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Thermal Decomposition of Solid Substances as a Method to Obtain Nanocrystalline Structurally Ordered Media

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Abstract

For one reactions class of thermal decomposition of the type of crystallohydrate dehydration, decompositions of carbonates, hydroxides and other compounds, we managed to go the entire way – from the starting reagent to the final morphology of the solid product. Possible phase formation mechanisms for this type of processes were considered. A general algorithm that allows theoretically predicting the size and shape of the particles of final product was proposed. The product of thermal decomposition is a porous compact formation that conserves the geometric dimensions and shape of the starting precursor particle (pseudomorphosis). There is a fraction of emptiness inside pseudomorphosis, equal to the difference between the molar volumes of the starting reagent and product. Pseudomorphosis consists of oriented product nanocrystals equally sized and shape interconnected, that is, represents a structured system.

It was demonstrated experimentally that pseudomorph obtained by dehydration of $CuSO_4 \cdot 5H_2O$ monocrystal behaves analogously to liquid crystals as an optically anisotropic medium, *i. e.*, possess birefringence. This is the evidence of the ordered locations of particles composing it. It was established that the spatial distribution of the intensity of small-angle X-ray scattering from pseudomorphosis obtained by dehydration of $CuSO_4 \cdot 5H_2O$ monocrystal (performed at the synchrotron radiation source of INP, SB RAS, applying a two-coordinate detector) possessed angular anisotropy. Based on the received data, the sizes of the rod-shaped particles were assessed: thickness (~8 nm), length (~100 nm) and their location in pseudomorphosis.

Key words: thermal decomposition, pseudomorphosis, nanocrystalline structurally ordered media, supercrystal, small-angle X-ray scattering

INTRODUCTION

Due to unique physical properties, different from properties both voluminous materials, and individual nanoparticles, forming a composite, nanocomposite media arouse of particular interest to researchers. Properties (structural, electric, optical, and magnetic) of new materials based on nanocomposite media are defined by the size, shape, mutual arrangement (orderliness) of the constituent nanoparticles and fill factor by nanoparticles. Ordered porous nanocomposite media, so called metamaterials, unusual properties of which are conditioned by not so individual physical characteristics of their components, how precisely their structural ordering, are most interesting from the viewpoint of practical applications. Metamaterials may possess by a negative refraction index of light, abnormal magnetic and dielectric permeability and other unique physical properties.

Known techniques of the synthesis of nanocomposite porous media allow preparing a limiting number of systems: porous silicon, oxidized porous silicon, porous gallium phosphide, porous aluminium oxide, as well as mesoporous photon-crystalline structures based on ordered polymer spheres (in the form of direct or inverse crystals), spheres from silicon dioxide [1] or zirconium dioxide [2]. At the same time, it is obvious that a successful development of nanotechnologies is impossible without developing and improving methods of the chemical synthesis of nanoproducts [3].

Having established the mechanism of the thermal decomposition of solid substances, we offered a new way of the targeted synthesis of porous nanocomposite media with the controlled dimensions and shape of nanoparticles. This approach to solid-phase reactions of thermal decomposition based on the concept of the reverse bond between the chemical reaction and destruction allows quantitatively predicting the size and shape of particles of the solid product [4]. The product of thermal decomposition represents a porous compact formation that preserves the geometrical sizes and shape of the starting particle of the precursor (pseudomorphosis). Inside pseudomorph, there is a proportion of emptiness, the size of which is equal to the difference of the molar volumes of the starting reagent and product. Herewith, pseudomorphosis consists of oriented nanocrystals of the product of the equal size and shape, connected between each other, *i. e.*, represents a structured system from monosize particles. It can be said that pseudomorphosis is a supercrystal based on highly ordered elements.

The goal of the present work is the development and experimental rationale of a new method of the preparation of nanocrystalline structurally ordered media by the thermal decomposition method.

RELAXATION OF MECHANICAL STRESSES BY DESTRUCTION AS A FACTOR DEFINING THE PARTICLE SIZE OF THE SOLID PRODUCT OF THERMAL DECOMPOSITION

Thermal decomposition of solid substances is one of the traditional methods of the preparative chemistry of the solid body for the preparation of small particles [5]. However, for the possibility to efficiently and purposively manage properties of the formed product, such as, for example, dispersity, defectiveness *etc.*, it is necessary to understand the decomposition mechanism, and namely, the processes proceeding in the reaction zone and determining its structure. Thermal decomposition, as a rule, occurs *via* the formation and growth of embryos that when overlapping give the reaction front. A chemical reaction is localized on the front that moves with a constant speed. These ideas represent postulates of topochemistry [6]. As mentioned above, reactions of the type of dehydration of crystallohydrates, decomposition of carbonates, hydroxides and other compounds lead to the formation of the highly crushed product formed in the form of so called pseudomorphosis.

The formation mechanism of pseudomorph is conditioned by relaxation of mechanical stresses emerging in the interphase boundary due to difference of molar volumes of the starting reagent and solid product [7]. The cracks formed in the reaction zone being efficient runoffs of the gaseous product accelerate decomposition. This is one of the concrete manifestations of the positive feedback at solid-phase reactions. The value of mechanical stresses and accordingly, destruction efficiency, *i. e.* the particle size of the resulting product, in the first turn, is defined by the magnitude of shrinkage when reacting.

The problem of the quantitative dependence of the size of fractured particles obtained in the course of these reactions from the magnitude of shrinkage was solved by us for some cases of the destruction geometry in the reaction zone and tested experimentally for a number of model reactions [7–13].

The most important parameter of our theory is the characteristic scale of the minimum possible destruction: $h_0 \approx \gamma/E\beta^2$, where γ is specific work of breaking; E is averaged modulus of elasticity; β is characteristic linear shrinkage. The minimum fractured particles (h_0) is a consequence of the energy conservation law: the work expended for the formation of a new surface should be equal to the energy of the field of mechanical stresses that is released as a result of the crack formation. It is well known that when at brittle destruction, the ratio of γ/E, as a rule, is equal to the interplanar distance, perpendicular to the direction of the crack propagation.

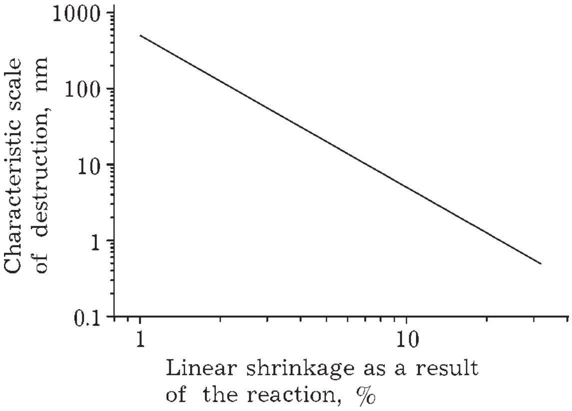

Fig. 1. Dependence of the characteristic scale of destruction on the magnitude of the linear shrinkage for thermal decomposition reactions of the dehydration type.

Without going into the details of the theory and complexity of exact calculations, in which the anisotropy of the mechanical properties of the reactant and product, as well as the dependence of the shrinkage on orientational correspondences between them that should be taken into account, one can make the lower-end estimate of the fractured particles for an arbitrary solid-phase chemical process depending on the magnitude of the linear shrinkage (Fig. 1).

The reactions, interesting to us, of thermal decomposition of the type of dehydration, decomposition of carbonates, hydroxides *etc.*, usually have the volume shrinkage $\Delta V/V \sim 30-60\ \%$, respectively, average linear shrinkage amounts to one third of this magnitude. It can be seen that the size of fractured particles for these chemical processes varies within the limits of 1–10 nm.

The theory allows not only predicting the size of fractured particles, but also indicating the existing limitations in respect to the preparation of the monodisperse nanosize product. It is obvious that in fine crystals, where the energy of mechanical stresses does not reach the destruction threshold, cracks will not form. Additionally, the size of the starting crystals should be sufficient for establishing the stationary mode of the movement of the reaction front. According to our assessments, the maximum and uniform crushing is realized in monocrystals with the sizes of above $\sim 10^3 h_0$. On a stationary moving front, the same conditions of destruction are constantly reproduced, which ensures the minimally possible size, maximally narrow distribution of the resulting particles of the product by sizes and preservation of an orderly arrangement of particles relatively to each other.

PHASE FORMATION AT SOLID-PHASE REACTIONS OF THERMAL DECOMPOSITION

It is obvious that reactions of thermal decomposition $A_{sol} \leftrightarrow B_{sol} + C_{gas}$ of the type of dehydration of crystallohydrates, decomposition of carbonates, hydroxides *etc.*, begin on the surface of the starting reagent, with which molecules of the gaseous product are removed and the layer representing a solid solution of the product in the starting reagent is formed. This layer is coherently connected with the matrix and mechanically tense, since the molar volume of the solid solution is smaller than the molar volume of the matrix. At this stage, the solid solution layer is thickened due to the diffusive removal of the gaseous product. The subsequent development of the solid-phase chemical reaction depends on the evolution of a solid solution of the product in the starting reagent.

There are the following possible evolution routes of the solid solution:

1) a solid solution may be stable or metastable, but stable in the course of the reaction in the whole concentration range (there is an unlimited mutual solubility of a solid product in the starting reagent);

2) when achieving the critical concentration the decomposition of a solid solution on individual phases occurs by the mechanism of the decomposition of solid solutions (limited solubility).

Why are we limited only by these two evolution variants of a solid solution? Once in the local area of reacting solid the chemical stage proceeded (for example, removing water from the surface layer), a rearrangement of the crystalline structure of the starting reagent into the product structure happens inevitably. And this is in fact a phase transition, which is according the total classic Ehrenfest classification can be first or second order phase ransition. The availability of the interface between of the initial phase and phase of the product is inalienable property of first order phase transition. At the phase transition of the second kind, the accumulation of a new phase in the starting reagent occurs continuously as far as passing a chemical reaction without forming the interface.

The theory of forming autowave fronts for these cases [7, 9, 11–13] that allows predicting the rate of a solid-phase chemical reaction was proposed by us. However, in this case, we are interested only the morphology of the resulting product.

It is obvious that for the considered number of solid-phase chemical processes regardless the type of the phase transition, the morphology of the solid product is uniquely determined by the relaxation of mechanical stresses by destroying. And this is the major factor. But between the case with localized precipitates and uniform proceeding chemical processes, there is an important difference, consisting in the fundamentally different distribution of deformations in the reaction zone. Allocations of the solid product mechanically associated with the starting reagent localize tensile stresses that are proportional to full shrinkage within themselves. At uniform proceeding the process, mechanical stresses, on average, are uniformly distributed over the reaction zone. This forces us to consider every case separately.

MORPHOLOGY OF THE SOLID PRODUCT FOR THE CASE OF UNIFORM OCCURRENCE SOLID-PHASE CHEMICAL REACTIONS

Consider the variant of homogeneous occurrence of a solid-phase chemical reaction, namely, a chemical reaction in the isotropic medium.

The removal of the gaseous product leads to the formation in the surface layer of a solid solution. Due to the difference of molar volumes of the starting reagent and product, this layer experiences mechanical stresses. The stress condition of the surface can be characterized as the plane stress state, *i. e.* along the surface voltage is proportional to the respective components of the shrinkage tensor at the reaction; the direction is perpendicular to the surface, free, therefore, the corresponding stress component is equal to zero. When achieving by stresses the critical conditions on fracture a crack propagating normally to the surface is formed. Due to breaking the symmetry of force fields on the normally propagating crack, the tangential component of the stresses starts acting, trying to rotate the toe crack to the left or right. A crack turn and movement along the surface with puncturing plate most efficiently unload the stress state. The plate thickness is proportional to $h_0 \approx \gamma/E\beta^2$. Ideally, the length of the plate should be commensurable with the sample dimension, but the multiple destruction of the surface leads to the length limitation of the split off plate. The repetition of acts: a chemical reactions along the crack facets, accumulation of mechanical stresses, and subsequent destruction with puncturing plate of the final product – leads to the emergence of the stationary moving joint front of the chemical reaction and destruction (Fig. 2). It is the picture of the disordered destruction that we observe at experimental studying the ionic exchange of sodium for

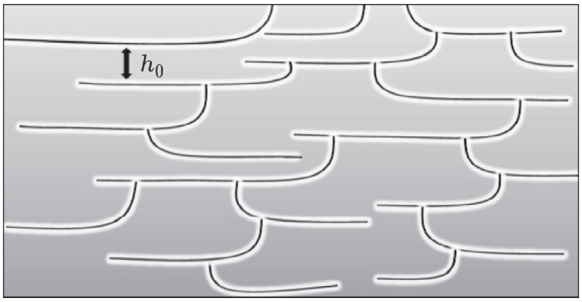

Fig. 2. Morphology type of the solid product for the case of homogeneous occurrence of the solid-phase chemical reaction.

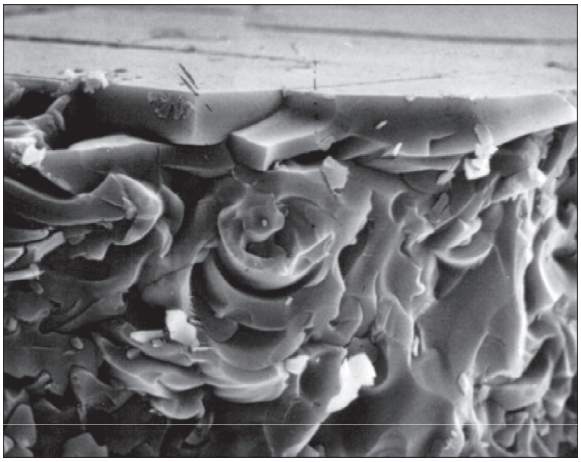

Fig. 3. Morphology of the solid product of the ion exchange of sodium ions for lithium ions in alkaline silicate glass.

lithium in alkaline silicate glass in nitrate lithium-containing melts (Fig. 3) [8–10].

Glass is an isotropic medium; therefore, here the picture described above is implemented most brightly. Due to the instability of the crack to turning, a solid product of plate geometry is formed. The plates length is limited and more likely, is determined by the size, within the limits of which the mutual influence of cracks is completely lost: at the plate thickness of 1.5–2 μm, its average length amounts to almost 10 μm, *i. e.* in 5–7 times exceeds the thickness.

The plates are separated by cracks and bound by joint isthmuses, which imparts the mechanical properties to the product. By characterizing such a type of structuring in respect of the origin one speaks of the determined chaos. At the destruction only the plate of the strictly certain thickness and size can be formed, but the place of the appearance of the crack is determined not precisely, as well as the rotation direction (to the left or right) depending on local fields of stresses near crack tip, what and brings the chaotic nature into the location of plates. The total volume of cracks is equal to the difference of molar volumes of the starting reagent and product, and the totality of cracks forms a topologically singly connected domain.

What alterations into the destruction picture at homogeneous occurrence the solid-phase chemical reaction the anisotropy of the starting crystalline reagent and anisotropic occurrence the reaction will bring in? Unfortunately, while we are not able to fully consider the action of these factors simultaneously and confine ourselves only to the consideration of the case of the anisotropic shrinkage in an isotropic or weakly anisotropic reagent that is characterized by the identical value of γ/E for various crystallographic directions. The presence of an anisotropic shrinkage and, accordingly, of the deformations tensor will lead to the fact that on each facet of the initial monocrystal of the reagent there will be own individual kind of the plane stress state. We are able to determine it by having found out projections of appropriate components of the deformations tensor on the corresponding monocrystal facets. The kind of the plane stress condition of the facet together with planes of the potential destruction (planes of the monocrystal cleavage) unambiguously sets the subsequent destruction picture. It is obvious that the destruction is facilitated along the planes that have the smallest adhesion, and this, as a rule, the planes with large interplanar distances and, accordingly, with the smallest reticular density of structural elements. It is also obvious that the destruction should be accompanied by the maximum relaxation of stresses, and this is implemented in that case, if the projection direction of the normal to the destruction plane will be close to the direction of the maximum stretch, *i. e.*, the maximum shrinkage.

Suppose that we know the kind of the plane stress state of the verge of the monocrystal, *i. e.*, the specific kind of the ellipse of deformations for the given facet. For this, it is sufficient to know the crystalline structures of the starting reagent and product and orientational ratios between them. The main axes of the strain ellipse will correspond to values of the characteristic scale of the minimum possible destruction for various directions of h_{0X} and h_{0Y}, moreover, for certainty, accept that $h_{0X} < h_{0Y}$.

As a result of the occurrence of a solid-phase chemical reaction, on this facet of the crystal the critical conditions on destruction will be achieved and, by cleavage planes, amounting to the minimum angle with the direction, perpendicular to the direction of the maximum shrinkage, cracks will emerge. The average distance between cracks will be equal to h_{0X}. The appearance of cracks in the direction of X with a larger number of stresses concentrators on their edges facilitates to the destruction in the direction, close to the direction Y with the average fractured particles h_{0Y}. The stored elastic energy in the reacted surface layer is sufficient for this. The surface of the monocrystal facet, thus, will become covered by cracks grid with a typical scale $h_{0X} \times h_{0Y}$. Due to the crack instability to turning at the depth of h_{0X}, a crack turns on the cleavage plane constituting the minimum angle with the surface of the crystal facet. It is most probable that this crack will move along the facet surface in case, if this natural growth facet presented in the crystal faces with the minimum Miller indices, *i. e.*, the plane of cleavage.

The final product will represent in the general case parallelepipeds coupled between each other by isthmuses with a characteristic scale of $h_{0X} \times h_{0X} \times h_{0X}$. The thickness of these parallelepiped-like particles is equal to the smallest size of fractured particles for the given specific facet of the monocrystal. It follows from here that for various facets of the starting crystal when occurrence a chemical reaction, its own individual fractured particles is characteristic in accordance with the deformation ellipse for the given facet. On the stationary front of a solid-phase chemical reaction, the conditions facilitating the repetition of acts of destruction with the identical fractured particles, characteristic for the given facet of the monocrystal, are reproduced. Consequently, by changing the habitus of the starting crystal, *i. e.* the ratio of facets in the faces of the crystal or forcing to enter into the reaction only certain facets, one can control the size and shape of particles of the formed solid product. Of course, this is not the sole possibility to manage the parameters of the fractured particles in a homogeneous occurrence chemical process but in our point of view, most nontrivial.

One can consider a great number of variants of reaction proceeding with various kinds of the ellipse of strains on a specific crystal facet, including cases, when its individual components are equal or higher than zero. However, in the frameworks of this work, this seems inappropriate. The algorithm of actions in the most general view was demonstrated by us, and the specific is better to apply to the chemical solid-phase process already experimentally studied. To explain pictures of destruction on individual facets at dehydration of barium acid oxalate dehydrate, the given algorithm was used by us [14] (Fig. 4). A quantitative coincidence of experimental values of parameters of surface fractured particles with theoretically calculated ones were obtained.

What can be said about the structuredness of the solid product formed upon the homogeneously proceeding solid-phase process in weakly anisotropic media? It is obvious that the most characteristic kind of structuring in this case

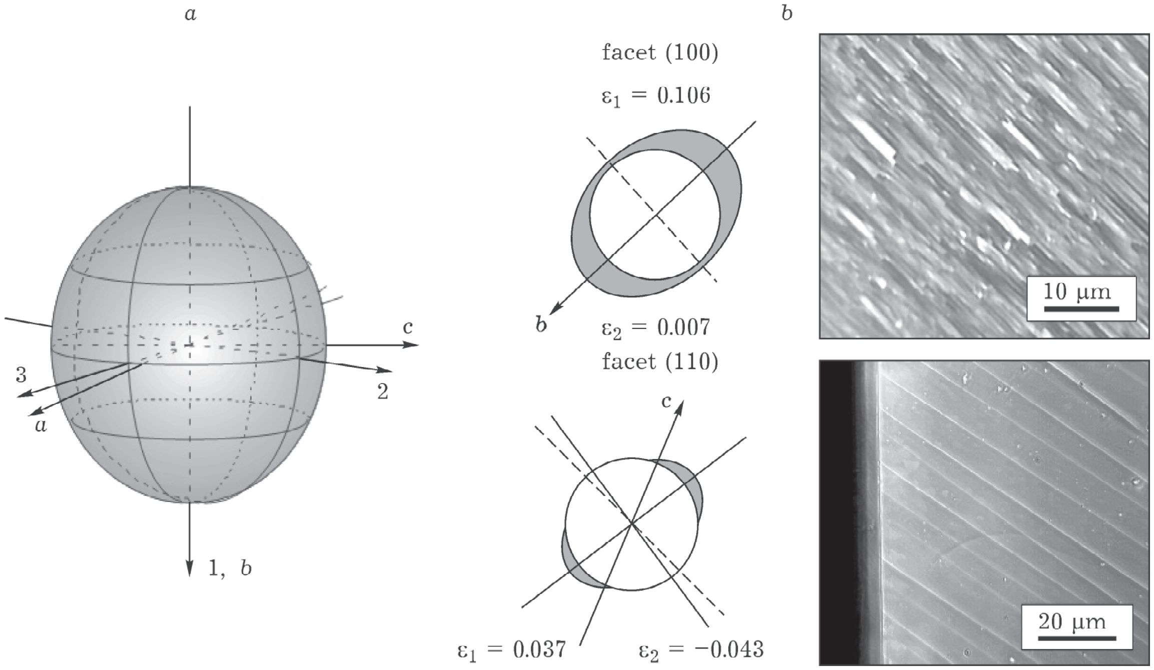

Fig. 4. Anisotropy of destruction on various facets of a crystal at the dehydration reaction $BaC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$: *a* – deformation ellipsoid at the reaction and the location of the crystallographic axes (*a*–*c*) of the starting hydrate and principal axes of the deformation ellipsoid (*1*–*3*); *b* – pictures of destruction and deformational condition on the facets (100) and (110) (deformation ellipses on the appropriate verges and deformation values along the main axes are represented; dashed lines indicate lines of the intersection of facets by the destruction planes).

will be so called determined chaos. This is associated with the fact that a new crack, perpendicular to the surface, is formed in an arbitrary place of the horizontal site of the previous crack and further can deflect to the left or right at gouging the corresponding plate. Thus, the fracture pattern is similar to the one described by us earlier for ion exchange in alkaline silicate glass and dehydration of barium acid oxalate.

Although the processes considered above possess by the probabalistic nature, they are based on some mechanisms of destruction, therefore, the structure formed nevertheless possess certain orderliness. The shape, sizes, mutual location and crystallographic orientation (in case of crystalline reagents) of particles have close characteristics, since the process occurs stationary, *i. e.* conditions of loading (including averaged boundary conditions and deformations profiles emerging in the reaction zone) and destructions are constantly reproduced. However, there are and other factors facilitating the formation of the ordered morphology of the solid product. For the start, consider the trivial case. Suppose that the ellipsoid of deformation of the solid-phase chemical reaction have a special kind: by one direction – shrinkage, by all the other ones – lengthening. The reaction causes the destruction only on certain facets of the crystal, herewith; plates of the length in the whole facet and thickness (h_0), in accordance with the tensor of the shrinkage are formed. By all other directions, disruption is banned. The final product will have the ordered plate-like morphology. A similar morphology will be observed at the condition, if the crystalline lattice of the reagent possess clearly pronounced anisotropic properties, for example, the layered character, which causes an essential difference (approximately by an order) in the specific work of fracture along various crystallographic directions. In these cases, as a rule, the ellipsoid of deformation of the solid-state chemical reaction and anisotropy of the crystalline lattice are interrelated. Under these conditions, as a rule, the ellipsoid of deformation of the solid-phase chemical reaction and anisotropy of the crystalline lattice are interrelated. Examples of the orderly plate-like morphology are well known for layered compounds [6]: molybdenum oxide dihydrate, potassium ferrocyanide, vermiculite, copper formiate tetrahydrate *etc*. Ordered geometry of destruction emerges in that case, if the movement of cracks in various crystallographic planes will be independent. If the tips of at least one type of cracks out of a possible set of cracks, moving perpendicularly to the surface facet, do not turn up to transverse splitting off, then in this case, in the bulk of the product, that orderliness will be conserved that formed on the surface of the crystal facet.

MORPHOLOGY OF THE SOLID PRODUCT OF A CHEMICAL REACTION THAT IS ACCOMPANIED BY THE FORMATION AND GROWTH OF LOCALIZED PRECIPITATES

If the solubility of the solid product in the reagent is limited, then in the surface layer, as far as the removal of the gaseous component, a supersaturation is quickly achieved and precipitates of the solid product mechanically coupled with a reagent are formed. These precipitates experience tensile stresses, proportional to the volumetric mismatch of phases, *i. e.* complete shrinkage at the reaction. Upon the growth of precipitates the elastic energy is accumulated in them. When achieving the size of precipitates $h_0 \approx \gamma/E\beta^2$ (typical scale of minimum possible destruction) their split off from the reagent occurs. Cracks serve as efficient runoffs, which accelerates the removal of the gaseous component. A loop of the positive reverse connection between the reaction and destruction arises, as a result of which an autowave front of the reaction is formed. In this case, the destruction scale is equal to h_0 and does not depend on the conditions of carrying out the reaction.

At the disintegration of a solid solution, the shape of the localized precipitate coherently associated with the starting reagent is determined by the minimum of the elastic energy [13, 14]. If the growth of the localized precipitate is quasi-equilibrium, then the shape of the precipitate is directly associated with the minimum of the elastic energy. If the growth of the localized precipitate is quasi-equilibrium, then the shape of the precipitate is directly connected with the minimum of the elastic energy. In the general case, in the anisotropic medium, the precipitate has the shape of parallelepiped, the lengths of the ribs of which are inversely proportional to the product of the Young's modulus on square of the linear shrinkage in the selected direction. The strain tensor can be calculated by the tensor of shrinkage that, in turn, is determined from experimental orientational correspondences between the product and starting reagent. And the tensor of the minimum fractured particles is placed in correspondence with the tensor of shrinkage. As soon as the precipitate size in some direction reaches the critical size h_0, the destruction will occur. Moving along the interphase boundary a crack splits off the precipitate, herewith, a complete relaxation of the mechanical energy stored in it occurs. The precipitate partially preserves the mechanical contact with the starting reagent along one direction. The repetition of the acts of the formation, growth and splitting off precipitates with subsequent "burning out" of the starting reagent on the contacts between neighbouring precipitates forms the final type of structuring the solid product of the solid-phase chemical reaction. It is hard to characterize unambiguously the structuredness of the formed product. Precipitates at the formation are coherently associated with the matrix and after splitting off preserve the original orientation, and the isthmuses bind precipitates in the coherent whole giving mechanical properties to the final product. Thus, the solid product consists of strictly oriented parallelepipeds of the same size (in general case) or other geometrically affined figures (plates, cubes, needles *etc.*) connected by isthmuses (Fig. 5). Cracks between precipitates form a topologically singly connected region, and their total volume is equal to the difference of molar volumes of the starting reagent and product. The existence of the far translational order in such a system is doubtful, but the presence of the far orientational order in the location of particles of the solid product is very probable, as in liquid crystals.

Thus, for one class of the reactions of thermal decomposition of the type of crystallohydrates dehydration, decomposition of carbonates, hydroxides and other compounds, we managed to come the whole way – from the starting reagent to the final morphology of the solid product. Possible mechanisms of the phase formation for this type of processes were considered and the overall algorithm that allows theoretically predicting the size and shape of particles of the final product was proposed. The product of thermal decomposition represents a porous compact formation preserving the geometrical sizes and shape of the initial particle of the precursor (pseudomorphosis). In pseudomorphosis, there is a proportion of the emptiness, the volume of which is the difference of molar volumes of the starting reagent and product. Herewith, pseudomorphosis consists of the oriented product nanocrystals connected between each other of the same size and shape, *i. e.* represents a structured system from monosize (on average) particles.

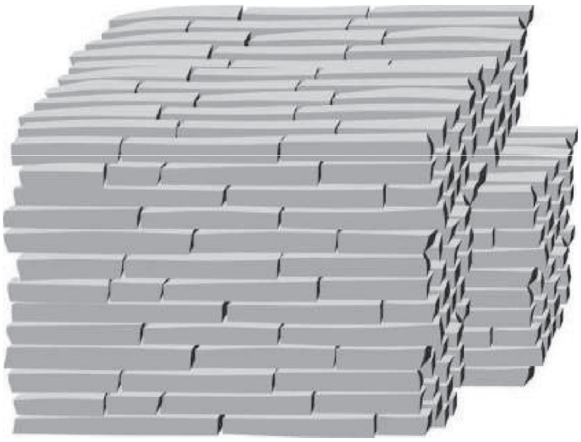

Fig. 5. Representation demonstration of the destruction of the crystal-precursor and the formation of pseudomorphosis of the reaction product.

PSEUDOMORPHOSIS OF THE SOLID PRODUCT OF THERMAL DECOMPOSITION: SUPERCRYSTAL, PARACRYSTAL OR FROZEN METASTABLE LIQUID CRYSTAL?

Is a pseudomorphosis of thermal decomposition product a supercrystal? We did not manage finding a rigorous definition of the term "supercrystal". Is it advisable to apply to them the rigid requirement of translational symmetry, as to usual crystals? *The supercrystal is an object that possesses a periodical three-dimensional structure built on the base of monosize highly ordered elements.* Opal-like photon crystals based on ordered polymeric monosize spheres, spheres from silicon, zirconium or titan dioxides to the full correspond to the above definition. But the attempt to construct such a supercrystal from ordered distributed by sizes, but, on average, monosize elements of a more complex shape that possess by anisotropy (for example, parallelepipeds) will hardly be successful. It is necessary to take into account that these parallelepipeds are bound between each other by local contacts forming a topologically simply connected region and are divided between each other by empty space with a volume, comparable with their own volume. It is obvious that for the fulfilment of this condition, parallelepipeds should have angular deviations from the direction, along which they, in average, are oriented. Highly textured objects of this kind built from distributed elements of an anisotropic shape with the angular disorientation from the average require a somewhat expanded determination softening the rigid requirement of the translation symmetry. If define supercrystals as the objects consisting of «*on average monosize weakly disordered elements possessing on average the periodic structure*», then it will completely correspond to our ideas about the structure of pseudomorph of product of the thermal decomposition.

More strictly, supercrystals of the considered type, analogously to liquid crystals, can be classified by the type of the density function $\mathbf{c(r)}$ and local orientation of particles $\mathbf{n(r)}$. A unit vector $\mathbf{n(r)}$ (director) points out the direction, along which on average selected axes of particles (for example, long) in the point with the coordinate$\mathbf{r}$ are oriented. According to this, as and in relation of liquid crystals, one can allocate three types of supercrystals: nematic, smectic and cholesteric. The existence possibility of nematic and smectic supercrystals does not raise a doubt. Our ideas about the internal structure of pseudomorphosis of the thermal decomposition product precisely correspond to the theoretical ideas about the structure of nematic and smectic supercrystals. There is only one big difference of the liquid-crystal state of the substance from the substance condition in pseudomorphosis. Liquid crystals are equilibrium objects, and the internal structure of pseudomorphosis is specified by specific conditions of thermal decomposition and further cannot be reversibly changed when varying external conditions.

One more theoretical approach developed for the diffraction description on the structures, close by the structure character, is known [17]. To describe structures characterized by a specific type of the disturbance of the translational order Hoseman introduced the concept of paracrystal. Paracrystal structures are based on the existence of only some probabalistic short-range order, equal for all particles of the structure, while the long-range order rapidly decreases from one “coordination sphere” to the next one. Apparently, the pseudomorphosis structure agrees well with such a model especially taking into account that the sizes and shape of the particles composing the structure also represents distributed values.

In general, these three approaches can be applied to the description of the internal structure of pseudomorphosis without any significant limitations.

By what physical methods can we experimentally substantiate that pseudomorphosis synthesized by us is a supercrystal? By analogy with the liquid crystals considered above, pseudomorphosis should possess by the properties of optically anisotropic medium, *i. e.*, birefringence, and in the convergent light give the conoscopic image.

High resolution electron microscopy and especially microdiffractional studies also demonstrate the ordered location of particles composing the pseudomorphosis.

We lay the biggest hopes on the method of small-angle scattering of X-ray, which will allow determining not only the size and shape of these particles, but also their mutual location.

HIGH ORDERLINESS OF THE DEHYDRATION PRODUCT $CuSO_4 \cdot 5H_2O$

Dehydration of $CuSO_4 \cdot 5H_2O$ already during almost a hundred years has been a model reaction for the study of the thermal decomposition mechanism [6]. It is known that at dehydration of $CuSO_4 \cdot 5H_2O$ in vacuum, the X-ray amorphous solid product of the chemical composition $CuSO_4 \cdot 5H_2O$ is formed.

Based on the results analysis of multi-year research the following mechanism of the reaction product formation is proposed. When placing the crystal $CuSO_4 \cdot 5H_2O$ in vacuum water molecules begin to remove oneself from its surface. A solid solution of vacancies of water molecules in the starting structure is formed in the near-surface layer of the crystal. When exceeding the critical concentration of vacancies of water the allocation of the reaction product – metastable $CuSO_4 \cdot H_2O$, nucleates and accrues. As a consequence, stresses arise, which increase with the rise of the particles size and when achieving some critical value the product particle splits off from the reagent phase. The mechanical stress is conditioned by the difference of molar volumes (shrinkage at the reaction is ~50 %) of the product and starting reagent. The reaction starts again on the freshly formed surface, the growth of the phase of the metastable monohydrate continues on the remaining inter-phase contacts, and the indicated sequence of the processes (reaction – formation and growth of the allocation of the product – mechanical stresses – destruction) is repeated. The sizes and shape of the particle formed are determined by anisotropy of the deformation in the course of the reaction. The product inherits certain structural elements of the starting reagent. It is supposed that in the reaction product, the chains formed by sulphate ions and copper ions that are coordinated by the remaining water molecules are preserved. Thus, according to the mechanism proposed, the reaction product consists of ordered particles of the same size and shape separated by an emptiness formed as a result of cracking. Unfortunately, for this reaction one cannot theoretically calculate the size and shape of the formed product particles, since the crystalline structure of the metastable product is unknown to us. It is also impossible to determine it, since the reaction product is X-ray amorphous. Since the external sizes of the starting crystal after the reaction are preserved (pseudomorphosis is formed), then the emptiness volume is equal to the decrease of the volume as a result of the reaction and reaches 50 %. Pseudomorphosis of the solid product, as we established, has the specific surface, equal to 79 m^2/g. The totality of all the available experimental data (anisotropy of embryo growth, directions of spreading cracks, both in the starting reagent, and in product *etc.*) allows suggesting that the direction of the large axis of the plate of the product coincides with the direction [110], along which copper-sulphate chains in the starting crystal $CuSO_4 \cdot 5H_2O$ are located. Particles of the reaction product should have the shape of rods with the thickness of approximately 10 nm elongated along the direction [110] of the starting copper sulphate pentahydrate. The thickness assessment of the rods was made based on the value measurements of the specific surface of pseudomorphosis of the reaction product.

What physical methods can we confirm the proposed dehydration mechanism of $CuSO_4 \cdot 5H_2O$ and experimentally substantiate that pseudomorph synthesized by us is a supercrystal? It is impossible to use high resolution electron microscopy that is the most direct method to study the dehydration product, since the product is destructed under an electron beam. Optical microscopy shows that the pseudomorphosis obtained by dehydration of the monocrystal $CuSO_4 \cdot 5H_2O$ in the polarized light behaves analogously to liquid crystals, as the optically anisotropic medium, *i. e.* has birefringence. This points out at the ordered location of the particles composing it but does not give any quantitative information.

Small-angle X-ray scattering is probably the sole method, capable of ensuring the data about anisotropy of the shape and texture of the reaction product. As the study object, the dehydration product of the monocrystal $CuSO_4 \cdot 5H_2O$ with the thickness of ~150 μm was used. Dehydration was carried out under vacuum at room temperature. The resulting pseudomorphosis was impregnated with vaseline oil to prevent the interaction with water vapours.

The study was performed on the source of synchrotron radiation of the Institute of Nuclear Physics, SB RAS (Novosibirsk) using a two-coordinate detector. It was established that the space distribution of the intensity of small-angle scattering of X-ray beams from pseudomorphosis obtained by dehydration of the monocrystal $CuSO_4 \cdot 5H_2O$ possessed by the angular anisotropy (Fig. 6). The scattering profiles in the opposite directions have in the general case the asymmetrical view. The signs of the existence, at least, of one axis of the second order are observed in the space distribution of the scattering intensity. The obtained results

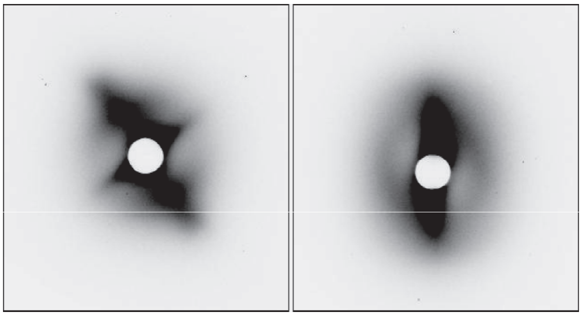

Fig. 6. Pictures of small-angle scattering X-ray beams from pseudomorphosis obtained by dehydration of the monocrystal $CuSO_4 \cdot 5H_2O$ at various orientations relatively to the incident beam.

testify the orderliness presence in the structure of the reciprocal laying of particles of the reaction product in the pseudomorphosis volume. The view of scattering profiles qualitatively agrees with the suggestion about the fact that the morphology of the dehydration product represents oriented packaging rod-like particles. On the basis of the data obtained, the sizes of the particles of the rod-like shape were assessed: thickness ~8 nm, length ~100 nm. Unfortunately, the absence of the theory of low-angle scattering X-ray beams by supercrystals or paracrystals does not allow reproducing in details the plate location in pseudomorphosis.

CONCLUSION

The reactions considered are very simple and, one can say, “poor” from the viewpoint of classical chemists. As a rule, the products are strictly determined. In fact, at complete decomposition of metal hydroxides or carbonates, as known, exclusively appropriate oxides with their own crystalline structure can form. But what endless possibilities open up in front of us when placing the emptiness on the product of the solid-phase chemical reaction! It is possible to banish it from the product, distribute chaotically or strictly orderly, in which connection, and implement this by various ways, purposefully controlling the size, shape and mutual location (orderliness) of its constituent particles. Variants of the distribution of the emptiness will inevitably attach new physical and chemical properties to the final solid product.

So far we have made only the first steps to understanding how the solid product morphology is formed and what determines spatial occurrence of a chemical reaction in the solid phase. But already one can say that there is a chance to purposefully create structurally organized media containing within themselves regular grids of open-loop ring resonators, the structure from nanoplates or nanorods or the configurations of the type “fish grid”, moreover, implement it in the mode of self-assembly.

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