Russian Chemical Reviews **63** (12) 965–976 (1994)
©1994 Russian Academy of Sciences and Turpion Ltd

UDC 539.8

Problems in mechanochemistry and prospects for its development

P Yu Butyagin

Contents

I. Introduction 965
II. The present state of research 965
III. Prospects for further development and expected results 971

Abstract. The results of studies on nonthermal chemical reactions induced by the deformation of solids are summarised in the review. Attention is concentrated on the analysis of processes involving the dissipation of elastic energy, the description of the nature and properties of the intermediate nonequilibrium states, and also studies of processes involving the low-temperature molecular mixing of solid reagents. The possible trends in further research are discussed. The bibliography includes 89 references.

I. Introduction

Mechanochemistry is the study of the influence of elastic and plastic deformations on the reactivities of solids. This definition is not quite complete and rigorous, but it emphasises the relation between mechanochemistry and other branches of chemical science. Chemical reactions unaccompanied by a change in volume and the appearance (or relaxation) of internal stresses are indeed rare; mechanochemistry is therefore an indissoluble component of the physical chemistry and chemistry of solids.

The vigorous development of mechanochemistry during the last decade became possible as a result of advances in fundamental research and the improvement of many technological processes, including the synthesis of new materials. The intersections of mechanochemistry with adjacent branches of knowledge such as the physics and chemistry of the solid state, the theory of strength, physicochemical mechanics, catalysis, chemical engineering, materials science, geology, biochemistry, the chemistry of medicinal drugs, etc. have been no less important. The application of mechanochemical methods in engineering (in the manufacture of building materials and ceramics, including superconducting ones, in powder metallurgy, in the food and pharmaceutical industries, etc.) have also attracted the attention of investigators and technologists to mechanochemistry.

The extensive possibilities of mechanochemistry as the chemistry of nonthermal low-temperature reactions are illustrated by the fact that refractory substances and intermetallic compounds, inorganic and organic compounds, and molecular complexes have been synthesised, polymers and pharmaceutical preparations have been modified, and composite materials have been created in the solid phase without dissolution or fusion of the reactants. Mechanochemical syntheses are carried out at a comparatively low temperature, where the formation of an ideal crystal structure is difficult. This opens a route to the synthesis of substances and materials in the nanocrystalline and amorphous states.

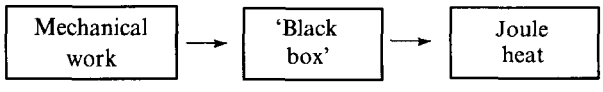
The rate of development of mechanochemistry is reflected by the growth in the number of publications. The total number of journal articles on mechanochemistry published throughout the world increased over the last ten years almost by a factor of five and exceeded one thousand in 1992. The number of studies on the mechanochemistry of metals and alloys and also on the synthesis of various materials for engineering has greatly increased (see Refs 1–43).

II. The present state of research

The period, lasting more than 100 years, in which mechanochemistry has been established as an independent field of knowledge has come to an end. During this time, mainly the results of qualitative observations of various effects have accumulated.

Nowadays no one believes that under the influence of mechanical action elastic energy is converted instantaneously, and without trace, into Joule heat.

It has been shown that, on deformation and disruption of solids, various energy-rich intermediate states arise in the first place, their subsequent decomposition resulting in the evolution of an appreciable proportion of the heat. In other words, there exists the so called 'black box' between work and heat; if energy is supplied to it faster than it can be converted into heat, it is possible to achieve various and unexpected chemical reactions.



Vibrationally an electronically excited bond, electrons and ions, metastable atomic structures, and other intermediate states may exist in the 'black box' and this list by no means exhausts its contents.

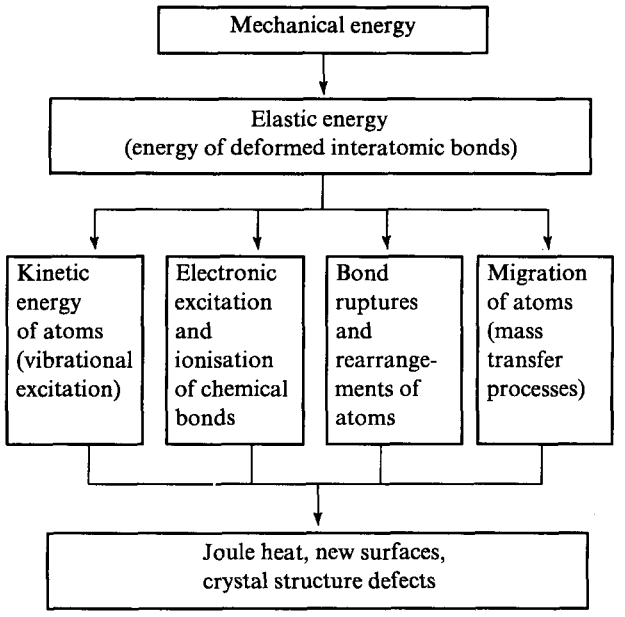
1. Transformations of elastic energy in solids

The scheme below illustrates the principal paths to the appearance and transformation of active nonequilibrium states arising when solids are subjected to mechanical influences.

Definite excess energy carriers with specific electronic and chemical structures, reactivities and relaxation mechanisms correspond to each of the pathways. Each state is characterised by a definite energy yield and lifetime. We shall consider the scheme below in greater detail.

P Yu Butyagin Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 117334 Moscow, Russian Federation. Fax (7-095) 938 21 56. Tel. (7-095) 299 73 25
E-mail: mechxim@glas.apc.org

Received 23 August 1994
Uspekhi Khimii **63** (12) 1031–1043 (1994); translated by A K Grzybowski



2. Deformed interatomic bonds

Deformed covalent bonds are detected by IR spectroscopy (Fig. 1) and the extent of deformation is calculated from the shift of the absorption band maximum.[7,22,32,35,44] In metals and other crystals, the average degree of lattice deformation is calculated from the line shape in X-ray spectra. The deformed bond and its reactivity have long been considered by theoreticians and experimenters. In the construction of a kinetic theory of the strength of solids, attention has been concentrated on the reactions involving the rupture of elastically stressed bonds.[35] The effect of stresses on the rate constant k for this reaction was calculated from the Eyring–Kauzmann equation:

$$k = k_0 \exp\left(-\frac{E_a - \sigma V^{\neq}}{RT}\right),$$

where k_0 and E_a are the pre-exponential factor and the activation energy for the thermal decomposition and $\sigma V^{\neq}$ is the work performed by the elastic stresses in the reaction step (σ is the stress and $V^{\neq}$ the volume of activation).

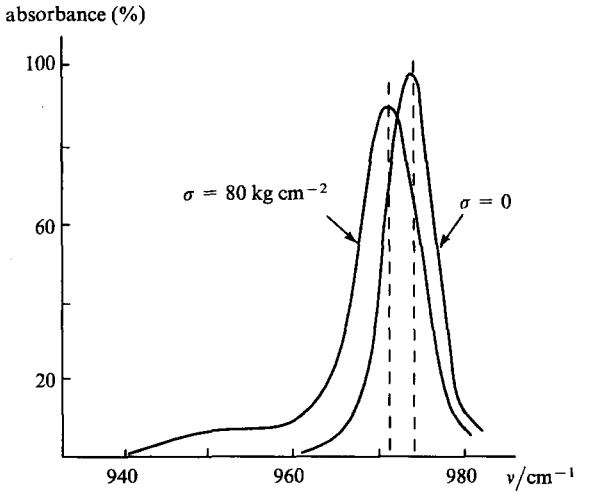


Figure 1. Skeletal vibrations of the main chain atoms in the IR spectrum of polypropylene in the initial state ($\sigma = 0$) and after extension by a load ($\sigma = 80\ \mathrm{kg\ cm^{-2}}$) (temperature 150 °C).[35]

In formulating this equation, it is implied that the active stresses facilitate the transitions through the energy barrier but do not affect its height. This approximation is apparently valid for the extension of bonds in the region of linear elasticity. For considerable deformations, one may expect a deviation from the linear energy relation. According to the results of quantum-chemical calculations,[45] a deformation of the C–C bond in the $\sim CH_2-CH_2-CH_2\sim$ chain close to the predissociation deformation lowers the ionisation potential of the hydrocarbon fragments almost by a factor of 2.

In substitution reactions, the reactivity of deformed fragments of organic molecules is characterised by the magnitude and sign of the coefficient of sensitivity to stresses.[14,32] Its value shows by what factor the rate constant changes following the extension or compression of a molecular fragment. For example, the rate constant for the hydrogen atom transfer reaction

$$R^{\cdot} + \sim CH_2-CH_2-CH_2\sim \rightarrow RH + \sim CH_2-CH^{\cdot}-CH_2\sim$$

is related to the deformation energy of the $-C-C-C-$ bond skeleton by the expression[32]

$$\ln\frac{k(\varepsilon)}{k(\varepsilon=0)} = \alpha\frac{\Delta E^{0.5}}{RT},$$

where k are the rate constants for the reaction in the deformed [$k(\varepsilon)$] and nondeformed [$k(\varepsilon = 0)$] fragments, ΔE the deformation energy, and α an empirical constant the value of which depends on the nature of the hydrogen atom acceptor (in the abstraction of a H atom by an ozone molecule, $\alpha = 57\ \mathrm{J^{1/2}\ mol^{-1/2}}$).[32]

The above relation is valid for small deformations. It has been suggested that strongly deformed Si–O–Si linkages on the SiO_2 friction surface have reactivities similar to those of the $\equiv Si^{\cdot}\ldots{}^{\cdot}O-Si\equiv$ radical pairs. So far this is only a hypothesis put forward on the basis of the analysis of the kinetics of the reactions of SiO_2 with H_2, CO, and other molecules.[9] The first quantum-chemical calculations for substitution reactions involving deformed bonds were carried out several years ago.[44] It may be hoped that, as a result of the development of computer techniques and programs, it will become possible in the immediate future to investigate in greater depth the deformed fragments of molecules and their reactivities.

3. Vibrationally excited states

Several decades ago, there was a widely held view that impact or friction give rise to regions with an increased temperature — 'hot spots'. The initiation of chemical reactions was attributed to the existence of such spots.[21] The controversy concerning the possibility of an increase in temperature at the entrance to a crack or on the friction surface has still not ended. Mention of 'hot spots' may be found also in modern literature. Calculations of local temperature carried out by various investigators imply that the rate of evolution of Joule heat is much higher than the rate of removal of heat. However, the real situation is far from this highly simplified model. Several relaxation pathways usually operate. One of them involves the relaxation of the disturbed atomic structure, which is known to be a slow process, and energy transformations are therefore extended in time.

Judging from indirect features, centres with a high temperature exist only under extreme conditions. These include, for example, the instant when cavitation bubbles are flooded following the absorption of ultrasound in liquids.[19,27,41] Not only have the rates of absorption and transformation of the energy via different paths been calculated rigorously for this case[19] but measurements have also been made of the emission spectra,[41] confirming the existence of 'hot spots' with a temperature up to several thousands of degrees.

The first direct spectroscopic measurements revealing the state of the solid material at the instant of decomposition have been carried out for poly(methyl methacrylate). Their results are

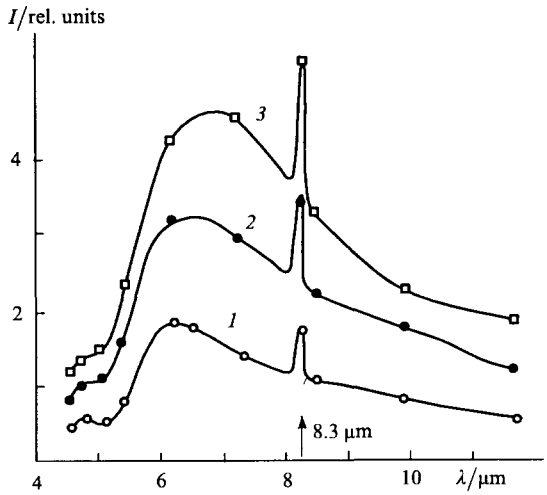


Figure 2. Thermal emission spectra obtained on disruption of a poly(methyl methacrylate) specimen.[37] Time elapsed from the start of disruption (μs): (*1*) 10; (*2*) 20, (*3*) 30.

illustrated in Fig. 2. The IR spectra measured at 10, 20, and 30 μs intervals after the initiation of the crack contain narrow lines, against the background of a broad thermal emission maximum, which correspond to vibrationally excited states. The lifetime of these states is short and the principal chemical mechanism of their destruction is the unimolecular isomerisation and decomposition of molecules accompanied by the ejection of fragments; bimolecular reactions with participation of 'hot' fragments of ruptured molecules have not been observed.

The first reports of the ejection of low-molecular-mass fragments on mechanical degradation of polymers appeared more than 25 years ago[46] and since then the decomposition of hot fragments has been frequently observed (see, for example, Zarkhin et al.[20] and Boldyrev[47]). The dynamics of the appearance, migration, and disappearance of excitations on dissociation of linear chains of atoms excited on rupture is investigated nowadays by molecular dynamics[43] or quantum-chemical methods.

For the occurrence of chemical reactions of highly excited states (decomposition, electron transfer, isomerisation, etc.), it is necessary that the energy level of the excited state should be close to the region where the potential curves corresponding to the initial and final states of the molecular or ionic fragment intersect. For example, when an ionic LiF crystal is cleaved, F atoms are ejected into the gas phase. The F^- anion must lose an electron in order to be able to leave the crystal: in contrast to F^-, the neutral F atom is not retained on the surface by electrostatic interaction forces. One of the hypotheses put forward to account for the emission of F atoms is as follows. Calculation[48] have shown that electron transfer in accordance with the scheme

$$F^-_{vib} \rightarrow F + e^-,$$

$$Li^+ + e^- \rightarrow Li,$$

is possible provided that the amplitude of the vibrations of the F^- ion, which are excited immediately after the dissociation of bonds at the entrance to the crack, exceeds 0.75 of the lattice parameter. Separation from the surface by this distance is equivalent to bond dissociation. In ionic crystals, decomposition into neutral atoms rather than ions is energetically more favourable.

It has been suggested that the ejection of hydrogen atoms on mechanical degradation of carbochain polymers[20] and of methane on degradation of polydimethylsiloxane[49] can be explained in this way. Apparently, after the dissociation of the chain, the amplitude of the vibrations of atoms in these polymers is such that, at the instant of their mutual approach, the distance between them diminishes so much that atomic rearrangements in accordance with the schemes

$$\sim CH(CH_3)\dot{C}H_2 \rightarrow \sim C(CH_3)=CH_2 + H^{\cdot}\text{(in polypropylene)},$$

and

$$=Si(CH_3)O^{\cdot} \rightarrow =Si=O + C^{\cdot}H_3\text{ (in polysiloxanes)},$$

became possible.

4. Electronic excitation and ionisation

All the consequences of electronic excitations and ionisation are usually combined in the group of mechanoemission phenomena. These include luminescence, static electrification, electron emission, and other effects associated both with the appearance of single electrically charged centres and with the effect of electric fields (static electrification). An extensive literature has been devoted to this problem.[9, 15, 30, 48]

Mechanical excitation of the electronic subsystem has been observed in crystals with different types of interatomic bonds. Examples of such processes in metallic copper[50] and magnesium oxide[9, 51] are presented below.

The 2.14 eV and 1.70–1.72 eV lines in the mechanoluminescence spectrum of copper (Fig. 3) correspond to electron transitions from surface electronic states to holes at the top of the *d* band of copper. The holes in the *d* bands are localised at dislocation nuclei, while electron–hole recombination, accompanied by the emission of light quanta, is induced by the emergence of dislocations onto the surface during the plastic deformation of the specimen.[30]

In magnesium oxide, electronic excitation with electron transition through the band gap may be represented as a chemical reaction involving electron transfer from the anion to the cation.[9]

$$\{Mg^{2+}O^{2-}\} \rightarrow \{Mg^+ \ldots O^-\}^*$$

Different distances between the ions correspond to the initial and excited states. When the excitation is induced by the absorption of UV light quanta, the lifetime of the $\{Mg^+ \ldots O^-\}^*$ excitons is short, since the necessary change in the interatomic distance is hindered by the rigid crystal matrix.

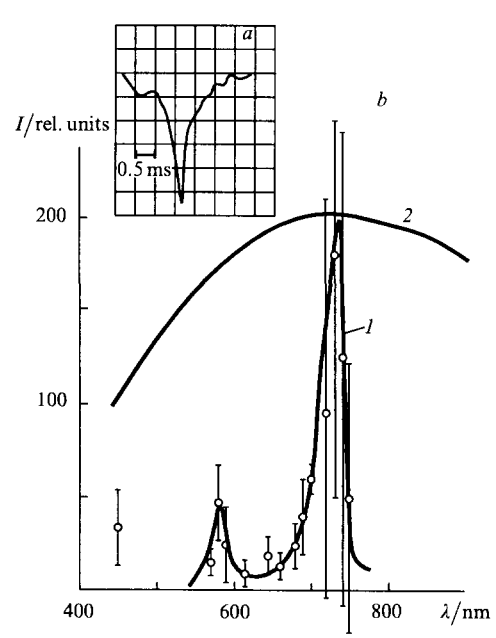


Figure 3. Oscillogram (*a*) and mechanoluminescence (*b*, curve *1*) and the thermal emission (*b*, curve *2*) spectra for copper at $T = 4000$ K.[50] The application of a load (impact) and the measurements (at the opposite end faces of a cylindrical specimen) were performed in vacuo at 10^{-5} GPa.

The same transition on friction is induced by the deformation of the surface, which increases the interionic distances to values corresponding to the $\{Mg^+ \ldots O^-\}$ structure, while electron transfer completes the stabilisation of this new state. At room temperature ($T \approx 0.1\ T_{pl}$), the thermal relaxation of the deformed surface is retarded and the long-lived quasi-exciton $\{Mg^+ \ldots O^-\}$ states may be preserved and investigated by spectroscopic, adsorption, and EPR methods.[51]

From the chemical point of view, the $\{Mg^+ \ldots O^-\}$ structures should be interpreted as radical pairs in which the oxygen radical-ion is one of the most active chemical species. In this case, the friction surface is distinguished by a high reactivity. The mechanical activation of the surfaces of many oxides is associated with the formation of quasi-exciton states.

Thus electronic excitation may be induced not only by the absorption of emission quanta but also by deformation, which creates configurations of atoms or ions favourable for electron transfer.

Other mechanisms also exist of the appearance of electrically charged centres and electric fields on disruption, deformation, and friction in crystals.[15,30,52] One of them is associated with the separation of the charges on the electrical double layer when contact between solid surfaces is broken.[15] On disruption and plastic deformation, the charges are separated between the dislocation nucleus and the compensating 'coat' (oppositely charged point defects). When a moving dislocation emerges onto the surface, the 'coat' remains in the bulk of the crystal. The growth of a crack as well as friction between surfaces are therefore a source of a wide variety of electrophysical effects.[30,52,53]

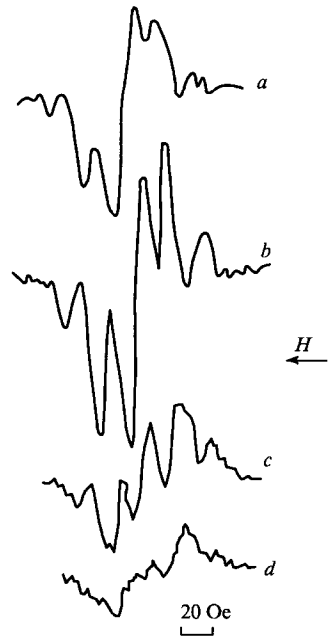


Figure 4. EPR spectra of the free radicals detected at the site of the mechanical rupture of DNA molecules isolated in a dilute frozen solution in D_2O: (*a*) and (*b*) different DNA specimens at 80 K; (*c*) and (*d*) the same specimens after raising the temperature to 195 and 217 K respectively (the rupture takes place in the deoxyribose unit).[54,55]

5. The dissociations and rearrangements of interatomic bonds

The mechanical properties of substances have been described fairly fully in the literature and constants such as the modulus of elasticity, the elastic limit, strength, hardness, etc. may be found in handbooks. On the other hand, quantitative data characterising the resistance of various substances to mechanical loads are not quite so extensive and studies on the kinetics and mechanisms of mechanical destruction have invariably attracted attention.

Indeed, failure is impossible without the dissociation of interatomic bonds and it therefore remains in essence a chemical step. The breakdown of polymers, molecular crystals, inorganic compounds, and metals is therefore regarded in mechanochemistry as a degradation process in the analysis of which it is necessary to take into account the nature of the bonds and the chemical structure of the corresponding substances.

Many examples of the chemical degradation of simple and complex substances on failure and deformation may be quoted (see, for example, Refs 1, 3, 5, 9, 14, 16, 20, 22, 35, 43, 46–49, 54–56, and 58).

The example of the mechanical destruction of polymers, in which not only the supermolecular structure is disrupted but macromolecules are cleaved, has become classical. The free radicals formed at the ends of the broken chain are detected and investigated by the EPR method. They have been observed on failure and deformation of polymers with different structures — ranging from polyethylene to DNA. In order to detect the primary radicals at the site of rupture, DNA molecules were isolated from one another in a dilute solution, the solution was frozen, and the destruction was observed at 80 K (Fig. 4).[54,55]

The radicals frequently initiate chain degradation and cross-linking. The chain degradation of three-dimensional polyacrylate esters,[16] cellulose,[55] and carbons[23] has been described. Polyethylene differs from these polymers by a tendency towards cross-linking.

On degradation of silicon dioxide, the dense network of siloxane bonds is ruptured and the radicals formed disproportionate. Two-coordinated silicon atoms and other irregular groups accumulate under these conditions.[9,56] The chemical properties of 'mechanical' radicals and their subsequent reactions in solids having directed bonds and on their surfaces are analysed within the framework of the theory of the reactivity of free radicals. The principal difference distinguishing radicals in solids is their high stability due to their fixation on the surface or in the bulk of crystals. Their destruction is usually induced by their involvement in chemical reactions and by the existence of various relay mechanisms of the migration of the free valence.

In metals, where there are no strictly directed bonds between atoms, the chemically reactive centres are atoms, with a low degree of coordination, within the dislocation nuclei and other structural defects. Prolonged mechanical treatment leads to extensive disordering with stabilisation of nanocrystalline or amorphous structures.[13,24,25,39,40,42,57,59–67] The degree of disordering is frequently characterised by the dimensions of microcrystalline blocks separated by intergrain boundaries. Their dimensions and residual deformation are calculated from the line shape in the X-ray spectra. The merging of the lines into a single broad band corresponds to the transition of the substance to the X-ray-amorphous state.

The degradation of ionic crystals[1,4,11,12,21,37,38] may be accompanied by the decomposition of complex anions and ionisation of the substance. Salts in which the cation is much smaller than the anion, for example, silver oxalate $Ag_2C_2O_4$, are distinguished by a high sensitivity to mechanical influences. The salt decomposes more than half during mechanical treatment at room temperature, this being detected by the liberation of the metal and carbon dioxide. Crystalline hydrates (for example, kaolin), which on mechanical treatment initially lose water of crystallisation, decompose even more readily. Finally, salts with unstable anions (azides, perchlorates, etc.) decompose explosively under impact.

Thus studies on the degradative phenomena in the course of disruption and deformation processes have shown that the macroscopic deformation pattern conceals profound changes in the chemical structure of the substance. Plastic deformation cannot therefore be regarded in isolation from chemical consequences.

Since the reactivity of solids is their structure-sensitive property, the disordering and degradation (activation) processes are used in chemistry and chemical engineering to accelerate processes involving dissolution, sintering, synthesis, and decomposition of solid reagents.

6. Mass transfer processes

Irreversible changes in the form and size of a solid on plastic deformation are inevitably accompanied by the displacements of atoms in its bulk relative to one another. Relay mechanisms of the migration of structural defects frequently predominate under these conditions.

a. Deformation mobility

The deformation mobility of atoms (molecules, ions) and its scale are demonstrated by the phenomenon of the miscibility of various substances under the conditions of joint mechanical treatment. One of the striking examples is the dissolution of tungsten in iron[65] and nickel[66] at room temperature (Fig. 5).

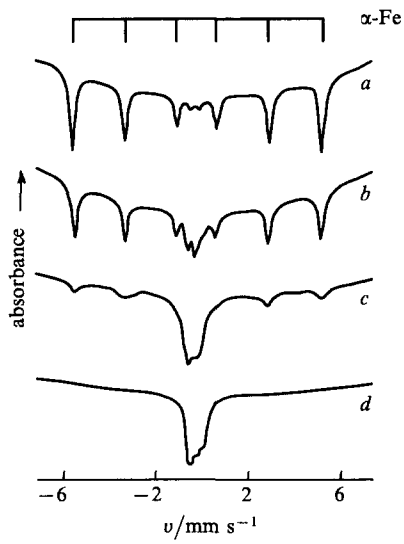
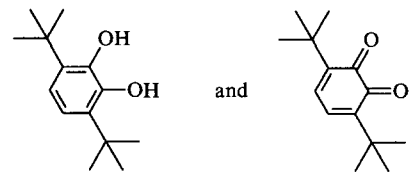


Figure 5. Mössbauer spectra of the 1 : 1 Fe/W mixture after mechanical treatment at room temperature in a vibromill.[29] Dose of supplied mechanical energy (kJ g^{-1}): (*a*) 5; (*b*) 10; (*c*) 60; (*d*) 100.

In terms of all their features, these are systems where miscibility is most difficult. Tungsten belongs to the strongest metals and the enthalpies of its mixing with iron and nickel are low: ~ -3 kJ mol^{-1} for mixing with nickel and ~ 0 kJ mol^{-1} for mixing with iron. The thermal mobility of atoms is almost frozen, since the temperature of the mechanical treatment does not exceed 0.2 T_m of the mixture components [T_m = melting point (Ed. of Translation)].

The initial stage of the dissolution of tungsten in nickel was detected from the increase in the nickel lattice parameter from 0.352 to 0.364 nm during the mechanical treatment of a mixture of the powders.[66] On more prolonged mechanical treatment, the nickel and iron crystal structures gradually break down; this can be seen from a series of Mössbauer spectra of the Fe/W mixture (Fig. 5). The growth of the amorphous halo in the spectra of the Fe/W mixtures is accompanied by the appearance of a single line in the spectrum, reflecting the formation of the paramagnetic iron compounds Fe_7W_6 or Fe_2W. Consequently tungsten atoms are inserted in the first coordination sphere of the iron atoms and the dissolution is not confined to the surface layer but involves the entire bulk of the substance.

The list of systems in which deformation mixing at the atomic or molecular level has been observed may be greatly expanded. It includes not only metals[17,24,25,37,39,40,42] and inorganic compounds,[1,5,8,12,21,26,28,53,59,67,68] but also plastic mixtures of organic substances.[39] The interest in molecular mixing has not disappeared to this day. Thus the appearance of an EPR signal has been observed recently when powders of a sterically hindered phenol and the quinone were mixed:[70]



The signal corresponds to the spectrum of radical pairs stable at room temperature (Fig. 6).

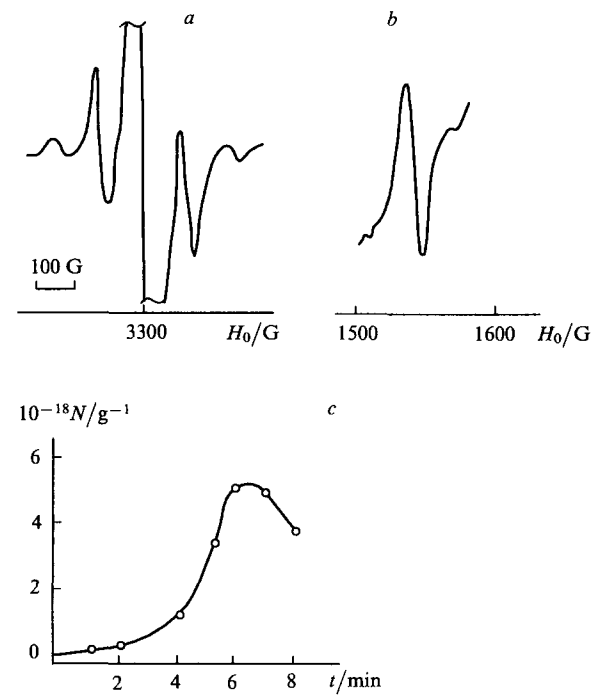


Figure 6. EPR spectra of the free radicals (central line) and radical pairs (outer lines) recorded on grinding a mixture of 3,6-di-*tert*-butyl-catechol and 3,6-di-*tert*-butyl-*o*-quinone powders in the region of 3000 G (*a*) and 1500 G (*b*). (*c*) Kinetics of the accumulation of radical pairs.[70]

On mixing, the molecules come into contact and the mobile hydrogen atom passes from the phenol to the quinone; this results in the formation of two adjacent radicals—a radical pair. The EPR spectrum of such a pair is illustrated in Fig. 6*a* and the kinetics of the accumulation of the radicals are illustrated in Fig. 6*c*. The number of pairs characterises the number of molecules in contact. During the mechanical treatment of a mixture of the phenol and quinone powders, the number of radical pairs increased to 5×10^{18} g^{-1} (in other similar systems, the increase was 1×10^{19} g^{-1}), which is a little less than 1% of the total number of molecules. When mixing is continued, the radical pairs begin to move apart, which is observed from the accumulation of the signals due to individual radicals (the average line in the spectrum of Fig. 6*a*).

Thus there is at present no doubt about the existence of the phenomenon of the low-temperature deformation mixing at the atomic (or molecular) level and its high effectiveness for both hard and soft substances.

b. Mechanochemical synthesis

Deformation mixing at the molecular level has led to the possibility of carrying out chemical reactions in mixtures of solids at room temperature whereupon diffusion is almost frozen. It is nowadays possible to find in the literature descriptions of several hundreds of such reactions, which have been achieved on Bridgeman's anvils,[8,18] in various mills,[1,21,24,25,38] attrition mills,[71,72] and disintegrators,[12] on rollers,[3,28] and in shock waves.[2]

It is important to emphasise that there are conditions under which the deformation mixing of solid reagents is completed by the formation of a new crystalline phase comprising the reaction products. Consequently the ordering of the product phase takes place under the same conditions as the disordering of the crystal structures of the starting materials.

Crystalline products may be formed in the reactions between simple and complex organic or inorganic compounds, between metals (mechanical fusion), and in mixtures of two or several solid components. As an example, Fig. 7*a* presents the kinetic curve for the synthesis of lead ferroniobate from a mixture of powders of three oxides:[36]

$$4\,PbO + Nb_2O_5 + Fe_2O_3 \rightarrow 4\,Pb(Fe_{0.5}Nb_{0.5})O_3\,.$$

The yield of the crystalline product phase was recorded by X-ray phase analysis (Fig. 7*b*). The figure shows clearly that the formation of the product is accompanied by its degradation. If the mechanical treatment is not stopped, then the content of the product synthesised in the mixture begins to fall.

During a prolonged mechanical treatment of a mixture of boron and carbon powders at room temperature, the accumulation of boron carbide was observed. There can be no doubt about the reality of the nonthermal mechanism of the synthesis of boron carbide, since the temperature in the apparatus was lower by 2000 K than the melting point of the components, while the heat of reaction is low. The formation of the nanocrystalline boron carbide was detected by X-ray diffraction despite the fact that the unit cell of B_4C contains more than 100 atoms. Thus plastic deformation induces not only the breakdown of the crystals of individual substances but also the formation of new crystal structures in mixtures of solid reagents.

The formation of the crystalline phase of the product in multicomponent reaction mixtures reveals yet another feature of the transformations of the elastic energy in solids, which is no less promising for chemistry. Under the same conditions, two at first sight incompatible processes are intertwined in the above process, namely, the decomposition and ordering of the crystal structures.

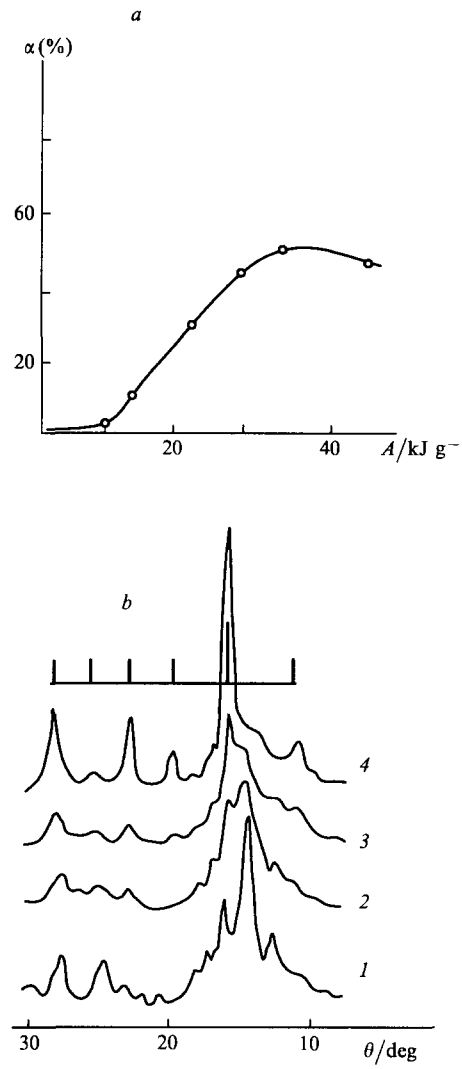


Figure 7. Kinetics of the mechanochemical synthesis of lead ferroniobate from a mixture of iron oxide, niobium oxide, and lead oxide powders at room temperature (*a*). Diffractometer traces for the mixture at different stages of the reaction (*b*) (the positions of the product lines are indicated in the top part of the figure).[36]

Table 1. Mechanochemical synthesis in metal–nonmetal mixtures (according to the data of Shelimov and Butyagin[81]).

Mixture	T_{ad}	T_m	Mixture	T_{ad}	T_m	Mixture	T_{ad}	T_m
Explosive reactions								
Zn + S	3380	693	Ti + C	3210	1941	Zr + 2S	5930	2128
Cd + S	2280	594	Ti + 2B	3190	1941	Hf + C	3900	2500
2In + 3S	2160	430	5Ti + 3Si	2390	1941	Hf + 2B	3520	2500
Sn + S	1640	505	Zr + C	3410	2128	5V + 3Si	2400	2190
Sn + 2S	1140	505	Zr + 2B	3310	2128	2Ni + Si	1590	1728
Pb + S	1620	600	Zr + 3Si	2480	2128			
Reactions without explosion								
2Cu + S	1267	1357	2As + 2S	580	1087	Ta + C	2730	3287
2Ag + S	695	1234	2Sb + 2S	880	904	Ti + B	2600	1941
Ge + S	1173	1210	Nb + 2B	2350	2740	2W + C	670	3700

Note. The data on the explosion in each reaction system have been taken from Refs 33, 75, 78–81, and 83; T_{ad} = adiabatic combustion temperature of the mixture; T_m = melting point of the metal.

The destabilising effect of elastic stresses on the crystals has proved favourable for the mixing of the components at the molecular (atomic) level. The formation of crystalline reaction products indicates a trend towards ordering. The greater the shift of the reaction equilibrium towards the products, the stronger is the manifestation of this trend.

In exothermic reaction mixtures, the formation of the product is accompanied by the evolution of heat. By varying the intensity of the mechanical treatment and the rate of removal of heat, it is possible to create in such systems conditions favourable for the mechanical initiation of thermal explosion. During the last decade, explosive mechanochemical synthesis has become the object of continuous attention by investigators.[29,33,73-81]

In the initial stage of the mechanical treatment, the size of the powder particles diminishes, the mixture is stirred, and the area of contact between the reactants increases. Under these conditions, the reaction begins to develop in the surface zone and heat is evolved. So long as the particles are large, the degree of their reaction is low and the temperature remains at a low level. After the increase in the area of the surface of contact to several square metres per gram, the rate of reaction increases so much that there is insufficient time for heat to be removed and the reaction passes into the self-acceleration regime.

In reaction mixtures for which the adiabatic reaction temperature is equal to or greater than the melting point of one of the components and the rate of application of the mechanical energy dose is above a critical level, the self-acceleration condition is replaced by thermal explosion (see Table 1 and Shelimov and Butyagin[81]).

* * *

Vibrational and electronic excitation as well as phenomena involving the degradation and disordering of crystals, deformation mixing, and synthesis represent the content of the large field of nonthermal physicochemical and chemical reactions. This field complements the classical thermal theory and significantly expands its possibilities. The phenomena considered are no less interesting for solid state physics, materials science, and other branches of natural sciences.

From the chemical point of view, reactions in mixtures of powders and processes involving the mechanical activation of solid reagents are the most promising. However, the experience accumulated in laboratories is being gradually assimilated in engineering. The list of mechanochemical reactions achieved on a small scale embraces various classes of solid-phase reactions.

Thus gas–solid reactions include the synthesis of nitrides, hydrides, and carbonyls on interaction of gases (nitrogen, hydrogen, carbon monoxide, etc.) with powdered metals and nonmetals.[61-64,82-85] The first experiments on pseudocatalytic reactions under the conditions of the mechanical treatment of a powdered catalyst have already been carried out.[83,85]

The list of solid–solid reactions is the longest. It includes the synthesis of carbides, borides, and silicides from the initial elements (TiC, TiB_2, B_4C, etc.[33,74-76,81]), the reduction of oxides by metals,[77] and the synthesis of ferrites, superconducting ceramics, and other oxide materials.[1,6,12,36] Mechanical fusion, i.e. the preparation of alloys, intermetallic compounds, and composite materials from them, also belongs to processes of this class[17,24,25,28,39,40,42,59,60,65,67,68,72,73]. Solid-phase organic synthesis[2,6,18] includes the preparation of phthalazole, amine acylation reactions, Diels–Alder condensation, the polymerisation of solid monomers, etc. Modification of medicinal drugs and the preparation of compositions with a controlled liberation of medicinal forms constitute a related field.

A by no means complete list of systems investigated has been presented here, but even these examples emphasise the breadth and scale of the accumulated knowledge. Nowadays there is a transition in mechanochemistry from laboratory research to technological developments. A diverse range of laboratory mechanochemical reactors has been created and exists. It is possible to activate and synthesise in them organic and inorganic substances.[1,8,71,72,86]

Unfortunately, the reactors have not always been successfully characterised (dose, rate of application of dose) to be able to compare the results obtained by different workers or to give recommendations concerning the scaling of experiments. Vigorous research is being prosecuted on these lines.[71,72,86]

However, the choice of manufacturing apparatus is as a rule restricted to equipment which has been created for other purposes—grinding, extrusion, etc. Theoretical studies on the conditions of the synthesis in large-scale mechanochemical reactors taking into account the dynamics and energy relations of specific processes can be counted on one's fingers, i.e. the laboratory experiment–technological tests link has not yet been established.

III. Prospects for further development and expected results

1. Reactivity of elastically deformed solids

Studies on the role of elastic stresses in solid-phase reactions were apparently developed in several directions. They can be given conventional names: (1) electronic structure and reactivity of elastically deformed interatomic bonds; (2) elastic model of solid-phase reactions; (3) reactions in structural relaxation processes. The first of these has already been examined in Section II. 2. The contents of the others will be briefly described below.

The second aspect of the above investigations deals with reactions in continuous media, where it is necessary to take into account the deformation of not only the reaction centre proper but also of its environment. Within the framework of the elastic approximation, the potential energy of the reaction centre is represented as the sum of the energy of the chemical interaction proper U_{chem} and the deformation energy U_{str}. The height of the energy barrier in the reaction involving such a reaction centre is equal to the difference between the energies of the system in the transition and initial states. The complex structure of the reaction barrier in the solid phase is illustrated by the scheme below:

$$E = (U^{\#}_{chem} + U^{\#}_{str}) - (U^{0}_{chem} + U^{0}_{str}).$$

The superscripts '#' and '0' denote the transition and initial states.

Computer calculations of the energy barrier in model reactions are not very complex (Fig. 8) when they are carried out by the method of molecular dynamics and do not involve changes in the electronic subsystem, but because of this the results of such calculations are approximate. Fig. 8*a* illustrates the model for the calculation of the barrier height when an extraneous atom is inserted in the crystal lattice. This atom, designated by a filled circle, is acted upon by a force F, which displaces it downwards at a constant rate. Here one calculates both the change in the energy of the atom (Fig. 8*b*, curve *1*), and the deformation of its environment (curve *2*), i.e. all the components of the barrier structure (the schemes in Figs 8*c* and 8*d* illustrate the macrokinetics of the deformation mixing). The first results of such calculations have shown that the deformation contribution may be dominant under certain conditions.[28,87] The calculations of the barrier structure are valid for both thermal and mechanochemical reactions.

The main difference between mechanical reactions and the usual thermofluctuation reactions is the use of different methods for overcoming the energy barrier separating the initial and final states in the elementary reaction step. It is as a rule understood that the form and height of the energy barrier are independent of the way in which it is overcome: under the influence of elastic stresses or by the thermofluctuation route.

However, systematic studies on the effect of elastic stresses and of the rate of deformation on the form of the potential surface and the route followed during the movement of the system of reacting species along the reaction coordinate have not been carried out.

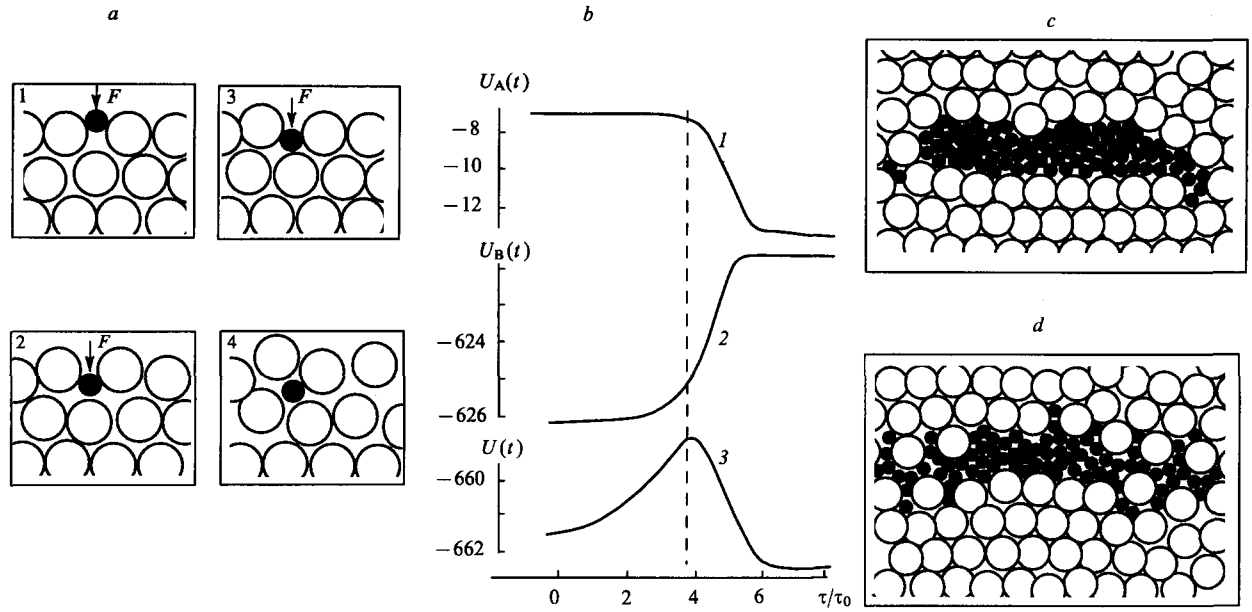


Figure 8. Modelling of deformation mixing by the method of molecular dynamics. Permeation of an atom through the surface: (*a*) scheme; (*b*) calculation of the changes in the energy of the atom itself [$U_A(t)$] (curve *1*) and of the crystal [$U_B(t)$] (curve *2*) and of the height of the energy barrier [$U(t)$] (curve 3) for a three-dimensional model; (*c*) and (*d*) stages in deformation mixing on uniaxial compression of a three-layer model.[9, 10, 28, 29]

The limits of the applicability of this approximation are therefore also unknown. It may be hoped that the search for answers to these questions will begin in the immediate future.

Mechanochemical reactions in solids are known to be induced not only by the direct action of elastic stresses but also by elastic energy relaxation processes. Studies on the kinetics and mechanisms of the reactions accompanying structural relaxation belong to the third aspect. Unjustifiably little attention has been devoted in the literature to the mechanisms of these reactions as well as relaxation itself, which can be accounted for by the difficulties in the experimental study of these processes.

One of the first studies[48] was devoted to calculations of the probability of the emission of atoms from the cleavage surfaces of alkali metal halide crystals. An experimental investigation of rapid structural relaxation has been recently carried out by synchrotron radiation diffraction methods.[5] It may be hoped that the results will stimulate the formulation of further studies.

Nowadays all the available theoretical models are restricted to the analysis of the relaxation of a one-dimensional chain of atoms and the secondary reactions occurring after its rupture.[20] However, it is no less important that, under certain conditions, the energy liberated in the elementary reaction steps assumes the form of a compression wave (soliton), which initiates the reactions in the neighbouring cells, etc. Such self-supporting relay reactions began to be observed recently in both computer and physical experiments.[20]

2. The mechanisms of mechanochemical reactions

a. Degradation

In the study of the disordering of crystals of simple and complex substances, much attention is devoted to the problem of the degradation or dispersion limit. The term 'limit' is given to the smallest dimension of the crystal block or another fragment of the initial structure remaining unchanged under the conditions of prolonged mechanical treatment.

The ideas about the degradation limit (dispersion limit), based on the results of calculations of the strength of microcrystals, which previously seemed unshakeable, restricted mechanical dispersion to crystal fragment dimensions of tens of nanometers. However, it has been observed recently that for many isotypical crystals (face-centred cubic metals,[57] alkali metal halides[53]) the degree of disordering is greater the stronger the substance. This finding gave rise to interest in problems of the concentration of elastic energy, the determination of the degradation limit, and the study of the mechanisms of dispersion.

Recently the views on the nature of mechanical dispersion have begun to change.[25, 89] Instead of the disruption of individual microcrystals, the deformation of complex polycrystalline structures, threaded by intergrain boundaries and interfaces, is now analysed. From this point of view, the decrease in the size of microcrystalline blocks on plastic deformation is equivalent to an increase in the density of the network of dislocation boundaries. Hence follow a series of consequences important for a deeper understanding of both the processes occurring in the material and of the mechanisms of the chemical reactions.

Thus, in the migration of dislocations, combined into boundaries and 'sweeping' through the bulk of the crystal during their motion, work is expended on the reorganisation of the crystal structure accompanied by rearrangements of atoms, the production of defects, and other processes favouring chemical reactions.

The denser the network of boundaries, the larger the 'swept' volume. If in the course of the operation of stresses, the boundaries 'sweep' the entire or almost the entire volume of the substance, one may speak of the possibility, in principle, of a global deformation disordering of the crystals. The transition to such a 'deformation-transparent' state requires that the average distance between the boundaries L, virtually equal to the size of the crystalline blocks, should decrease to a critical value L_{cr} satisfying the condition:

$$L = L_{cr} \quad \text{when} \quad \dot{\varepsilon}_{cr} = \frac{1}{L}\frac{dL}{dt} = \frac{1}{\tau},$$

where τ is the duration of the operational stresses, and $\dot{\varepsilon}_{cr}$ the critical rate of deformation, which depends on many factors. The quantity $\dot{\varepsilon}_{cr}$ may be estimated from the equations of the theory of plasticity. It may be hoped that a rigorous theory of 'deformation transparency' will appear in the immediate future. It will then become possible to relate the observed dispersion limit not to the indivisibility of the nanocrystals but to the establishment of a dynamic equilibrium between the processes involving global disordering and spontaneous relaxation,[25, 89] which is induced by

the tendency of the substance to return to its natural ordered state (plastic deformation creates the mobility necesary for this purpose).

This incipient concept is much more fruitful for chemistry, since it removes the limitations to the scale of the mobility of the structural elements of the solid and draws attention to the extent of the possible chemical consequences of deformation processes in the regions corresponding to the motion of the intergrain boundaries and interfaces.

The possibility, in principle, of profound changes in the chemical and physical properties of substances on deformation should not encounter serious objections. Thus many inorganic crystals consist of species (ions) which are stable only in a powerful crystal field generated by the electrostatic interaction forces. When the deformation weakens the crystal field, then the species constituting the crystal also lose their stability and their properties change.

Thus the weakening of the crystal field in the narrow-band oxides GeO_2 and SnO_2 as a result of the disordering of the crystal structure is accompanied by a decrease in the width of the band gap with a corresponding change in physical and chemical properties: colour, conductivity, and reactivity, including catalytic activity.[51]

The examples examined demonstrate the extensive possibilities of the phenomenon of mechanical activation, to which several monographs have been devoted.[1,6,21,38] This field of research has a solid experimental basis and in future years one may expect the discovery, if not of new phenomena, then of new relations between the sensitivity of substances to mechanical loads and the change in reactivity on activation, on the one hand, and the nature of the interatomic bonds and the chemical structure of specific compounds, on the other.

b. Solid–solid reactions

The reactions between solid substances at a low temperature, carried out without preliminary dissolution, fusion, or sintering of the reactants, constitute one of the most promising branches of mechanochemistry, which, as before, has attracted the attention of investigators.

The mechanisms and kinetics of the processes in mixtures of solid reactants, where elastic stresses and chemical forces act simultaneously while the deformation and the reaction are closely intertwined, are not considered in either mechanics or chemical kinetics. Here there are no ready solutions from other branches of solid state physics and chemistry.

The kinetic description of solid-phase reactions is complicated by the fact that the dispersity, phase composition, and the defect structure and mechanical properties of the reaction medium vary continuously during its mechanical treatment.

The development of a theory of solid-phase reactions is still not complete. It is necessary that it should allow a description of the mechanisms and kinetics of solid phase reactions in such a way that they would permit the use in mechanochemistry of the large body of knowledge in classical thermochemistry. The problem is not quite so simple as might appear at first sight. Analysis of the results of the studies in recent years suggests the following logic for the development of the theory.

The interpenetration of atoms begins on the surface of contact of the components, so that the work involved in the formation of the interface is one of the important factors in the initial stage of the reaction. Together with elastic stresses, chemical forces operate here also; they in fact determine to a large extent the intensity of the mixing.[1,28,87,88] The results of computer experiments have revealed the specific role of chemical affinity in deformation mixing.[28] Experiment shows that the greater the energy of the mixing in the system

$$A + B \rightarrow AB,$$

and the more extensive the contact zones, the more complete and thorough the mixing.

The insertion of an atom A in a crystal B is hindered by a definite energy barrier. At a low temperature, this barrier is overcome by the action of elastic stresses. The barrier is lower, the greater the energy gain on interaction of the atoms A and B. Therefore, for the same level of elastic stresses, the probability of overcoming the barrier increases with increasing energy of mixing.

An excess energy accumulates in the reaction mixture during mechanical treatment. There are several carriers of this energy; these are the residual elastic stresses, interfaces, intergrain boundaries, amorphous regions, regions of supersaturated solid solutions, and other metastable structures. The accumulation of energy cannot be infinite, the accumulated energy being discarded at some stage and the structure of the reaction mixture becoming ordered. In mixtures of solid reactants, the equilibrium state to which the system passes on relaxation may prove to be the crystalline phase of the reaction products.[87,88] The more thorough the mixing and the higher the level of the stored energy, the greater the probability of the formation of the product phase on relaxation.

It may be expected that a two-stage mechanism of solid-phase reactions, namely deformation mixing–relaxation, will again attract the attention of investigators in the coming years. It is essential to select key parameters characterising the dynamics of the deformation mixing and the critical state of the reaction mixture, to examine the conditions under which mixing is replaced by relaxation, and to discover the specific mechanisms of the relaxation for substances with different types of interatomic bonds.[25,87,88]

Apart from deformation mixing, in real plastic materials it is necessary to take into account also diffusional processes, which may facilitate structural relaxation. Indeed, a dense network of interfaces and intergrain boundaries may play the role of accelerated-diffusion channels even in the absence of deformation. Furthermore, a decrease in the size of the microcrystalline blocks to 10^{-9}–10^{-8} m is equivalent to the shortening of the diffusion pathways (X) and of the duration of permeation (t) by many orders of magnitude ($t = X^2/D$). Therefore nanocrystalline particles become diffusionally transparent in reaction mixtures where the diffusion coefficient (D) is close to 10^{-20} m^2 s^{-1}.

Simultaneously with the theory of deformation mixing, the theory of quasi-explosive and explosive mechanochemical reactions in exothermic systems, where the energy liberated in relaxation processes is sufficient for the self-acceleration of the reaction, will develop. Furthermore, the range of reaction systems investigated will probably expand greatly.

The intense development of the mechanochemical synthesis of inorganic substances, intermetallic compounds, and alloys is associated with their successful employment in materials science (superconducting ceramics, heat resistant and ultrastrong materials, amorphous alloys, nanocrystalline materials, etc.). In creating such materials, it is important not only to synthesise a substance with a specified chemical constitution but also to achieve the specific formation of its structure. Mechanochemical methods make this possible.

The advantages of mechanochemical methods—ecological purity (the absence of solvents or annealing furnaces), simplicity, and the possibility of the chemical and structural modification of the product—are being comparatively slowly realised in organic chemistry. However, the first signs that such conservation attitudes will be soon overcome have already appeared: the mechanochemistry of medicinal drugs, the mechanochemistry of carbons, etc. has been developed. As time goes by, the efforts of investigators will be distributed uniformly between the mechanical syntheses of organic and inorganic substances. The search for methods of synthesis, optimal in mechanochemistry and unrelated to the mechanisms adopted in thermochemistry, will be continued.

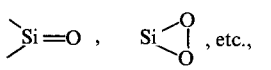
c. Gas–solid reactions

A fresh surface which is exposed following the disruption of a solid or produced as a result of friction is, as it were, designed for participation in chemical reactions. The atoms of such a surface

are coordinatively unsaturated and the problem is merely to select their partners in the reaction. Otherwise, the active surface ceases to exist in rearrangements and oxidation or hydration processes.

In order to account for the mechanisms of the chemical reactions occurring with participation of a freshly formed surface, it is essential to know the valence state of the atoms on this surface, their reactivity, and the rates of structural rearrangement (relaxation). These studies have already been combined in an independent field (mechanical chemisorption or tribosorption [9,21,51,56,85]).

Hitherto the majority of studies have been carried out for the freshly formed silicon dioxide surface.[9,56] Silicon and oxygen atoms with ruptured bonds ($\equiv Si^{\cdot}$, $=Si:$, $\equiv SiO^{\cdot}$) in the ground and electronically excited states, new atomic groups



deformed siloxane linkages, and other centres have been detected on it. The electronic structure and constitution of these fragments have been described and measurements have been made of the rate constants for the reactions of the principal centres with gases and their course has been determined. The nature and properties of the active surfaces of ionic oxides, graphite, silicon, and individual metals have also been investigated.

It has recently become clear that the spectrum of nonequilibrium chemically reactive states is much wider than appeared previously. The energy liberated on reaction with gases is sufficient to excite the electronic subsystem of the crystals with ejection of fragments comprising complex anions, emission of electrons, including those with energies up to tens of kiloelectronvolts [15]), and also the emission of neutrons on disruption of deuterium-containing crystals.[53] The theory of mechanoemission phenomena continues to be developed (see, for example, Molotskii [30]) and the experimental and theoretical studies in this interesting field will continue for many decades.

The chemisorption of gases on a freshly formed surface is widely used as a kind of instrument for the determination of the degree of damage of the crystal structure. Chemisorption is the first stage in the interaction of solids with gases; however, solid–gas reactions are not always restricted to monomolecular surface coverage. Three examples of a more far-reaching development of these reactions are presented below.

Thus volatile carbonyl complexes are formed on the active surface of nickel in the presence of CO, nickel pentacarbonyl being desorbed from the metal surface into the gas phase. The renewal of the surface continues until almost the entire metal has been converted into $Ni(CO)_5$.[21]

Molecules of gases such as N_2, NH_3, O_2, CO, and others dissociate into atoms on chemisorption, as a result of which surface compounds are stabilised on the active surface.[9] On plastic deformation and friction, increasing numbers of fresh atoms from the bulk of the solid particles are carried to the surface, where they interact with the gas. The repeated renewal of the surface in the gaseous atmosphere leads ultimately to the formation of the solid–gas reaction product phase (the corresponding nitride, oxide, or another compound).[82]

Reactions of yet another type have been discovered in the $Zr-(H_2+CO)$ and $Zr-(H_2+C)$ systems.[83,85] Thus mechanical treatment of zirconium powder promotes the acceleration of the dissolution of hydrogen in it. The hydrogen dissolved in the metal hydrogenates either the CO molecules which have been chemisorbed on the surface or the graphite added to the hydride powder. The reaction

$$CO + H_2 \rightarrow CH_4,$$

during the mechanical treatment of the metal powder under a $(CO+H_2)$ atmosphere can be regarded as the prototype of future mechanocatalytic processes.

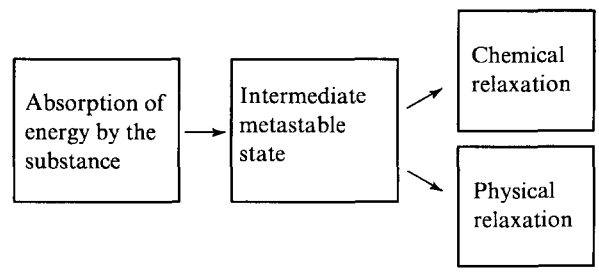
There is no doubt that examples of solid–gas and solid–liquid reactions will multiply in the immediate future and that the first hypotheses concerning their mechanisms will be revised or rejected. Conditions ensuring a high effectiveness of low-temperature mechanical reactions between solids and the external medium will be found on the basis of the study of these reactions. The reactions can be used not only for the chemical syntheses but also in catalysis and in the modification of solid surfaces—their stabilisation, improvement of their corrosion resistance, etc.

It is noteworthy that phenomena involving mechanical chemisorption, catalysis, and synthesis are part of the more general problem of the interactions of the solid undergoing deformation and the external medium. Here mechanochemistry will become ever more closely intertwined with physicochemical mechanics and colloid chemistry.[34] These sciences are concerned with the study of the effect of the medium on processes involving the mechanical treatment of solids—their disruption (dispersion, friction, and plastic deformation (the Rebinder effect). Therefore all the manifestations of chemical reactivity, reflecting the development of deformation and revealing the dissipation of elastic energy, are equally interesting for both mechanochemistry and for different manifestations of the Rebinder effect (strengthening or facilitation of disruption, etc.).

3. Kinetic models of mechanochemical reactions

One of the principal problems in the theory of nonthermal chemical reactions is the elucidation of the relation between the expenditure of energy and the reactivity of the reactants. The current state of research does not permit the establishment of a complete balance for the energy transformations, while a quantitative description of all the relaxation pathways in mechanochemical reactions is hardly likely to be achieved soon.

The route involving the search for a kinetic description of nonthermal reactions appears more realistic. Among those possible, the following scheme remains more attractive:



It is similar to that presented at the very beginning of the review. The kinetic equation corresponding to this scheme has the following form:

$$\frac{\delta\Delta\varphi}{\delta t} = I - \frac{\Delta\varphi}{\tau_{chem}} - \frac{\Delta\varphi}{\tau_{phys}},$$

where $\Delta\varphi$ is the excess energy of the intermediate states (it can be represented as $\Delta\varphi = N\varphi g$, where N is the concentration of excess energy carriers, and φ and g are their energy and yield), I is the supplied energy flux, τ_{chem} is the characteristic chemical relaxation time, and τ_{phys} is the characteristic physical relaxation time. Chemical relaxation is understood as the employment of part of the excess energy in chemical or physicochemical reactions, while physical relaxation includes the remaining energy dissipation channels.

Under stationary conditions, the rate of a chemical reaction W_{chem} is

$$W_{chem} = Ig\frac{\tau_{phys}}{\tau_{phys} + \tau_{chem}},$$

and its energy yield G_{chem} is given by

$$G_{chem} = \frac{W_{chem}}{I} .$$

Evidently, the advantage of this scheme consists in the fact that it makes it possible to relate the conditions in the mechanical treatment, the rate of the chemical reaction, and its energy yield G (in mol MJ^{-1}). Naturally, in each specific case the scheme will be specified in greater detail and expanded. However, the above advantage will be preserved.

The energy yield G is one of the principal quantitative characteristics of mechanochemical reactions.[9] It can be calculated or predicted, provided that the mechanism or physical model of the process is known. For example, if the height of the energy barrier is E in the elementary step of a nonthermal reaction, then the maximum energy yield G_{max} is given by $G_{max} = 1/E_a$. For the experimental determination of the yield, it is sufficient to measure the amount of products and the work performed.

As a rule, in degradation reactions the energy yield is small and lies in the range from 10^{-4} to 10^{-1} mol MJ^{-1}. Its numerical value characterises the sensitivity of the given compound to mechanical influences. The generation of defects is (with rare exceptions) an energy-consuming process. Systems in which chain degradation develops or there is a possibility of other self-acceleration mechanisms are an exception.

Deformation mixing and synthesis are usually characterised by comparatively high yields — up to 1–10 mol MJ^{-1}. Even in the most difficult case involving the mixing of tungsten with iron (Fig. 5), the yield is 0.1 mol MJ^{-1}. Naturally, the yield depends on the conditions in the mechanical treatment — the rate of deformation and the frequency of the influences, temperature, the nature of the surrounding medium, and other factors.

The measurements and calculations of the energy yields lead to the possibility of using in mechanochemistry data banks comprising the kinetic and thermodynamic characteristics of thermochemical reactions. For example, the relation $G_{max} = 1/E_a$ includes the activation energy for the reaction. A correlation between G and thermodynamic parameters in a series of isotypical reactions has been observed more than once.[1] It may be hoped that systematic measurements and calculations and analysis of the energy yields will lead to the creation of a quantitative picture of mechanochemical reactions which will possess predictive power.

* * *

Summarising the results of numerous studies on mechanochemistry, one may differentiate several aspects of fundamental investigations with which the development and further progress in this interesting and promising field of knowledge are associated.

These include primarily the following:

the discovery of the molecular mechanisms of the deformation of simple and complex substances as well as their mixtures combined with the elucidation of the nature of the intermediate nonequilibrium states;

the kinetic description of the mechanical degradation, atomic migration, and molecular mixing processes as well as chemical reactions involving the formation of new crystalline or amorphous structures under deformation and energy dissipation conditions;

the study of the relation between thermal and nonthermal reactions in which the energy barrier is overcome either via a thermal fluctuation mechanism or under the influence of elastic stresses.

Altogether, these aspects are combined into the problem of the systematic description of the laws governing chemical reactions under the conditions of the joint action of mechanical and chemical forces.

References

1. E G Avvakumov *Mekhanicheskie Metody Aktivatsii Khimicheskikh Protsessov* (Mechanical Methods for the Activation of Chemical Processes) (Novosibirsk: Nauka, 1986)
2. G A Adadurov, V I Gol'danskii, P A Yampol'skii *Zh. Vses. Khim. O-va im. D I Mendeleeva* **18** 80 (1973)
3. N K Baramboim *Mekhanokhimiya Vysokomolekulyarnykh Soedinenii* (Mechanochemistry of High-Molecular-Mass Compounds) (Moscow: Khimiya, 1978)
4. V V Boldyrev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2228 (1990)
5. V V Boldyrev, N Z Lyachov, Yu T Pavlyukchin, E V Boldyreva, E Yu Ivanov, E G Avvakumov *Sov. Sci. Rev. B, Part 3* **14** 105 (1989)
6. V V Boldyrev *Eksperimental'nye Metody v Mekhanokhimii Tverdykh Neorganicheskikh Veshchestv* (Experimental Methods in the Mechanochemistry of Solid Inorganic Substances) (Novosibirsk: Nauka, 1983)
7. V A Bershtein *Mekhanogidroliticheskie Protsessy v Napryazhennykh Tverdykh Telakh* (Mechanohydrolytic Processes in Stressed Solids) (Leningrad: Nauka, 1987)
8. P Bridgman *Phys. Rev.*, **48** 825 (1935)
9. P Yu Butyagin *Sov. Sci. Rev. B, Part 1* **14** 1 (1989)
10. P Yu Butyagin, in *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii: Sb. SO AN SSSR* (Mechanochemical Syntheses in Inorganic Chemistry: Collected Papers. Siberian Division of the Academy of Sciences of the USSR) (Ed. E G Avvakumov) (Novosibirsk: Nauka, 1991) p. 32
11. M V Vlasova, N G Kakazei *Elektronnyi Paramagnitnyi Rezonans v Mekhanicheski Razrushennykh Tverdykh Telakh* (Electron Paramagnetic Resonance in Mechanically Disrupted Solids) (Kiev: Naukova Dumka, 1979)
12. I A Chint, in *Desintegrator* (Tallin: Valgus, 1979) Vol. 1, p. 3
13. E M Gutman *Mekhanokhimiya i Zashchita Metallov ot Korrozii* (Mechanochemistry and Protection of Metals against Corrosion) (Moscow: Metallurgizdat, 1981)
14. A Casale, R S Porter *Polymer Stress Reactions* Vols 1, 2 (New York: Academic Press, 1978, 1979)
15. B V Deryagin, N F Krotova, V P Smilga *Adgeziya Tverdykh Tel* (Adhesion of Solids) (Moscow: Nauka, 1973)
16. A M Dubinskaya *Sov. Sci. Rev. B, Part 3* **14** 37 (1989)
17. A E Ermakov *Fiz. Met. Metalloved.* 11 (1991)
18. A A Zharov *Zh. Vses. Khim. O-va im. D I Mendeleeva* **18** 73 (1973)
19. H G Flinn, in *Physical Acoustics: Principles and Methods* (Ed. W P Mason) (New York: Academic Press, 1964) Vol. 1, Part B, p. 7
20. L S Zarkhin, S V Sheberstov, N V Panfilovich, L I Manevich *Usp. Khim.* **58** 644 (1989) [*Russ. Chem. Rev.* **58** 381 (1989)]
21. G Heinike *Tribochemistry* (Berlin: Academie-Verlag, 1987)
22. H H Kaush *Polymer Fracture* (Berlin: Springer, 1978)
23. T M Kchrenkova *Sov. Sci. Rev. B, Part 3* **14** 1 (1989)
24. C C Koch *Annu. Rev. Mater. Sci.* **19** 123 (1989)
25. C C Koch *Nanostruct. Mater.* **2** 109 (1993)
26. E G Avvakumov (Ed.) *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii: Sb. SO AN SSSR* (Mechanochemical Syntheses in Inorganic Chemistry: Collected Papers. Siberian Division of the Academy of Sciences of the USSR) (Novosibirsk: Nauka, 1991)
27. E A Margulis *Zvukokhimicheskie Reaktsii i Sonolyuminestsentsiya* (Sonochemical Reactions and Sonoluminescence) (Moscow: Nauka, 1986)
28. P H Shingu (Ed.) *Mechanical Alloying, Mater. Sci. Forum* **88–90** (1992)
29. P Yu Butyagin (Ed.) *Mekhanokhimicheskii Sintez* (Mechanochemical Synthesis) (Vladivostok: Izd. Dal'nevost. Gos. Univ., 1990)
30. M I Molotskii *Sov. Sci. Rev. B, Part 3* **13** 1 (1989)
31. A Popov, N Rapoport, G Zaikov *Oxidation of Stressed Polymers* (New York: Gordon and Breach, 1991)
32. A A Popov, G E Zaikov, in *Polymer Yearbook* (Ed. R A Pethrick) (London: Harwood Acad. Publ.) Vol. 10, p. 257

33. A Popovich, V Vasilenko, in *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii: Sb. SO AN SSSR* (Mechanochemical Syntheses in Inorganic Chemistry: Collected Papers. Siberian Division of the Academy of Sciences of the USSR) (Ed. E G Avvakumov) (Novosibirsk: Nauka, 1991) p. 168
34. P A Rebinder, E D Shchukin *Usp. Fiz. Nauk* **108** 3 (1972)
35. V R Regel', A I Slutsker, E E Tomashevskii *Kineticheskaya Priroda Prochnosti Tverdykh Tel* (The Kinetic Nature of the Strength of Solids) (Moscow: Nauka, 1974)
36. A N Streletskii, A B Borunova, N P Kozina, V I Lapshin, P F Relushko, in *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii: Sb. SO AN SSSR* (Mechanochemical Syntheses in Inorganic Chemistry: Collected Papers. Siberian Division of the Academy of Sciences of the USSR) (Ed. E G Avvakumov) (Novosibirsk: Nauka, 1991) p. 66
37. *The First International Conference on Mechanochemistry: Proceedings, INCOME Košice, Slovakia 1993* (Ed. K Tkačova)
38. K Tkačova *Mechanical Activation of Minerals* (Amsterdam: Elsevier, 1989)
39. *The Second International Conference on Mechanical Alloying for Structural Applications: Proceedings. ASM International, Materials Park, Ohio, 1993* (Eds J J Barbadillo, F H Froes, R B Schwarz)
40. R B Schwarz, in *Synthesis and Consolidation of Amorphous, Metallic Powders. Rapidly Solidified Alloys* (Ed. H Lieberman) (New York: Marcel Dekker, 1993) p. 157
41. K S Suslik *Science* **247** 1439 (1990)
42. A W Weber, H Bakker *Physica* **153** 95 (1988)
43. L S Zarkhin, L I Manevich, N S Enikolopyan *Macromol. Chem. Macromol. Symp.* **26** 431 (1989)
44. B E Krysyuk, E V Polianchik *Khim. Fiz.* **12** 253 (1993)
45. A I Gubanov *Mekh. Polim.* (5) 771 (1978)
46. V A Radtsig, V S Pudov, P Yu Butyagin *Vysokomol. Soedin., Ser. B* **9** 414 (1967)
47. V V Boldyrev *Kinet. Katal.* **13** 1411 (1972)
48. L M Belyaev, Yu N Martyshev, Yu Ya Yushin *Acta Phys. Acad. Sci. Hung.* **33** 307 (1973)
49. A M Dubinskaya, A N Streletskii *Vysokomol. Soedin., Ser. A* **24** 1924 (1982)
50. K B Abramova, Doctoral Thesis in Physicomathematical Sciences, Ioffe Physicotechnical Institute, St Petersburg, 1991
51. A A Bobyshev, Candidate Thesis in Physicomathematical Sciences, Institute of Chemical Physics, Academy of Sciences, Moscow, 1983
52. R B Whitworth *Adv. Phys.* **24** 233 (1975)
53. V A Kuznetsov, A G Lipson, D M Sakov *Zh. Fiz. Khim.* **67** 782 (1993); A G Lipson, V A Kuznetsov, B V Deryagin *Dokl. Akad. Nauk SSSR* **318** 636 (1991)
54. G V Abagyan, P Yu Butyagin *Biofizika* **10** 763 (1965)
55. G V Abagyan, P Yu Butyagin *Vysokomol. Soedin., Ser. A* **26** 1311 (1984)
56. V A Radtsig *Izv. Sib. Otd. Akad. Nauk, Ser. Khim.* (5) 60 (1987)
57. J Eckert, J C Holzer, C E Krill, W L Jonson, in *Mechanical Alloying* (Ed. P H Shingu) *Mater. Sci. Forum* **88–90** 505 (1992)
58. P Butyagin, V Radzig *Plaste Kautsch.* **19** 81 (1972)
59. V V Neverov, V N Burov *Fiz. Met. Metalloved.* **46** 978 (1989)
60. S Surinach, M D Barro, J Segura, Clavaguera-Mora *Mater. Sci. Eng. A* **134** 1378 (1991)
61. K Susuki, M Sherif El-Eskanrdarany, K Aoki, in *Mechanical Alloying* (Ed. P H Shingu) *Mat. Sci. Forum* **88–90** 81; 325; 339; 801 (1992)
62. K Susuki, M Sherif El-Eskanrdarany, K Aoki *J. Non-Cryst. Solids* **150** 472 (1992)
63. K Susuki, M Sherif El-Eskanrdarany, K Aoki *Metal. Trans.* **23A** 2133 (1992)
64. K Susuki, M Sherif El-Eskanrdarany, K Aoki *J. Appl. Phys.* **72** 2665 (1992)
65. P F Relushko, I V Berestetskaya, P Yu Butyagin, L I Trusov, V I Novikov, V V Moskvin *Zh. Fiz. Khim.* **64** 2858 (1990)
66. A O Aning, Z Wang, T H Courtney *Acta Metall. Mater.* **41** 165 (1993)
67. E Yu Ivanov, in *Mekhanokhimicheskii Sintez v Neorganicheskoi Khimii: Sb. SO AN SSSR* (Mechanochemical Syntheses in Inorganic Chemistry: Collected Papers. Siberian Division of the Academy of Sciences of the USSR) (Ed. E G Avvakumov) (Novosibirsk: Nauka, 1991) p. 190
68. V I Fadeeva, A V Leonov, in *Mechanical Alloying* (Ed. P H Shingu) *Mater. Sci. Forum* **88–90** 481 (1992)
69. D S Tipikin, Candidate Thesis in Physicomathematical Sciences, Moscow Physicotechnical Institute, Moscow, 1993
70. D S Tipikin, Ja S Lebedev, O G Poluectov, J Schmidt *Chem. Phys. Lett.* **215** 199 (1993)
71. R W Rydin, D Maurice, T H Courtnay *Metal. Trans.* **24A** 175 (1993)
72. P A Vityas, A A Kolesnikov, A A Stephanovich, V F Nozdrin, in *Mechanical Alloying* (Ed. P H Shingu) *Mater. Sci. Forum* **88–90** 619 (1992)
73. M Atzmon *Phys. Rev. Lett.* **64** 487 (1990)
74. A A Popovich, V P Reva, V Vasilenko, O A Belous, in *Mechanical Alloying* (Ed. P H Shingu) *Mater. Sci. Forum* **88–90** 737 (1992)
75. V Rusanov, Chr Chakurov *J. Solid State Chem.* **79** 181 (1989)
76. G B Schaffer, P G McCormick *Metal. Trans.* **21A** 2789 (1990)
77. Chr G Tschakarov, Doctoral Thesis, Burgas, Bulgaria, 1983
78. Chr G Tschakarov, G G Gospodinov, Z Bontschev *J. Solid State Chem.* **41** 244 (1982)
79. Chr Tschakarov, V Rusanov, G G Gospodinov *J. Solid State Chem.* **59** 265 (1985)
80. Chr Chakurov, V Rusanov, J Koichev *J. Solid State Chem.* **71** 522 (1987)
81. K B Shelimov, P Yu Butyagin *Dokl. Akad. Nauk SSSR* **316** 1439 (1991)
82. A Calka, J I Nikolov, B V Ninham, in *The Second International Conference on Mechanical Alloying for Structural Applications: Proceedings, ASM International, Materials Park, Ohio 1993* (Eds J J Barbadillo, F H Froes, R B Schwarz) p. 189
83. P Yu Butyagin, A N Streletskii, O S Morozova, I V Berestetskaya, A B Borunova *Dokl. Akad. Nauk* **336** 771 (1994)
84. M Senna, K Okamotu *Solid State Ion* **32/33** 453 (1989)
85. G Cocco, G Mulas, M Pintore, G Piliu, L Schiffini *The Second International Conference on Mechanical Alloying for Structural Applications: Proceedings, ASM International, Materials Park, Ohio, 1993* (Eds J J Barbadillo, F H Froes, R B Schwarz)
86. M Magini, in *Mechanical Alloying* (Ed. P H Shingu) *Mat. Sci. Forum* **88–90** 121 (1992)
87. P Yu Butyagin *Dokl. Akad. Nauk SSSR* **319** 384 (1991)
88. P Yu Butyagin *Dokl. Akad. Nauk* **331** 311 (1993)
89. A R Yavari, P J Desre *Phys. Rev. Lett.* **65** 2571 (1990)