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STRUCTURAL EVOLUTION IN CERAMIC TECHNOLOGY AND PROCESSING

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A survey of the development trends in ceramic technology and processing from the standpoint of synergetics and chemistry of imperfect crystals is given.

The major goal of any technology is producing materials with tailored properties. Based on this principle, I. V. Tananaev has formulated the central challenge for physicochemical analysis as finding a solution to the tetradic problem "dispersity – composition – structure – property." In the particular case of ceramic technology, it can be imagined as the sum total of processes involving two major stages: (i) preparation of precursor materials which ends in making semi-finished products (preforms) of a particular shape and size, and (ii) sintering of the preforms to achieve the required structural properties on which other useful properties rely. In other words, in all technological operations — from processing of raw material to production of finished components — the major goal is to control the evolution of the structure in the right direction. It is important to emphasize that all technological operations (preparation of powders and molding mixtures, molding, removal of sacrificial bond, sintering) are to a certain extent controlled by the input of the mechanical energy and its accumulation during structural deformation or degradation followed by dissipation involving mass transfer and thermal activation of sintering. In a sense, the original raw materials for ceramic production undergo a number of states each characterized by a definite composition and structure. Thus, the preparatory and intermediate steps can be characterized in terms of the structural features of powders, molding mixtures, and preforms, whereas the final step — in terms of the structure of the finished product. Precisely in this sense should the structural evolution of ceramic technology be rationalized.

It is important to note that ceramics prepared from man-made inorganic materials compositionally and structur-

ally may be ranked among the most complex products [1]. The actual structure of such ceramics is, strictly speaking, irregular, that is, lacks translational properties; still, in most cases, one can identify a statistically averaged cell with definite characteristics which provide an acceptably adequate description of the properties of a particular material. The size of the cell, assumed to be a real object, is normally taken into account as a structural factor in all processing steps of the original material.

Until the present, no generally recognized classification for structural elements of ceramic materials has been developed, and the definitions and notations used frequently lack strict formulation.

A classification was proposed by K. K. Strelov [2] in which, depending on the resolving power of measuring instruments used, several structure scales, or structure orders, could be distinguished for structural elements. Structures of first order can be identified by the unaided eye; those of second order can be distinguished under an optical microscope, and those of third order, by electron microscopy. Now we consider this classificatory principle in some more detail. We assign elements with a size of < 1 μm (including electrons and atoms) to a substructure, those with a size from 1 μm to 1 mm, to a microstructure, and those with a size of > 1 mm (comprising the whole of a component), to a macrostructure (Fig. 1) [1]. The demarcating bounds proposed are somewhat conventional in character; still, they are based on the potentialities of instrumental methods, with the actual elements of which a structure is composed falling into the above size ranges. The description of a structure involves determination of the chemical and phase composition, the shape and size of the structure's constituent elements taken on an appropriate scale, and the mutual arrangement of elements in space and their quantitative proportions. It should be noted that, in this

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context, the chemical composition is included in the notion "structure," since individual atoms differ in structure and nature of their smaller constituent elements. This approach provides a means for describing the evolution of a structure in all steps of production technology — from the precursor powder to the finished ceramic component.

Mass and heat transfer processes play a role in the ceramic technology; these processes are typically irreversible and non-equilibrium processes that occur in all real systems [3 – 7]. These open systems (as distinct from closed (isolated) systems treated by the equilibrium thermodynamics) continually exchange matter, energy, and information with their environment.

Environmental processes in open systems may lead to self-organization, that is, the occurrence of structures capable of the dissipation [5] or accumulation [8] of matter, which may involve a decrease in entropy. The proportion of accumulative and dissipative structures is controlled by the actual conditions, primarily, by the extent of nonequilibrium between matter and environment. The system tends to decrease its energy (matter) and to transfer it to the environment through the mediation of dissipative structures. If the exchange is too rapid or if barriers are set within the system that inhibit dissipation, the system accumulates matter by building up accumulative structures. It should be noted that the occurrence of accumulative and dissipative structures may be regarded as a manifestation of the self-organization process and, depending on the course taken by the process, each of these structures may play a prevailing role.

Development of an actual system involves a range of states: stability – instability – stability. The stable state of a system may be an ordered (determinate) one or disordered (chaotic). An actual system can be regarded as a combination of both ordered and disordered (chaotic) states resulting from the involvement of equilibrium and non-equilibrium processes. A steady state can be described in terms of a dynamic equilibrium involving a continual exchange between matter and environment. A steady state (or a state close to it) obeys Prigogine's theorem of minimum entropy production and the Le Chatelier – Broun principle according to which a system counteracts internal and external forces as they tend to disturb the system from an equilibrium condition. The negative feedback thus generated tends to minimize small effects which, however, are incapable of throwing the system out of the region of stability [5].

A system that persists in a state of instability evolves under the action of a force applied to it, and the effect produced by this force is further increased by the positive feedback. The system in such a state displays an enhanced sensitivity to noise (the sum of small uncontrolled internal fluctuations and external disturbances). The external disturbances may come from variations in temperature, pressure, or physical fields; the internal fluctuations may be associated with structural elements or technological implications (prehistory) [9]. In certain situations, transformations experienced by the system are purely probabilistic (stochastic) in character; in this,
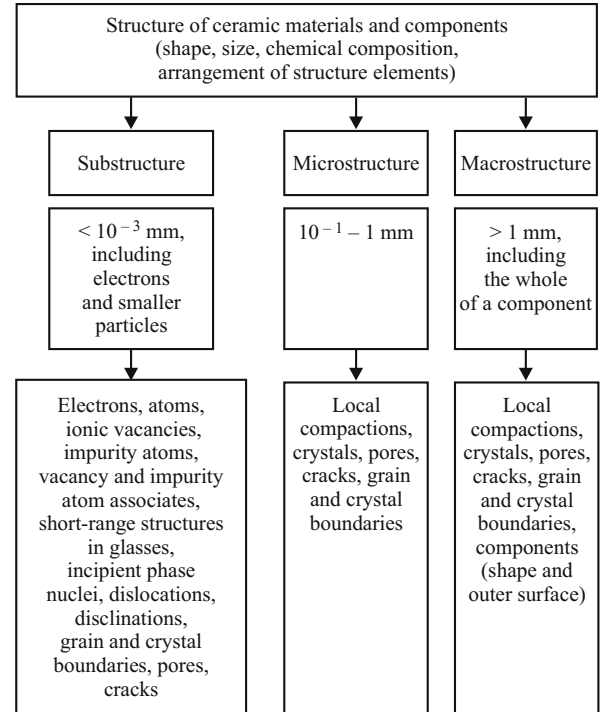

Fig. 1. A classification of structural elements (ceramic constituents).

the number of independent (controlling) parameters that determine the evolution of the system tends to decrease, and the evolution of the system is determined by the extent of nonequilibrium between matter and environment [9].

A situation has been considered in mathematics for a system undergoing transition from an unstable state into one of the two final equivalent states. This effect is referred to as the bifurcation (branching) of a process, and the transition point (that is, the point of instability) is called a bifurcation point. The foundations of a mathematical theory of bifurcations were laid down by A. Poincare and A. N. Lyapunov and further developed by A. A. Andronov and his disciples. Mathematically, bifurcation is understood to mean a change in the topological partition of the phase space of a dynamic system into trajectories under small perturbations of the system's parameters [10]. Staying within the bifurcation theory, one can analyze the behavior of a differential equation without resort to its integration.

Viewed mathematically, such a situation occurs when the solution of a differential equation describing a process loses stability, and the system undergoes transition from one solution to two alternative solutions (mathematically, this results in a change of the symmetry of solution). It is important to emphasize that these two states of the evolving system are equivalent, and the preferential choice for one of the two is made accidentally, depending on small external disturbances or internal fluctuations.

In a complicated situation described by a set of equations, a number of stable states for a system may occur; into

one of these the system may go accidentally after it has lost stability due to perturbations or fluctuations; this situation is referred to as multistability. An alternative point of view can be considered according to which the bifurcation is merely a convenient idealization; in a realistic approach, one would rather prefer a concept of instability. In practice, this offers an advantage, since it becomes unnecessary to prove the existence of two equivalent states for the system. On the other hand, in reality a pure bifurcation is an exceptionally rare occurrence; usually, one of the two states at the presumed bifurcation point is always preferred for a range of reasons, including those originating in perturbations and fluctuations.

Actual systems (in our case, intermediate products at different stages of technological process) frequently display a set of coexisting stable states (multistability). If these states differ markedly in properties and have a close probability of being recorded, then the final result will show a poor reproducibility [11]. A system in an instable state and with high sensitivity to external perturbations and internal fluctuations can be easily controlled. The unstable state may either be or not be a bifurcation. The transition through a bifurcation (a nonequilibrium phase transition) entails the "loss of memory" of the previous state (prehistory). Multistability, that is, a set of stable states with strongly differing properties into which a system may fall after it has passed through an unstable state, results in a poor reproducibility of structure and performance characteristics of the processed ceramic [11]. Still, the states may lie sufficiently close to each other, which provides the possibility of developing a reasonably stable technology.

Technologists have always been concerned with principal unstable states (without recourse to concepts of synergetics) which were of primary importance for structural evolution of the material at a particular technological stage [9]. Control of the system with a view to eliminate multistability provides an effective route to improving the reproducibility of the ceramic structure. In case the unstable state is a bifurcation, then a way to proceed may be to remove the bifurcation [3, 4]. To make the structural evolution predictable, one should scan the region of instable states with a control signal of intensity above the noise level.

The evolution of a structure is to a significant extent dependent on the degree of nonequilibration to which the system is exposed. At the same time, the behavior of a system under nonequilibrium conditions allows a general description, which formally opens the way to the use of far-reaching analogies: equations proposed for treating particular processes can be applied with success to other processes that are physically quite different from the former. To be specific, it makes possible following the structural evolution not only in a shaped preform or sintered components, but also at the stage of preparation of the precursor powder or molding mixture. If so, then the preparatory stages of ceramic technology may be regarded as mass-transfer processes which, through the mediation of plastic deformation or brittle fracture, can be used to control the structural evolution of the material in the needed direction.

Diffusional mass transfer performs a pivotal role throughout the successive stages of ceramic processing (primarily, high-temperature processes); a traditional basis for understanding these processes is the concept of point defects in crystals [12]. A quasi-chemical approach to the formation of defects gives a clear idea of the importance of the gas medium in the structural evolution during sintering and doping.

The notions "physics of open systems," "thermodynamics of irreversible processes," "nonequilibrium thermodynamics," and "synergetics" as applied to physicochemical systems are in fact synonyms. Synergetics is an interdisciplinary science explaining the formation and self-organization of patterns and structures in 'open' systems far from thermodynamic equilibrium. Staying within the framework of this concept, one will see that the processes that occur at different stages of ceramic technology share many common features. In our opinion, this allows a deeper insight into these processes and their interrelation.

Ceramic materials at relatively low temperatures (typically, below 0.5 – 0.7 of the melting point) show a brittle behavior and breakdown when subjected even to a slight elastic strain. With increase in temperature, as the thermal activation comes into play, the material changes over to plastic strain or viscous flow although rather small. Phenomenologically, with increase in temperature and load applied, the ceramic material undergoes either an instantaneous (at the speed of sound) fracture under a slight elastic strain applied, or a relatively slow irreversible (plastic) deformation.

The plastic deformation is accompanied by continuity violations, however not tending to bring about fracture at either the macrolevel or at the micro- and sublevel (in conventional definitions of plasticity, they are omitted). They lead to the occurrence of inner surfaces and the corresponding energy losses; in fact, this implies the origination of cumulative structures. The amount of stored energy is controlled by the balance of plastic and brittle properties in the material as well as by internal and external conditions. The internal conditions primarily involve the type of chemical bond and the unit cell of the material: the higher the covalency of chemical bond and the more complicated the type of unit cell (the number and structure of sublattices), the more pronounced the brittle behavior exhibited by the material. The external conditions involve the mechanical load applied, temperature, heat removal (especially their variation in time), etc.; the higher the degree of nonequilibrium of the mechanical action, the higher the probability for a particular ceramic to reveal its brittle properties.

Viewed in this light, it is important to note that there are two temperature regions in which the behavior of ceramic materials as regards the storage of energy and their brittle and plastic properties are drastically different. In the first region, energy is stored through generating new outer interfaces; in the second, energy is additionally stored through intervention of inner violations of continuity (structure imper-

fections, or defects). In technology at moderate temperatures, in order to reduce brittleness and to impart plasticity to the semi-finished product, a plasticizing additive (polymers) is introduced. In many processes, plastic raw materials, in particular clays, are also used. In what follows, we discuss these technological techniques from the standpoint of synergetics and chemistry of imperfect crystals.

In practice, nonplastic precursor materials are treated under elastic strain conditions to initiate brittle fracture and thus to achieve the major goal — to obtain a powder with required properties. The particles of a highly dispersed powder interact to form a maximum of cumulative structures which normally persist to the stage of sintering. Subjected to size reduction, the material, in conformance with the Le Chatelier – Brown principle, resists the external action to form dissipative structures; note that increasing the intensity of external action promotes self-organization. The powder particles, assembled into aggregates by adhesive forces, prove to be effective dissipators of mechanical energy; here the stress is partly relieved by shifting particles with respect to each other (plastic strain of the aggregates formed). The size reduction process becomes retarded, which, viewed technologically, is an undesirable effect. At the same time, structure defects in the particles continue to accumulate.

In the final stages of size reduction, the surface of particles undergoes amorphization. The amorphitized layer thus formed exhibits plastic properties, which decreases the efficiency of mechanical action. The amorphitized layer promotes the formation of rather strong aggregates capable of withstanding plastic strain, which results in the dissipation of energy put into the system. In a sense, it can be assigned to dissipative structures. At the same time, amorphization arises from the accumulation of point defects and can therefore be associated with the occurrence of cumulative structures as well as with the formation of new interfaces and other violations of continuity embracing cracks, pores, and vacancies. The major function of the system is to provide maximum dissipation of input energy rather than to protect the particles from degradation. Under intense grinding conditions, the particles (formally material subsystems) are too slow to dissipate energy into the environment (neighboring particles, dispersion medium, walls of the grinding mill), and part of the energy is accumulated to be spent on new interfaces during brittle fracture, which intensifies size reduction. Evolution of energy and material during size reduction is shown schematically in Fig. 2.

The liquid added to the mixture during wet grinding provides favorable conditions for dissipating energy, which prevents the formation of accumulative structures. The amorphitized layer has a thickness and the aggregates associated therewith have dimensions much smaller than those during dry grinding. In a material with a complex crystalline structure containing highly covalent chemical bonds, the input energy cannot be transferred fast enough from atom to atom, and a significant part of it becomes accumulated within the system. Precisely for this reason, quartz and sugar, subjected
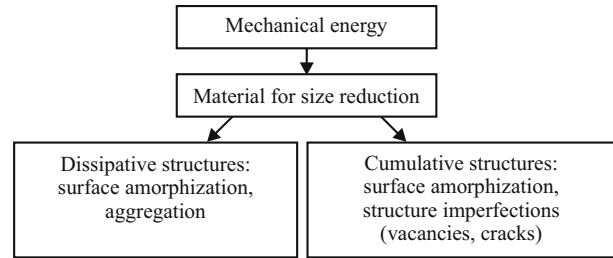

Fig. 2. Scheme for the formation of dissipative and cumulative structures during size reduction.
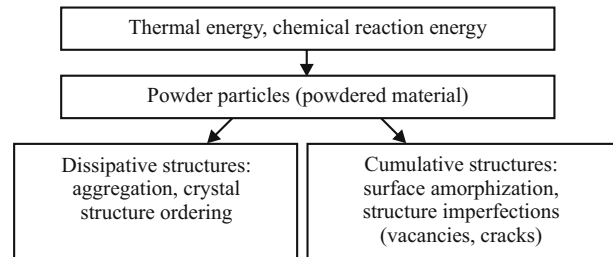

Fig. 3. Scheme for the formation of dissipative and cumulative structures of ceramic powders prepared by chemical methods.

to prolonged dry grinding, become amorphized, whereas NaCl resists such operation. The energy accumulated within the system during dry grinding is spent on powder aggregation. The prolonged dry grinding makes it possible to obtain nanoparticles capable of accumulating much energy; for this reason, they are occasionally referred to as energy-saturated [13].

Highly dispersed powders are normally prepared using chemical methods [14]. The driving force of this process is the difference between the chemical potentials of the initial (intact) phase and that of the powder produced; the vast variety of self-assembled particles provide conditions for cooperative processes. Despite the obvious dissimilarity of powders prepared by mechanical grinding and chemical methods, the schemes for energy evolution in these materials are pretty much alike (Fig. 3).

The powder energy, like that in mechanical grinding, tends to decrease through particle aggregation. Because of the strongly nonequilibrated synthesis combined with the complex crystalline structure of the material, the small particles, assembled into aggregates with large surface, accumulate part of the energy; this process is accompanied by the occurrence of multiple imperfections of micro- and substructures and finally by the amorphization of the system. The temperature controlling the rate of diffusional mass transfer of chemical reactions plays a pivotal role in this process, in which the internal energy tends to decrease owing to the structural ordering of particles.

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(to be continued)