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MECHANOCHEMISTRY OF INORGANIC SOLIDS*

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The content of the paper is a review of the results in mechanochemistry of inorganic solids which were carried out in the Institute of Solid State Chemistry and directed by the author. The mechanochemical processes which proceed in the apparatus like mills have two main features : locality of processes and their impulse character. When processes occur in the top of the crack propagated in the solid, the transition from low energy vibron level exitation to a high one is possible. The impact of preliminary mechanical treatment on the reactivity of solids is connected with the effect of defects formed during the treatment. The results obtained are discussed in terms of technological application.

Key Words : Mechanochemistry; Locality of Processes; Mechanical Treatment

INTRODUCTION

THE reactions occurring during deformation, friction or fracture of solids have long been considered as physical phenomena and an approach to their control, optimization was based primarily on investigation of physical causes and effects. However, our experience of experimental data accumulated for the past forty years has shown that such chemical processes are significant.

Strictly speaking, the fact that mechanical action can lead to chemical consequences was not a discovery. Since the first attempts by Man to obtain fire by friction and to the more recent data on the possibility of ignition and detonation of certain solid explosives, it has come to light that chemical reactions may be initiated by mechanical means. But it was unexpected that while on one hand, the mechanochemical processes embrace a wide range of effects in nature and engineering on the other they are unusual and are not confined to reactions induced by heat evolved during mechanical action which phenomenon became known quite recently.

Striking effects have been found and unusual chemical reactions have been discovered. Thus, gold which is well known to everybody not to be attacked by oxygen of the air under ordinary conditions, at the moment of mechanical action reduces even carbon dioxide;[1] mechanical treatment of metals changes their position in electromotive series.[2] Oxides and salts hardly soluble even in concentrated acids being dissolving in diluted aqueous solutions of the acids and even in

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water.[3–7] The data are available that at the moment of mechanical action the diffusion coefficients of solids may increase many times over. At the moment of mechanical action certain compounds begin decomposing through unusual mechanism quite unlike the thermal one.[8]

At the same time the progress of present-day engineering raises a problem of development of new uncommon, non-thermal methods for initiating reactions in order to intensify such important industrial processes as the leaching of mineral raw materials in metallurgy, the activation of components of binding agents in construction industry, an increase in reactivity of ingredients of metallic or non-metallic powder-mixtures in powder technology, the new and uncommon methods for solid-state synthesis in chemical industry, etc. Taken together these factors make investigations of chemical processes, brought about by mechanical action, extremely urgent and important.

The questions which should be answered first of all are : how and where do these processes take place. The question of where these reactions proceed is not usual for classical inorganic chemistry. Indeed, when investigating a reaction in gases and liquids, except in a few special cases, the probability for the reaction to proceed is generally the same all over the bulk. Mechanochemical processes, like most other heterogeneous processes, occur locally and therefore, the question of the exact site of the reaction course is quite natural. Experience shows that it is normally either the site of contact between the reactant and an object which produces mechanical action on the system or the sites of contact between particles of the solid—where pressure and stresses are primarily concentrated.

From the sites of contact the reaction zone can spread over the neighbouring regions of the crystal due to various processes of relaxation—heating, formation of a new surface, or imperfections or chemical transformations. The rate of these processes of relaxation may be highly different. Thus, a crack in brittle solids can propagate at a velocity close to that of sound; the velocity of heat wave is determined by the magnitude of thermal gradient and by the thermal conductivity; the

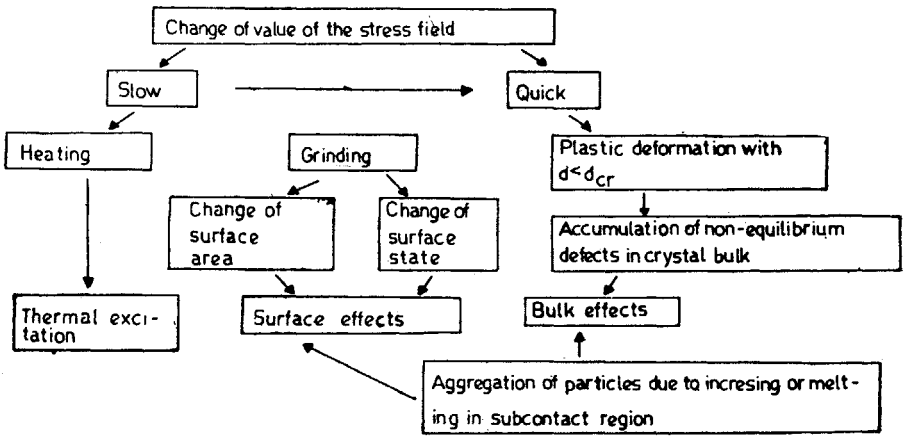

CHART 1

process of elastic stress relaxation due to formation of lattice defects may proceed very slowly requiring hours, days and even years to obtain equilibrium. The change-over from one way of stress field relaxation to another depends on the nature of substance, conditions of mechanical interaction between particles (relations between the loading of the sample and the shear), and, with other conditions being equal on the amount of energy absorbed by the solid. Chart I shows the change-over from one way of a relaxation to the others as the absorption of energy increases resulting in occurrence of the stress field. At the bottom of Chart I, chemical consequences of energy relaxation by different routes are presented.

Mechanical treatment of the system, altering conditions of the chemical reactions course, may be permanent or periodical.

In the first case we have examples of change in reactivity of solids under the influence of permanent stress field generated, for example, in a Bridgeman's anvil device. It is known that these processes depend on the time of treatment, and their degree of transformation depends on mechanical work done on the system. In the case of Bridgeman's anvil device this work is determined rather uniquely by the turning angle of the anvil. These processes are well covered in detail in literature and will not be discussed in this paper.

The other case is a change in reactivity and the excitation of chemical processes in solids after mechanical treatment at regular intervals, as it takes place, for example, in various apparatus, mills. The characteristic property of such processe is their locality : the region where the process occurs is normally confined to the region of contact between the particle deformed and a grinding object, or other particles. The second peculiarity of this process is its pulsed character which we have pointed out previously.[9] In apparatus commonly used for grinding, the formation of the stress field and its relaxation occur at regular intervals by subjecting a solid to a sequence of mechanical pulses following one after the other. A schematic representation of these pulses is shown in Fig. 1. Every pulse characterises the occurrence of the stress field in the region being treated (the left-hand side of the pulse) and its relaxation leading to various physical and physico-chemical consequences (the right-hand side of the pulse).

Being characteristic properties, both locality and pulsed behaviour of mechanochemical processes, however, present experimental difficulties in studies of mechanochemical processes if the study is performed correctly (i.e. with averaging

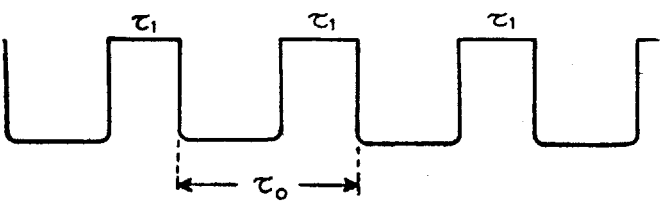

FIG 1 Pulsed character of mechanical action. The left-hand side of the pulse—the formation of stress field. The right-hand side—its relaxation by different routes.

neither the site where the reaction proceeds, nor the time of the process, what some investigators used to do).

As an example of this one may consider study of chemistry of processes occurring at the tip of a moving crack. During early twenties of this century Griffith suggested that at the tip of a moving crack high temperatures and pressures were developed. Their existence was then supported by direct experimental studies carried out at Cambridge, Karlsruhe, Leningrad, and Novosibirsk. It was shown that the tip of the moving crack is surrounded by the field of high temperatures and pressures which can very with the velocity of crack propagation and physico-chemical properties of the substance through which the crack passes.

In the early seventies in one of the papers dealing with a kinetic model of mechanochemical processes,[9] the present author suggested that if the chemical reaction, induced at the tip of the moving crack, proceeds through several concurrent or successive stages then a change in the reaction mechanism should be expected as compared with the same reaction excited by thermal way. The concentration of energy at the tip of the crack and pulsed behaviour of the process are responsible for this.

For the last twenty years experimental data were accumulated which supported our assumption. These experiments were performed jointly by our laboratory and the physicists of the Leningrad Physico-Technical Institute.[8,10] The set-up used in these experiments is represented schematically in Fig. 2, where 1 shows the support for crystals in the ion source of a transit-timed mass-spectrometer; 2, the knife for

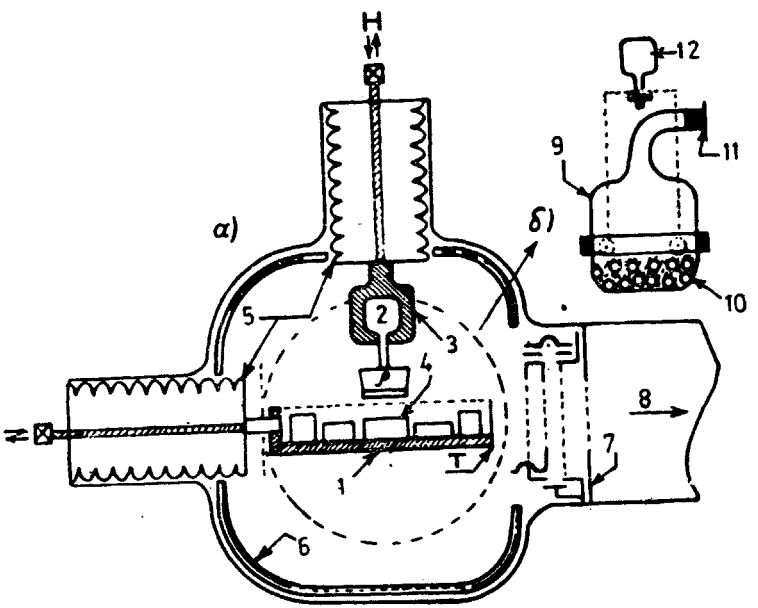

FIG 2 Schematic representation of experimental set-up for investigation of gas content formed at the tip of a moving crack (see explanation in the text).

cleavage inserted into a holder 3; 4 indicates the crystals of substance under study; 5 the system of silphons allowing the displacement of the support in a horizontal direction and that of the knife in vertical one; 6 shows the camera of the ion sources; 7 the net; and 8 the tube of the spectrometer. For example, this was shown in experiments on mechanical cleavage of alkali nitrates single crystals directly in the ion source of a mass-spectrometer. It is shown that if the velocity of crack propagation is sufficiently high, nitric oxide rather than oxygen is evolved as a gaseous product, during the cleavage of bromates from rather than oxygen is evolved, etc. The composition of products of the reaction differs from that of the thermal decomposition products. When the crack velocity decreases this effect disappeared and a usual thermal mechanism of decomposition is realized.

The cause of the observed effect appears to be the fact that at high crack velocities, the higher vibronic states are excited and at low velocities, as well as during thermal decomposition, the lower states are excited.

Recently, it has been possible to observe this effect with other compounds, for instance, iodates, chlorates, and to employ it for investigation of the crack multiplication along the curves of gas evolution.[11]

As the first approximation, this may be shown in the following scheme in Fig. 3, where various ways of decomposition of the nitrate-ion are represented. The excitation of nitrate to the lowest vibronic state corresponds to its transition to the metastable state on account of nitrate-ion stretching; oxygen and nitrate ions are the products of the reaction. If the next vibronic state is excited (deformation of the nitrate ion by compressing rather than by stretching corresponds to it), the rupture of bonds occurs within the nitrate-ion to give nitrous oxide and the O_2^- ion.

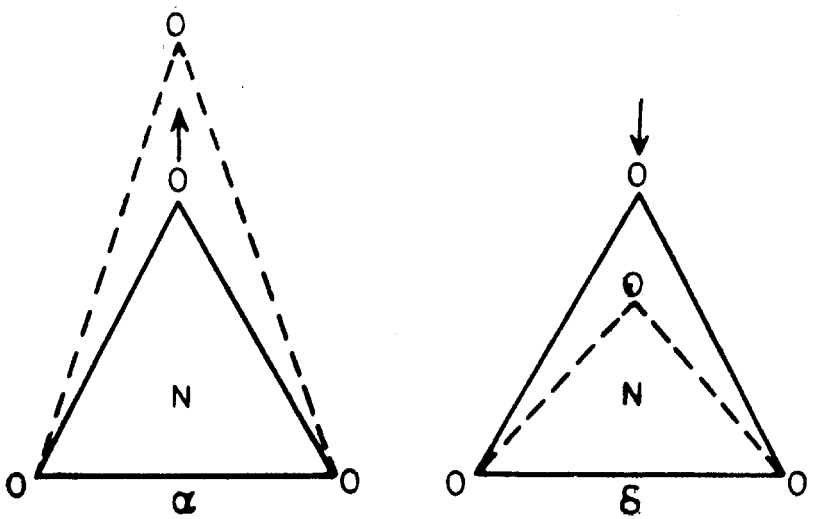

FIG 3 A scheme illustrating possible ways of the nitrate ion decomposition.

Another aspect of the question is the investigation of quick local variations in the crystal structure at the moment of mechanical action on the substance. Until recently, this problem was considered to be very difficult and even hopeless in respect of the short-lived metastable structural states.[12] However, the use of accelerators as a source of synchrotron radiation, which has intensity of radiation several orders greater than that for X-ray tubes, makes it possible to study structural changes in solids during mechanical action.

The Institute of Solid State Chemistry of the Siberian Branch of the Academy of Sciences of the USSR and the Institute of Nuclear Physics devised jointly a diffractometer for synchrotron radiation which enables one to record a diffraction pattern and to put it into storage of an electronic computer in 10^{-5} sec, and also to resolve points with an accuracy of 1 hair space msec for repeated processes. Such a high resolution enables one to record the development of distortions in metals under deformation, relaxation of distorted structures, and to identify quick phase transitions. Since the intensity of the beam is high, it is possible not only to increase the time resolution, but also to follow the changes localized in small regions of the sample. Thus, during deformation of tin metal with a ruby cutter it was found that in the local regions with a size not above 0.1×0.1m, an increase in pressure occurs and the transformation of tin into a metastable crystalline modification with the area of stability above 10kbr proceeds. When unloaded, the metastable modification very rapidly transforms into the stable state.[13]

Similar results concerning very strong but rapidly vanishing distortion of the lattice were obtained from silver single crystals.

In addition to detecting structural changes occuring as a result of the stress field relaxation (i.e. process relating to the right-hand side of the mechanical pulse), the synchrotron diffractometer may be used for studying processes occurring during formation of the stress field (i.e, the left-hand side of the mechanical pulse). As an example, Fig. 4 presents the results of studies on changes in the linewidth of lithium fluoride during mechanical action. It is seen that after the stress field has appeared, the formation of lattice distortions, which leads to line broadening, proceeds not immediately, but after some milliseconds.

The influence of mechanical pretreatment is another problem under study in mechanochemistry of inorganic solids. From the above it follows that, in essence, the consequences of the stress field relaxation is also the question, the consequences being long-lived. In spite of the fairly widespread opinion that the primary effect of mechanical pretreatment is the dispersion of solids and formation of a new surface, the formation of linear and point defects was found to occur along with the formation of a new surface (*see* Chart I). The characteristic feature is that in this case the defects are formed with non-equilibrium density and the state of solids thus obtained should be classed as a metastable one. Thus, mechanical treatment when affecting a solid by short but powerful pulses results in formation of the "active" or the so-called "metastable" state.

In connection with the great present interest shown in the properties of metastable states, their production and application in technology, we shall dwell on

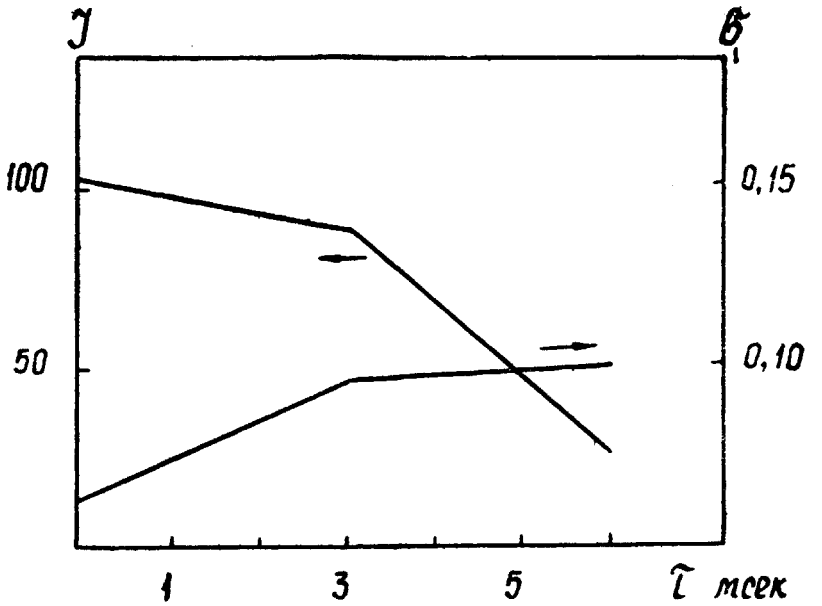

FIG 4 Change of half-width of line and amplitude in Debye diffraction pattern from lithium fluoride in the course of its deformation recorded with a diffractometer SI.

this question particularly. Metastable states are known to be formed as a result of storing energy by solids and the following quenching of excited states in the crystal.

There are many various methods for obtaining metastable states. Among these are the rapid freezing of metals, and vapour condensation on a cooled surface, and intensive light and electron beams irradiation. Sometimes reactions frozen in the certain stages of their course are used for this purpose. Plastic deformation of a solid may be also used to obtain metastable states. As it is seen from Table I, the mechanical method for obtaining metastable states may lead to three basic types of sources of metastability : compositional, structural and morphological. A fairly large amount of energy accumulated by a solid is achieved (0.2–0.8 RT).

There are two approaches to estimate the influence of mechanical pretreatment on the reactivity of solids. One of them takes into account an increase in the free energy of solids occurring as a result of increase both in enthalpy and entropy terms in the equation for the Gibbs thermodynamic potential in the course of mechanical treatment A change in the potential (or the free energy, since the solid state is the question) may be defined using the notion of activity A introduced by Huttig.[14]

$$G^{\alpha} - G = A^{\alpha}$$

As the free energy changes so the equilibrium constant related to it by the relation $\Delta G = -RT \ln K_0$ must also change. An increase in activity as a

TABLE I

Methods of obtaining metastable states

Methods	*Types of disturbances*	*Rate of quenching* sec^{-1}	E, $RT_m/10$
Quick Cooling of Melt or Crystal	*C*		
(*a*) freezing of melt on cooled surface	*S*	10^3–10^5	0.2–0.4
(*b*) Lazer melting		10^{13}	0.8
Condensation			
(*a*) of vapours	C	10^{12}	0.9
(*b*) electrochemical			
(*c*) chemical	*M*		
Irradiation			
(*a*) with heavy particles	*C*	10^{12}	0.5
(*b*) ionic implantation			
(*c*) cross beams condensation			
Action of Mechanical Pulse	*C*, *S*, *M*		
Mechanical apparatus (*a*) free shock		10^{+1}	0.2–0.8
(*b*) shear			
(*c*) shock + shear			
Shock waves		10^{12}	
C–compositional			
S–structural			
M–morphological			

consequence of mechanical treatment both for exothermal and endothermal reactions always lead to increased deviation from equilibrium and therefore to increased reaction rate.

The storage of the excess energy accumulated by a solid can be checked either by calorimetric measurements (for example, by determining heats of dissolution) or by using DTA technique[17–19] (as a difference between enthalpies of activated and non-activated samples).

The other approach to estimation of effect or preliminary mechanical treatment is in consideration of properties of specific defects generated during mechanical treatment, and of peculiarities of solid-state reaction mechanism.[20] Not only is the amount of energy accumulated by a solid important for accelerating one or another chemical solid-state reaction, but the types of defects involving this energy are also of importance. The point is that depending on what mechanism of the reaction is and what step is rate determining, different chemical processes are sensitive to various types of defects in a different manner. Therefore, the task of investigation is to find, which defect this reaction is especially sensitive to, in order to select such a way of treatment of a solid, which involves the maximum concentration of these defects.[21]

With such a statement of the question one can not restrict oneself to measuring integral quantities such as excess heat of dissolution, X-ray line broadening, etc. The problem inevitably arises to obtain by various physical methods a direct information on what processes occur during mechanical treatment and what defects are therewith generated. As an example of such an approach, the results of investigations undertaken by us jointly with the Institute of Physical Chemistry of the Academy of Sciences of GDR can be cited. These investigations were carried out on mechanical activation of apatite with the aim of developing new methods for obtaining phosphate fertilizers without processing the ore by acid.[22,23] As is well known, this problem confines to the increase of reactivity of apatite towards acids. Apatite is hardly soluble in aqueous solutions of weak acids therefore, it should be expected that the rate-determining stage of the process is not the processes of transfer through the layer of saturated solution which borders on the surface, but a chemical reaction on the surface.

The mechanism of this reaction is in the reaction of complexing between ions of the ligand available in the solution or water molecules (if it is aquacomplex) and cations or anions composing the lattice. Whether the ions go into the solution or the process confines to the adsorption of the ligands on the surface depends upon the relation between the energy required for removing the ion from the lattice and the energy released as a result of interaction between the ligand and the ion of the complexing agent. With a given composition of the solution we can alter the first of these two components by generating various crystal defects which loosen chemical bonds in the lattice. Dislocations and boundaries of blocks may be such defects first of all. Therefore, the treatment of a solid with high-power mechanical pulses leading, as was said, to the formation of such defects may be used as a method for increasing the reactivity of apatites and phosphorites. Recently, Australian chemists have managed to show by direct observations with electron microscope that it is dislocations which are the sites where the dissolution of apatite crystal begins.

Experimental investigations undertaken by us have shown that, in fact, if mechanical treatment results in plastic deformation and accumulation of defects in

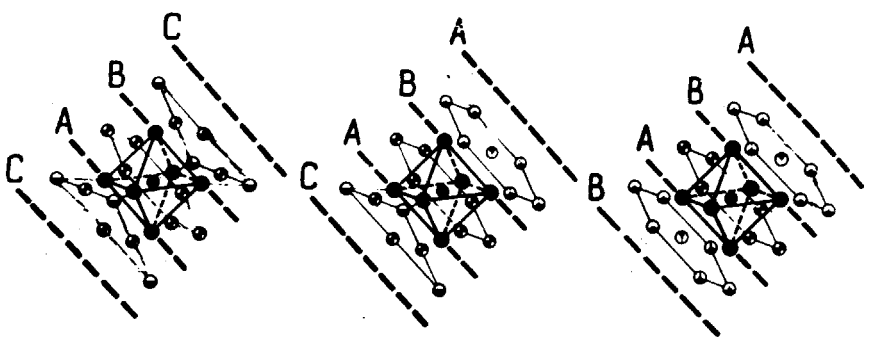

FIG 5 A scheme showing the change in environment of the iron-oxygen group in the course of mechanical treatment : (A) crystallochemical scheme ; (B) relative position of cations.

apatite crystals (as determined from line broadening in Debye diffraction patterns and changes in structure of EPR spectra for paramagnetic marks in apatite crystals), the solubility of apatite in initators of soil acids—the solutions of ammonium citrate and critic acid increases. In some cases this increase may be fifteen-fold or even twenty-fold, allowing the mechanical treatment of apatite to be used as a non-acid method for preparing phosphate fertilizers.

If mechanically activated apatite is heated to 350–400 °C the crystal defects are annealed and hence the reactivity of apatite decreases.

In contrast to the activation of apatite, where the accumulation of energy occurs due to the formation of the large number of dislocations, the mechanical activation of forrites offers an instance where the formation of metastable states takes place due to the redistribution of three- and two-valence cations over octa and tetra-positions.[26–28] Experimental data, obtained in our Institute, have shown that, in the course of mechanical treatment, it is to carry out the deformation of the crystal in such a manner that the shear of the oxygen planes with respect to each other is realized. The displacement is especially considerable in the (111) planes where they are shifted on vector which is shorter and not coincident with the vectors of the face-centered cubic oxygen lattice typical for spinels. As a result, the spatial arrangement of oxygen ions exhibits no long-range order through the cubic close packing of oxygen sublattice is retained. Locally, the oxygen sublattice may comprise, for example, a superposition of cubic and hexagonal layers. In consequence, the number of the nearest octa-sites corresponding to the angle of the cation-anion-cation bond changes (Fig. 5). This bond is known to be responsible for the main physical and chemical properties of spinels. As this takes place, there appear exchange-bound pairs cation anion-cation with an angle of the bond different from the right angle (90°) typical for common ferrites-spinels (Table II).

TABLE II

The number of the nearest octa-sites for an arbitrarily chosen cation as a function of the type of oxygen sublattice packing in spinels

Local type of oxygen sublattice packing	The number of the nearest octa-sites corresponding to the angle of the cation-anion-cation bond			
	71°	90°	122°	180°
Cubic CA (cation) BC	0	12	0	6
Hexagonal BA (cation) BA	2	6	12	0
Hybrid I BA (cation) BC	1	9	6	3
Hybrid II CA (cation) BA	1	9	6	3

Due to this, a change in magnetic properties of spinels takes place. Mechanical activation results also in amorphization of structure. The model of the structure of amorphous solids is a random close packing of rigid spheres.[29] According to

this model, the vacant large octa-sites have the highest occupancy probability in the oxygen sublattice.[30] This is also supported by experimental data of the Mössbauer spectroscopy, according to which, all the cations initially occupying tetrahedral interstices are moved into octa-positions in the course of mechanical activation.[27] The physical consequence of this influence upon ferrites spinels is an increase of magnetic ordering during mechanical activation (fact is of interest by itself, since we used to think the reverse). The chemical result is unusual properties of spinels treated in such a way. Thus, it is well known that when treating zinc ferrite with acid solutions, the zinc cations are leached out from zinc ferrite in the first instance, then the three-valency iron ions go into the solution. In the case of mechanically activated ferrite, the opposite picture is observed.[31]

Thus, mechanical activation leads to a new method of obtaining amorphous ferrites-spinel. Its obvious advantage is the possibility to carry out amorphization through several stages and to control the degree of disordering at each stage.

Similar results are obtained for other compounds related to ferrites-spinels in structural type. For example, in the case of binary sulphides, mechanical treatment leads to the change of iorn coordination from tetrahedral to octahedral.[32]

The use of mechanochemical methods for intensification of processes occurring between solids offers radically new and promising possibilities. It is well known that the rate of these rections in their initial stages is determined by the number of contacts between the reactant particles and by the area of these contacts. As the reaction proceeds, the resulting layer of the solid product separates the reactants, and the diffusion of the reactants through the product layer becomes a rate-determining stage of the process. Conducting simultaneously mechanical treatment and heating one may achieve a permanent renewal of contacts between solid particles and permanent change of the reaction mechanism from the diffusion range to the kinetic one.[6] Thus, it has been shown in a paper[33] that if a mixture of oxides forming ferrite is heated and treated simultaneously in a vibratory mill the temperature of the synthesis can be decreased by several hundred degrees.

If, along with two components, there is a liquid in the system, for example, water and the relation between the solid and liquid phases is so that the solid particles can form a labile framework structure,[34] it may be expected that when a mechanical pulse is delivered to the system a pressure pulse initially occurs in the system. Since the liquid is more mobile than the solid particle forming the frame the liquid will pass from the region of elevated pressure to the region with lesser pressure. The filtration of the liquid through pores will lead ultimately to elevated temperature, so some time there will be condition of elevated pressures and temperatures in the system. In Fig. 6, the shaded area corresponds to these conditions. This enables one to realize mechanochemical processes, such as hydrothermal synthesis pressure leaching, which require special apparatus.[9]

Finally, the so-called "mechanical alloying" should be also classed to the processes occurring between solids. This process is in obtaining metastable states

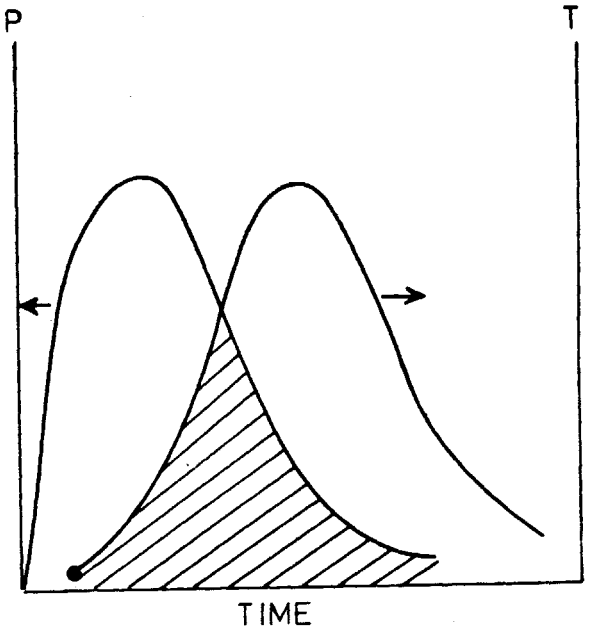

FIG 6 A scheme showihg the occurence of high pressures and temperatures during mechanical treatment of pulp.

due to the consequent alternation of the grinding and welding stages is mixtures of two metal powders.[35,36]

Not concerning with the physical and metallographic consequences of mechanical alloying, well known from literature, we shall dwell here in more detail on the chemical consequences of mechanical alloying. Very often mechanical alloying leads to a sharp increase of reactivity of solids. The formation of the so-called supercorroding alloys for the quick preparation of hydrogen from water can be cited as a good example.[37]

Another example is a rise in reactivity of metals towards hydrogen during their treatment in mixture. Thus, mechanical alloying of a mixture of magnesium and nickel powders results in an increase of reactivity up to the level close to that which is reached in this mixture by the way of fairly complicated technology comprising several alternating stages of melting and sintering of resulting powder.[38,39] An increase in reactivity of the metallic mixture takes place not as a simple result of increased interphase surface but as a consequence of formation of defect region bordered on this surface. Thus, experimental data obtained in our laboratory have shown that in mechanical alloying of a mixture of magnesium and nickel the displacement occurs, favouring the process of hydrogenation.

III. TECHNOLOGICAL PROBLEMS—THE USE OF MECHANOCHEMISTRY, THE CHOICE OF AN ACTIVATOR AND REGIME OF MECHANICAL TREATMENT

Based on the above scientific approach to the understanding of mechanochemical processes and changes of reactivity of solids in consequence of mechanical treatment,

it is also possible, in a number of cases, to make specific recommendations or intensification of technological processes with the methods of mechanochemistry and on the choice of apparatus for this purpose.

The first that one should know in such an approach is the peculiarities of the process which is to be controlled and first of all which stage of the process is rate-determining. Knowing the rate-determining stage and the peculiarities of the process we should determine then to which type of defects the process under study is especially sensitive and which conditions must be realized for its best course. Depending upon the peculiarities of the process all the processes can be divided in several groups so as it is shown in Table III. In the left column of the table the

TABLE III

Type of transformation	What is to be changed upon mechanical treatment	Examples
$^{I}T \rightarrow T_{(S)}$	*S*	
	Surface, number of active sites	Preparation of (*a*) minerals of flotation (*b*) preparation of fillers for composites (*c*) Preparation of sorbents
$^{II}T \rightarrow T_{(V)}$	*A*	
	Generation of non-equilibrium defects in crystal bulk, point, one-dimensional, two-dimensional, face of blocks	(*a*) Polymorphous transitions (*b*) Tetragonal displacement (*c*) Abnormal distribution of ions in lattice (*d*) Topotaxical transformation
$^{III}T + L(G)$	*S, A*	
	Surface, presence of defects in crystal structure	(*a*) Reduction of oxides with hydrogen (*b*) Leaching of ores (*c*) Formation of carbonils (*d*) Grouting
$^{IV}T + T$	*S, A, N*	
	Surface, Presence of defects, number of contacts between particles	(*a*) Preparation of titanates, ferrites, alumosilicates by reaction solid-solid (*b*) sintering of solid-phase mixtures
$^{V}T + T_{(L)} \rightarrow T_M$	*S, A, N*	
	Surface. Presence of defects number of contacts, local increase of N at points of contacts	(*a*) Preparation of metastable solid solutions of alloys (*b*) Hydrothermal synthesis

type of the process is given, in the middle—the factor (or factors) producing decisive influence on the course of the process. In the right column, the examples of specific processes are given.

Assume that the process takes place on the surface and its rate is determined by the value of specific surface or by active sites on the crystal surface as it takes place, for example, in flotation when the sorption of flotoreagents by minerals occurs; in the preparation of high-filled polymers, catalysis, etc. In these cases, the chief condition for conducting mechanical treatment must be the realization of such regime which provide the maximum disperisation of the solid at minimum power expenditures.

In the case when the process comprises a transformation involving the rearrangement of the crystal lattice and this transformation may be facilitated, in contrast, or hindered under the influence of various defects mechanical treatment must be carried out in the activation regime, i.e. plastic deformation must be the main channel of the elastic stress field relaxation. This is the case, for example, if one needs with the help of mechanical treatment to carry out the transformation of one polymorphous modification onto another, to obtain the abnormal distribution of ions on interstitial sites, to conduct the mechanochemical decomposition of a solid. If the transformation, which is to be affected, has a cooperative character e.g. martansitic transitions by incorporating defects into the lattice with the help of mechanical treatment one can prevent the polymorphous transition rather than accelerate it. This is the case, for example, in the transformation of tetragonal modification of copper ferrite into the cubic one.[40]

The peculiarity of the processes which course or intensification require activation is the availability of the threshold energy of mechanical pulse, below which activation does not take place. This markedly restricts and, sometimes, make impossible the employment of apparatus with low power intensity (for example, common ball mills) for activation.

Such processes as the leaching of minerals and rocks, the reduction of oxides with gaseous reducing agents, various reactions of inorganic synthesis involving interaction of a liquid or geneous reactant with solids which beings on the surface and then propagate into the bulk crystal, all of them for require course the maximum contact of reactants, on the one hand, and the availability of potential centres of the reaction—defects in the solid phase, on the other. Since the first is realized by the way of fragmentation of the solid component of the reaction and the second-due to its activation, one should chose such a regime of mechanical treatment which involves both the grinding and activation of the solid.

When conducting such solid-phase processes as the synthesis of ferrites, silicates from solid components one should and to the two above factors—the value of specific surface and crystal activity and the third—the number of contacts between particles of the solid components. Thus, it is essential to conduct mechanical treatment of each component and then that of mixture so as to grind, activate and mix both the components. Thus, in preparing the solid-phase mixture to the reaction and in the course of the reaction one should be able to control not

only the processes of grinding and activation, but also the mixing process of the components.

Finally, the course of some solid-phase processes requires besides the above three factors another one : the generation of extreme values of temperature and pressure at the point of contacts between particles of the solid at the moment of mechanical action This leads to the possibility of obtaining metastable compounds and states at the sites of contact and their following quenching. Mechanical alloying and hydrothermal synthesis, which we have mentioned above, may be examples of such processes. For their course, besides factors providing the contact of the reactants, i.e. surface, particles, the number of contacts between particles of different components and activity of solids, associated with defects available in them, a sufficiently high-power mechanical pulse is required to create extreme conditions at the point of contact.

From the above-stated it is seen that different processes require different regimes of mechanical treatment. This determines also the choice of apparatus for conducting mechanical activation. In spite of the apparent variety and diversity of apparatus applied in mechanical activation, all of them can be divided into three main classes depending on the character of elementary physical processes providing mechanical action (Fig. 7). The process of mechanical action, which confines mainly the operation of shear is realized in various apparatus such as rollers of cone-type, crushers, etc. The collision of a moving object with a barrier is realized in various apparatus such as jet-mills, disintegrator, etc. Peculiarity of these apparatus is that the action is produced upon each specific particle.

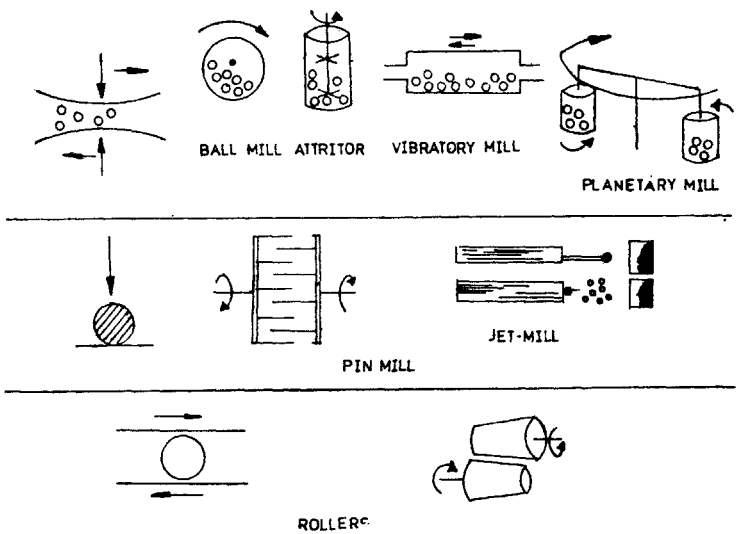

FIG 7 Types of mechanical action when employing various machines for conducting mechanical activation.

And, finally, numerous grinding apparatus, from ball mills and to vibratory, planetary, mills, and attritors a combination of shock and shear loading is realized. In contrast to apparatus of jet-mills type, these machines enable one to carry out the solid state reaction between particles of specific components and, among these the presence of liquid phase. Taking all this into account, one can recommend common apparatus for grinding applied in industry, i.e. mills for realization of the processes of the first group showing in Table III. The chief criterion for their application is both productivity and economical operation. For the solution of some specific problems some specific requirements are necessary (for example, such as the prevention of contamination of the sample, etc.). In the case of the processes relating of the second group, the value of energy pulse delivered to a solid is of importance and the expected effect is achieved only with the existence of some threshold energy or special character or pressure—shear relation during deformation. The employment of common grinding apparatus—mills for activation dose not give the desired effect and it is necessary to create special apparatus with high power intensity and sufficient time of system being under extreme conditions (such as planetary mills, attritors, vibratory mills with large amplitude, etc).

The employment with this aim of jet-mills, desintegrators is restricted in spite of their high power intensity, because of the little time of excitation of the system. For intensification of the processes relating to the third group, where simultaneous increase of the surface and its activation are required, it is essential to carry out the operation of mechanical treatment at first in the regime of grinding and then in the regime of activation. This can be done either by the consequent use of two apparatus : mill and mechanochemical activator or due to the work of one activator in different regimes. Recently, new types of apparatus have appeared in which these two consequent operations are carried out simultaneously.[41]

Finally, the processes relating to the fourth and fifth groups in Table II can be carried out in apparatus where mechanical action is produced not upon a specific particle, but upon some number of them. If in doing this besides a simple increase of the surface and the number of contacts between particles, the reactivity of the components is also important, a requirement arises that mechanical pulse should be of sufficient power. The confines the field of application of apparatus to vibratory mills, attritors and planetary mills.

In conclusion, a few words should be said on the procedure of choosing a method of mechanochemical treatment for solving specific technological problems. It must comprise in our opinion, several research stages :

1. Based on the peculiarities of the reaction mechanism one should determine which type of defects the reaction is especially sensitive to.

2. To determine which form of mechanical action should be chosen in order to obtain maximum concentration defects with minimum power imput. What a correlation between shear and pressure must be, what an amplitude pulse and its duration must be, whether there is a correlation between the time of system being in metastable high excited state and the time needed for the completion of the reaction. In doing this it is important to take into account a necessity of precise

measuring delivered in the form of mechanical pulses. Deviations from this rule both with insufficient power of mechanical pulses[42–44] and with excess energy delivered to the system[45] or excess time of treatment[46] lead to considerable decrease in efficiency of mechanical activation and sometimes even to the reverse effect.

3. Then one should determine how the shear stress and pressure are distributed among the particles and how to obtain optimum conditions. Specific realization depends upon the type of apparatus used for mechanical activation. If in the case of jet-mills or disintegrators the problem confines mainly to the consideration of collision between a particle and a barrier, in the case of ball mills and similar apparatus with high power intensity (attritors, vibratory and planetary mills), the distribution of pulse loading among the particles is the main thing.

4. Finally, one should imagine how to repeat optimum conditions of the treatment of a power or a particle in order to calculate the required productivity of apparatus.

Additional requirement to be taken into consideration depending upon specific conditions of the process are such as minimization of the wear of working parts of apparatus, possible causes of contamination of the probe, reduction of specific quantity of metal and power consumption of apparatus.

It is quite clear that all this procedure of choosing a method may be realized when necessary investigations in the field of mechanochemistry of inorganic substances—the subject of the present lecture—will be carried out.

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