaction of polycrystalline systems. *J. Appl. Chem. of the USSR*, 1992, **65**(7), P. 1478–1488.

[10] Gusarov V.V., Suvorov S.A. Transformation-transport processes in polycrystalline systems and creep of materials. *J. Appl. Chem. of the USSR*, 1992, **65**(10), P. 2377–2380.

[11] Gusarov V.V., Suvorov S.A. Thickness of 2-dimensional non-autonomous phases in locally equilibrium polycrystalline systems based on one bulk phase. *J. Appl. Chem. of the USSR*, 1993, **66**(7), P. 1529–1534.

[12] Gusarov V.V., Popov I.Yu., Gugel Yu.V. Transformation-transport processes of formation of dynamic structures in 2-dimensional non-autonomous phases during thermomechanical processing of oxide and polycrystalline systems. *J. Appl. Chem. of the USSR*, 1994, **67**(7), P. 1116–1120.

[13] Smirnova Zh.N., Gusarov V.V., Malkov A.A., Malygin A.A., Suvorov S.S. Stabilization of the γ-form of aluminum oxide in the $AlO_{1.5}$–SiO_2 system with different levels of spatial conjugation of components. *J. Appl. Chem. of the USSR*, 1995, **68**(12), P. 1950–1954.

[14] Gusarov V.V., Malkov A.A., Malygin A.A., Suvorov S.A. Thermally stimulated transformations of 2-dimensional non-autonomous phases and compaction of oxide polycrystalline materials. *Inorg. Mater.*, 1995, **31**(3), P. 346–350.

[15] Gusarov V.V., Almjasheva O.V. The role of non-autonomous state of matter in the formation of structure and properties of nanomaterials. Chapter 13 in the book Nanomaterials: properties and promising applications. Ed A.B. Yaroslavtsev. Scientific World Publishing House, Moscow, 2014, P. 378–403. (in Russian)]

[16] Gusarov V.V. Statics and dynamics of polycrystalline systems based on refractory oxides. Abstract of diss. Doctor of Chemical Sciences. St. Petersburg, 1996, 44 p.

[17] Sanfeld A. *Introdaction to the thermodynamics of charged and polarized layers*. Wiley, N.Y., 1969, 258 p.

[18] Gusarov V.V. The thermal effect of melting in polycrystalline systems. *Thermochim. Acta*, 1995, **256**(2), P. 467–472.

[19] Sanfeld A., Steinchen A. Surface stress of isotropic solid under irreversible condition. *Comptes Rendus Chimie*, 2003, **6**(7), P. 677–682.

[20] Urusov V.S., Tauson V.L., Akimov V.V. Geochemistry of solids. GEOS, Moscow, 1997, 500 p. (in Russian)

[21] Tauson V.L., Parkhomenko I.Yu., Smagunov N.V., Babkin D.N., Menshikov V.I. Non-autonomous surface phases in the synthesis of sulfides and their geochemical role. Electronic scientific and information journal "Bulletin of the Department of Earth Sciences of the Russian Academy of Sciences", 2003, **1**(21).

[22] Tauson V.L., Akimov V.V., Lipko S.V., Loginov B.A. Nonautonomous phases as potential sources of incompatible elements. *Doklady Earth Sciences*, 2006, **407**(2), P. 280–283.

[23] Tauson V.L., Babkin D.N., Lipko S.V., Kravtsova R.G., Grebenshchikova V.I., Lustenberg E.E. Nonautonomous nanophases on a hydrothermal pyrite surface and its geochemical significance. *Doklady Earth Sciences*, 2008, **423**(2), P. 1501–1506.

[24] Akimov V.V., Gerasimov I.N., Tauson V.L., Loginov B.A. Mucrostructure and chemical composition of nonautonomous surface phases in crystals of pirrohotine ($Fe_{1-x}S$). *Bulletin of the Russian Academy of Sciences: Physics.*, 2006, **70**(7), P. 1051–1054.

[25] Glavatskiy K. *Multicomponent Interfacial Transport*, Springer, Berlin Heidelberg, 2011.

[26] Sanfeld A. Ordering induced by chemical, thermal and mechanical constraints at solid interfaces. *Pure and Appl. Chem.*, 1984, **56**(12), P. 1727–1738.

[27] Novoselov A.R. Point contact and linear interfaces as non-autonomous phases, their role in wetting and heterogeneous condensation processes. *Russ. J. Phys. Chem.*, 1991, **65**(2), P. 459–463.

[28] Lipko S.V. Non-autonomous phases on the surface of mineral and inorganic crystals and their role in the concentration of impurity elements. Abstract of diss. ... candidate of chemical sciences, Irkutsk, 2010, 18 p. (in Russian)

[29] Neiman A.Ya., Trafieva M.F., Kostikov Yu.P. Chemistry and mass transfer routes during formation of phases of the V_2O_5-MoO_3 system. *Russ. J. Inorg. Chem.*, 2005, **50**(10), P. 1582–1595.

[30] Neiman A.Ya., Uvarov N.F., Pestereva N.N. Solid state surface and interface spreading: An experimental study. *Solid State Ionics*, 2007, **177**(39-40), P. 3361–3369.

[31] Neiman A.Ya., Guseva A.F., Trifonova M.V., Sukhankina I.V. Surface reaction diffusion in the synthesis of molybdates and tungstates: the role of the phase composition of the products. *Russ. J. Inorg. Chem.*, 2005, **50**(3), P. 367–372.

[32] Neiman A.Ya., Kulikova T.E. Electrochemistry of solid-phase reactions: Phase formation in the In_2O_3-WO_3 system. Processes at the $WO_3|In_2O_3$ and $WO_3|In_6WO_{12}$ interfaces. *Russ. J. Electrochem.*, 2007, **43**(6), P. 682–694.

[33] Neiman, A.Y., Pestereva, N.N. Tsipis, E.V. Surface diffusion, migration, and conjugated processes at heterophase interfaces between WO_3 and $MeWO_4$ (Me = Ca, Sr, Ba). *Russ. J. Electrochem.*, 2007, **43**(6), P. 672–681.

[34] Pervov V.S., Makhonina E.V., Zotova A.E., Kireeva N.V., Kedrinsky I.-M.A. New possibilities to obtain ceramic nanoheterostructures with enhanced ionic conductivity. *Nanotechnol Russia*, 2014, **14**(9), P. 347–355.

[35] Krasnenko T.I., Rothermel M.V. Conditions for the formation of a non-autonomous phase during chemical and thermal deformations of complex oxides. In the book: Solid State Chemistry and Functional Materials – 2018. Thermodynamics and Materials Science. Abstracts of the Russian Conference with International Participation and the 12-th Russian Symposium with International Participation. edited by V.V. Gusarov, 2018, P. 21. (in Rassian).

[36] Tauson V.L., Lipko S.V., Arsent'ev K.Y., Smagunov N.V. Crystal growth through the medium of nonautonomous phase: Implications for element partitioning in ore systems. *Crystallogr. Rep.*, 2019, **64**(3), P. 496–507.

[37] Krasnenko T.I., Rotermel M.V., Samigullina, R.F. Stabilizing the associated non-autonomous phase upon thermal expansion of $Zn_2V_2O_7$. *Russ. J. Inorg. Chem.*, 2017, **62**(4), P. 413–417.

[38] Gerasimov I.N. Modeling of non-autonomous phase formation on the surface of inorganic mineral substances. Dissertation for the degree of candidate of chemical sciences. Irkutsk State University. Irkutsk, 2010. (in Russian).

[39] Samsonov V.M., Bazulev A.N., Sdobnyakov N.Yu. On surface non-tension of small objects. Chemistry and computer modeling. *Butlerov communications*, 2002, **10**, P. 267–271. Supplement to special issue. (in Russian).

[40] Luo J., Chiang Y.-M. Existence and stability of nanometer-thick disordered films on oxide. *Acta Materialia*, 2000, **48**(18–19), P. 4501–4515.

[41] Kaul A.R., Gorbenko O.Yu., Kamenev A.A. The role of heteroepitaxy in the development of new thin-film oxide-based functional materials. *Russ. Chem. Rev.*, 2004, **73**(9), P. 861–880.

[42] Magomedov M.N. On the dependence of surface energy on the size and shape of a nanocrystal. *Physics of the Solid State*, 2004, **46**(5), P. 924–937. (in Russian).

[43] Zhang H., Banfield J.F. Thermodynamic analysis of phase stability of nanocrystalline titania *J. Mater. Chem.*, 1998, **8**(9), P. 2073–2076.

[44] Samsonov V.M., Khashin V.A. Thermodynamic approaches to the problem of phase state of nanoparticles. *Condensed matter and interphases*, 2007, **9**(4), P. 387–391. (in Russian).

[45] Rempel A.W., Wettlaufer J.S., Grae M. Worster Premelting dynamics in a continuum model of frost heave. *Journal of Fluid Mechanics*, 2004, **498**, P. 227–244.

[46] Batsanov S.S. Features of solid-phase transformations induced by shock compression. *Russ. Chem. Rev.*, 2006, **75**(7), P. 601–616.

[47] Ogbezode J.E., Offia-Kalu N.E., Bello A., Anye V. Ch, Onwalu P.A. Phase structure transformation and growth mechanism for iron oxide nanoparticles synthesized by mechanochemical method: A mini-review. *J.Alloys and Metallurgical Systems*, 2024, **7**, P. 100103

[48] Kozlova T.O., Sheichenko E.D., Vasilyeva D.N., Kozlov D.A., Kolesnik I.V., Tronev I.V., Teplonogova M.A., Baranchikov A.E., Ivanov V.K. Ultrasonic-assisted hydrothermal synthesis of nanoscale double ceric phosphates. *Nanosyst.: Pysh., Chem., Math.*, 2024, **15**(2), P. 215-223.

[49] Kozlova T.O., Vasilyeva D.N., Kozlov D.A., Kolesnik I.V., Teplonogova M. A., Tronev I.V., Sheichenko E.D., Protsenko M.R., Kolmanovich D.D., Ivanova O.S., Baranchikov A.E., Ivanov V.K. A Comparative study of cerium(III) and cerium(IV) phosphates for sunscreens. *Molecules*, 2024, **29**(9), P. 2157–2157.

[50] Al'myasheva O.V., Korytkova E.N., Maslov A.V., Gusarov V.V. Preparation of nanocrystalline alumina under hydrothermal conditions. *Inorg. Mater.*, 2005, **41**(5), P. 460–467.

[51] Korytkova, E.N., Maslov, A.V., Pivovarova, L.N. et al. Synthesis of nanotubular $Mg_3Si_2O_5(OH)_4$-$Ni_3Si_2O_5(OH)_4$ silicates at elevated temperatures and pressures. *Inorg Mater.*, 2005, **41**(7), P. 743–749.

[52] Enikeeva M.O., Proskurina O.V., Motaylo E.S., Danilovich D.P., Gusarov V.V. The influence of conditions of the monazite structured $La_{0.9}Y_{0.1}PO_4$ nanocrystas sintering on thermal and mechanical properties of the material. *Nanosyst.: Phys. Chem. Math.*, 2021, **12**(6), P. 799–807.

[53] Lomanova N.A., Tomkovich M.V., Osipov A.V., Ugolkov V.L., Panchuk V.V., Semenov V.G., Gusarov V.V. Formation of $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ (m = 4–9) nanocrystals upon thermal decomposition of coprecipitated hydroxides. *Russ. J. Inorg. Chem.*, 2021, **66**(5), P. 755–764.

[54] Gyrdasova O.I., Samigullina R.F., Vladimirova E.V., Medyankina I.S., Buldakova L.Yu., Yanchenko M.Yu., Pasechnik L.A. Precursor method for the synthesis of highly dispersed ZrO_2 doped with scandium. *Mendeleev Communications*, 2024, **34**(5), P. 640–642.

[55] Zhang K., Ma Ch., Paul S., Zaffran J. Unveiling the phenol direct carboxylation reaction mechanism at ZrO_2 surface. *Molecular Catalysis*, 2024, **569**, P. 114606.

[56] Boykobilov D., Thakur S., Samiev A., Nasimov A., Turaev K., Nurmanov S. Prakash J., Ruzimuradov O. Electrochemical synthesis and modification of novel TiO_2 nanotubes: Chemistry and role of key synthesis parameters for photocatalytic applications in energy and environment. *Inorganic Chemistry Communications*, 2024, **170**(3), P. 113419.

[57] Sozarukova M.M., Proskurnina E.V., Baranchikov A.E., Ivanov V.K. CeO_2 nanoparticles as free radical regulators in biological systems. *Nanosyst.: Phys. Chem. Math.*, 2020, **11**(3), P. 324–332.

[58] Popova N.R., Shekunova T.O., Popov A.L., Selezneva I.I., Ivanov V.K. Cerium oxide nanoparticles provide radioprotective effects upon X-ray irradiation by modulation of gene expression. *Nanosyst.: Phys. Chem. Math.*, 2019, **10**(5), P. 564–572.

[59] Qi Junnan, Liu Huimin, Liu Guihong, Chen Yao Innovation of TiO_{2-x} nanomaterials in the biomedical field: synthesis, properties, and application prospects. *Chemical Engineering Journal*, 2024, **491**, P. 151773.

[60] Priya Dhuria, Satnam Singh Bhamra Influence of LTSSR and TSSR synthesis methods on the structural properties of $YFeO_3$ orthoferrite. *Materials Science and Engineering: B*, 2022, **285**, P. 115960.

[61] Tretyakov Yu.D. *Solid-phase reactions*. Chemistry, Moscow, 1978, 360 p. (in Russian)

[62] West A.R. *Solid State Chemistry and Its Applications*. Wiley India Pvt. Limited, 2007, 744 p.

[63] Rao C.N.R., Gopalakrishnan J. *New directions in solid state chemistry*. Nauka, Moscow, 1990, 520 p. (in Russian)

[64] Schmalzried H. *Chemical Kinetics of Solids*. Weinheim, VCH, 1995, 700 p.

[65] Guseva A.F., Neiman A.Ya. New data on the mechanism of mass transfer in solid-phase reactions: 1. Reactions in an electric field. *Kinetics and catalysis*, 1994, **35**(1), P. 1–7

[66] Chebotin V.M. *Chemical diffusion in solids*. Science, Moscow, 1989, 208 p.

[67] Andrievsky R.A. Fundamentals of nanostructured materials science. Possibilities and problems. *Laboratoriya znaniy*, Moscow, 2029, 228 p. (in Russian)

[68] Suzdalev I.P. Multifunctional nanomaterials. *Russ. Chem. Rev.*, 2009, **78**(3), P. 249–282. (in Russian)

[69] Eliseev A.A., Lukashin A.V. *Functional nanomaterials, Fizmatlit*, Moscow, 2010, 456 p. (in Russian).

[70] Guozhong Cao, Ying Wang. *Nanostructures and Nanomaterials: Synthesis, Properties, and Applications*. World Scientific, 2011, 581 p.

[71] Aaga G.F. Zinc oxide and its engineered derivative nanomaterials: Insight into energy, environmental, medical, agricultural, and food applications. *Materials Today Sustainability*, 2024, **28**, P. 101051.

[72] Karmakar D., Karmakar S., Ghosh A., Jana D. A comparative overview of the recent progress of some novel metal oxide and sulfide nanomaterials-based photocatalyst. *Materials Today Communications*, 2024, **40**, P. 110115.

[73] Sadykov V.A., Eremeev N.F., Shlyakhtina A.V., Pikalova E.Yu, Advances in alternative metal oxide materials of various structures for electrochemical and catalytic applications. *International Journal of Hydrogen Energy*, 2024, **94**, P. 179–208.

[74] Faraday M. On certain conditions of freezing water. *Athenaeum*, 1850, **1181**, P. 640–641.

[75] Faraday M. XXIV. On Regelation, and on the Conservation of Force, *Philos. Mag., Ser.*, **417**, 1859, 162 p.

[76] Mendeleev D.I. On the influence of touch on the course of chemical transformations. *ZhRHO*, 1886, **18**(8). (in Russian)

[77] Gibbs D. *Thermodynamic works*. GITTL, Moscow-Leningrad. 1950, 492 p. (in Russian)

[78] Rusanov A.I., Shchukin E.D., Rebinder P.A. On the theory of dispersion. I. Thermodynamics of monodisperse systems *Colloidal journal*, 1968, **30**(5), P. 573–580.

[79] Kuni F.M., Rusanov A.I. Statistical theory of aggregative equilibrium. *Theor. Math. Phys*, 1970, **2**(2), P. 192–206.

[80] Kligman F.I., Rusanov A.I. On the thermodynamic equilibrium states of disperse systems with suspended particles. *Koll. Zh.*, 1977, **39**(1), P. 44–47. (in Russian)

[81] Gusarov V.V. Statics and dynamics of polycrystalline systems based on refractory oxides: dis. Doctor of Chemical Sciences: 02.00.04. St. Petersburg, 1996, 598 p.

[82] Tomkovich M.V., Andrievskaya E.R., Gusarov V.V. Formation under hydrothermal conditions and structural features of nanoparticles based on the ZrO_2–Gd_2O_3 system. *Nanosyst.: Phys., Chem., Math.*, 2011, **2**(2), P. 6–14.

[83] Smirnov A.V., Fedorov B.A., Tomkovich M.V., Almjasheva O.V., Gusarov V.V. Core-shell nanoparticles forming in the ZrO_2-Gd_2O_3-H_2O system under hydrothermal conditions. *Doklady Physical Chemistry*, 2014, **456**(1), P. 71–73.

[84] Almjasheva O.V., Smirnov A.V., Fedorov B.A., Tomkovich M.V., V.V. Gusarov. Structural features of ZrO_2-Y_2O_3 and ZrO_2-Gd_2O_3 nanoparticles formed under hydrothermal conditions. *Russ. J. Gen. Chem.*, 2014, **84**(5), P. 804–809.

[85] Eshmakov R., Sherstobitov A.V., Filatova D., Konstantinova E., Rumyantseva M. SnO_2/MnO_x composite systems as VOCs sensors: Influence of manganese chemical state and distribution on functional performances. *Materials Chemistry and Physics*, 2024, **328**, P. 129992

[86] Shaposhnik A.V., Shaposhnik D.A., Turishchev S.Y., Chuvenkova O.A., Ryabtsev S.V., Vasiliev A.A., Vilanova X., Hernandez-Ramirez F., Morante J.R. Gas sensing properties of individual SnO_2 nanowires and SnO_2 sol–gel nanocomposites. *Beilstein J. Nanotechnol*, 2019, **10**, P. 1380–1390.

[87] Almjasheva O.V., Krasilin A.A., Gusarov V.V. Formation mechanism of core-shell nanocrystals obtained via dehydration of coprecipitated hydroxides at hydrothermal conditions. *Nanosyst.: Phys., Chem., Mathem.*, 2018, **9**(4), P. 568–572.

[88] Voronin G.F. Fundamentals of Thermodynamics Publishing House, Moscow, Moscow University, 1987, 192 p.

[89] Almjasheva O.V. Formation and structural transformations of nanoparticles in the TiO_2–H_2O system. *Nanosyst.: Phys., Chem., Math.*, 2016, **7**(6), P. 1031–1049.

[90] Dzhevaga E.V., Chebanenko M.I., Martinson K.D., Lobinsky A.A., Popkov V.I. One-step combustion synthesis of undoped c-ZrO_2 for Cr(VI) removal form aqueous solutions. *Nanotechnology*, 2022, **33**(41), P. 415601.

[91] Proskurina O.V., Sokolova A.N., Sirotkin A.A., Abiev R.S., Gusarov V.V. Role of hydroxide precipitation conditions in the formation of nanocrystalline $BiFeO_3$. *Russ. J. Inorg. Chem.*, 2021, **66**(2), P. 163–169.

[92] Gusarov V.V., Malkov A.A., Malygin A.A., Polyakova E.V., Khabibova S.V., Petrova L.I., Suvorov S.A. Evolution of $AlO_{1.5}$–TiO_2 systems with different prehistories. *Russ. J. Applied Chemistry*, 1991, **64**(5), P. 1134–1135.

[93] Eliseev A.A., Falaleev N.S., Verbitskiy N.I., Volykhov A.A., Yashina L.V., Kumskov A/, Zhigalina V.G., Vasiliev A.L., Lukashin A.V., Sloan J. Size-dependent structure relations between nanotube and encapsulated nanocrystal. *Nano Letters*, 2017, **17**, P. 805–810.

[94] Popkov V.I., Martinson K.D., Kondrashkova I.S., Enikeeva M.O., Nevedomskiy V.N., Panchuk V.V., Semenov V.G., Volkov M.P., Pleshakov I.V. SCS-assisted production of $EuFeO_3$ core-shell nanoparticles: formation process, structural features and magnetic behavior. *J. Alloys and Compounds*, 2021, **859**, P. 157812.

[95] Koroleva E., Naberezhnov A., Rysiakiewicz-Pasek E., Vakhrushev S., Sysoeva A., Kumzerov Yu. Dielectric response of potassium nitrate in a restricted geometry. *Composites Part B: Engineering*, 2016, **94**, P. 322–326.

[96] Alekseeva O.A., Naberezhnov A.A., Fokin A.V. Effect of restricted geometry on phase transitions in nanostructured sodium nitrate. *Physica B: Condensed Matter*, 2025, **696**, P. 416676.

[97] Alekseeva O.A., Enikeeva M.O., Naberezhnov A.A., Sysoeva A.A. Stabilization of the monoclinic phase of KH_2PO_4 under limited geometry conditions. *Technical Physics Letters*, 2024, **50**(11), P. 7–10.

[98] Naberezhnov A.A., Alekseeva O.A., Kudryavtseva A.V., Chernyshov D.Yu., Vergentiev T.Yu., Fokin A.V. Structural transition and temperature dependences of thermal expansion coefficients of $NaNO_3$ embedded in non-pressurized glass. *Physics of the Solid State*, 2022, **64**(3), P. 365–370.

[99] Mikhailin N.Y., Shamshur D.V., Parfen'ev R.V., Kozub V.I., Gal'perin Y.M., Kumzerov Y.A., Fokin A.V. Size dependences of the magnetic properties of superconducting lead-porous glass nanostructures. *Physics of the Solid State*, 2018, **60**(6), P. 1068–1072.

[100] Belotitskii V.I., Kumzerov Y.A., Kalmykov A.E., Kirilenko D.A., Romanov S.G., Sorokin L.M., Sysoeva A.A., Peschel U., Zhuromskyy O. Optical properties of metal nanoparticles in chrysotile channels, *Technical Physics Letters*, 2016, **42**(6), P. 656–658.

[101] Kumzerov Y.A., Naberezhnov A.A. Effect of restricted geometry on the superconducting properties of low-melting metals (review article). *Low Temperature Physics*, 2016, **42**(11), P. 1028–1040.

[102] Gatina E.N., Maslennikova T.P. Formation of chrysotile nanotubes with titania in the internal channel. *Nanosyst: Phys, Chem, Math.*, 2024, **15**(3), P. 380–387.

[103] Almjashev O.V., Gusarov V.V. Effect of ZrO_2 nanocrystals on the stabilization of the amorphous state of alumina and silica in the ZrO_2–Al_2O_3 and ZrO_2–SiO_2 systems. *Glass Physics and Chemistry*, 2006, **32**(2), P. 162–166.

[104] Al'myasheva O.V., Gusarov V.V. Nucleation in media in which nanoparticles of another phase are distributed. *Doklady Physical Chemistry*, 2009, **424**(2), P. 43–45.

[105] Al'myasheva O.V., Gusarov V.V. Features of the phase formation in the nanocomposites. *Russ. J. Gen. Chem.*, 2010, **80**(3), P. 385–390.

[106] Zlobin V.V., Krasilin A.A., Almjasheva O.V. Effect of heterogeneous inclusions on the formation of TiO_2 nanocrystals in hydrothermal conditions. *Nanosyst.: Phys., Chem., Mathem.*, 2019, **10**(6), P. 733–739.

[107] Tammann G, Mansuri Q.A. Metallographische mitteilungen aus dem Institut für physikalische chemie der universität göttingen CXIII. Zur Rekristallisation von Metallen und Salzen. Zeitschrift für anorganische und allgemeine Chemie, 1923, **126**, 119 p.

[108] Hüttig G.F., Theimer H., Breuer W. Über reaktionen fester stoffe: 126. Mitteilung. Über die entgasung fester stoffe. Zeitschrift für anorganische und allgemeine Chemie, 1942, **249**(2), P. 134–145.

[109] Kaur I., Gust W. Fundamentals of grain and interphase boundary diffusion. Stuttgart: Ziegler Press, 1989, 422 p. (Russ. ed.: Kaur, I., Gust, W. Diffuziya po granitsam zeren i faz. Moscow: Mashinostroenie, 1991, 446 p.)

[110] Hwang J.C.M., Ho P.S., Lews J.E., Campbell D.R. Grain boundary diffusion of aluminum in polycrystalline silicon films. *J. Appl. Phys.* 1980, **51**(3), P. 1576–1581.

[111] Hwang J.C.M., Amos D.E., Nelson G.C. Analysis of grain-boundary diffusion in thin films: Chromium in gold. *J. Appl. Phys.*, 1976, **47**(9), P. 3769–3775.

[112] Wuttig M., Brinbaum H.K. Self-Diffusion along edge dislocations in nickel. *Phys. Rev.*, 1966, **147**, P. 495.

[113] Fletcher N.H. The Chemical Physics of Ice Cambridge Univ. Press. 1970, 271 p.

[114] Barer S.S., Klividze V.I., Kurzaev A.B., Sobolev V.D., Churaev N.V. Thickness and viscosity of thin non-freezing layers between the surface of ice and quartz. *Doklady USSR Academy of Sciences*, 1977, **235**(3), P. 601. (in Russian)

[115] Gilpin R.R. A model for the prediction of ice lensing and frost heave in soils. *Water Resour. Res.*, 1980, **16**(5), P. 918.

[116] Clarke D.R. On the equilibrium thickness of intergranular glass phases in ceramic materials. *J. Am. Seram. Soc.*, 1987, **70**(1), P. 15–25.

[117] Kikuchi R., Cahn J.W. Grain-boundary melting transition in a two-dimension lattice-gas model. *Phys. Rev. B.*, 1980, **21**(5), P. 1893.

[118] Mizuno Y. Hanafusa N. Studies of surface properties of ice using nuclear magnetic resonance. *J. Phys. Colloques*, 1987, **48**, P. C1-511–C1-517.

[119] Dash J.G. Surface melting. *Contemp. Phys.*, 1989, **30**(2), P. 89.

[120] Elbaum M., Schick M. Application of the theory of dispersion forces to the surface melting of ice. *Phys. Rev. Lett.*, 1991, **66**(13), P. 1713.

[121] Elbaum M., Lipson S.G., Dash J.G. Optical study of surface melting on ice. *J. Cryst. Growth.*, 1993, **129**, P. 491.

[122] Dash, J.G., Haiying Fu, Wettlaufer, J.S. The premelting of ice and its environmental consequences. *Reports Prog. Phys.*, 1995, **58**, P. 115.

[123] Wettlaufer J.S., Worster M.G., Wilen L.A., Dash J.G. A theory of premelting dynamics for all power law forces. *Phys. Rev. Lett.*, 1996, **76**, P. 3602

[124] Shultz M.J. Ice surfaces. *Annu. Rev. Phys. Chem.*, 2017, **68**, P. 285.

[125] Slater B., Michaelides A. Surface premelting of water ice. *Nat Rev Chem*, 2019, **3**, P. 172–188.

[126] Canale L., Comtet J., Nigu'es A., Cohen C., Clanet C., SiriaA., Bocquet L. Nanorheology of interfacial water during ice gliding. *Phys. Rev.*, 2019, **X9**, P. 041025.

[127] Richhariya V., Tripathy A., Carvalho O., Nine J., Losic D., Silva F.S. Unravelling the physics and mechanisms behind slips and falls on icy surfaces: A comprehensive review and nature-inspired solutions. *Materials & Design*, 2023, **234**, P. 112335.

[128] Boxe C.S., Saiz-Lopez A. Influence of thin liquid films on polar ice chemistry: Implications for Earth and planetary science. *Polar Science*, 2009, **3**, P. 73–81.

[129] Pavlovska A., Dobrev D., Bauer E. Orientation dependence of the quasi-liquid layer on tin and indium crystals. *Surface Science*, 1994, **314**, P. 341–352.

[130] Smit W.J., Bakker H.J. The Surface of Ice Is Like Supercooled Liquid Water. *Angew. Chem.*, 2017, **129**, P. 15746–15750.

[131] Bluhm H., Ogletree D.F., Fadley C.S., Hussain, Z., Salmeron M. The premelting of ice studied with photoelectron spectroscopy. *J. Phys. Condens. Matter.*, 2002, **14**, P. L227–L233.

[132] Conde M. M., Vega C. Patrykiejew A. The thickness of a liquid layer on the free surface of ice as obtained from computer simulation. *J. Chem. Phys.*, 2008, **129**, P. 014702.

[133] Pickering I., Paleico M., Sirkin Y.A.P., Scherlis D.A., Factorovich M.H. Grand canonical investigation of the quasi-liquid layer of ice: is it liquid? *J. Phys. Chem. B*, 2018, **122**, P. 4880–4890.

[134] Dosch H., Lied A. & Bilgram J.H. Glancing-angle X-ray scattering studies of the premelting of ice surfaces. *Surf. Sci.*, 1995, **327**, P. 145–164.

[135] Frenkel Ya.I. Liquid state and theory of melting. I. Continuity of solid and liquid states. Collection of selected works. Scientific articles. Publishing house of the USSR Academy of Sciences, Moscow-Leningrad, 1958, Vol. 2, P. 269–279. (in Russian)

[136] Frenkel Ya.I. Liquid state and theory of melting. II. Theory of melting and crystallization. Collection of selected works. Scientific articles. Publishing house of the USSR Academy of Sciences, Moscow-Leningrad, 1958, Vol. 2, P. 269–279. (in Russian)

[137] Ubbelode A. The Molten State of Matter. London University, London, 1978, 384 p.

[138] Ubbelode A. Melting and Crystal Structure. Clarendon Press, 1965, 325 p. M, Mir, 1969, 420 p.

[139] Pastukhov E.A., Vatolin N.A., List V.L., Detsov V.M., Kachin S.V. Diffraction studies of the structure of high-temperature melts. Ekaterinburg; Ural Branch of the Russian Academy of Sciences, 2003, 353 p. (in Russian).

[140] Ladyanov V.I., Logunov S.V., Kuzminykh E.V. On the viscosity of micro-inhomogeneous liquid metals. *Metalls*, 1997, **4**, P. 22. (in Russian).

[141] Ladyanov V.I., Novokhatsky I.A., Logunov S.V. Estimation of the lifetime of clusters in liquid metals. *Metalls*, 1995, **2**, P. 13. (in Rissian).

[142] Psarev V.I., Ivanov A.L. On the pre-crystallization structural state of supercooled selenium melt. *Russ. J. Phis. Chem.*, 1992, **66**(3), P. 788–790. (in Russian)

[143] Skripov V.P., Koverda V.P. Spontaneous crystallization of liquids. Nauka, Moscow, 1984, 232 p. (iv Russian).

[144] Filippov E.S. Structure, chemistry and physics of metallurgical melts. *Metallurgy*, Moscow, 1995, 303 p. (in Russian)

[145] Chivilikhin S.A., Gusarov V.V., Popov I.Yu., Svitenkov A.I. Model of fluid flow in a nano-channel. *Russ. J. Math. Phys.*, 2008, **15**(3), P. 409–411.

[146] Popov I.Y., Rodygina O.A., Chivilikhin S.A., Gusarov V.V. Soliton in a nanotube wall and stokes flow in the nanotube. *Tech. Phys. Lett.*, 2010, **36**(9), P. 852–855.

[147] Ershova A.A., Popov I.Y., Chivilikhin S.A., Gusarov V.V. Waveguide modes and adhesion conditions for flow in a nanochannel. *Dokl. Phys.*, 2010, **55**(6), P. 271–273.

[148] Popov I.Yu., Chivilikhin S.A., Gusarov V.V. Model of fluid flow in nanotube: Classical and quantum features. *J. Phys.: Conf. Ser.*, 2010, **248**, Art. No 012006.

[149] Chivilikhin S.A., Popov I.Yu., Gusarov V.V. Planar flows in nanoscale regions. *Nanosyst.: Phys., Chem., Math.*, 2011, **2**(3), P. 49-52.

[150] Chivilikhin S.A., Popov I.Yu., Aryslanova E.M., Vavulin D.N., Gusarov V.V. Liquid flow in nanotubes. *J. Phys.: Conf. Ser.*, 2012, **345**, Art. No 012036.

[151] Chivilikhin S.A., Gusarov V.V., Popov I.Yu. Flows in nanostructures: hybrid classical-quantum models. *Nanosyst.: Phys., Chem., Math.*, 2012, **3**(1), P. 7–26.

[152] Belonenko M.B., Chivilikhin S.A., Gusarov V.V., Popov I.Yu., Rodygina O.A. Soliton-induced flow in carbon nanotube. *Europhysics Letters.*, 2013, **101**(6), P. 66001.

[153] Rodygina O.A., Chivilikhin S.A., Popov I.Yu., Gusarov V.V. Crystallite model for flow in nanotube caused by wall soliton. *Nanosyst.: Phys., Chem., Math.*, 2014, **5**(3), P. 400–404.

[154] Chivilikhin S.A., Gusarov V.V., Popov I.Yu. Charge pumping in nanotube filled with electrolyte. *Chinese J. Phys.*, 2018, **56**(5), P. 2531–2537.

[155] Almjasheva O.V., Popkov V.I., Proskurina O.V., Gusarov V.V. Phase formation under conditions of self-organization of particle growth restrictions in the reaction system. *Nanosyst.: Phys., Chem., Math.*, 2022, **13**(2), P. 164–180.

[156] Almiasheva O.V. Formation of oxide nanocrystals and nanocomposites under hydrothermal conditions, structure and properties of materials based on them: dis. Doctor of Chemical Sciences: 02.00.21. Moscow, 2018, 362 p.

[157] Gilpin R.R. A Model of the "Liquid-Like" layer between ice and a substrate with applications to wire regelation and particle migration. *J. Colloid and Interface Science*, 1979, **68**(2), P. 235–251.

[158] Frenkel J. The Liquid State and the Theory of Fusion. *Acta Physicochimica URSS*, 1935, **3**, P. 633–648.

[159] Gusarov V.V., Popov I.Yu. Dynamic structure formation during high-temperature deformation of polycrystalline oxides. *Izvestiya Universiteta. Physics.*, 1995, **38**(8), P. 69–75.

[160] Gusarov V.V., Popov I.Yu. Flows in two-dimensional nonautonomous phases in polycrystalline system. *Nuovo Cimento della Societa Italiana di Fisica D.*, 1996. **18D**(7), P. 799–805.

[161] Döppenschmidt A., Butt H.J. Measuring the thickness of the Liquid-like layer on ice surfaces with atomic force microscopy. *Langmuir*, 2000, **16**, P. 6709.

[162] Kornienko M.E., Sheiko N.L., Kornienko O.M., Nikolaienko T.Y. Discrete properties of quasi-liquid water film in the ice premelting range. 1. Temperature dependences of water nanofilm thickness and viscoelastic properties of polycrystalline ice. *Ukr. J. Phys.*, 2013, **58**, P. 151.

[163] Conde M.M., Vega C., Patrykiejew A. The thickness of a liquid layer on the free surface of ice as obtained from computer simulation. *J. Chem. Phys.*, 2008, **129**, P. 014702.

[164] Wettlaufer J.S. Ice surfaces: Macroscopic effects of microscopic structure. *Phil. Trans. R. Soc. A*, 1999, **357**, P. 3403.

[165] Schmalzried H. Chemical kinetics of solids. Weinheim: VCH, 1995, 700 p.

[166] Gusarov V.V., Ishutina Z.N., Malkov A.A., Malygin A.A. Peculiarities of the solid-phase chemical reaction in formation of mullite in the nanosize film composition. *Doklady Akademii Nauk.*, 1997, **357**(2), P. 203–205. (In Russian)]

[167] Smirnova Zh.N., Gusarov V.V., Malkov A.A., Firsanova T.V., Malygin A.A., Suvorov S.A. High-speed synthesis of mullite. *Russ. J. Gen. Chem.*, 1995, **65**(2), P. 199–204.

[168] Gusarov V.V., Malkov A.A., Ishutina Zh.N., Malygin A.A. Phase formation in a nanosized silicon oxide film on the surface of aluminum oxide. *Tech. Phys. Lett.*, 1998, **24**(1), P. 3–8.

[169] Kol'tsov S.I., Aleskovskii V.B. Effect of degree of dehydration of silica gel on mechanism of hydrolysis of adsorbed titanium tetrachloride. *Russ. J. Phys. Chem.*, 1968, **42**(5), P. 630–632.

[170] Aleskovskii V.B. Chemistry and technology of solids. *J. Appl. Chem. of the USSR*, 1974, **47**(10), P. 2207–2217.

[171] Malygin A.A. Molecular Layering Nanotechnology. *Nanotechnologies in Russia (Rossiiskie Nanotekhnologii)*, 2007, **2**(3-4), P. 87–100. (In Russian)

[172] Malygin A.A., Drozd V.E., Malkov A.A., Smirnov V.M. From V.B. Aleskovskii's "Framework" hypothesis to the method of molecular layering/atomic layer deposition. *Chemical Vapor Deposition*, 2015, **21**, P. 216–240.

[173] Sosnov E.A., Malkov A.A., Malygin A.A. Nanotechnology of Molecular Layering in Production of Inorganic and Hybrid Materials for Various Functional Purposes (a Review): I. History of the Development of the Molecular Layering Method. *Russ. J. Appl. Chem.*, 2021, **94**(8), P. 1022–1037.

[174] Almjasheva O.V., Gusarov V.V. Effect of ZrO_2 nanocrystals on the stabilization of the amorphous state of alumina and silica in the ZrO_2-Al_2O_3 and ZrO_2-SiO_2 systems. *Glass Physics and Chemistry*, 2006, **32**(2), P. 162–166

[175] Bachina A., Almajasheva O.V., Danilovich D.P., Popkov V.I. Synthesis, crystal structure and thermophysical properties of $ZrTiO_4$ nanoceramics. *Russ. J. Phys. Chem. A: Focus on Chemistry*, 2021, **95**(8), P. 1529–1536.

[176] Artamonova O.V., Almyasheva O.V., Mittova I.Ya., Gusarov V.V. Sintering of nanopowders and properties of ceramics in the ZrO_2–In_2O_3 system. *Advanced Materials*, 2009, **1**, P. 91–94.

[177] Khadidja Laziri, Amar Djemli, Djaida Redaoui, Foudil Sahnoune, Essebti Dhahri, S.F. Hassan, Nouari Saheb. Kinetics of formation, microstructure, and properties of monolithic forsterite (Mg_2SiO_4) produced through solid-state reaction of nano-powders of MgO and SiO_2. *Ceramics International*, 2024, **50**(22), Part A, P. 45179–45188.

[178] Zargar H.R., Bayati M.R., Rezaie H.R., Golestani-Fard F., Molaei R., Zanganeh S., Kajbafvala A. Influence of nano boehmite on solid state reaction of alumina and magnesia, *J. Alloys and Compounds*, 2010, **507**(2), P. 443–447.

[179] Gusarov V.V. Fast Solid-Phase Chemical Reactions. *Russ. J. Gen. Chem.*, 1997, **67**(12), P. 1846–1851.

[180] Kirillova S.A., Panchuk V.V., Semenov V.G., Almjasheva O.V. Solid-phase interaction in the ZrO_2–Fe_2O_3 nanocrystalline system. *Nanosys.: Phys., Chem., Math.*, 2018, **9**(6), P. 763–769.

[181] Kingery W.D. Regelation, surface diffusion and ice sintering. *J. Appl. Phys.*, 1960, **31**(5), P. 883–838.

[182] Jonson D.L. New method of obtaining volume, grain-boundary and surface diffusion coefficient from sintering data *J. Appl. Phys.*, 1969, **40**(1), P. 192–200.

[183] Kingery W.D., Berg M. Study of initial stages of sintering solids by viscous flow, evaporation – condensation end self-diffusion. *J. Appl. Phys.*, 1955, **26**(10), P. 1205–1212.

[184] Coble R.L. Diffusion model for hot pressing with surface energy and pressure effect as driving forces. *J. Appl. Phys.*, 1970, **41**(12), P. 4798–4807.

[185] Fedorov P.P. Determination of annealing duration in the study of phase equilibria in the solid state of binary systems. *Russ. J. Inorg. Chem.*, 1992, **37**(8), P. 1891–1894. (in Russian).

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