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Mechanochemistry and mechanical activation of solids

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Contents

I.	Introduction	177
II.	Studies of the influence of high pressure on the matter	178
III.	The influence of pressure and shear on the physicochemical properties of solids and chemical reactions with them	179
IV.	Mechanical activation and mechanochemical reactions in mills	179
V.	The use of mechanochemistry and mechanical activation for the solution of applied problems	184

Abstract. The effects of the hydrostatic and shear-inducing pressure on the physicochemical properties of solids are analysed. The mechanochemical reactions and mechanical activation are illustrated with various types of chemical transformations ranging from polymorph transitions to solid-state reactions. The prospects for the use of mechanochemistry for the solution of applied problems are discussed. The bibliography includes 299 references.

I. Introduction

The term 'mechanochemistry' was first introduced by W Ostwald in the 'Textbook of General Chemistry',† where he considered, in particular, various methods for the simulation of chemical processes. This term refers to chemical reactions involving reagents in any state of aggregation, although most frequently it is applied to solid-state processes and reactions either initiated by a mechanical means or involving reagents preactivated by a mechanochemical treatment.

The history of emergence and maturation of mechanochemical investigations has been reviewed elsewhere.[1,2] M Carry-Lea, an American chemist, is commonly recognised[3] as a pioneer of mechanochemistry owing to his works on the decomposition of silver halides,[4,5] where he established specific features of the mechanochemical processes and clearly differentiated them from thermally activated ones. There are equally good reasons to consider M Faraday, who observed an acceleration of the dehydration of crystalline hydrates upon the mechanical treatment, as another father of mechanochemistry.

The first work in this field performed in Russia is likely the study of solid-state reactions with powders upon the mechanical activation by F M Flavitskii.[6] Later, these investigations were continued in the Leningrad State University within the scope of development of a method for the qualitative analysis of ores and minerals,[7] and further in the Tomsk State University.[8–10] In the Soviet Union, in the 1940s, the nature of the shock sensitivity of explosives was systematically investigated.[11,12] In approximately the same period, the importance of polymers in economics greatly increased and thus mechanochemistry attracted specialists working in the field of macromolecular chemistry.[13–16]

There were four major research centres actively involved into mechanochemical investigations.[2,17]

1. The Institute of Physical Chemistry and the Institute of Chemical Physics of the Academy of Sciences in Moscow, where important theoretical studies on the nature and mechanisms of the mechanochemical processes in various systems have been accomplished.[14,16,18–20]

2. The A F Ioffe Physico-Technical Institute in Leningrad, where the mechanisms of chemical reactions of polymers under the mechanical treatment have been elucidated by the research team of S N Zhurkov.[21,22] More recently, a series of works on thermodynamics of the mechanochemical processes have been performed in St Petersburg by A I Rusanov and co-workers.[23,24]

3. The Siberian scientific school of mechanochemistry of inorganic compounds. The first works in this field were performed in the mid 1950s in the Tomsk State University,[8–10] but then the 'centre' of research activities moved to Novosibirsk, where studies on both the theory of the mechanochemical processes in inorganic systems and the use of mechanochemistry for the solution of applied problems related to the processing of minerals, inorganic synthesis, materials science, catalysis, *etc*. were deployed in the Institute of Chemical Kinetics and Combustion, the Instutitute of Geology and Geophysics, the Institute of Physico-Chemical Foundations of Mineral Processing, and the Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences.[25–37]

4. The Scientific Production Association 'Dezintegrator' and the Tallinn Polytechnic Institute in Estonia, where I A Hint and co-workers mainly elucidated the industrial applications of the rod disintegrator mills of their own design.[38–40]

In addition, investigations in the field of mechanochemistry were conducted on a systematic basis in scientific and technological centres in Kiev,[41] Ivanovo,[42,43] Sverdlovsk,[44] Ufa,[45] Minsk,[46] and other cities of the former Soviet Union.

Nowadays, the interest of researchers to mechanochemistry does not subside but, in contrast, the community of scientists dealing with mechanochemistry and the mechanical activation expands and the number of publications in these fields rapidly increases.[47,48] New dedicated mechanochemical centres appears in France, Italy, Germany, USA, China, South Korea, Japan, India, Canada, *etc*.

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† W Ostwald *Lehrbuch der Allgemeinen Chemie. Stöchiometrie* Bd. 2 (Leipzig: Engelmann, 1891).

II. Studies on the influence of high pressure on the matter

A mechanical action on a solid can typically be represented as a combination of pressure and shear. Therefore, it is important to establish the role of each of the two factors in the modification of the physicochemical properties of substances subjected to a mechanical treatment. In this regard, studies on the effects of isostatic pressure, *i.e.*, the behaviour of a sample under equal loads from all directions, became important. This field was pioneered by works by G Tammann [49] and P V Bridgman,[50] which still retain their significance although they were done in the first half of the 20th century.

So far, the effects of pressure on solid-state reactions have been less explored than the temperature effects. The major reason for this is difficulties related to the experimental instrumentation and monitoring of processes taking place at elevated pressures. Nevertheless, three major aspects of the influence of high pressure on the course of chemical reactions in the solid state can be distinguished.[51]

The first aspect includes the influence on the intergrain interactions in mixtures of reacting solids. As has been pointed out by W Komatsu,[52] it is important to correctly account for the total number and the overall area of the intergrain contacts, since it is they rather than the mere ratio of surface areas of reacting particles that govern the rate of a solid-state reaction, at least in its early steps.

This has been shown by W Poch [53] by the example of the synthesis of nickel ferrite and zinc and magnesium aluminates from the respective oxides at a pressure ranging from atmospheric to 60 kbar. The experimentally observed significant acceleration of the reactions under elevated pressures can be explained by an increase in the contact area between the reacting particles, which promotes the diffusion across the interface. The optimum pressure as regards the reaction rates is 40 kbar. A further increase in pressure decelerates the reactions, since under these conditions, the vacancy-mediated diffusion in the bulk of particles becomes the rate-limiting step and it is impeded by high pressures. In some cases, changes in the reaction rates and conversion levels are indicative of the involvement of an intermediate gas phase.[54]

The second aspect of the pressure effects includes the changes within the particles of solid reagents themselves.[55] The changes can be subdivided into ones occurring with the real structure (primarily, concentrations of various defects), a modification of the interatomic distances and bond angles, and the changes inside the atoms or ions. The direction of the pressure-induced changes in the concentration of point defects is determined by whether the formation of a specific defect gives rise to a lattice dilation or shrinkage. Consequently, the concentration of the ion vacancies should always decrease and that of the interstitial ions increase with an increase in pressure, all other factors being the same. This explains the different possible net effects of pressure on the diffusion in solids and, consequently, on the solid-state chemical reactions, for which the diffusion through the layer of a solid product is the rate-limiting step.

An increase in pressure also modifies the properties dependent on the interatomic distances and bond angles.[56] In particular, this gives rise to a narrowing of the band gap so that a dielectric starts to behave as a semiconductor and even sometimes as a metal. Thus the effect predicted by K T Herzfeld [57] and N F Mott [58] in the beginning of the previous century has been successfully confirmed experimentally.

H G Drickamer and C Frank proposed [55] a classification of all transformations in solids under the isostatic compression into four groups. The first group includes the transformations accompanied by a rearrangement of atoms, molecules or ions in a crystal without substantial changes in the electronic subsystem. The conversion of the face-centred cubic lattices of alkali metal halides into primitive cubic lattices under the mechanical load can be taken as an example of this type of transformations. The second group includes similar transitions that are accompanied by changes in the electronic subsystem. As a consequence, such transitions result in an alteration of the electrical or magnetic properties of the substance. The transition of ferromagnetic α-iron into paramagnetic γ-form can be mentioned as an example. The third group includes the structural and bulk transformations, which are characterised by the existence of a specific transition point and are accompanied by a change in the type of the electronic structure. The $\sigma \rightarrow d$ hybridisation of bonding in rubidium and potassium crystals and the transition from the f- to the d-character of bonding in crystals of cerium and other rare-earth metals upon compression fall into this group. Finally, the fourth group comprises the transformations accompanied by continuous changes in the bonding character, such as those observed in iron acetyl acetonate (the transition $Fe^{3+} \rightarrow Fe^{2+}$) as well as in some complex compounds with donor-acceptor bonds and molecular crystals upon compression.

Presently, this classification does not cover all the available experimental data and thus it cannot be considered comprehensive. Still, it can be taken as a basis for the analysis of the isostatic pressure effects on solids. Apparently, the consideration of the isostatic compression effects on molecular crystals as well as the analysis of pressure-induced changes in molecules and intermolecular interactions realised through the van der Waals and H-bonds may help to substantially extend this classification.[59]

The range of studies devoted to the influence of high pressure on physicochemical properties of solids is constantly expanding. Over the recent years, the emphasis in such investigations has shifted exactly to molecular crystals.[60–79] Probably, this relates to broad capabilities offered by this approach in the elucidation of the intermolecular interactions in biological systems and in the characterisation and modification of molecular crystals applied as functional materials (*e.g.*, a pressure-induced transition of an organic ferromagnet into an antiferromagnet).

The experimental results on the behaviour of molecular and ion-molecular crystals under the isostatic pressure have been reported. In particular, it has been established that the isostatic compression of a crystal of deuterated oxalic acid gives rise to a shortening of two hydrogen bonds and an elongation of the third one.[59] The pressure-induced structural changes in crystals with hydrogen bonds have been explored in detail by Katrusiak.[60–64] It was demonstrated that the compressibility of an H-bond under the isostatic compression depends on its type, local environment and the type of molecular packing in the crystal.

The compressibility of hydrogen bonds in molecular crystals has been also investigated by other authors.[65–71] In particular, it has been shown that the two NH···O hydrogen bonds present in the crystal structure of $Co(NH_3)_5NO_2Cl_2$ are characterised by different compressibilities: the longer bond proves more compressible. As a result of the compression, the nitro ligand is rotated, which results in a change in the bond lengths between the cobalt atom and the ligands. The NH···Cl bonds present in the structure behave differently: the *cis*-NH_3Cl bonds continuously shorten with an increase in pressure, whereas one of the two H-bonds in the *trans*-position elongates.[76, 77]

The deformation of the H-bonds in crystals of the monoclinic paracetamol modification subjected to the isostatic compression is accompanied by a change in the molecular conformation: the angle between the planes of the acetamide group and the benzene ring is diminished. In contrast, similar compression of molecular layers in the orthorhombic paracetamol modification is isotropic. The results obtained made it possible to rationalise the mechanism of the polymorph transition of the monoclinic paracetamol modification to the orthorhombic one.[65–68, 78, 79] Glycine polymorphs also produce different responses to pressure. The α-modification shows no phase transitions up to pressures of 4 GPa and the pattern of changes in the unit cell parameters is generally similar to that observed upon a temperature decrease.[65, 66, 69–72] Meanwhile, the β-modification undergoes a phase transition already at 0.76 GPa,[79] whereas the γ-form converts in the pressure

range of 2.7–2.8 GPa into a new previously unknown modification referred by the authors to as δ-glycine.[74,75]

The investigations into the influence of pressure on biochemical objects is getting increasingly important. In particular, valuable information on the carbonyl–carbonyl interactions giving new insights into the nature of the β-folds and α-helices in proteins has been gained [80] and the structural changes in nucleic acids have been elucidated.[81] Studies on the permeability of cell membranes as a function of pressure occupy a special place. Pressure can affect both the structure of the membrane itself and the conformations of its constituent molecules.[82]

Changes in the intermolecular distances and mutual orientations of molecules at elevated pressures can result not only in the intermolecular changes but also in the intramolecular changes. This was evident already to Bridgman, who observed polymerisation of benzene at a pressure increased to 23–30 GPa.[50] Also, it has been found [61] that the OH···O bonds joining molecules into chains, layers and helices in the crystal structures of cyclohexane-1,3-dione and dimedone are differently shortened upon compression. A more detailed review concerning the changes in molecular crystals subjected to the isostatic compression can be found elsewhere.[82]

Studies on the influence of the isostatic pressure on reactions with inorganic compounds are rather numerous. Below, we consider only selected examples of systems, in which an increase in pressure either changes the chemical properties of components or initiates chemical reactions.

Semenenko *et al.*[83,84] investigated the formation of ternary intermetallics in pseudobinary systems Hf_2Fe-Hf_2Cu, Hf_2Ni-Hf_2Mn and Hf_2Ni-Hf_2Cu and their interactions with hydrogen. A model for the location of inserted hydrogen atoms within the cavities of the intermetallic matrices was proposed [83,84] as well as a dependence of the valence state of hydrogen atoms on their concentration therein.

An interesting inversion of the electronic levels with different symmetries has been observed, which can occur not only under the direct action of the external pressure but also in the course of a pressure-induced chemical reaction, as in the case of the alkali metal intercalation into graphite [83] or the formation of intermetallics containing an alkali metal as a component.

Goryainov *et al.*[85–88] measured the Raman and IR spectra of natrolite at a pressure of 4 GPa. The experimental results were compared with the theoretical calculations of the crystal structure. According to the results obtained, natrolite behaves differently upon compression in water, which can penetrate into its cavities (in particular, the phase transitions occur at 0.75 GPa and 1.25 GPa), and glycerol, which cannot penetrate into the cavities (the compression in glycerol does not result in any phase transitions).

Therefore, the experimental data discussed above clearly indicate that studies of the behaviour of solids under pressure are necessary not only because they give important insights into the mechanisms of the mechanochemical processes but also because they represent a powerful method for the elucidation of structural and intermolecular interactions.

III. The influence of pressure and shear on the physicochemical properties of solids and chemical reactions with them

In addition to the studies of solids under the isostatic pressure discussed above, experiments providing conditions simultaneously for the compression and shear deformation yield valuable information. To the best of our knowledge, this type of studies were pioneered by Bridgman, who designed a dedicated apparatus, which provided control over the values of pressure and shear, deformation rate and sample temperature.[89,90]

Modified Bridgman anvil cells were utilised by R Roy *et al.*[91–93] for the elucidation of various solid-state processes ranging from polymorph transitions to decomposition reactions. They showed that the shear component strongly affects the process rates sometimes accelerating the reactions by a factor of a few hundred and thus increases the conversion levels, although it does not shift the equilibrium between the reactants and reaction products. For instance, the degree of decomposition of jadeite into nepheline and albite

$$2\,(Na_2O\cdot Al_2O_3\cdot 4\,SiO_2) \longrightarrow$$
$$\longrightarrow Na_2O\cdot Al_2O_3\cdot 2\,SiO_2 + Na_2O\cdot Al_2O_3\cdot 6\,SiO_2$$

does not exceed 10% under the action of the hydrostatic pressure at 350 °C, whereas it increases up to 60% under the simultaneous action of pressure and shear at the same temperature.

A similar apparatus was employed for the synthesis of alloys with anomalous concentrations of components and intermetallics.[94,95] A A Zharov *et al.*[20,96] demonstrated in a series of experiments that organic syntheses are possible under shear deformation and high pressure in a special reactor similar to the Bridgman anvil cells.

Studies of mechanochemical solid-state syntheses of organic compounds in anvil cells are worth a special discussion. However, the mechanisms of such processes as well as the mechanisms of solid-state reactions between organic compounds are significantly less explored as compared to inorganic synthesis.

More recently, studies of mechanochemically activated interactions between low-molecular-weight solid organic compounds appeared. As a result of these research efforts, new reactions of polymerisation of various classes of organic compounds and opening of benzene and pyridine rings were discovered and the dramatic acceleration of the polymerisation with respect to analogous reactions in the liquid phase was achieved.

Dadali *et al.*[97] demonstrated that the mechanically activated solid-state reactions between two reactants, one of which is an electron donor, while another is an electron acceptor, yield free radicals.

IV. Mechanical activation and mechanochemical reactions in mills

The mechanical activation in a mill is the most common operation in mechanochemistry. Probably, this is mainly due to two factors, *viz.*, the simplicity of the experiment and the interest of technologists, since mills are the most common devices realising the mechanical treatment of solids. Nevertheless, both mechanics and physics of the processes occurring in this type of devices remain a subject of numerous investigations.[98–116] The vast majority of these studies are devoted to the optimisation of the grinding step for maximising the active surface area of the solid at the minimum energy consumption. The number of studies, in which mills are used exclusively for the mechanical activation, is significantly smaller.

Such studies are based on two main principles: the pulse time structure of the process (the regular alternation of two processes, *viz.*, the development of a stress field and its relaxation [29,98–100]) and the spatially local character of the mechanical treatment on solids (indeed, the stress field develops not in the whole volume of a solid particle but only in the areas of its contact with other particles or with the working medium).[101–103] As a rule, this type of studies are aimed at the determination of the size of the area, where the stress field is developed under the mechanical treatment, as well as the lifetime and the actual form (*e.g.*, a pressure burst) of the field.[104,105] Additionally, possible relaxation channels of the stress field (*e.g.*, a temperature rise or formation of various metastable forms and new interfaces, *etc.*) and related secondary processes are explored.[106] Not pretending to the comprehensive survey of works in this filed, we shall just make mentions of several important contributions, *viz.*, by Maurice and Courtney,[106–108] Gaffet *et al.*,[109] Tkačova *et al.*,[110] Delogu *et al.*[111] performed abroad and by Urakaev *et al.*[112–116] accomplished in Russia.

Studies in this field are far from being complete and probably they even should be intensified due to the potential applications of the mechanochemical processes in industry. As an example, we cite the results regarding temperatures developed in the contact areas estimated by different authors for the systems similar in terms of their chemical compositions and conditions of the mechanical treatment. The scatter in the reported values is as large as from 38 to 600 – 700 °C.[109]

1. Mechanical activation of single-phase systems

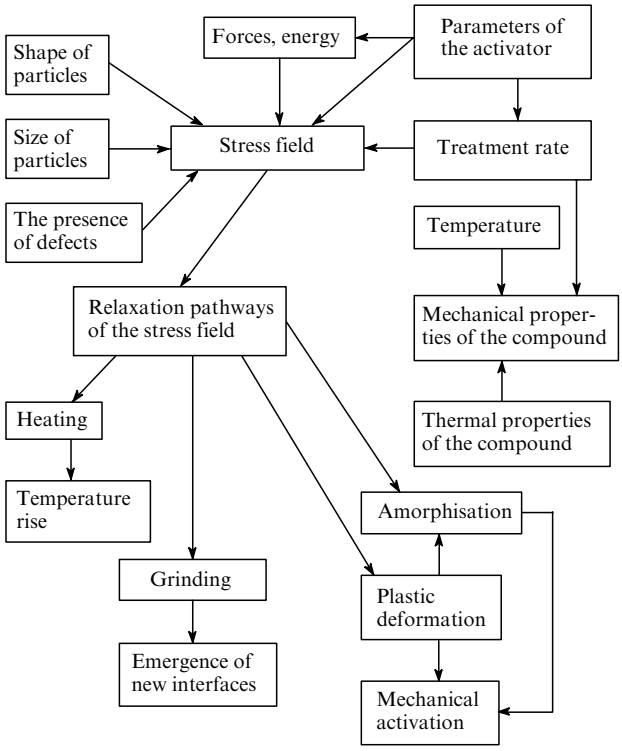
If a compound subjected to the mechanical treatment is strictly single-phase, then the relaxation of the stress field can proceed by several independent pathways and be accompanied by various secondary processes, such as the heat liberation, emergence of new interfaces, accumulation of defects in crystals, formation of metastable polymorphs, amorphisation of solids and chemical transformations.

The exact share taken by each of the channels depends on the conditions of the mechanical load (*e.g.*, the energy input and the loading rate), physical properties of the solid, treatment temperature, *etc*. In some cases, the preferable relaxation channel can be altered at the course of the process. For instance, an increase in the propagation rate of a main crack during decomposition of oxy-acid salts switches the decomposition mechanism in its tip: the thermal decomposition is replaced with the mechanochemical one.[117, 118] A gradual decrease in the size of particles subjected to the mechanical treatment results in a transition from grinding to plastic deformation.[119, 120]

The factors affecting the formation of a stress field are depicted in Scheme 1, together with the main pathways of its relaxation.[121] The left side of the Scheme relates to the grinding process, which is covered in detail in the literature, and thus it will not be considered here. The processes listed in the right half of the Scheme are typically classified as the mechanical activation.

Normally, grinding is used to create the maximum active surface of a powder at the minimum energy consumption, whereas the aim of the activation is to accumulate energy in the form of defects or other structural modifications of a solid, which makes it possible to decrease the activation energy or improve steric conditions for its subsequent chemical transformations.

Scheme 1



There are two distinct cases of the mechanical activation. In the first case, the duration of the mechanical treatment involving the formation of a stress field and its relaxation is longer than the chemical reaction time (these processes are commonly referred to as mechanochemical). In the second case, *vice versa*, the duration of the mechanical treatment involving the formation of a stress field is shorter than the chemical reaction time or these processes take place separately. The latter case is associated with the mechanical activation.

There are different forms of the energy storage upon the mechanical activation. Usually, they can be described as the formation of defects in crystals subjected to the activation.[121, 122] Thermodynamics of the energy accumulation upon the mechanical load has been considered elsewhere.[23, 24] Most frequently, the mechanical treatment gives rise to the plastic deformation and subsequently to the formation of linear defects, such as dislocations, ion and atom vacancies and interstitial ions. Recently, computer simulations of such processes have been surveyed by Gainutdinov *et al*.[123] In addition, this results in changes in the bond angles, emergence of broken bonds and further in the formation of free radicals (in covalent crystals) or amorphisation (in molecular crystals).

Since the defect formation in metal salts, oxides and carbides has been extensively discussed in numerous reviews and monographs (see Refs 122, 124 – 127), below we consider only those cases of the mechanical treatment, which are non-typical, in our opinion. These include, for instance, the activation of spinels, *i.e.*, ferrite-type complex oxides. Upon the mechanical treatment, the densely packed oxygen sublattice in spinels remains unchanged. The most important changes occur in the cation sublattice, which are manifested in the redistribution of bi- and trivalent cations over the tetrahedral and octahedral cavities.[101 – 103, 128 – 131] This redistribution gives rise to a substantial change in the physical and chemical properties of spinels. An annealing of spinels at 500 – 600 °C results in the return of the cations to their typical positions so that the normal properties of spinels are restored. Similar results were obtained upon the activation of chalcogenides.[132]

The mechanical activation enables relatively easy modification of both physical (*e.g.*, changes in the Neel temperature) and chemical (*e.g.*, changes in the leaching order of cations) properties of ferrospinels.[133 – 137]

The discovery of the quasi-crystalline state, in which compounds manifest unusual physical and chemical properties, in 1984 (Ref. 138) gave a strong incentive to the search for the alternative methods for the production of quasi-crystals, in addition to the traditional method of quenching of alloys. Among other methods, the mechanochemical one was also evaluated. In 1989, Ivanov, Konstanchuk and Bokhonov [139 – 141] obtained for the first time quasi-crystals by the mechanochemical treatment of intermetallics $Mg_{32}(Zn,Al)_{49}$, $Mg_{32}(Cu,Al)_{49}$ with the Frank – Casper structure.

They established that the formation of the icosahedral phase starts already in the early steps of the mechanical treatment. According to the high-resolution electron microscopy results, the nucleation and growth of the icosahedral phase are initiated by the production of rotational twinning defects, whereas the parent and the transformed phases are topotactically related to each other.[142]

The same authors found [143, 144] that the mechanochemically prepared icosahedral phase $Ti_{45}Zr_{38}Ni_{17}$ manifests a high hydrogenating activity. Similar studies were started abroad approximately at the same time.[145]

In general, we note that the period of preliminary experimental information gathering in the field of mechanochemistry and mechanical activation of simple metal, oxide and salt systems comes to its conclusion. Likely, novel results may be anticipated in

mechanochemistry of complex oxygen-containing (*e.g.*, spinels or silicic acid derivatives) and coordination compounds, where unusual (at least from the viewpoint of the compounds already elucidated) pathways of the energy accumulation due to the changes in the non-equilibrium concentrations of linear and point defects, emergence of shear structures or other pathways related, for example, to the isomerisation processes, changes in the bond angles or rotational defects can be realised.

Nevertheless, we believe that it would be more important for the moment to rationalise the whole array of the experimental information collected up to present. Very often, the results obtained are interpreted in the very standard way, something like: 'The mechanical activation gives rise to the accumulation of defects in reacting crystals thus increasing their reactivities', which is rather meaningless and worthless. Actually, no strict conclusions on the particular type of defects produced upon the activation can be derived based solely on the line broadening in powder diffraction patterns or the calorimetrically estimated enthalpies. Indeed, various defects differently affect chemical processes [146] and therefore a deeper analysis of the activation consequences is necessary, which is ignored by the majority of researchers.

As for the mechanical activation of molecular crystals, the number of studies devoted to the emergence and relaxation of stress fields in these systems is very limited. Although mechanochemistry of polymers is studied in sufficient detail, very little is known about the behaviour of molecular crystals under the conditions of the mechanical treatment.[147–153] It is known [149, 150] that structural disordering is frequently observed, which is manifested in the broadening of diffraction lines. In some cases, the H-bonds that join the molecules in the pristine crystal structure into dimers or more complex aggregates break down. Sometimes, zwitter-ionic groups are formed [150] or free radicals appear, if the mechanical treatment results in the scission of strong covalent bonds.[97, 151–153]

2. Mechanical activation of multi-component mixtures

In addition to studies of the influence of the mechanical activation on single-component systems discussed above, similar studies of multi-component mixtures have been getting increasingly important over the recent years. Three major classes can be distinguished among such systems, *viz.*, solid–gas, solid–liquid and solid–solid mixtures.

a. Mechanical activation of solid–gas systems

As has been established already in the early studies (for instance, see Refs 126 and 154), the mechanical treatment affects both the sorption of gases upon their interaction with various solids and subsequent chemical reactions of adsorbed gases with solids.

The enhancement of adsorption of gases on solid surfaces upon the mechanical treatment is accompanied in some cases by the penetration of gas molecules into the mechanically deformed lattice. The sorption time *vs.* duration of the mechanical treatment function is characterised for many gases by the existence of an optimum value due to the competition of the mechanically activated adsorption and desorption processes as the active surface centres are getting gradually filled with gas molecules.

The adsorbed gas molecules can react with molecules of other compounds co-adsorbed on the same surface. As an example of such a reaction, the co-oxidation of hydrogen and carbon monoxide on quartz surfaces subjected to the mechanical activation can be mentioned. P Yu Butyagin was one of the first to start the elucidation of gas–solid reactions both under the conditions of mechanical preactivation and exactly during the activation.[14, 18, 19] It was found [155–157] that the mechanical treatment of metallic and oxide catalysts enhances their activity, which is traditionally associated with the accumulation of various defects in the catalysts, including point and extended defects (typically, dislocations) and changes in the ratio of areas of different crystal faces (*i.e.*, changes in the crystal habitus).

It is important to stress that not only the reaction rate but also the mechanism of the catalytic reaction changes due to the mechanical activation. This fact makes it possible to increase the selectivity of catalysts with the mechanical activation. Among recent works, studies by R A Buyanov *et al.*[34, 35] devoted to the mechanocatalysis, *i.e.*, catalytic reactions under the simultaneous action of the mechanical treatment, deserve special attention. They accomplished a number of interesting and important catalytic transformations (*e.g.*, pyrolysis of butane over magnesium oxide or hydrogenation of butadiene over metal hydrides). Additionally, they elaborated a promising technique for the conduction of mechanochemical reactions under high pressures (10 MPa) of hydrogen, oxygen or ammonia.

The adsorbed gas molecules can not only react with the solid on its surface but also diffuse into the bulk of the solid in the course of the reaction. The influence of the mechanical activation on reactions in gas–solid systems was studied most thoroughly for oxidation, nitridation, hydrogenation and carboxylation of metals and various metal oxides. The influence of the mechanical activation on reactions of gases with polymers has been elucidated in substantially less detail, whereas the influence on molecular crystals remains virtually unexplored.

The influence of the mechanical activation on reactions of gases with metals yielding volatile products have been carefully investigated by the example of the formation of nickel carbonyl.[126, 154] Owing to the mechanochemical treatment of nickel foil, the synthesis of nickel carbonyl can be realised under atmospheric pressure, although typically it is performed in an autoclave. During the activation process, the active centres are generated on the nickel surface, which are characterised by a weak (if any) dependence of the reaction rate on temperature. This suggestion explains the anomalies of the dependence of the reaction rate on temperature (*i.e.*, the negative temperature coefficient) and pressure.[126]

The silicon chlorination is another example of the same type of processes. Both mechanical preactivation and the activation of silicon directly during the chlorination substantially accelerate the reaction and increase the yield of the product, methylchlorosilane.[155, 156]

If the product of a mechanically activated reaction is solid, then the chemisorption of gaseous reactant on the active sites is followed by the generation and growth of the product nuclei and further by the formation of the product layer.

Since no thermal activation is involved, the occurrence of specific thermodynamically forbidden reactions under the conditions of mechanical activation was suggested, in particular, the oxidation of gold by carbon dioxide.[157]

After the formation of a product layer, the process continues either in the kinetic or diffusion mode, depending on the ratio of molecular volumes of the solid reactant and product.

The mechanochemical hydrogenation of metals is one of the most common processes utilising the mechanical activation. The rapt attention of researchers to the hydrogenation of mechanically activated metals is likely caused by its potential in the technology of hydrogen storage. The first investigations in this direction were conducted in the Soviet Union in the mid-1980s.[158–161] It was discovered that the mechanical activation of magnesium noticeably accelerates its hydrogenation. The conversion level can be dramatically increased by the addition of a catalytic amount of nickel, iron or chromium to the basic metal being activated.[160] Later, these studies were extended by foreign researchers [162–172] to the influence of the mechanical activation on the rates and conversion levels of the hydrogenation of both traditional hydrogen absorbers (*e.g.*, FeTi, $LaNi_5$ or $MgYNi_4$) and the novel ones.[158–161] As has been recently established,[143, 144] the icosahedral structures produced mechanochemically or using the mechanochemical activation of some intermetallics act as highly efficient hydrogen absorbers.

More detailed information on the application of the mechanical activation for the metal hydrogenation can be found elsewhere.[173]

In the case of the mechanochemically activated oxidation of metals with oxygen or halogens, the metal surface is constantly renewed due to the grinding with the product being fully or partly removed mechanically. The oxidation rate first increases until the minimum particle size is achieved and then starts to decrease.[174]

The metal nitridation reaction proceeds through the intermediate formation of a solid solution of nitrogen in metal followed by the precipitation of the nitride phase above a specific critical nitrogen concentration in the solid solution. The further activation gives rise to the overstoichiometric accumulation of nitrogen.[175] The mechanically-assisted nitridation of titanium is only efficient if the nitridation is carried out directly during the activation, whereas the preactivation gives only insignificant gain in the reaction rate.[176]

The nitridation of stainless steel in the atmosphere of ammonia is more efficient than in nitrogen. The activation however is accompanied by the conversion of γ-iron into α-modification.[177]

The mechanical treatment of silicon in the atmosphere of ammonia at 100 °C yields α-Si_3N_4; the complete conversion requires 48 h. At room temperature, the complete conversion is reached only after $\sim$168 h.[178]

Kalinkin *et al.*[179] demonstrated that the mechanical activation of diopside $CaMgSi_2O_6$ is accompanied by the carbon dioxide adsorption on the surface of the sample.

b. Mechanochemistry of solid – liquid reactions

The investigations into the mechanical activation of solid – liquid reactions are dominantly stimulated by the progress in two industries broadly exploiting these processes. In hydrometallurgy, such processes offer a route to increase the efficiency and selectivity of leaching of valuable components from ores and minerals.[26, 37] In pharmaceutics, the mechanical activation is employed for the solubilisation of poorly soluble medicines.[149, 152, 180]

As has been established already in the early works devoted to the mechanical activation, it is the accumulation of various defects in the reacting solid rather than mere increase in the specific surface area upon grinding that is responsible for the increase in reactivity. Extended defects, *i.e.*, dislocations, play a crucial role in the process of dissolution so that the dissolution rate correlates with the dislocation density.[181, 182]

When a mixture of two components forming a galvanic pair rather than a single-component solid is dissolved, the mechanical activation of the components can change their electrode potentials and thus affect the dissolution rate.[183 – 186]

It should be however taken into account that under specific values of viscosity of the slurry and the intensity of the mechanical load, the conditions suitable for hydrothermal processes can evolve in the system upon mechanically assisted dissolution.[29, 187]

The dissolution of molecular crystals has certain distinctive features as regards the effects of the mechanical activation. Typically, the mechanical activation of such crystals induces either polymorph transitions or amorphisation. The exact mechanism of the process remains unclear: whether it proceeds through the intermediate step of the accumulation of extended defects or through the step of contact melting followed by the recrystallisation.

In some cases, the mechanical activation results in the decomposition of dimers initially present in the crystal structure. The amorphisation of molecular crystals or transition into metastable modifications increases the rates of dissolution and the solubilities (in the case of the micellar mechanism of the dissolution).

The influence of the mechanical activation on the processes of dissolution of solids has been elucidated not only for water but for other solvents as well. In particular, the mechanical activation increases the rate and the conversion level in the interaction of propyl iodide or bromide with aluminium,[188, 189] initiates the styrene polymerisation[190, 191] and pyrazine oxoalkylation.[192] However, very little information is available concerning the mechanisms of the activation for all these processes, despite their significance in chemistry.

c. Mechanochemistry of solid – solid reactions

Mechanochemically initiated solid-state processes have recently become a subject of intense investigations. Probably, this is due to the potential applications of such reactions in technology, in particular, for the development of the so-called dry processes, which are more environmentally friendly and cost efficient than the currently adopted technologies.[193]

Any chemical interaction between solids proceeds neither in the entire volume of the reacting compounds nor on their entire surface but rather exclusively in the contact areas between the particles.[194] Thus the total number of such contacts between reacting particles plays the decisive role at the initial steps of a solid-state reaction. This means that it is always desirable to grind and mix components in such a way as to prevent the aggregation of particles of the same component (this dramatically decelerates the reaction). The mechanical alloying is often classified as a variant of the mechanochemical reactions. As a rule, the mechanical alloying is used for the preparation of solid solutions and metastable intermetallides provided that the traditional methods for their synthesis are either difficult or inconvenient for other reasons.[195 – 208] Furthermore, a mechanochemical synthesis yields the respective product as a highly dispersed phase, which can be useful for the subsequent technological steps.[195]

In order to illustrate such an approach, we mention the systems Mg – Ti or Al – Nb, in which the boiling point of the first component lies below the melting point of the second component.

By means of mechanochemistry, it proves sometimes possible to shift the boundaries of the formation of substitution solid solutions beyond the thermodynamical limits established for the equilibrium state. In particular, the ultimate solubility of aluminium in nickel, according to the respective equilibrium diagram, is13.5 at.% at 1000 °C; it decreases by a factor of 3.5 at 500 °C and becomes fractions of a percent at room temperature. Notwithstanding, the mechanochemical method enabled preparation of solid solutions of aluminium in nickel with the aluminium content as high as 28 at.% (Ref. 198).

Solid solutions can be synthesised not only by the mechanical treatment of the respective mixtures but also by the mechanical activation of the intermetallic compounds that are characterised by low enthalpies of formation. In particular, solid solutions NiV and CoV manifesting anomalous magnetic properties have been prepared in this way.[199, 200] Mechanochemical approach has been applied to prepare several solid solutions with positive enthalpies of mixing, such as solid solution of copper in iron.[208, 209]

The similarity between the atomic sizes and general structures of the components are the main factors governing the possibility of the formation of solid solution under the mechanical alloying.[197, 203 – 205] As has been established for the systems Ni – In, Cu – Sn and Cu – In, the formation of solid solutions proceeds as follows. First, after the complete intermixing of the alloy components, the respective intermetallics compounds, *viz.*, $Ni_{10}In_{27}$, Ni_2In_3, Cu_6Sn_5 and Cu_9In are produced. Then, their structures are distorted due to the second order microdeformations giving rise the deformational packing defects.[204, 205]

Investigations into the mechanochemical transformations in the systems Fe – X (X = C, Si, Sn or Ge) can be illustrated by the results of E P Yelsukov *et al.*[206 – 211] According to their model, the formation of binary compounds in these systems proceeds in several steps. First, nanostructures with a domain size of $\sim$10 nm are generated due to the diffusion of X along the intergrain boundaries of iron. Then, the intermetallic compounds and the amorphous phase emerge. Further, the atoms X diffuse from the boundaries into the bulk of the iron grains thus giving rise to the intermixed solid solutions.

The sequence of transformations upon the mechanochemical iron carbonisation below 32 °C have been established by X-ray diffraction.[211] If the carbon content [C] < 20%, the product is amorphous; whereas for [C] > 20%, crystalline iron carbides Fe_3C and Fe_7C_3 are formed. The initial steps of the process include grinding of the components, their intermixing and the generation of nanocomposites with a particle size of ~10 nm. In parallel, the atoms of the second component X diffuse into α-iron along the intergrain boundaries. In the case of metalloids with the atomic radius comparable to that of iron (*i.e.*, Si, Ge and Sn), the intermetallics ($FeSi_2$, $FeGe_2$ and $FeSn_2$, respectively) are directly nucleated in the areas of their local concentration, *i.e.*, along the intergrain boundaries. The further mechanical treatment affords solid solutions. In the case of metalloids with the atomic radius substantially smaller than that of Fe (*i.e.*, C), the emergence of the carbide phase is preceeded by the formation of an amorphous phase.

A similar sequence of steps was observed in the solid-state synthesis of intermetallics Fe–Ti,[209] Fe–Zr,[210] Ni–Ge[212] and Ni–Bi.[213]

P Yu Butyagin[214] proposed a classification of all mechanochemically activated solid-state reactions into two groups, depending on the rate-limiting step of the overall process: either the development of contacts (*e.g.*, as in the synthesis of lead niobate, where the reaction proceeds in the near-surface regions) or the mass-transfer into the bulk (as in the synthesis of nickel aluminide).

Very high diffusion coefficients of atoms or ions constituting a solid phase is a distinctive feature of mechanochemical solid-state syntheses. To be distinguished from the ordinary diffusion determined by the concentration gradients, this type of diffusion is denoted with a special term, 'deformational atomic intermixing', or 'ballistic diffusion'. Several hypotheses regarding the mechanism of this process have been suggested. Butyagin proposed[122] that the interstitial sites of the lattice are responsible for the diffusion, whereas Schwarz argued[215] that the diffusion proceeds through the dislocations, the number of which increases continuously upon the mechanical treatment. Therefore, the exact mechanism of the deformational atomic intermixing remains a subject of debate.

Sometimes, particular contact conditions are realised so that the direction of the mechanochemical process contradicts the thermodynamical calculations. For instance, the rate of the solid-state interaction of tungsten trioxide with alkali-earth metal carbonates is the maximum in the case of barium carbonate, although this should be opposite, assuming that the rate should correlate with the change in the free energy during the process.[216] A similar situation is observed for the interaction of potassium persulfate with methyl- and phenyl-substituted imidazoles.[217] According to both computer simulations[218,219] and experiments,[220] the mechanical treatment substantially accelerates the diffusion processes in solid phases. In particular, the coefficient of chromium diffusion into iron is 10^{-12} cm^2 s^{-1} and 2×10^{-8} cm^2 s^{-1} at room temperature and at 1400–1600 K, respectively. Meanwhile, it can be increased up to 10^{-5}–10^{-7} cm^2 s^{-1} with the mechanical activation.

Karagedov *et al.*[221] suggested that the accumulation of defects cannot be the only factor driving the marked acceleration of mechanically activated solid-state synthesis of complex oxides from simple oxides since the defects can be cured even before the initiation of the reaction. The most significant result is the adjustment of the size distribution of particles in the reaction mixture in such a way as to provide the densest packing and preventing aggregation.

The mechanochemical synthesis in multi-component systems represents yet another direction in the field of solid-state inorganic synthesis.[200]

The possibility of participation of fluidic (gaseous or liquid) phases in the processes at their intermediate steps has become increasingly important over the recent years. Indeed, a process, which is formally considered as a solid-state reaction, can actually represent a certain combination of solid + gas or solid + liquid reactions. In this regard, the control over such processes requires alternative tools as compared to the case of truly solid-state reactions.[222]

The presence of water in solid-state systems either before or after a reaction is of particular interest. E G Avvakumov, E G Devyatkina and N V Kosova[223,224] elaborated an original method referred to as the mild mechanochemical synthesis. Essentially, two hydroxides, one of which is acidic, while the other is basic, can be used as precursors in the synthesis of a complex oxide instead of simple oxides. The rate of the mechanically activated neutralisation reaction appears higher than the rate of the interaction of non-hydrated oxides.

Studies in the same directions were then continued by M Senna and co-workers[225] The results of these joint research efforts were summarised in a monograph.[226] The authors demonstrated that the mechanical activation converts the bridging metal–oxygen–metal bonds in the acidic component into the bridging bonds between the basic and acidic components, *i.e.*, in the case of the reaction of $Ca(OH)_2$ with $TiO_2\cdot0.82\,H_2O$, the Ti–O–Ti bonds are converted into the Ca–O–Ti bonds.

Water released in the neutralisation process can act as an additional factor for the reaction acceleration. Conditions suitable for hydrothermal processes can evolve in the system. The first assumptions that hydrothermal reactions can be initiated under the mechanical activation of oxides containing water have been made already in the very early works devoted to the mechanochemical synthesis (see, for instance, Ref. 227). However, the comprehensive argumentation in favour of this hypothesis has been given later.[29,228,229] There is serious experimental evidence of the attainability of hydrothermal synthesis in mechanochemical activators.[230,231]

The heat delivered in a system as a result of a chemical reaction and the relaxation of a stress field upon the mechanical treatment can actuate the transition from the mechanochemical synthesis regime to the self-propagating high-temperature synthesis.[232–234] Apart from the cognitive interest, this phenomenon holds some promise for applications. First of all, the self-propagating high-temperature synthesis can be realised in those systems, where the adiabatic temperature is not sufficient for sustaining the combustion. Second, this switch of the modes can eliminate the possible negative combustion impacts on the product, such as sintering and oxidation.[235,236]

P G McCormick and co-workers[237] discovered that if a system composed of two reactants that react to yield two solid products is diluted with one of the products, then the second target product can be produced in the form of nanoparticles. In particular, cadmium sulfide with the particle size of the order of a few nanometers can be produced by the solid-state reaction of cadmium chloride with sodium sulfide, if the reaction mixture is diluted with sodium chloride. The optical properties of such nanoparticles, the so-called quantum dots, differ substantially from those of crystalline cadmium sulfide.[238] Similar syntheses have been realised for nanoparticles of metals,[239] simple and complex oxides,[240–245] nitrides[246] and salts.[247,248]

Balaž *et al.*[249] reported on a mechanochemical method for the preparation of nanoparticles of cadmium, lead and zinc sulfides by the reaction of the respective metal acetates with sodium sulfide.

Gras *et al.*[250] demonstrated that the mechanochemical synthesis of molybdenum silicide from elements yields particles with a size of ~90 nm, whereas only larger particles can be produced by the self-propagating high-temperature synthesis due to the sintering of particles in the combustion wave. Boron nitride nanotubes were successfully prepared by Chen *et al.*[251] by the mechanochemical reaction of boron with ammonia.

Investigations into the mechanochemical solid-state reactions of molecular crystals is a rather new but promising direction. The potential importance of this field relates not solely to the tradi-

tional fields of applications of molecular crystals, such as pharmaceutics, but also to the newly discovered possibilities of their utilisation as functional materials for molecular electronics, molecular magnets and so on.

Within this field, mechanochemically assisted reactions of organic synthesis play the key role. Studies in this direction were started back in the 1950s.[252] Later, the possible implementation of a number of organic syntheses in reactors similar to the Bridgman anvil cells and extruders [253, 254] was demonstrated by A A Zharov *et al.*[20, 96] and by N S Enikolopov.[16] More recently, various mills were tested as activators, especially ones providing the high energy input, such as vibrational planetary mills and attritors. It was established that many types of organic reactions (*e.g.*, halogenation, esterification, acetylation, *etc.*[255–258]) can be realised with these devices. Furthermore, in some cases, the mechanochemical method has proven to be not only simpler and faster than the traditional syntheses but more selective as well.

The number of publications devoted to the use of mechanochemical approach in the synthesis of various organic compounds constantly increases. As selected examples, one can mention the solid-state synthesis of tris(4-imino-2-pentanonato)chromium by the mechanically activated reaction of chromium(III) chloride with (4-imino-2-pentanonato)sodium,[259] the synthesis of oxazolidines by the mild mechanical treatment of mixtures of β-aminoalcohols with aldehydes and the synthesis of Shiff bases from mixtures of crystalline aldehydes and amines.[260, 261] One of the traditional methods for the oxidation of organic compounds is the reaction with lead tetraacetate or manganese triacetate in a liquid phase. Nikishin *et al.*[262] implemented this process in the mechanochemical mode by the activation of the reaction mixtures in a vibrational mill.

The phosphorus atoms can be incorporated into the aluminosilicate framework of zeolites by the mechanically activated solid-state interaction of the respective sodium zeolites with aluminium phosphate. This gives rise to the variation in the lattice parameters, which makes it possible to design molecular sieves with improved thermal stability.[263, 264] In a similar way, various organic molecules can be intercalated into the interlayer space of kaoline by the reaction between them in the presence of alkali metal halides.[265–268] The mechanochemical method is also useful for other reactions. In particular, Hihara *et al.*[269] utilised the mechanical activation for the synthesis of nickel and copper complexes with dimethylglyoxime. The use of solid-state mechanochemical synthesis for the preparation of various boron compounds, including diborane, borane adducts with nitrogen-containing organics, borazine and transition metal tetrahydroborates, have recently been reviewed by Volkov and Myakishev.[270]

As has already been mentioned, the mechanisms of the solid-state reactions of molecular crystals are less elucidated as compared to the reactions of ionic crystals. In some cases, even the actual solid-state character of the process cannot be proven, since the contact melting or sublimation of components in intermediate steps of the reaction cannot be decisively ruled out. In the case of macromolecular compounds (*e.g.*, cellulose), the interaction can be truly solid-state, whereas the involvement of fluidic phases is highly probable in the intermediate steps of reactions with crystals of low-molecular-weight organics.

Summarising all the experimental evidence discussed above, we note that the extensive experimental data have been gathered thanks to numerous investigations accomplished both in Russia and abroad. Nevertheless, the mechanisms of many processes realised in the mechanochemical reactors remain poorly understood. Partly, this is explained by the complexeity of the processes under study. However the main problem, in our opinion, is that the elucidation of the mechanisms is rarely formulated as an aim of the investigation and researchers often limit themselves to the preparation of a material with desired properties or the realisation of a process with the target parameters. However, the deep understanding of the mechanisms is a prerequisite for the fine control over the processes.

V. The use of mechanochemistry and mechanical activation for the solution of applied problems

Initially, such large-scale industries as hydrometallurgy,[1, 26, 37, 271] production of construction materials and fertilisers [39, 40, 272–274] were envisaged as potential fields of application of mechanochemistry. Nevertheless, despite very promising results obtained in laboratories, industrial implementations of the mechanochemical processes remain challenging owing to the lack of high-energy-input devices with sufficient performance. The available equipment (typically, mills) does not provide the energy input that is high enough for the large-scale mechanical activation.

Several attempts have been undertaken to perform industrial validation of the mechanochemical methods in these fields. In particular, mechanochemical processes were implemented in a plant for the hydrometallurgic processing of chalcopyrite into copper and sulfur in Wittenberg, in a facility for the acid-free production of fertilisers from natural phosphates in the Hubsugul deposit in Mongolia and in the production of silicalcite in Estonia. Unfortunately, no anticipated benefits from the implementation of these processes were achieved.

On the other hand, mechanochemistry has proven its efficiency in smaller-scale factories aimed at the production of more expensive goods. In non-ferrous metallurgy, the mechanical activation is successfully applied to the opening of tungsten and gold ores.

Nowadays, the mechanochemical methods are in the wide use in the production of catalysts,[34, 42] functional ceramics,[275, 276] diverse special-purpose materials,[277–283] materials for hydrogen storage,[173] ligatures for metallurgy, *etc.* In pharmaceutics, the mechanochemical methods are commonly employed for the production of medicines and control of their stability with respect to grinding, mixing, pelletisation and preparation of dosage forms from substances.[149–152, 284–286]

The mechanical activation is actively employed in the production of pigments and cosmetics.[287] The use of this method opens new avenues in preparative chemistry, including both organic and inorganic synthesis.[259–264]

The mechanical activation is used in processing of organic wastes, including poly(vinyl chloride), bromo- and chloro-containing aromatics.[288–292] The mechanical treatment of hexachlorobenzene, 1,4-dichlorobenzene, octachloronaphthalene or *o*-nitrochlorobenzene in the presence of alklaline agents, such as calcium oxide or hydride, yields [288] recyclable phenols and naphthols. The dechlorination can afford different products, depending on the intensity of the treatment. In particular, *o*-nitrochlorobenzene and 3-chloro-2-nitrophenol are obtained as the main products under mild and drastic conditions, respectively.

The mechanical treatment of clay minerals can be utilised for the extraction of phenol from aqueous solutions [266, 267] and water purification from radionuclides.[293, 294] It is of note that these efforts aimed at the application of the modern achievements of mechanochemistry to the intensification of small-scale expensive industrial processes are based on the specific results of dedicated fundamental investigations to the largest extent than ever before.[295–299]

We believe that industrial implementations of mechanochemical processes should be expected in these directions. However, it would be a mistake to think that the process will be smooth and seamless, and this is due to several reasons.

The apparent simplicity of the method acts simultaneously as an advantage and a disadvantage of the method. Historically, experimentalists armed with ordinary mortars were commonly considered to be prepared for the conduction of mechanochemical investigations. Moreover, a team equipped with a mill instead of mortars was often recognised as one specialised in mechanochemistry.

As a result, the number of successful implementations of mechnochemistry in technology is relatively small despite the huge total number of related studies (as we have mentioned before, the number of publications and patents in this field has increased dramatically over the last decade). It is of no surprise taking into account the fact that the trial-and-error method remains the key methodological tool in the vast majority of the experimental works. In essence, all such studies fall into one simple scheme: a researcher takes a compound or a mixture of compounds, treats it mechanically and looks at the result. It is rather surprising that even this methodology sometimes yielded positive results at all.

Up to the present, mills are most commonly used for the mechanical activation, although these devices are not designed for this purpose, strictly speaking. The purpose of a mill is to treat the material in order to generate the maximum surface area at the minimum energy consumption for the grinding process. In contrast, the purpose of an ideal device for the mechanical activation is to insert the maximum amount of energy into the treated solid to enable the accumulation of the input energy as defects mostly affecting chemical reactivity. This requires high energy inputs to be transferred from the working medium to the treated solid during the mechanical activation, which cannot be achieved with ordinary disintegrators. The ordinary mills have to be redesigned (and sometimes quite significantly) to take this requirement into effect. This, however, can lead to another problem related to the possible contamination of the compound subjected to the mechanical activation with the materials composing the working medium and the reactor body. This problem becomes more and more prominent as the energy input increases.

In order to relieve this problem, hard materials, such as tungsten carbide or silicon nitride coated with teflon or other inert substances can be utilised. The most efficient way is to operate in the self-lining mode, *i.e.*, to use the treated compound itself as a material forming the protective coating of the working medium and the reactor body.

The mechanical activation of mixtures creates even more serious problems. As has already been mentioned above, in order to activate a solid-state process it is necessary, first, to grind the components of the mixture, second, to mix them in such a way as to generate the maximum number of contacts between the particles of reacting components and, third, to create conditions for the mutual diffusion of the atoms or ions involved into the reaction, formation of the intermediate solid solution and withdrawal of the reaction product. Naturally, the currently adopted simultaneous realisation of these three totally different physical operations in the same apparatus does not make much sense. It would be more advisable to separate these operations, which should be taken into account in the design of the activator (the use of three specialised machines could be an alternative). Another possibility is to combine the mechanical activation of a solid-state synthesis with other methods, *e.g.*, with the preliminary mixing of the components by co-precipitation or by the sol – gel technology.

We considered above only several main problems impeding the wide industrial utilisation of the recent advancements in the field of mechanochemistry. Although they are to be solved in different ways, all the ways include one common factor: fundamental investigations in the field of mechanochemistry should be stimulated and developed at the utmost in order to make progress towards applications. As for the character of the most topical investigations, the information gathering step should be already replaced with the systematisation of the available information and construction of models for the mechanical activation and mechanochemical reactions. So far, this has been accomplished only in a few particular cases. The accumulation of experimental facts is still underway but it should not last forever.

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