

Reviews

Mechanochemical processes with the reaction-induced mechanical activation. Chemo-mechanochemical effect

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The review addresses the special case of mechanical activation of solid-state chemical reactions when the stress field, strain, and defects in crystals are induced by the chemical reaction itself rather than by the external mechanical impact (chemo-mechanochemical (CMC) effect). This review presents the analysis and state-of-the-art of research activities in this area. Different cases of the CMC effect in homogeneous and heterogeneous systems are considered: with or without changes in the chemical composition, with or without formation of solid products, *etc.*

Key words: mechanochemistry, mechanical activation, chemo-mechanochemical effect, feedback in solid-state processes, mechanochemical activation as a result of the reaction itself, reactivity of solids.

Introduction

In recent years, the number of publications devoted to the effect of the external mechanical impact on chemical reactions (mechanochemical reactions and mechanical activation)^{1–16} or mechanical phenomena induced by chemical reactions (photo- and thermomechanical effects) has been markedly increased.^{17–31} At the same time, scarce information is available on the processes when the reaction-induced stress field in solids exerts a certain effect on the reaction pathway, rate, propagation topography, and morphology of the formed product. These problems featured the mainstream direction of the second half of

the XX century.^{31–38} At that time, many key principles of this effect have been formulated, important ideas and hypotheses have been advanced, and simple but convincing and reliable model experiments have been conducted. It was the time when the scarcity of experimental resources gave plenty of time for reflections and thoughts on the design of experiments and on the subsequent analysis of the experimental results. Unfortunately, at that time, in turn, underdevelopment of experimental techniques and insufficient level of theoretical calculations did not allow the going beyond the limits of the qualitative description and validation of the proposed trivial mathematical models by quantitative experimental data. Nowadays when exper-

iments and calculations can be performed at much higher level, this challenge has been to some extent subsided because old generation of scientists involved in the solution of this problem has changed. Nevertheless, the importance and relevance of this unsolved challenge is still high. Without the insight into the correlation between transformations in solids and induced mechanical stresses, the control over solid-state reactions and properties of the formed products is impossible; this understanding underlies the fundamentals of materials science, development of innovative "solvent-free" technologies, design of the devices based on solid materials and utilizing their transformations.

The objective of this review is concerned with the identification of still unsolved challenges and with the description of recent achievements in this direction to our knowledgeable readers and to unaccustomed newcomers.

1. Terminology

For the description of the correlation between the chemical reaction and reaction-induced mechanical stresses, we will use the term "chemo-mechanochemical effect" (CMC effect). This term seems to be advantageous to avoid the misleading confusion with some related terms, which are widely used in literature for the description of chemomechanical and mechanochemical effects.

The term "*chemo-mechanochemical effect*" is used when the role of a foreign chemical reactant is reduced to the modification of the physical properties of solids (this phenomena is well known as the Rehbinder phenomenon and the Roscoe phenomenon).^{39,40} The term "mechanochemical effect" is applicable when the reaction is triggered by the external impact.^{1–16} The same term but in somewhat different meaning is being used in biochemistry when the mechanical output is closely related to chemical processes (for example, upon ion transfer through a membrane upon muscle contraction, *etc.*).⁴¹

Several models have been proposed for the description of the steady-state propagation of the failure front in solids induced by structural transformations in the sample.^{42–44} These models differing by specific details of underlying approaches provide the prediction of the possible development of the process, however, the related calculations have not been verified by the experimental evidence, which could give the ground for the quantitative assessment and could reveal the difference in the behavior of diverse systems. Therefore, recognizing the contribution of the authors of the above publications to the statement and solution of the general problem, this particular aspect is beyond the scope of this review and we will focus our attention on the discussion of the works, in which the hypothesis on the correlation between the chemical reaction and induced activation of the initial substance due to the mechanical impact has been experimentally validated.

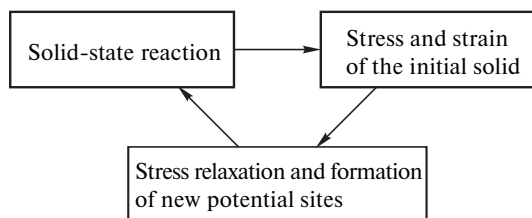


Fig. 1. The scheme illustrating the feedback reaction upon the CMC effect.

In this review, we will focus our attention on the processes in solids with the induced feedback reaction: the reaction itself leads to the generation of mechanical stresses, which, in turn, control further evolution of this reaction (Fig. 1). At the time, these processes were referred to as chemomechanical.³⁸ In our opinion, the term "chemo-mechanochemical effect" (CMC effect) seems to be more appropriate because this ideology allows the identification of the processes with the feedback reaction in comparison with the processes when the chemical reaction leads to the generation of mechanical stresses and strains (for example, bending of a metal plate) but does not induce any further changes in the reactivity of the sample.

2. Principal reasons of CMC effects

The development of the CMC effect can be induced by several events.

1. The development of mechanical stresses in the initial sample due to the misfit between the molecular volumes of the initial substance (V_i) and the reaction product (V_r) — dilation component by Nabarro.³² Two cases should be distinguished: $V_r > V_i$ and $V_r < V_i$.

2. Misfit between the lattice parameters of the initial substance and the reaction product in the case of the topology — interfacial energy component by Nabarro.³²

3. Change in the number of sites with increased surface curvature in the course of the reaction (the Kelvin—Thomson principle).⁴⁵

The development of the CMC effect is controlled by the mechanical properties of the sample related to its structural features (including their anisotropy) as well as by the sensitivity of the chemical process to the induced mechanical stresses and consequences of stress relaxation, in particular, mechanical deformation of the sample. This aspect of the CMC effects allows their classification as a mode of mechanochemical processes.

The development of stress relaxation processes is independent of the origin of the stress source (internal or external). Several mechanisms of stress relaxation depending on the external impact and temperature are known⁴⁶ (Fig. 2). For the adequate comparison of stress relaxation processes in different substances, it seems convenient to

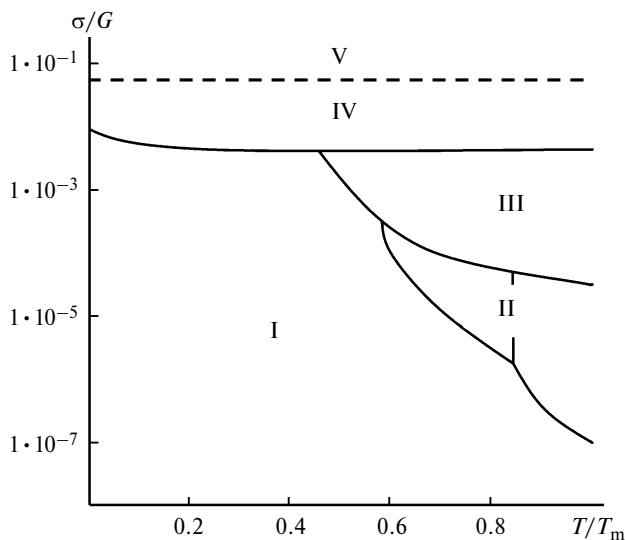


Fig. 2. Diagram of the regions corresponding to operation of different mechanisms of plastic deformation depending on the ratio between the current temperature and the melting temperature (T/T_m) and on the ratio of stress to shear modulus (σ/G):⁴⁶ I, elastic region; II, diffusion flow; III, dislocation creep; IV, slip of dislocations; V, theoretical strength.

express the corresponding parameters in relative units: stress in fractions of shear modulus (G) or Young's modulus, temperature in fractions of the melting temperature (T_m). At low temperatures, $T \leq 0.6 T_m$, the diffusion process with the participation of the pointlike defects are frozen and stress relaxation and the concomitant mass transfer are allowed at a certain stress level only *via* the movement of dislocations (slip or, at $T \geq 0.5 T_m$, dislocation creep). The particular cases of dislocation slip are concerned with twinning and domainization. When the stress threshold providing the dislocation slip is higher than the breaking stress (strength), the initial sample experiences fragmentation, and the fractured fragments (splinters) have the kinetic energy, which is sufficient for their spray (the example is the thermolysis of big-sized KMnO_4 crystals). At higher temperatures, $T \geq 0.6 T_m$, the diffusion flow *via* the movement of pointlike defects (in most cases, vacancies) is allowed.

The knowledge on the mechanisms of stress relaxation due to chemical transformations allows not only prediction of the possible scenario of this process but also offers the route for the control over the rate of transformations of solids through changes in their mechanical properties. For example, for brittle solids, where the dislocation slip is hindered, one can expect the fracture at low temperatures due to phase transformations. Fragmentation takes place only when the size of the initial sample exceeds a certain critical value. In some cases, the mechanisms of stress relaxation were shown to be directionally controlled and this approach allows controlled changes in rate and topography of the transformation *via* the CMC effect (see the examples below).

The CMC effect feature a possible mode of feedback upon solid-phase chemical reactions. This feedback is one of the reasons behind localization and auto-localization of the process,³⁷ in addition to some other reasons such as self-heating and self-cooling, catalytic action of the reaction product, *etc.* The possibility of the auto-localization of the process (also due to the development of mechanical stresses) should be taken into account when studying and use of chemical reactions in solids.

The CMC effect can be observed both in homogeneous and heterogeneous systems.

3. Homogeneous systems

In the case of the homogeneous chemical reactions, the CMC effect appears as a cooperative response of the environment to local structural excitations, which are induced by light absorption of a molecule or by its chemical transformation.^{47,48} The size and the shape of the molecule are changed, and the molecule starts to serve as an admixture, a defect, or a dilation site for the initial structure. If an excited molecule remains in the same structural position similar to its neighbors (apart from the overall structural distortion), the process proceeds homogeneously without any critical structural rearrangements with the formation of a two-phase system and an interface between the initial substance and the reaction product. Accumulation of the clusters of excited states entails the depression in activation energy and acceleration of the process, whose kinetics shows the character typical of auto-catalytic reactions.

For example, the model has been advanced^{49–51} in which the mechanical stresses induced by changes in each separate molecule lead to the distortion of the surrounding of this molecule; this structural distortion is transferred from the site where the reaction took place to the intact (unreacted) part of the crystal due to the interaction between the molecules (Fig. 3). According to the authors, the study of homogeneous chemical solid-phase reactions requires the account for not only intramolecular changes but also for intermolecular interactions. Hence, if we deal with the photochemical reaction, all specific features of electron excitation should be taken into account. The point is that, in the solid phase, excitation is always accompanied by the phonon-mediated interaction with neighboring molecules or, in other words, the individual process is transformed into the collective one when excitation is transferred to the environment.

To take into account all additional forces generated in the crystalline structure due to the excitations induced by the chemical reaction, the authors introduced the term "*chemical pressure*". Distortions in structural nodes lead to changes in the chemical potential due to the transformation and, additionally, due to the distortion of the nearest environment, which is induced by an excited or unreacted

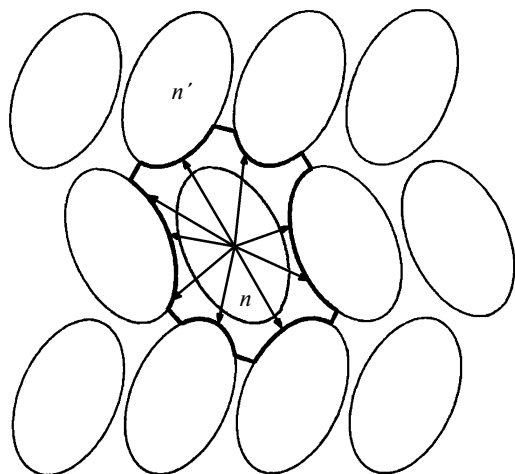


Fig. 3. Interaction of excited molecules with neighboring molecules.⁴⁷

molecule. A specific cluster composed of locally strained structural sites is formed; in turn, different clusters can interact with each other. As a result, activation energy decreases, and the process is auto-accelerated.

"Chemical pressure" can be the consequence of the diverse homogeneous chemical reactions, first of all, photochemical reactions in molecular crystals. Experimental verification of this model has been performed in the pioneering study on photopolymerization of 2,5-distyrylpyrazine.⁵²

Photochemical reactions in organic crystals (in particular, composition of the formed products) are assumed to be controlled by the mutual arrangement of molecules not in the initial crystalline structure but in the regions whose structure has been rearranged as a result of the disturbing action of the light-absorbing molecules (the concept of "pre-reaction" reorganization").⁵³ The formation of radicals in the crystals of organic compounds also leads to changes in the mutual arrangement of the surrounding molecules and to the generation of mechanical stresses, which control further transformation.^{54–57} Conformational changes of the molecule in the crystal are accompanied by simultaneous changes in structural and/or electron characteristics of the crystal (for example, intermolecular hydrogen bonds).⁵⁸ The problem of the feedback in glasses and crystals has been described in detail.⁴⁸

4. Heterogeneous systems

4.1. Polymorphic transitions

Let us start with the analysis of the processes of reorganization of the crystalline structure with invariable chemical composition.

Martensite transformations. The classical example illustrating the CMC effect is the low-temperature austenite–martensite transformation.⁵⁹ This process proceeds in the diffusion-free manner and is accompanied only by the displacement of Fe atoms by low (as compared with the lattice parameters) distances. As a result of these atomic displacements at the (reaction product)–(initial substance) interface, elastic deformation arises. Elastic deformation ahead of the front triggers the phase transformation, which acquires the cooperative character. In austenite, the transformation rate becomes high and approaches the sound speed.

Polymorphic transformation in ammonium salts. Another example illustrating the feedback upon phase transition is provided by the results of the works on polymorphic transformations in halides and ammonium rhodanide.^{60–62} In these systems, the mechanical stress field at the interface between the initial substance and the reaction product arises due to the misfit in their molecular volumes and crystalline lattice parameters.

In these compounds, the limiting stage of polymorphic transitions is the stress relaxation stage. The mechanism of stress relaxation is likely to be related to the outflow of dislocations from the surface of the interface between two polymorphic modifications inside the initial crystal along sliding planes as in the case of the $\beta \rightarrow \alpha$ transition in ammonium chloride and bromide.

The effect of stress field on the propagation of the interfacial boundary and on the formation of initial nucleating sites of a new phase may be appreciably different. This behavior was observed for the nucleation upon the polymorphic $\beta \rightarrow \alpha$ transition in NH_4Cl .⁶³ As follows from Fig. 4, the formation of the nucleation sites of a new phase hinders the formation and growth of new nucleation sites. The reason behind this scenario is related to the accumulation of numerous dislocations in the vicinity of a newly formed nucleation site, and these dislocations prevent the sliding of the dislocation that provides the propagation of the transformation front.

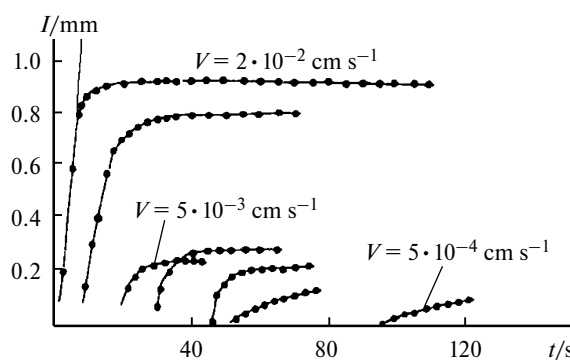


Fig. 4. Inhibition effect of the nucleation of a new phase on the formation of new nucleation sites upon the $\beta \rightarrow \alpha$ transition in NH_4Cl (V is the rate of the nucleation site growth).

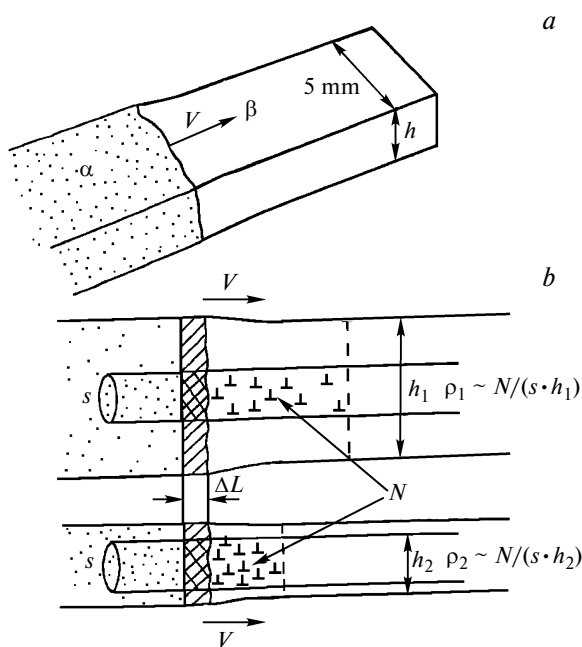


Fig. 5. Propagation of the reaction front of polymorphic $\beta \rightarrow \alpha$ transformation of tin (a) and the dependence of the dislocation density on the geometry of the sample (b); N is the number of dislocations.

In the case of the polymorphic III \rightarrow II transition in ammonium rhodanide when the polymorphic transformation is accompanied by the decrease in the molecular volume rather than by its increase, the stress relaxation pathway is concerned with the diffusion of vacancies from the interfacial surface into the initial phase to compensate its changes in the bulk. The additional mechanism of stress relaxation providing the acceleration of interfacial bound-

ary propagation is the fragmentation into the domains of a new phase.

In the case of the polymorphic transition in ammonium iodide, stress relaxation at the interfacial boundary proceeds due to the development of cracks at the interfacial boundaries between two phases; as a result, this process leads to the self-dispersion of crystals of the initial substance.

On the basis of the studies on stress relaxation mechanisms in the course of polymorphic transitions, the approaches for the control over the rates of these processes have been advanced.⁶⁰

In the case of the processes related to the movement of dislocations (transitions in NH_4Cl and NH_4Br), the method of the incorporation of stoppers preventing the movement of dislocations has been proposed, and this approach is well known in the physics of metals. Stoppers are not only dislocations by themselves, the excessive number of which prevents their movement but also the incorporated admixtures. For example, homogeneous additives (Cu^{2+} in the case of NH_4Cl and Ni^{2+} in the case of NH_4Br) were used as dislocation stoppers in the structure of halides.^{60–62} As was expected, the incorporation of these additives provides the inhibition of polymorphic transformations in halides, which is seen as an increase in the temperature corresponding to the onset of this transformation and in the depression in the nucleation rate.

Polymorphic $\beta \rightarrow \alpha$ transformations in tin. As was shown,^{64–66} by varying the conditions of stress relaxation upon the polymorphic $\beta \rightarrow \alpha$ transition in tin, the rate of the process and the morphology of the reaction products can be controlled. In this transition, the orientational matching of tetragonal (β) and cubic (α) modifications is missing. Change in the molar volume is 26%. This change is the reason behind the stress development at the inter-

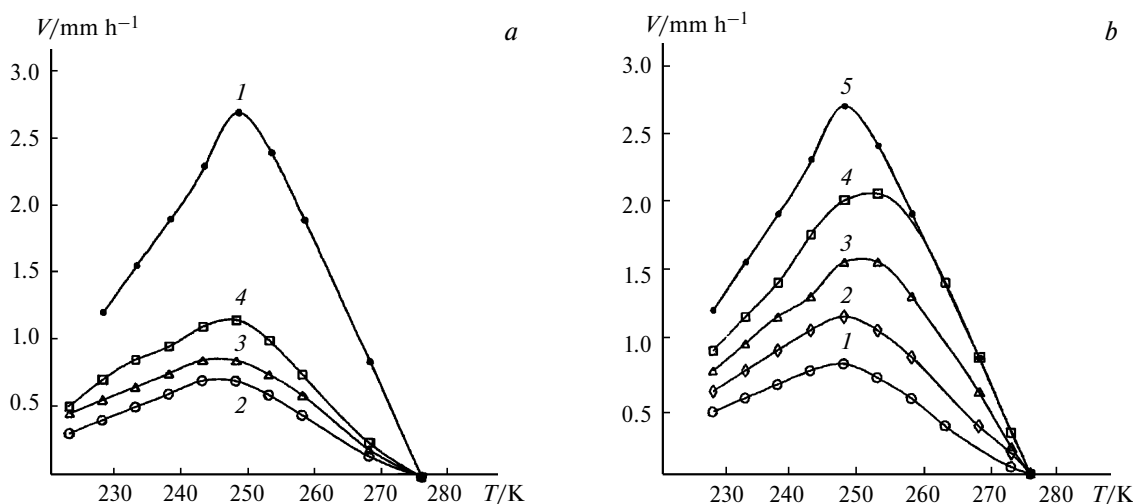


Fig. 6. (a) Propagation rate of the interfacial surface (V) versus temperature (T) for the initial tin sample (1) and at different concentrations of germanium in the sample: 0.3 (2), 0.2 (3) и 0.1 at.% (4); (b) the dependence of V on T at different thicknesses of the sample: 5–7 (1), 10–12 (2), 50 (3), 100–200 (4) and $>500 \mu\text{m}$ (5).⁶⁵

Table 1. Summary on studies of the CMC effect upon polymorphic transitions*

Substance	Transformation	$\Delta V/V$ (%)	T_{pt}/T_m	Stress relaxation mechanisms	Methods for process control
NH ₄ Cl	Type CsCl→NaCl	19	0.58	Slip of dislocations, dislocation-diffusion creep	Introduction of homogeneous additives — stoppers of dislocations
NH ₄ Br	Type CsCl→NaCl	18.2	0.50	Idem	Idem
NH ₄ I	Type NaCl→CsCl	-17	0.31	Slip of dislocations	Use of the Rehbinder phenomenon
NH ₄ SCN	Monoclinic phase → → rhombic phase	-1.8	0.80	Diffusion flow, domainization	Temperature regime
Sn	Tetragonal phase → → cubic phase	26	0.55	Dislocation-diffusion creep	Introduction of homogeneous additives for retardation of dislocation climb, scale effect

Notes. T_{pt} is the phase transition temperature, T_m is the melting temperature.

* Composed by A. P. Chupakhin.

facial boundary. Stress relaxation proceeds due to the plastic deformation *via* the movement of dislocations (Fig. 5).

To control the process, two approaches have been applied: introduction of germanium species into tin and changes in the geometry of the samples (Fig. 6).⁶⁵

The first approach is based on the use (similar to the above case of ammonium salts) of foreign atoms as stoppers preventing the movement of dislocations and thus hindering the propagation of the interfacial boundary. The second method of the control over the process rate is based on the application of the dependence of the density of dislocations on the thickness of the sample and slowdown of the front propagation as a result of mutual interaction between dislocations with increasing density (see Fig. 6).

The examples of polymorphic transitions, which can be controlled on the basis of the knowledge on the CMC effect, are listed in Table 1.

4.2. The CMC effect in the systems, in which composition is changed but no marked change in the structure takes place

Ionic diffusion in glasses. The nature of the feedback upon cation exchange in an isotropic medium between the melt with lithium and sodium salts in the alkali-silicate glass was studied.^{67,68} The reason behind the feedback is the strain induced by the misfit between the radii of substituting and substituted ions. The onset of the exchange process is characterized by the induction period; during this period, lithium ions diffuse from the surface to the bulk of the glass whereas sodium ions diffuse in the opposite direction. Since the strain induced by ionic exchange is initially insufficient for the failure of a solid matrix, the whole process is limited by the diffusion rate of lithium ions. Once a certain critical level of the stored mechanical energy is achieved, cracks are formed, and the matrix breaks down; hence, the rate of the exchange process

increases due to the formation of a new surface. Further propagation of the reaction front is provided by interconnected processes of ionic diffusion and fracture, and the diffusion process is limiting. Depending on the composition of the melt containing lithium ions and temperature, the crack tip can be blocked due to the crystallization of the ionic exchange products; as a result, the rate of further process and the morphology of the ion-exchange product (transition from the disordered platelet structure to the ordered system of hexagonal columns) are changed.

The model for the quantitative description of the steady-state front propagation and morphology of the reaction product has been advanced^{68–71} (Figs 7 and 8). This model allows the prediction of the dimensions of the particles of the reaction product. The key parameter of the model is h_0 , which is the characteristic scale of the minimally possible fracture:

$$h_0 \approx \gamma / (E\beta^2),$$

where γ is the specific work of fracture, E is the mean elastic modulus, β is the characteristic linear shrinkage. Limitations on the minimally allowed size of the fractured fragment (h_0) are governed by the law of energy conservation: the work spent on the formation of a new surface is equal to the energy of the mechanical stress field, which is released upon crack nucleation. It is well known that, upon brittle fracture, the numerical value of the ratio γ/E usually characterizes the interplanar distance, which is perpendicular to the direction of crack propagation. This allows the estimation of the lower size of the fractured fragment for an arbitrary solid-phase chemical process depending on linear shrinkage; and this estimation is important for the prediction of the properties of the formed solid product.

For the reactions of thermal decomposition (dehydration, decomposition of carbonates, hydroxides, *etc.*), the volume shrinkage $\Delta V/V$ is equal to ~30–60%, and, cor-

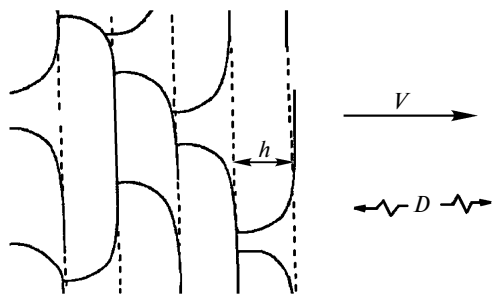


Fig. 7. The scheme illustrating the propagation of the reaction front according to the model:^{68–71} V is the front propagation rate, D is the diffusion coefficient, h is the scale of fracture.

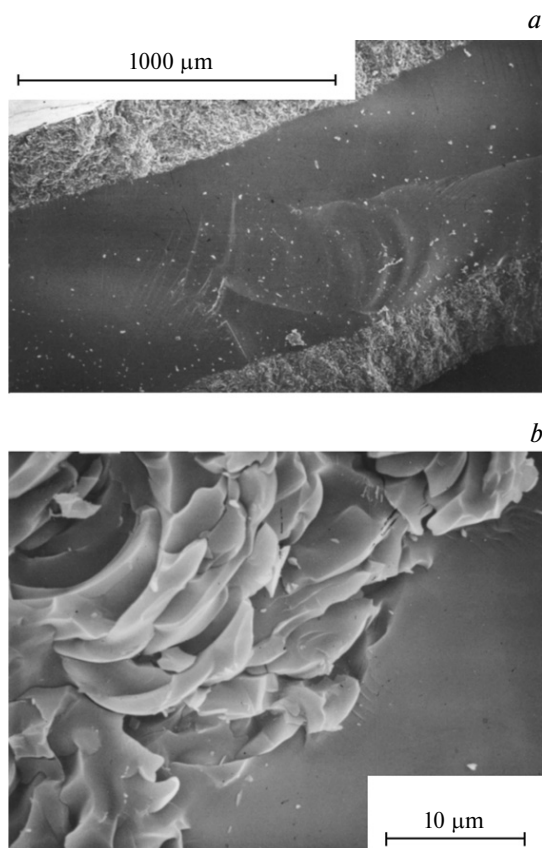


Fig. 8. Micrographs (*a*, *b*) of the boundary of the reaction front.^{68–71}

respondingly, the average linear shrinkage is one-third of this value. For these chemical processes, the size of the fractured block lies within the interval of 1–10 nm.

Among all works on experimental and theoretical study of the nature of the feedback and the CMC effect, the above studies seem to be most promising for the application of this model for the description of the CMC effect in some other systems. One of the results of the above studies is concerned with the development of the procedure for the preparation of the final product with a given mor-

phology (shape and size of blocks, their mutual arrangement, *etc.*) *via* thermal decomposition of diverse compounds, primarily salts and their crystalline hydrates, and this approach offers a new avenue for the preparative solid-state chemistry.^{72–75}

The CMC effect in intercalation reactions. A vivid example of the CMC effect is concerned with the interaction of lithium salts with crystalline aluminum hydroxide, hydrargillite; this process proceeds toptaxially *via* intercalation of lithium cations, anions, and water molecules to the space between aluminum hydroxide layers in hydrargillite with the formation of binary aluminum and lithium hydroxides (DHAL-An, where An = Cl, Br, I, NO₃, SO₄).^{76–91} The reaction commences in the regions adjacent to edges (001) of the hydrargillite crystal and proceeds from the periphery to the center of the crystal along the [hk0] directions; then, deeper regions of the crystals are involved in the reaction, and this behavior leads to the formation of the V-shaped reaction front (Fig. 9).

Structural and volume misfit between the structures of the initial hydrargillite and the intercalation product leads to the development of mechanical stresses in the region of the interfacial boundary, which were visualized by the methods of the single crystal X-ray diffraction and optical microscopy. Stress relaxation is provided by the fracture of the matrix along the basal planes (001) and by the ductile deformation of the hydrargillite crystalline region located ahead of the reaction front due to the formation and movement of partial dislocations. As a result, for hydrargillite, adjacent aluminum hydroxide layers are displaced along the *a* axis by $\pm a_0/3$ in the region ahead of the interfacial boundary, whereas the structure of the DHAL-An product is characterized by the unidimensional disorder along the *c* axis (see Fig. 9). Therefore, mechanical stresses induced in the course of the reaction and stress relaxation processes affect the spatial development of intercalation of lithium salts to hydrargillite, thus providing the conditions for auto-localization of the process.

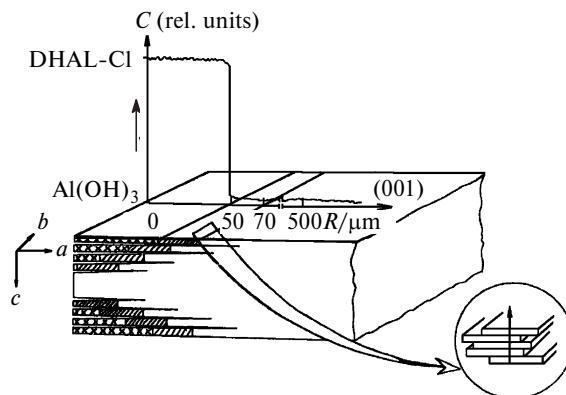


Fig. 9. Changes in the relative concentration of chloride ion in the direction along the plane (001) of the single crystal of hydrargillite upon intercalation of lithium chloride (C is the content of Cl).⁷⁶

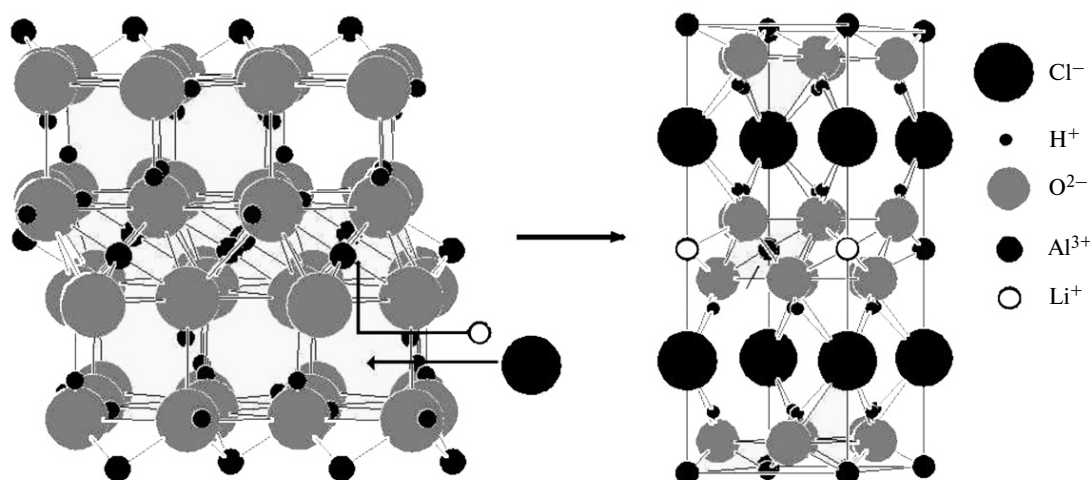


Fig. 10. The scheme illustrating intercalation of LiCl from the aqueous solution to hydrargillite.⁸⁰

Several models differing by the position of Li^+ ion have been advanced for the description of the structure of the intercalation product. According to the work,⁷⁹ Li^+ is located in the space between the electroneutral aluminum hydroxide layers. Neutron diffraction and NMR methods^{81–84} show that, due to intercalation, lithium ions are transferred from the interlayer hydrargillite space to octahedral cavities of the layers, whereas anions remain in the interlayer space. As a result, interlayer distance is changed, and stresses are induced in the layer; due to stress relaxation, the structure of layers becomes disordered, and this disordering is preserved even after deintercalation (Fig. 10). Preliminary mechanochemical treatment leads to the improvement in the intercalation conditions. The main factor responsible for this effect is the deformation of the hydrargillite layer rather than dispersion, which, starting at certain dimensions of small-sized particles, entails the deterioration rather than improvement of intercalation⁸⁰ (Fig. 11).

Detailed study on the reaction mechanism allows the use of intercalation–deintercalation processes for the selective recovery of lithium from high-mineralized natural and associated oil waters, which serves as a basis of the related industrial process.^{85–87} Selective recovery of lithium from brines is based on the fact that the dimensions of cavities in the structure, which accommodate lithium cations, are appreciably smaller than the dimensions of sodium and calcium.

Increased interlayer distance and the transition of the charged lithium cations into the layers of the structural framework allow the introduction of anions into the interlayer space; prior to intercalation, the anions were unable to enter this space due to their large dimensions. For example, chlorine anions can be substituted by various even big-sized organic anions.⁸² Deformation of the structural framework due to intercalation allows the use of the interlayer space for diverse modes of inorganic synthesis of complex compounds with a given geometric position of

ligands,^{88,89} metallic nanoparticles for different functional purposes,⁹⁰ as well as in the medicine for the development of the long-acting antidepressant drugs.⁹¹

4.3. The CMC effect in the systems with changes in structure and composition in the course of the process

Thermal decomposition of solids. Thermal decomposition is the prime example of the process with the CMC effect. Upon hydration of sodium silicate hydrate, dehydration at the early stages is shown to proceed without any marked changes in the solid — water slowly leaves the initial structure *via* diffusion to the surface.⁹² Next, due to the misfit between the molecular volumes of the initial substance and the reaction product, stresses are accumulated, and their action leads to the distortion of the lattice of the initial substance. Stress relaxation results in the development of cracks in the initial substance. The development of these cracks implies the formation of a new surface where dehydration takes place. The above sequence of the processes is repeated but now new cracks grow perpendicular to the surfaces of the early formed cracks,

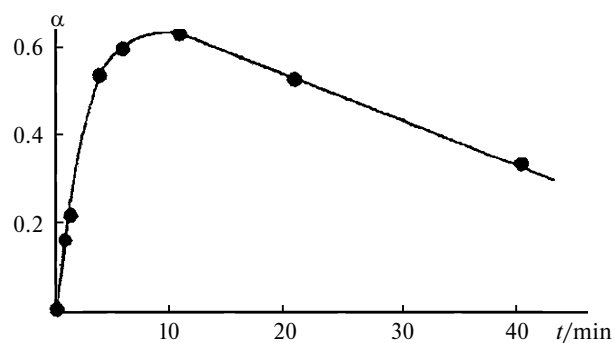


Fig. 11. The degree of intercalation of lithium chloride to hydrargillite plotted against the duration of preliminary mechanical activation of $\text{Al}(\text{OH})_3$ in the aqueous medium.⁸⁰

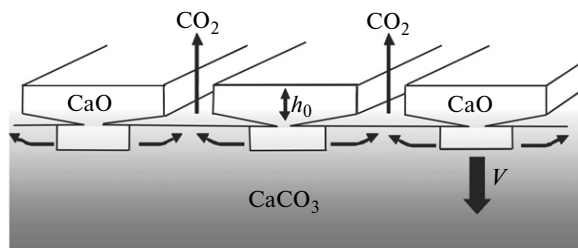


Fig. 12. The scheme illustrating the fracture of CaCO_3 crystal upon thermolysis due to the misfit of molecular volumes of initial CaCO_3 and decomposition product, CaO .^{93,94}

and the branched pattern of cracks is produced. Dehydration process is auto-catalyzed.

The model for the thermal decomposition of calcium carbonate has been proposed:^{93,94} This model is based on the feedback between the thermal decomposition reaction and deformation of the initial crystal and its breakdown (Fig. 12). Thermal decomposition leads to the formation of calcium oxide needles with a length of 100 nm and with a lateral size of 10 nm, and these needles are oriented with respect to the crystallographic axes of the initial calcite crystal. Molar volumes and unit cell parameters of the initial crystal and the thermolysis product are different; hence, at the interfacial boundary between the initial substance and the reaction product, marked tensile stresses arise. Finally, these stresses lead to the nucleation of cracks and fracture of the crystal. Upon fracture, a new surface is produced. Iteration of stages corresponding to the formation of calcium oxide and formation of the new surface provides the propagation of the reaction front inside the crystal.

This scenario is also responsible for the development of the positive feedback between the reaction and the induced breakdown of the crystal upon dehydration of other crystalline hydrates. Structural anisotropy of the

crystal controls fracture and morphology of the formed product so that one can identify the planes, along which the crystalline hydrate breaks down. For example, upon dehydration of the crystalline hydrate of acidic barium oxalate, structural deformation serves as the reason explaining the different character of crystal fracture on edges (100) and (110). Dramatic fracture proceeds along the edge (110) because the interplanar distance in the plane (002), along which the crystal breaks down, is maximum, and the projection of the normal with respect to the fracture plane (002) onto the edge (110) nearly coincides with the direction of the maximal distance (Fig. 13).^{73,94}

The knowledge on the feedback between the chemical reaction and fracture allows the quantitative prediction of the size and shape of solid particles, which are produced as a pseudomorph. A pseudomorph is a porous compact structural unit with preserved geometrical shape and dimensions of the initial crystal, which can be visualized as a structured system of unidimensional nanoparticles.

A pseudomorph is formed due to the relaxation of mechanical stresses induced at the (initial substance)/ (reaction product) interface due to the misfit in their molecular volumes. Stress relaxation leads to the nucleation of cracks (additional surface) and channels, which serve as pipelines for the removal of the gas product and provide the positive feedback of the solid-state chemical reaction.

Studies on the feedback for the thermal decomposition reactions (primarily, dehydration) entailed the development of a method for the preparation of solid products with a desired morphology (shape and size of blocks, their mutual arrangement, *etc.*), and this approach opens a new avenue for the preparative solid-state chemistry.⁷²

Thermal decomposition reactions with the CMC effect and other modes of feedback. These reactions can be exemplified by a well-known fact of a dramatic dispersion

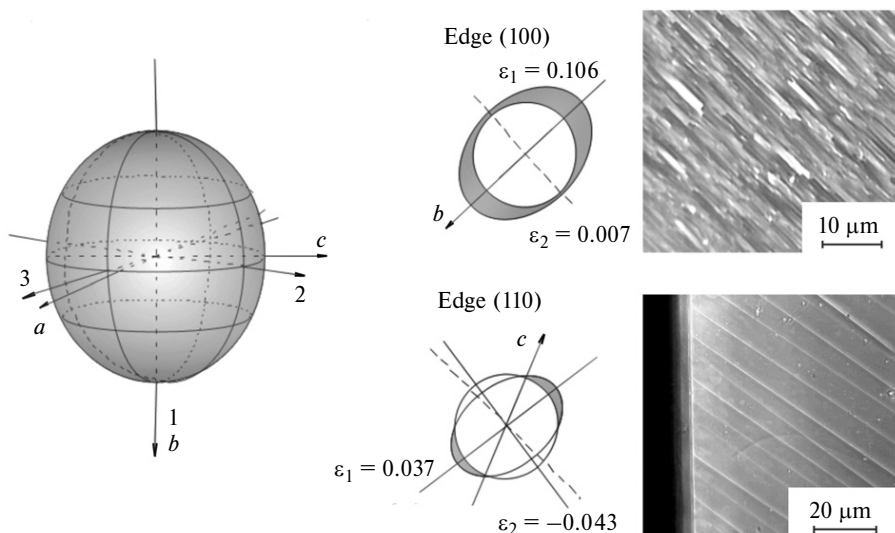


Fig. 13. Anisotropy of strain upon dehydration of $\text{Ba}(\text{HC}_3\text{O}_4)_2$.^{73,94}

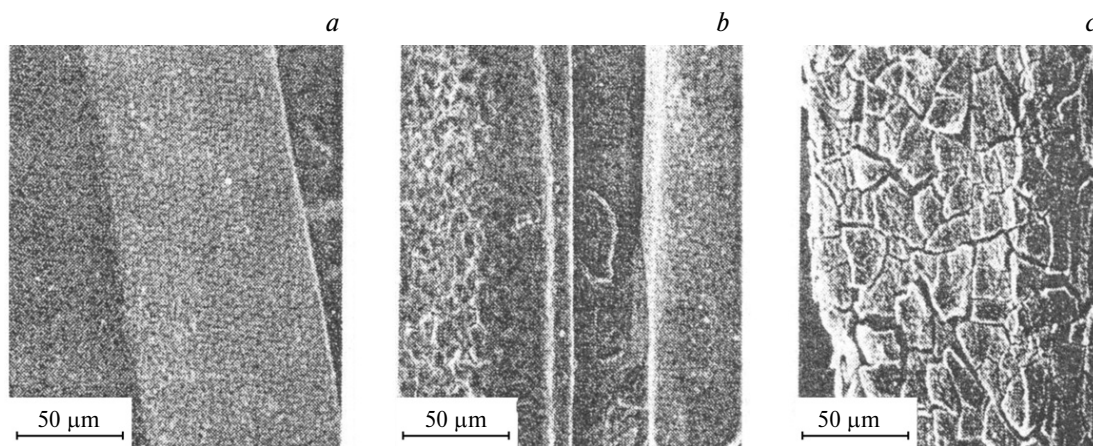
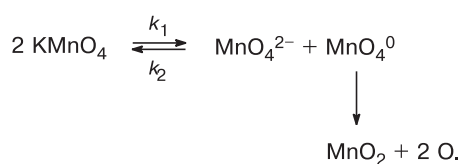


Fig. 14. Dispersion of KMnO_4 upon thermal decomposition (a–c).⁹⁶

of potassium permanganate in the course of its thermal decomposition.^{95,96} The initial stage of thermal decomposition of potassium permanganate is accompanied by the nucleation and further growth of cracks on its surface. Cracks quickly propagate inwards the crystal and their branching occurs. Thus, the formation of not only external surface takes place (Fig. 14).

Seemingly, there exist two reasons behind the feedback between the reaction and the dispersion of the unreacted substances, which provide the acceleration of the thermal decomposition process. These reasons are related to the mechanism of thermal decomposition of potassium permanganate, which proceeds in two stages.^{97,98} The first stage involves the electron transfer from one permanganate ion to another. This stage results in the formation of a stable manganate ion MnO_4^{2-} and an unstable radical MnO_4^0 , which decomposes into MnO_2 and oxygen:



Since the work of withdrawal of the electron from MnO_2 is higher than that from KMnO_4 , manganese dioxide being in contact with unreacted permanganate, will "hoover" the electrons from its lattice, thus shifting the equilibrium k_1/k_2 to the left. As a result, concentration of MnO_4^0 increases, and the conditions of thermal decomposition are improved. This scenario leads to the development of a purely chemical feedback between the reaction and its consequences. Owing to structural transformation, which is accompanied by the formation of the double salt $\text{K}_3(\text{MnO}_4)_2$ by K_2MnO_4 and KMnO_4 and by the reduction in the molecular volume and shrinkage, surface of the crystal is compressed and its dispersion takes place.^{99–101} Finally, formation of a molecule from two oxygen atoms, independently of the place where this event takes place (in

the bulk of the crystal or at the boundary of microblocks), can also be the reason of the self-dispersion of the sample.

Hence, upon decomposition of KMnO_4 , three possible sources exist which can explain the effect of the product (the development of the feedback) on the reaction pathway, and the contribution from each source remains vague:

- changes in the concentration of MnO_4^0 ;
- deformation of the lattice by the atoms due to the reaction $\text{K}_2\text{MnO}_4 + \text{KMnO}_4 = \text{K}_3(\text{MnO}_4)_2$;
- release of a gas product (oxygen).

Dispersion upon thermal decomposition of potassium permanganate is a well-known fact.^{102–104} The pioneering work on the mechanism of this process and reasons providing self-dispersion dated back 200 years.¹⁰⁴ However, the works devoted to the elementary stages of the process, morphology of the related decomposition products, and the kinetics have been published much later. With the account for new practical applications of the thermolysis of potassium permanganate, the problem concerning the mechanism of this process is still relevant^{105,106}

The CMC effect of "solid + gas = solid product" systems. Interaction of potassium bromide with chlorine in the vicinity of the growing potassium chloride nuclei in the bromide crystals was shown to be accompanied by the development of a stress field, which can be easily visualized in the polarized light.¹⁰⁷ Detailed study of this process shows that this process commences at the site where agglomerates of dislocations come to the surface of potassium bromide (Fig. 15).¹⁰⁸

Localization of the process is followed by its auto-localization or, in other words, the process proceeds *via* the growth of the nucleation sites formed at the stage of the nuclei localization. Fractured surfaces of potassium bromide crystals containing the formed nucleation sites were prepared so that the plane of fracture crosses the nucleation sites, and further etching with glacial acetic acid was performed. Examination of the fractured surfaces shows that, near the boundary between the initial substance and the reaction product, the density of dislocations markedly

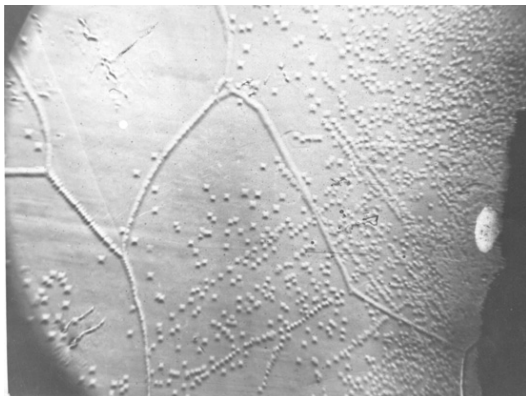


Fig. 15. Changes in density of dislocations in KBr at the boundary with the product reaction $\text{KBr} + \text{Cl}_2 \rightarrow \text{KCl} + \text{Br}_2$.¹⁰⁸

increases (see Fig. 15). This increased density of dislocations near the growing nucleation site rapidly decreases with moving away from the interface, and this scenario can be considered as the evidence of the development of the feedback in the reaction of interaction of chlorine with potassium bromide. This reaction commences at the agglomerates or the boundaries of blocks formed by dislocations. As this process progresses, stresses arise in the region adjacent to the interface (due to different reasons, for example, due to the misfit in molecular volumes or due to the misfit of lattice parameters of potassium bromide and chloride). The above stresses and their relaxation lead to the development of new dislocations, which serve as new potential sites necessary for the further progress of the process.

Subsequent studies on the $\text{KBr} + \text{Cl}_2$ system show that the above scenario of auto-localization of the process and the feedback mechanism demands further clarification because this version ignores the role of a liquid phase, which is formed at the intermediate stages of the process or, in other words, the effect of the external environment.^{109,110}

According to the results^{111,112} on the mechanism of the reduction of iron oxides, these processes are also accompanied by occurrence of the CMC effect. For example, upon reduction of wustite to iron, this process is provided by the diffusion of iron ions to the interfacial surface. At the initial stage of the process, oxygen sublattice is preserved. Stresses in the lattice induced due to the misfit of molecular volumes of the initial substance and the reaction product lead to the enhanced transfer of iron ions to the interstitial sites, thus favoring the reduction process. As follows from Fig. 16, the higher the flow of iron ions from the volume of the to-be-reduced substance to the reaction region (as compared with the same flow along the surface), the higher the probability of auto-localization of the process. This behavior can be responsible for the formation of iron "whiskers". Their growth can induce swelling of iron nuggets upon industrial reduction of iron oxide, which

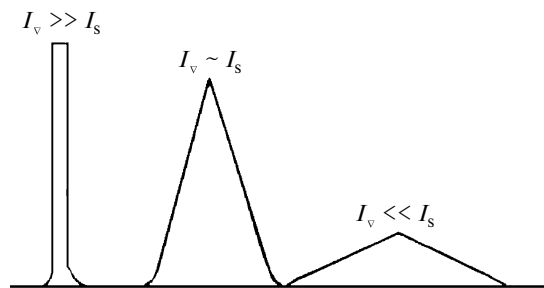


Fig. 16. The scheme illustrating the release of the reaction product upon reduction of wustite at different ratios of flows from the bulk of the matrix and along its surface (I_v and I_s , respectively).¹¹¹

can achieve 400% and presents a serious challenge for the metallurgical process for the production of iron.^{113,114}

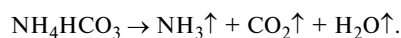
In the case of the interaction of gases with solids when the molar volume of the product is higher than the molar volume of the initial substance, the development of the feedback effect is well known and is related to the transformation of the process from the kinetic to diffusion regime. Numerous examples of this feedback are known. Well-known and well-studied examples are the processes of oxidation of metals, their sulfurization, *etc.*^{115,116} Let us also mention the works illustrating the specific character of this unusual feedback upon oxidation of silicon. In this process, of special importance are the stresses induced at the silicon—(silicon dioxide) interface.^{117–119} Relaxation of these stresses is provided by the viscoelastic flow in the dioxide layer as well as due to the breakdown of the bond between Si atoms with the formation of pointlike defects in the silicon structure and their diffusion to the interfacial boundary where silicon dioxide is formed.

Understanding of the feedback mechanism upon oxidation seems to be very important when this process is used in electronics, for example, for the production of integrated circuits and other devices.

The CMC effect upon the reactions, in which the solid product is absent. Among the reactions of thermal decomposition, a particular group involves the reactions, in which decomposition proceeds without the formation of a solid product, for example, upon thermal decomposition of ammonium bicarbonate and perchlorate.

According to the physics of surface, the sites with the maximum surface curvature are characterized by the free energy maximum. For chemists, this statement means that these sites should show the enhanced reactivity (the edge effect). In the case of crystals, these sites are primarily apexes and edges of the crystal. The importance of this effect for the processes of adsorption, catalysis, and dissolution has been highlighted.¹²⁰ The same effect can be the reason of auto-localization of the topochemical reactions, where a solid product is absent.^{121–123}

This reaction can be exemplified by thermal decomposition of ammonium bicarbonate in vacuum:



This reaction does not yield any solid products as the removal of the formed reaction products — ammonium, carbon dioxide, and water — prevents their chemical effect on the process; nevertheless, auto-localization of thermal decomposition takes place. This process proceeds *via* the formation and growth of cavities; by their shape, they resemble the nuclei of the product in the reactions, in which solid products are formed. This peculiar character of the evolution of the reaction zone is explained by the specific features of the initial crystalline structure. As follows from Fig. 17, this process commences at the apex of the crystal and progresses inside the crystal; upon its movement, this process reiterates the sites of the crystal where this reaction has started. This behavior is the reason behind the increase in the number of sites with enhanced reactivity or, in other words, auto-localization of the process.

Evidently, this explanation is simplified. In addition to the trivial increase in the coordination number in the course of the thermal decomposition, this process leads to changes in the properties of the molecules that remain in the structure in the vicinity of the sites where the reaction has started. Depending on a given reaction, reactivity can also be controlled by changes in length and angles of directed chemical bonds, by changes in the dynamics of the lattice and electron structure. In these systems, the CMC effect is less studied as compared with the reactions with the formation of a solid product.

The CMC effect upon dissolution of solids. The CMC effect upon interaction of the solutions of electrolytes and metals has been studied.^{38,124} The advanced mechanism of the feedback effect is concerned with the formation of a depression — a two-dimensional nucleation site of dissolution — and further opening of the layer of atoms along the crystalline plane *via* the movement of a single-atom

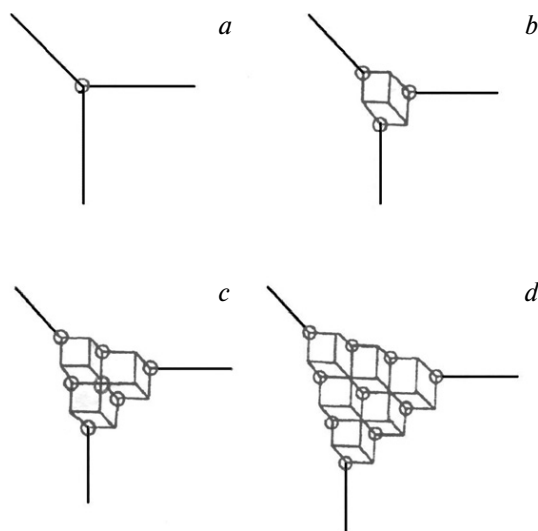


Fig. 17. Iteration of reactive sites in the course of the process due to the edge effects.¹²²

step and further iteration of the layer-by-layer dissolution. Taking into account the fact that the atomic steps can serve as the source of dislocations, one can conclude that the development of the additional source of dislocations due to the dissolution of surface atoms by the corrosion current is provided by the nucleation and operation of new surface sources of dislocations, which arise due to the heterogeneous dissolution of the surface with the formation of single-atom steps. According to the author's definition, chemomechanical effect is concerned with changes in physicochemical properties and fine structure (plasticization) of a solid due to the action of chemical (electrochemical) reactions on its surface, thus providing the additional flow of dislocations; several approaches based on the knowledge concerning the mechanism of this effect and its monitoring have been advanced for the protection of metallic articles from corrosion.

This group of phenomena also includes the effect of chemical reactions taking place upon wetting of the surface of a solid by aqueous solutions on the mechanical properties of solids, including those that control the wetting process.¹²⁵

The CMC effect upon decomposition of ammonium perchlorate. Ammonium perchlorate is widely used as an oxidizer in diverse areas of industry as well as a component of certain types of mixed missile fuels. For practical applications, it is necessary, on one hand, to provide its shelf stability and, on the other hand, to ensure its complete conversion upon in-service decomposition. The solution of these conflicting challenges is possible only due to the detailed study on the mechanism of its decomposition and, in particular, on the nature of the CMC effect.

Even early studies on thermal decomposition of ammonium perchlorate^{126,127} demonstrated that this process commences not over the entire surface of the crystal but at certain surface sites (precisely, in the near-surface region). Then, the reaction progresses near the region of its onset or, in other words, localization and auto-localization of the thermal decomposition process (formation and growth of nucleation sites) are observed.^{128,129} These nucleation sites are shown to be formed not on the surface but at a certain depth below the surface (20–30 μm). Noteworthy is that the nucleation sites are not dense but they are composed of separate micronuclei with dimensions of ~1 μm (Fig. 18).¹³⁰ The shape of the nuclei corresponds to the edge where these nuclei are formed: rhombic on the rhombic edge and rectangular on the prismatic edge. There exists the correlation between the topography of the arrangement of the decomposition nuclei and the sites where the dislocations and their agglomerates come to the surface of the crystal.

According to the results,¹³⁰ decomposition nucleus of ammonium perchlorate is composed of three zones: (1) the zone of the porous core of the nucleus, where the unreacted ammonium perchlorate is accommodated; (2) the zone where the chemical reaction proceeds; (3) the

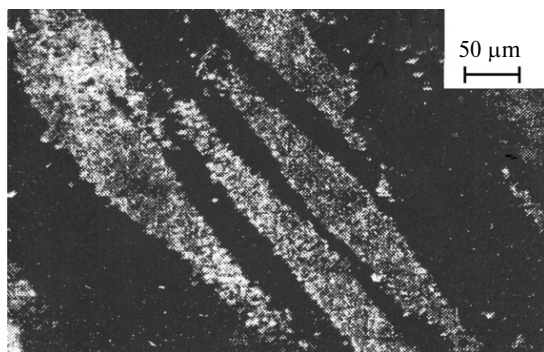


Fig. 18. Nuclei formed upon thermal decomposition of NH_4ClO_4 .¹³⁰

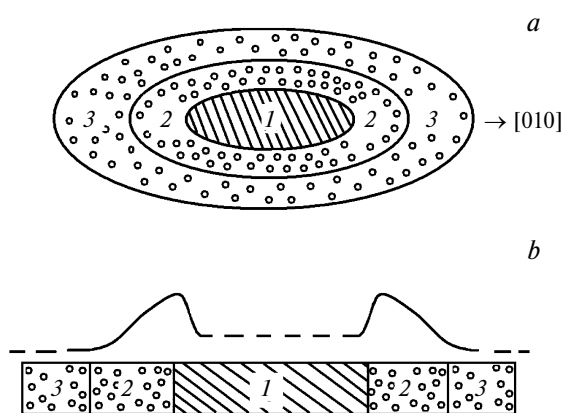


Fig. 19. The scheme illustrating distribution (a, b) of separate zones (1–3) in the nucleus.

stressed zone near a growing nucleus (Fig. 19). The key aspect is concerned with the deformation of the initial crystal in the region, which is characterized by a marked

increase in the density of dislocations in the vicinity of a growing nucleus.

The above evidence and results of additional studies offer the following scenario of thermal decomposition of ammonium perchlorate.^{131–133}

The initial stage of the reaction is concerned with the transition of the proton from NH_4^+ to the ion ClO_4^- . If this transition occurs on the surface or in the dislocation-free crystals of ammonium perchlorate (as in the grown "whiskers" of ammonium perchlorate), the whole process is reduced to the trivial (for ammonium salts) dissociation into ammonium and perchloric acid, which are removed from the surface. When the crystal contains linear structural defects (dislocations and their agglomerates, boundaries of blocks, which stand for the so-called inner crystal surface, pores), they serve as the sites for the accumulation of the dissociation products. Moreover, these structural defects are the regions of the accumulation of foreign ClO_3^- ions, which serve as traps for protons.^{132,133} Proton entrapment leads to the formation of the acid HClO_3 , which is unstable and decomposes with the formation of the radical ClO_2 .¹³⁴ This radical interacts with the ClO_4^- ions of the lattice; as a result, ClO_3^- ion is formed, and the process is repeated. As a result of the decomposition of perchloric acid and oxidation of ammonium, the products are accumulated within the pores, thus creating the excessive pressure, which can achieve, by estimates, 20 atm.¹³⁰ Deformation of the crystal induced by this excessive pressure serves as the source of the development of new dislocations, and the process is repeated (Fig. 20). Figure 21 illustrates the general scheme of the feedback in this system.^{135,136}

Guidelines for the optimization of the consumer-oriented characteristics of ammonium perchlorate are based on the comprehensive analysis of the complex feed-

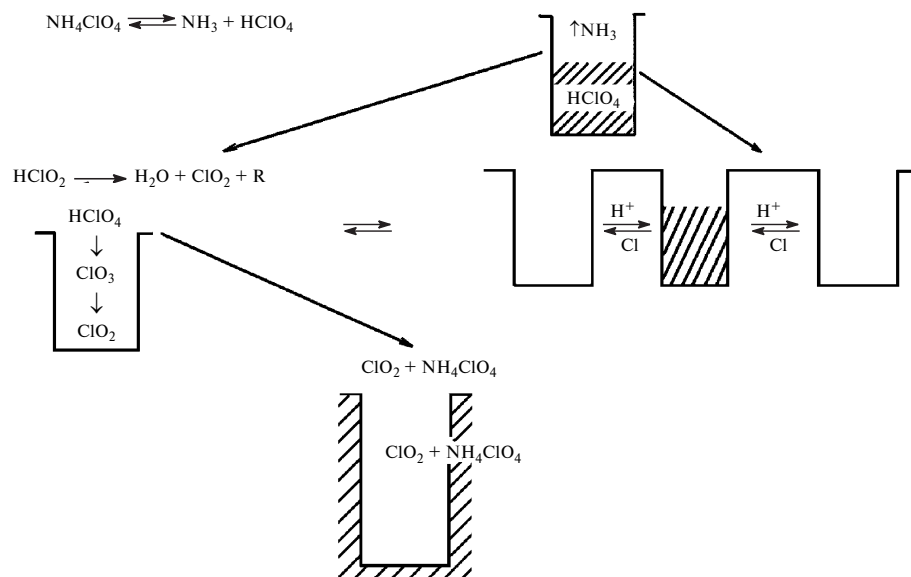


Fig. 20. The scheme illustrating the low-temperature decomposition of NH_4ClO_4 .¹³³

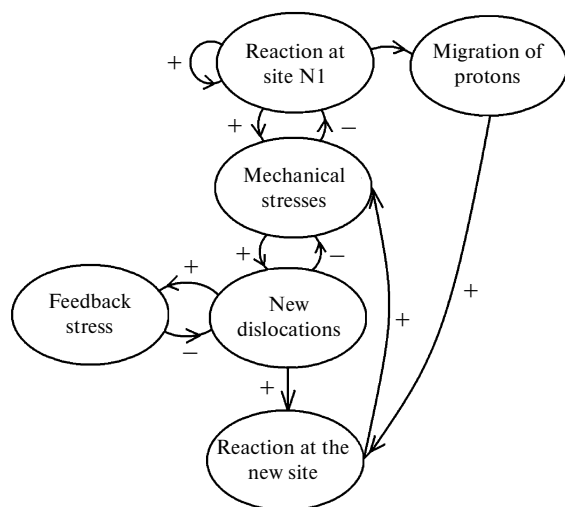


Fig. 21. Complex of feedback loops upon thermal decomposition of NH_4ClO_4 .^{135,136}

back loop. These guidelines are concerned with the control over the content of certain admixtures in order to govern "the chemical pathways of the feedback" (*via* purification from one admixtures and doping with others, preliminary irradiation or prevention of irradiation) and to control the density of dislocations and mechanical properties in order to regulate the process *via* the CMC effect (control over the dimensions of particles, concentration of dislocations, prevention of undesired mechanical impact upon storage and transport operations).

Conclusion

The importance of the CMC effect can hardly be overestimated. From the viewpoint of the macrokinetics of solid-state chemical reactions, the account for the CMC effect is the key component for the construction of the models illustrating the process in space, elucidation of the reasons behind localization and auto-localization or, in other words, the origin of its "topochemistry".

Several practical applications of the studies on the CMC effect in certain processes have been discussed. The list of the above examples could be lengthened. Practical applications should rely on the knowledge on the mechanism of the CMC effect in order to control the process and predict its scenario. Further development of works in this direction should involve the search of the systems where the CMC effect is best pronounced, and the reaction is sensitive to mechanical stresses and stress-induced structural distortions. Studies on the CMC effect should involve, for example, detailed study of the mechanical properties of solids, thorough examination of the product—(initial substance) boundary, and comprehensive study on the nature of the distortions in the crystal. The studies on the CMC effect in molecular crystals seem

to be very promising. Nowadays, principal attention is focused on external effects such as macroscopic deformation of molecular crystals due to the reaction. The next stride is the study how this deformation affects further development of the process, and this step is very important not only for the fundamental science but also for the development of crystals with photo- and thermo-mechanical phenomena for molecular devices, sensors, actuators.¹⁷

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