Mechanochemistry in Nanoscience and Minerals Engineering

Peter Baláž

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Dedicated to the memory of my son Pali
who passed away on one Spring sunny day

Preface

There are three keywords in title of this book. *Mechanochemistry* is a branch of science concerned with chemical and physico-chemical changes of solids due to the influence of mechanical energy. Very frequently, the small particles are product of this mechanical treatment. *Nanoscience* is a branch of science dealing with particles less than the size of 100 nm, giving to nanostructures built from them extraordinary properties. It has been experienced that mechanochemistry and nanoscience have impact on several technologies. *Minerals engineering* as well as many others applications serves as an good example.

The first chapter *Mechanochemistry in Nanoscience* deals with both disciplines. History, theories and models and synthesis routes are described. Special attention is devoted to nanogeoscience and application of nanoparticles in medicine which is hot topic for scientists and technologists.

The second chapter *High-Energy Milling* is devoted to energetically intensive treatment with which special structures in mechanochemistry and nanoscience are created. Various mills are described, the process variables which govern their mechanical effect as well as important phenomena accompanying the milling process.

Special techniques needed for investigation and characterization of solids in mechanochemistry and nanoscience are described in the third chapter named *Selected Identification Methods*.

The fourth chapter *From Minerals to Nanoparticles* show many examples how it is possible to obtain nanoparticles from minerals.

Mechanochemistry in Minerals Engineering is exclusively described in the fifth chapter. Here, various combinations of mechanochemical processing is illustrated for extraction of elements from minerals as well as their behaviour in leaching and sorption operations.

The largest sixth chapter *Applied Mechanochemistry* is devoted to applications of mechanochemistry in various technological fields. The effect of high-energy milling on particles (very frequently in nanodimensions) in scaled-up processes is illustrated for technological applications in mineral processing, extractive metallurgy, chemical engineering, materials engineering, coal industry, building industry, agriculture, pharmacy and waste treatment.

Košice, Slovakia *Peter Baláž*
Spring 2008

Contents

Acknowledgements

The completion of this book would not have been possible without influence of many people on my professional life. Wish to thank my first teacher in science Ivan Žežula, the learner of the only Czechoslovak Nobel laureate Jaroslav Heyrovský, who arouse my enthusiasm for science. Klára Tkáčová, a founder of the Slovak mechanochemical school, supervisor of my PhD. thesis first introduced me to the charm of mechanochemistry.

As early workers in the field of mechanochemistry it was pleasure to personally meet such pioneers as Peter Adolf Thiessen, Gerhard Heinicke, Hans-Peter Heegn and Eberhard Gock of Germany, Vladimir Vjačeslavovič Boldyrev, Pavel Yurievič Butyagin and Evgenij Grigorievič Avvakumov of Russia, Emmanuel Gutman of Israel, Zoltán Juhász of Hungary and Mamoru Senna and Fumio Saito of Japan. Of course, the list is not complete and several hundreds of contributions from laboratories of active mechanochemists throughout the world can be traced at the end of each chapter of the book. My best thanks is extended to all mechanochemists whose contributions created this work.

The completion of this book would have been impossible without the tremendeous help of Erika Dutková, my post-doc student, who gave the final shape to the manuscript.

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I would like to thank my wife Ela, for her encouragement, patience, and love.

Chapter 1
Mechanochemistry and Nanoscience

1.1 Mechanochemistry of Solids

Mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical changes of substances of all states of aggregation due to the influence of mechanical energy.

1.1.1 History of Mechanochemistry

The above mentioned definition is based on theoretical considerations of *Ostwald* (Nobel Prize 1909) concerning the relationship between chemical and mechanical energy. The German scientist significantly contributed to the development of modern chemistry by systemization of chemical disciplines. Ostwald (Fig. 1.3) was engaged in the systematization of chemical sciences from the energetic point of view. The term mechanochemistry has been used for the first time in his early works [Ostwald 1887, 1909]. He understood mechanochemistry in a wider sense when compared with the present view, regarding it as a part of physical chemistry like thermochemistry, electrochemistry or photochemistry.

From twenties, the further activities in mechanochemistry can be observed. The colloidal mill was developed (Fig. 1.1) and practically forgotten book on mechanochemistry was published [Pierce 1928]. Here author defines mechanochemistry as "the new science of mechanical dispersion involving the use of principles in physical chemistry". He hesitated to name this science because of his remark "... we shall call it mechanochemistry for lack of a better name, as it involves dispersion or defflocculation by mechanical means, thereby bringing about so-called colloidal dispersions".

However, the fact that mechanical activation can lead to chemical consequencies was not a discovery. Since the first attempts by man to obtain fire by friction and to the more recent data on the possibility of ignition and detonation of certain solid explosives, it has come to light that chemical reactions may be initiated by mechanical means [Boldyrev 1986]. That is a reason to look for the beginnings of the written history of mechanochemistry in the very early times.

P. Baláž, *Mechanochemistry in Nanoscience and Minerals Engineering*,

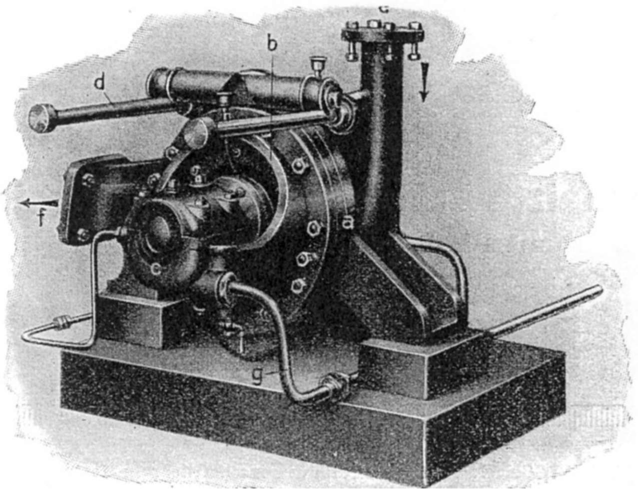

Fig. 1.1 Colloid mill Plauson-Oderberg for wet milling [Ostwald 1927]

Several studies has been published to find the very early traces of mechanochemistry [Takacs 2000, 2003, 2004; Baláž 2001].

1.1.1.1 Mechanochemistry in Antic Greece and Old Europe

The beginning of mechanochemistry of sulphides might be probably dated to antic area. *Theophrastus of Eresus* (Fig. 1.3) was student of Aristotle and served as his successor as the head of the Lyceum in Athens from 322 B.C. until his dead. His book, "On Stones or De Lapidibus" is the earlier surviving scientific book on minerals. In this book the sentence … "native cinnabar was rubbed with vinegar in a copper mortar with a copper pestle yielding the liquid metal … " is given. This is a very clear description of a mechanochemical process. The first described mechanochemical reduction probably followed the reaction

$$\mathrm{HgS} + \mathrm{Cu} \rightarrow \mathrm{Hg} + \mathrm{CuS} \tag{1.1}$$

and vinegar was smartly used to prevent the side effects which usually accompany dry milling on air. It remains a mystery why the mechanochemical preparation of mercury from its sulphide according to reaction (1.1) was forgotten during the Middle Ages.

However, as published recently, examples of other mechanochemical reactions between 300 B.C. and the end of the 18th century can be also traced in medieval literature [Takacs 2000]. *Agricola* documented several examples of chemical reactions under influence of mechanical action which can be connected with mining and metallurgical operations [Agricola 1546, 1556].

It is interesting to note that in the 17th century *Bacon* (Fig. 1.3) referred to four treatments that, in essence, are still among the most important procedures to prepare active solids: one of them is milling [Bacon 1658]. It was *Wenzel* who stressed out the fact that by heterogeneous reactions the degree of conversion depends mainly on the surface area of reacting solids and is not proportional to their amount [Wenzel 1777].

1.1.1.2 Faraday's Contribution to Mechanochemistry

Faraday, famous English physicist noticed in 19th century that certain hydrated salts dehydrated spontaneously when mechanically treated [Faraday 1834]. However, as stated recently his contribution to mechanochemistry started earlier [Takacs 2007]. In his book published in 1827, a twenty-page chapter was dedicated to mortars and comminution [Faraday 1827]. A very direct reference to a mechanochemical process was published in 1820 on the decomposition of silver chloride [Faraday 1820]. The reaction proceeds according to the equation

$$2\mathrm{AgCl} + \mathrm{Zn} \rightarrow 2\mathrm{Ag} + \mathrm{ZnCl}_2 \tag{1.2}$$

and the experiments applying "mortar milling" have been repeated with Sn, Cu and Fe metals. According to Faraday's description, the reaction between silver chloride and zinc is fast and highly exothermic, raising the possibility a mechanochemically induced self-sustaining reaction [Takacs 2002].

The reaction (1.2) was studied recently with modern mechanochemical tools. The mechanically induced self-sustainity of the process has been verified [Takacs 2007]. However, Faraday's contribution to solid state chemistry exceeds the frame of mechanochemistry. He contributed also to nanoscience (see later in this chapter). One of the first bridges between mechanochemistry and nanoscience has been built.

1.1.1.3 Carey Lea, the First Mechanochemist

The interesting papers concerned with the effect of mechanical energy on properties of substances were published by American scientist *Lea* [Lea 1891a, b, 1892–1894]. His contribution to the mechanochemistry has been analyzed recently by contemporary mechanochemists [Baláž 2001; Takacs 2003].

Lea published many works in his brilliant carrier, starting with the groundbreaking papers on colloidal silver [Lea 1866, 1891a, b]. He discovered, what he called three allotropic forms of silver: "soluble silver", "insoluble silver", and "gold-yellow or copper-coloured silver". He recognized that these allotropic forms, which formed colloids containing particles too small to be seen in any microscope of the day, suggested numerous applications [Smith 1972; Whitcomb 2006].

After studying the transformations of silver metal, he turned attention to halides of Ag, Hg, Pt and Au. From halides, chlorides, bromides and iodides were studied. Investigation of these compounds were summarized and a paper was red before American National Academy of Science in April 1892 when Lea was elected to membership. In case of AgCl and AgBr two modes of mechanical effect were applied: simple pressure and shearing stress. The observation recorded proved the existence of perfect uniformity in the action of both kinds of mechanical energy on the halides. When heated, AgCl melts without decomposition, but under the effect of low stress it decomposes with the formation of elemental silver

$$2AgCl \rightarrow 2Ag + Cl_2 \tag{1.3}$$

The reaction probably preceeds through silver subchloride formation.

On the other hand, mercurous chloride Hg_2Cl_2 sublimes under effect of temperature. However, under pressure (a glass rod was used in these experiments) the decomposition reaction leading to elementary mercury and chlorine was observed

$$Hg_2Cl_2 \rightarrow 2Hg + Cl_2 \tag{1.4}$$

This is one of Lea's frequently cited results, the first example of a mechanochemical reaction that brings about an outcome different from the effect of heat [Takacs 2004].

These initial results were followed by systematic investigations published in a series of articles during 1893–1894. As an example can serve the reaction

$$2NaAuCl_4 \rightarrow 2Au + 2NaCl + 3Cl_2 \tag{1.5}$$

The reaction has been performed under influence of mechanical stress. However, the decomposition cannot be produced by heat. Many others compounds were studied by Lea under the effect of sharp stroke of the pestle like silver tartrate, carbonate, citrate, oxalate, arsenate, sulphite, salicylate, orthophosphate and ferricyanide. The main objective of these studies was the initiation of endothermic reactions, specifically the decomposition of compounds with negative heat of formation, by the application of mechanical force.

Lea has shown for the first time the parallelism between the action of electricity, heat, light, chemical action and mechanical force on the silver halides and allotropic silver. He experimentally proved the theoretical ideas of Ostwald's who in his textbooks on general chemistry understood the equivalency of electrochemistry, thermochemistry and photochemistry with mechanochemistry. There is an interesting note in Ostwald's book "Die Welt der vernachlässigten Dimensionen" about Lea investigations [Ostwald 1927]. Ostwald appreciated him as one of the most known American researchers in the field of colloid chemistry (colloid chemistry studies small particles including nanoparticles).

This is one of the first documented traces of evidence the mutual connection between mechanochemistry and nanoscience.

1.1.1.4 From Simple Decompositions to Solid State Reactions in a Mill

Another American chemist *Parker* also appreciated the Lea's results but on the other hand critized that almost entirely his research was devoted to single compounds [Parker 1914]. Parker studied the solid-solid reaction (1.6) by trituration

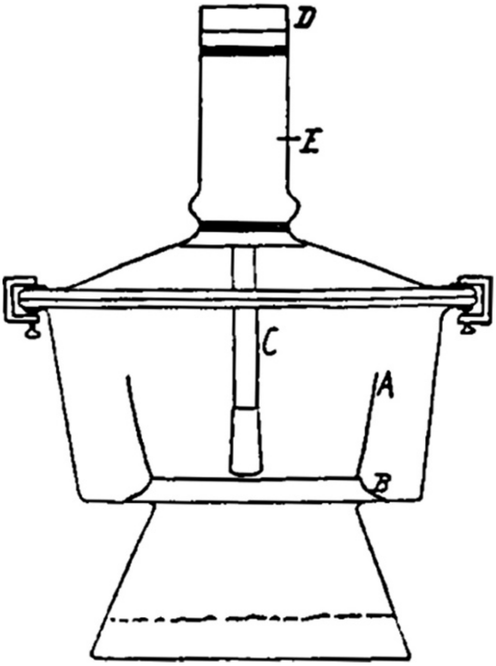

Fig. 1.2 The first mechanochemical reactor: A – mortar, B – iron collar, C – pestle, D – handle, E – rubber tubing [Parker 1914]

$$Na_2CO_3 + BaSO_4 \rightarrow Na_2SO_4 + BaCO_3 \tag{1.6}$$

However, during milling (5–30 min) the sodium carbonate was transformed only very slightly: yield of reaction (1.6) was only 1–3%. In further study he has shown that under certain conditions it is possible to bring about interactions between solid substances by means of a shearing stress, at ordinary temperatures, or at least very greatly to increase the velocity of these reactions [Parker 1918]. In accordance with Lea he concluded that shearing stress, such as could be applied by hand between a pestle and mortar, is widely different in its effects from simple pressure, and that one of the main reason why it is able to bring about reactions between apparently solid substances is that local or surface fusion of the reacting substances is occasioned.

Parker published as the first the picture of mechanochemical reactor (Fig. 1.2). Together with Lea they drew attention on the importance of controlling the atmosphere during milling process. In order to avoid the side effects in the reactor, the pestle and mortar as milling means were fixed in the desiccator.

1.1.1.5 Mechanochemistry in Europe: Traces in a Previous Century

In several review papers on mechanochemistry [Boldyrev and Tkáčová 2000; Boldyrev 2002, 2006] the Russian scientist *Flavickij* is quoted frequently with his contributions in solid state reactions performed by milling [Flavickij 1903, 1909].

As for the time scale his papers were published before Parker's contributions and their works can be appreciated as the pioneer works on solid state reactivity induced by milling.

Later on, a big gap in mechanochemistry of inorganic solids can be traced in literature. Particularly in western countries little seems to have been done except of one area of mechanically initiated explosion reactions in solids, an interest stimulated by the last World War [Fox 1975]. These investigations are linked with researches performed in England, France and Russia [Bowden and Tabor 1958; Bowden and Yoffe 1952, 1958]. The investigations resulted in the elaboration of hot spots theory (see later) which explained the initiation and development of explosion by local increase of temperature at the contact of two solids under mechanical action. Later, this theory was expanded for other theories, like oxidation of metals [Boldyrev and Tkáčová 2000].

In the 1920s the effect of mechanical energy on metals was investigated [Tammann 1929]. *Tamman* working in Göttingen found that not all energy is transformed into the heat but 5–15% of the expended energy remains in the metal as potential energy and increases the thermodynamic potential of the solid. As a consequence of the treatment a displacement of the thermodynamic potential and a significant increase of dissolution velocity occurs. Later Tamman and his co-workers studied the powder reactions in oxide and carbonate systems. They observed that by mechanical contact of quartz (SiO_2) with calcite ($CaCO_3$) the monomolecular layer of Na_2SiO_3 is formed

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \tag{1.7}$$

The old alchymist dogma (unfortunately accepted also for a long time later) that the solid state reactions can not proceed without liquid or gas medium was definitively overcome. *Hedvall*, another outstanding German scientist though not working in mechanochemistry supported by his observations Tamman's results [Hedvall 1938].

The other field of mechanochemistry has its traces in Tamman's time. In twenties, mechanochemistry of organic molecules was first elucidated. The first published papers [Wanetig 1921, 1922, 1927] were inspired by the needs of the pulp and paper industry. The benefitial effect of milling on cellulose solubility by the mechanical destruction of the macromolecule and creation of new hydrophilic groups in the place of discrupted valence bonds was explained [Boldyrev and Tkáčová 2000]. The research into mechanochemistry of organic molecules practically started with works of *Wanetig*. The mechanical degradation of polymers illustrated on polystyrene case started at about the same time. It was found that increase of the reactivity of polymers, e.g. of solubility is parallel to the decrease of the molecular weight [Staudinger and Dreher 1936; Hess et al. 1942]. The investigations in this field were continued in Germany [Berlin 1958; Grohn et al. 1962; Grohn and Paudert 1963] as well as later [Baramboin 1970; Simionesku and Oprea 1971].

In subsequent 3 decades *Fink* and *Bowden* and *Tabor* in particular investigated oxidation reactions of metals, decomposition reactions and conditions of rolling and sliding friction [Fink and Hofmann 1932, 1933; Bowden and Tabor 1958]. Thus during the rolling friction of iron rolls on the stressed surface tarnishing layers come into existence within a few minutes, which without mechanical stress would normally require about 10^{17} years for their growth. Fink excluded the influence of temperature for the interpretation of this effect and discussed plastic deformation as a cause of the acceleration of the reaction [Fink and Hofmann 1932; Heinicke 1984]. The experiments were made with steel as well as with pure metals like iron, nickel and copper. Bowden and Tabor alledge that temperatures over 700°C can be observed at the contact of solid substances exposed to frictions. These high temperatures, however, last only 10^{-4}–10^{-3} s.

The transformations of solids caused by milling were studied as early as 1940 by *Clark* and *Rowan* (1941) followed by *Dachille* and *Roy* (1960). These studies showed that both PbO transformations (massicot→litharge, litharge→massicot) can take place as a result of milling in a ball mill, depending on the amount of hydrostatic pressure generated in the mill. They suggested that pure hydrostatic pressure causes the litharge-massicot transformation, whereas bond breakage at low pressures, due to the action of displacive shear, causes its reverse.

The small excursion into history of mechanochemistry is not exhausted by the above given paragraphs and photographs of important players (Fig. 1.3), of course.

Theophrastus of Eresus
(371–286 B.C.)

Georgius Agricola
(1494–1555)

Francis Bacon
(1561–1626)

Michael Faraday
(1791–1867)

Matthew Carey Lea
(1823–1897)

Fridrich Wilhelm Ostwald
(1853–1932)

Fig. 1.3 Photogalery of important players in history of mechanochemistry

Table 1.1 Review papers on history of mechanochemistry

Title	Author(s)
Mechanochemische Reaktionen	Peters 1962
Review of the Phase Transformation and Synthesis of Inorganic Solids obtained by Mechanical Treatment (Mechanochemical Reactions)	Lin and Nadiv 1970
Mechanically Initiated Chemical Reactions in Solids	Fox 1975
Mechanochemistry of Inorganic Solids	Boldyrev 1986
Accelerating the Kinetics of Low-Temperature Inorganic Synthesis	Roy 1994
Colloid-chemical Aspects of Mechanical Activation	Juhász 1998
Mechanochemistry of Solids: Past, Present and Prospects	Boldyrev and Tkáčová 2000
Mechanochemistry in Extractive Metallurgy: The Modern Science with Old Routes	Baláž 2001
M. Carey Lea, the First Mechanochemist	Takacs 2004
Mechanochemistry: The Mechanical Activation of Covalent Bonds	Beyer and Clausen-Schaumann 2005
Mechanochemistry and Mechanical Activation of Solids	Boldyrev 2006

After these fundamental works the investigations continued as is in the following decades summarized in a series of review papers (Table 1.1), starting with the first pioneer review on mechanochemistry published by *Peters* and presented on the 1st European Symposium on Size Reduction which was held in Germany [Peters 1962].

1.1.2 Theories and Models in Mechanochemistry

1.1.2.1 Hot-Spot Theory

The first trial in mechanochemistry to explain the reason of mechanical initiation of chemical reactions was developed by Bowden, Tabor and Yoffe. They found that with friction processes for 10^{-4}–10^{-3} s temperatures of over 1000 K on surfaces of about 1 μm^2 can occur, and that these represent and important cause of mechanically initiated reactions [Bowden and Yoffe 1952, 1958; Bowden and Tabor 1958]. These temperatures can also be found near the tip of a propagating crack [Weichert and Schönert 1974]. Later this theory was expanded for other processes, like oxidation of metals. However, the controversy concerning the possibility of an increase in temperature at or on the friction surface has still not ended. Judging from indirect features, centers 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 [Suslick 1990; Butyagin 1994]. The phenomenon was experimentally proved and interpreted for three substances as given in Table 1.2.

Table 1.2 The maximum temperatures at the propagating crack [Weichert 1976]

Material	Glass	Quartz	Sugar
Temperature (K)	3200	4700	2500

To study the chemical processes occurring at the tip of a propagating crack a set-up has been used which allow a crystal to be cleaved directly in the vicinity of the ionic source of a mass spectrometer [Fox and Soria-Ruiz 1970]. Their experiments have shown that during the cleavage of inorganic crystals (calcite, magnesite, cerussite, lead and sodium azides) gas evolution can be substantial which suggests that high temperatures exists at the crack tip. However, since in brittle substances the rate of crack propagation can approach the sound velocity, i.e. 10^3 m/s, the life time excitation on the chemical bond must be 10^{-13} s. It is evident that under these conditions the term temperature can be used only symbolically. Later it was proved that the processes occurring at the tip of a crack during the cleavage of a crystal may proceed by different mechanisms depending on the speed of crack motion [Boldyrev et al. 1990; Boldyrev 1993].

1.1.2.2 Magma-Plasma Model

In the sixties, the first model in mechanochemistry – *the magma-plasma model* was proposed [Thiessen et al. 1967]. According to this model a great quantity of energy is set free at the contact spot of colliding particles. This energy is responsible for formation of a special plasmatic state which is characterized by emission of fairly excited fragments of solid substance, electrons and photons over a short time scale (Fig. 1.4).

The surface of contact particles is rather disordered and local temperatures can reach more than 10000 K. Thiessen distinguishes the reactions which occur in the plasma from the reactions taking place at the surface of particles during the significantly excited state, or immediately after its expiration. These considerations led to

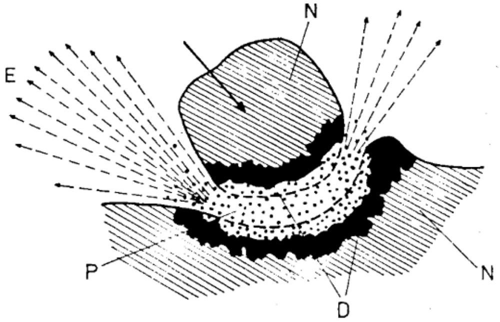

Fig. 1.4 Magma-plasma model: E – exo-electrons, N – undeformed solid, D – highly deformed surface layer, P – plasma [Thiessen et al. 1967]

an important conclusion which is valid for mechanically activated reactions – these reactions do not obey a single mechanism.

The German school elaborated the concept of "hierarchy" of energetic states which appeared to be very important for analysis of the processes induced by the effect of mechanical energy [Thiessen et al. 1967; Thiessen 1979; Thiessen and Sieber 1979a, b; Heinicke 1981]. In this concept, a large number of excitation processes occur due to mechanical activation which are characterized by different relaxation times (Table 1.3).

Heinicke shown the value of classifying tribochemical reactions according to the excitation processes initiating the individual reactions and to subdivide these excitation processes in their temporal courses. This way one will arrive at *a hierarchic model*, in which the most highly excited states having the shortest excitation times stand at the beginning and the numerous other states with smaller excitation incorporate themselves according to their temporal occurrence in the dissipation phase into the model [Heinicke 1981].

Long-lived states including defects and dislocations have been analyzed by equilibrium thermodynamics [Heegn 1989]. Mechanically disordered solids have an actual free energy content G which is higher than the equilibrium free energy G*:

$$G = G^* + G^E \tag{1.8a}$$

The excess free enthalpy is made up of the contributing defects and their disturbance enthalpy

$$G^E = \sum_i c_i H_i^* + T k_b \, \mathrm{NA} \sum_i C_i \ln c_i \tag{1.8b}$$

Table 1.3 Relaxation times of excitation processes in mechanically activated solids [Heinicke 1981]

Excitation process	Relaxation time
Impact process	$> 10^{-6}$ s
Triboplasma	$< 10^{-7}$ s
Gaseous discharge	$\sim 10^{-7}$ s
"Hot spots"	10^{-3}–10^{-4} s
Electrostatic charging	10^{2}–10^{5} s
Emission of exoelectrons	10^{-6}–10^{5} s
Triboluminescence	10^{-7}–10^{3} s
Lattice defects	10^{-7}–10^{6} s
Dislocation motion	10^{5} cms^{-1}
Lattice vibrations	10^{-9}–10^{-10} s
Fracture formation	10–10^{3} cms^{-1}
Fresh surface	at 1.3.10^{-4} Pa: 1–10^{2} s
Lifetime of excited metastable states	at 10^{5} Pa: $< 10^{-6}$ s
	10^{-3} s
	10^{-2} s

with major contributions from step and screw dislocations, outer specific surface, particle size of primary crystallites and amorphous regions and different phases [Hoffmann et al. 2005].

1.1.2.3 Spherical Model

During one of the first conferences on mechanochemistry in Berlin 1983 Thiessen demonstrated the different stages of an impact stress by *a spherical model* (Fig. 1.5). By this simplifying model it could be shown that the impact stress is combined with the appearance of different species. This state is limited to very small spaces and very short times and qualified as triboplasma [Thiessen et al. 1967]. The concept of triboplasma was later developed from thermodynamic and kinetic point of view.

The short life of triboplasma causes no Maxwell-Boltzmann distribution so that an equilibrium temperature cannot be given and the chemical process taking place in this excitation phase cannot be described by the laws of thermodynamics. The conversions in triboplasmas are of a stochastic nature. The highest stage of energy excitation changes dynamically into the next stage, characterized by the relaxation of the plasma states and termed “edge-plasma” and “post-plasma”. A step diagram of the energy dissipation was composed for the total process in the form of a hierarchy of the energy states (Fig. 1.6). A number of physical processes (see Table 1.2) take place in this step, such as the recombination of plasma products, the propagation of dislocations, fracture processes, the propagation of photons and the emission of electrons and photons which have important functions for the initiations of chemical reactions [Heinicke 1984].

1.1.2.4 Dislocation and Phonon Theory

The authors of *dislocation theory* allege that the mechanical action on solid substances gives rise to dislocations which come to the surface and subsequently become areas with increased chemical activity [Gutman 1974]. The motion of dislocations in solid substance is accompanied by the formation of phonons due to interactions between dislocations and other dislocations, defects, admixtures or interfaces. *The phonon theory* then emphasizes the distribution, mutual effect and origination of phonons in the course of disordering of solid substances by milling [Bertenev and Razumovskaya 1969].

1.1.2.5 Theory of Short-Live Active Centers

The essence of the theory consist in the idea that new surface arising during mechanical treatment is unable to stabilize in the 10^{-9}–10^{-11} s of thermal excitation. During the 10^{-4}–10^{-7} s required for stabilization, chemical bonds are liable to

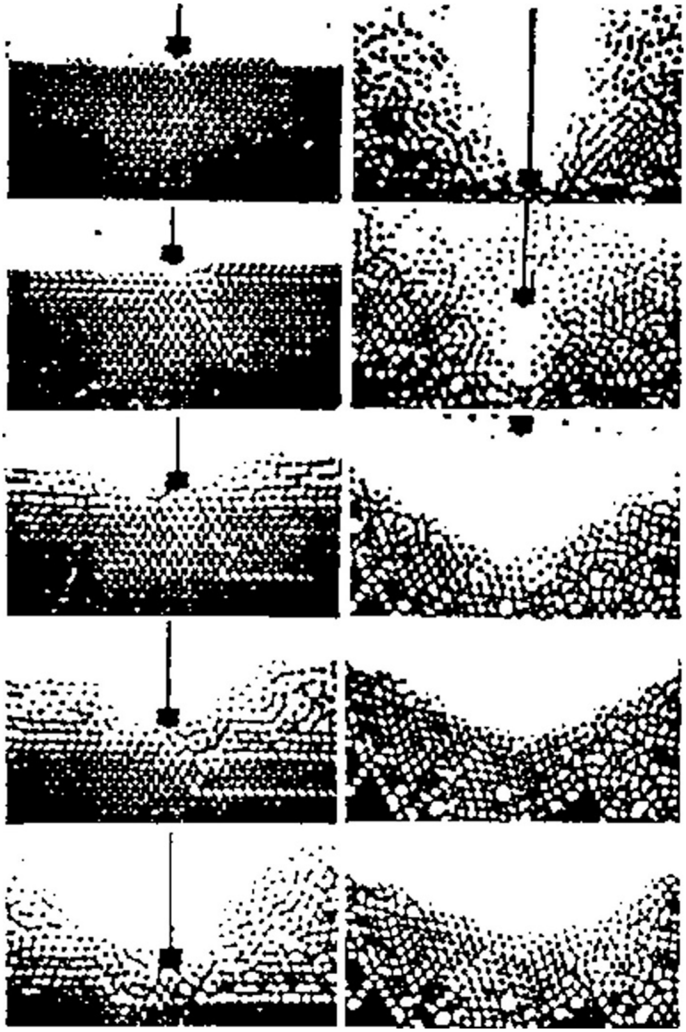

Fig. 1.5 Different stages of the impact stress schematically shown by *the spherical model* (↓ – penetration into the lattice of the solid, ↑ – decay phase up to the condition of frozen lattice distortion) [Heinicke 1984]

rearrangement, the electric surface relief is formed and further relaxation processes proceed. The decay of short-lived centres is related to the relaxation of excess energy. In vacuo, this relaxation is due to rearrangement of chemical bonds, whereas the interactions of short-lived centres with the molecules of surrounding medium are responsible for relaxation in chemically active medium. This is a case of exothermic process which can be accompanied e.g. by luminiscence or other phenomena involving radiation of energy [Butyagin 1973].

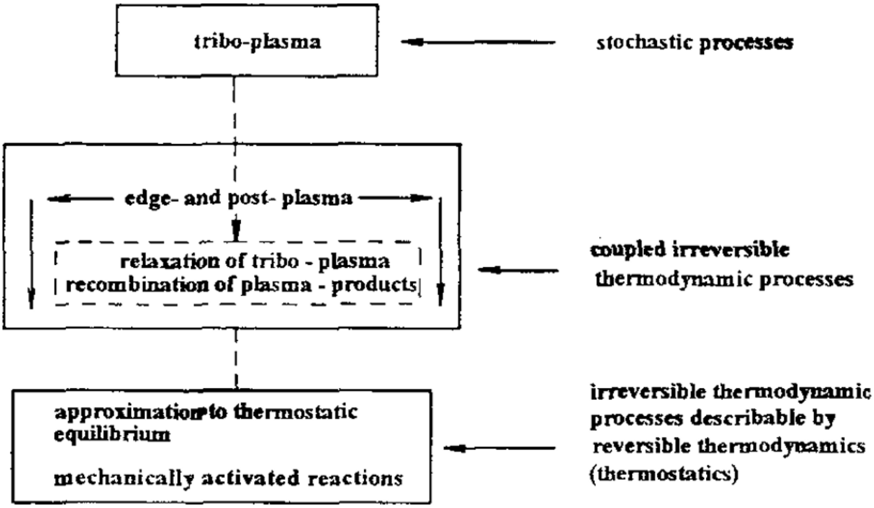

Fig. 1.6 Step diagram of the energy dissipation in solids stressed by impact [Thiessen and Sieber 1979a]

1.1.2.6 Kinetic Model

The specific features of mechanochemical effects have been analyzed from the viewpoint of limiting stages of the process [Boldyrev 1972]. The decomposition process of solid substance can be evaluated according to activation, deactivation and proper chemical reaction. We can discern two boundary cases: the decay is limited either by the processes of excitation and bond splitting (e.g. thermal decomposition) or by following stages (e.g. transformation of intermediates arising in the primary stage). Two characteristic features of mechanochemical effects have been determined: pulse action and local character of action. Both these features form the grounds of the kinetic model of mechanical activation. The kinetic model proposed by Boldyrev was experimentally verified.

1.1.2.7 Impulse Model

The model is based on the idea that the kinetics of the reaction is determined by the time in which substance is liable to be in contact with balls owing to the impulse effect of milling balls on solid substance [Lyachov 1984]. This time is different from the overall time of milling and is connected to the temperature rise during the impulse. The author succeeded in determining the equivalent temperatures corresponding to the contact of milling balls with solids and verified this idea [Boldyrev 1972, 1986].

In mills, the formation of stress field and its relaxation occur at regular intervals by subjecting a solid to a sequence of mechanical pulses following one after the

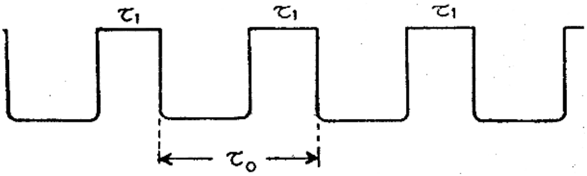

Fig. 1.7 Impulse character of mechanical action. The left side of the impulse – stress field formation, the right side – stress relaxation [Boldyrev 1986]

other. A schematic representation of these pulses is shown in Fig. 1.7. Every pulse characterizes the occurrence of stress field in the region being treated (the left-hand side of the pulse) and its relaxation leading to various physical and physico-chemical consequences (the right-hand side of the pulse) [Boldyrev 1986].

1.1.2.8 Theory of the Energy Balance

In this theory it was shown that the individual mill parameters as well as the different mill types lead to characteristic changes of the crystal lattice of solids [Heegn 1989, 1990].

1.1.2.9 Analogy Model

This model has been based on similarity of energy transfer in mill with the energy transfer in an electric circuit [Tkáčová et al. 1988]. The concept was experimentally verified with a great deal of minerals and has enabled a description of the mechanical action for variable specific energies of structural disordering of solids.

1.1.3 Mechanical Activation

The term mechanical activation was introduced by Smékal who regarded it as a process involving an increase in reaction ability of a substance which remains chemically unchanged [Smékal 1942]. Provided the activation brings about a change in composition or structure, it is a mechanochemical reaction. In this case, the mechanical activation procedes the reaction and has no effect during the course of this reaction. The definitions of mechanical activation published later were always dependent on the observed effect.

It was Butyagin who contributed to a certain unification. He considered the behaviour of the solids exposed to the effect of mechanical energy from the view-point of three main aspects: structural disordering, structure relaxation and structural mobility. Under real conditions, three factors simultaneously affect the reactivity of a

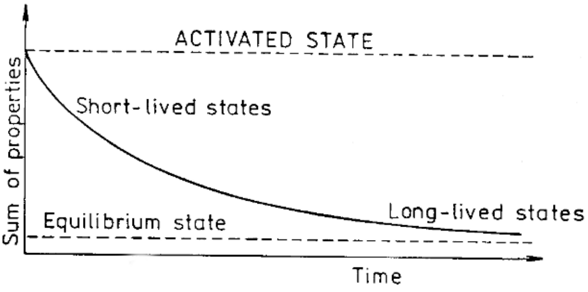

Fig. 1.8 A generalised relaxation curve of mechanically activated state [Lyachov 1993]

solid. The mechanical activation is defined as an increase in reaction ability due to stable changes in solid structure [Butyagin 1984].

However, structural relaxation plays the important role in mechanical activation. The concept of slowly changing states after interrupting the action of mechanical forces by activation has been described [Lyachov 1993]. Lyachov published a generalised relaxation curve for activated solids where individual parts of the curve correspond to processes with different characteristic times of relaxation (Fig. 1.8).

By this theory there is no possibility of influencing the reactivity of activated solids via states whose relaxation time is less than characteristic time of reaction itself. On the contrary, some long-lived states (e.g. surface area) may be regarded as constant during the course of a reaction and their influence has to be a subject of mechanical activation studies.

As for the kinds of relaxation processes various processes were described: heating, formation of a new surface, aggregation, recombination, adsorption, imperfections, chemical reaction between adjoing particles, etc. [Boldyrev 1986; Juhász and Kolláth 1993]. The rate of these relaxation processes may be vastly different and the processes can change from one way of relaxation to the other (Fig. 1.9).

Thus, mechanical activation can be regardered as a multi-step process with changes in the energetic parameters and the amount of accumulated energy of solids in each step. The four processes, namely, the accumulation of defects, amorphization, the formation of metastable polymorphous forms, and chemical reaction, are united by the term mechanical activation [Boldyrev and Tkáčová 2000].

Juhász proposed that processes under the influence of mechanical activation can be subdivided into primary and secondary ones [Juhász 1974, 1985, 1998; Juhász and Kolláth 1993]. The primary process (e.g. increase of internal and surface energy, increase of surface area, decrease of the coherence energy of solids) generally increase the reactivity of the substance. The secondary processes (e.g. aggregation, adsorption, recrystallization) take place spontaneously in activated systems and may appear even during milling or after milling has been completed.

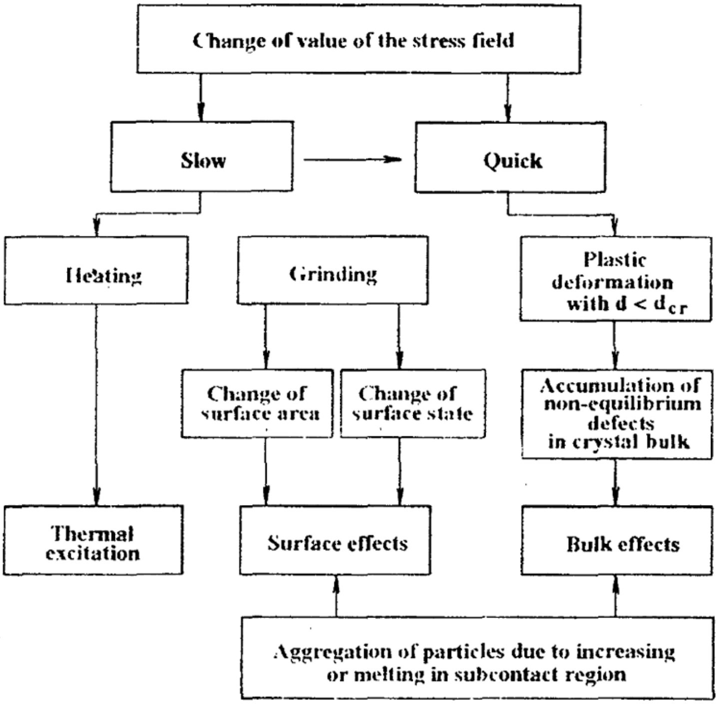

Fig. 1.9 Flowsheet of changes of relaxation processes [Boldyrev 1986]

1.1.4 Thermodynamics in Mechanochemistry

Chemical interactions between solids proceed through the consumptions of educts and the formation of products. These processes occur in agreement with physico-chemical laws and can be characterized using the fundamental thermodynamical equations. According to the Gibbs-Helmholtz equation it holds

$$\Delta G = \Delta H - T\Delta S \tag{1.9}$$

where ΔH is enthalpy and ΔS is entropy. If entropy ΔS is small (crystal structure is preserved and its disordering is slight), the term TΔS is small and the Gibbs free energy ΔG is predominantly determined by change of enthalpy ΔH. For highly disordered solids the entropy ΔS becomes significant and the term TΔS cannot be omitted.

A principal possibility for one or another chemical reaction to occur is determined by the sign of ΔG. According to the laws of thermodynamics, the process occurs spontaneously in the direction of decreasing the free Gibbs energy. A reaction between the substances proceeds with the formation of products, if

$$\Delta G_{\text{reac}} = \sum \Delta G_{\text{final products}} - \sum \Delta G_{\text{initial products}}, \Delta G < 0 \tag{1.10}$$

and takes the back direction if $\Delta G > 0$. In case when a system is in equilibrium $\Delta G = 0$. For example, in the reaction $A_{solid} + B_{solid} = AB_{solid}$, Gibbs energy is estimated as

$$\Delta G_{\mathrm{reac}} = \Delta G^0_{\mathrm{reac}} + RT \ln a_{AB}/(a_A a_B) \tag{1.11}$$

where a_A, a_B, a_{AB} are the activities of the initial and final products. However, since the activity of solids is equal (or close) to unity at normal pressure and room temperature, then

$$\Delta G_{\mathrm{reac}} = \Delta G^0_{\mathrm{reac}} \tag{1.12}$$

Thus, in order to determine the possibility for a reaction to proceed, it is sufficient to know $\Delta G^0_{\mathrm{reac}}$ in standard state ($p = 0.1$ Mpa, $T = 298$ K) which is calculated as the difference between Gibbs energies of the formation of final and initial products in standard state. These values are listed in reference books, see for example [Kubaschewski and Alcock 1979].

If a reaction in a mixture of solids is accompanied by the formation of gas or fluid phases (melts, solutions), solid solutions, or by the generation of defects, then, for a more strict thermodynamic forecast, it is necessary to take into account the changes of entropy and specific heat capacity during phase transitions of the components (melting, vaporization, dissolution), changes of volume and other parameters. If these factors are not taken into account, one can come across the contradictions between experimental data and thermodynamic calculations [Avvakumov et al. 2001].

The interpretation of the relation between the state of the solid before and after mechanical activation requires data for describing this state to be available. In contrast to gases and liquids, these solid particles are not able to be characterized with only a few thermodynamic factors related to these states. Even at the absolute zero point temperature, activated solids possess a finite zero point entropy caused be the disorder of lattice components. The inner thermodynamics equilibrium is first attained above the melting temperature. The state of any lower temperature depends considerably on the preliminary treatment, e.g. kind, intensity and duration of mechanical stress. The type and concentration of defects (Fig. 1.10) resulting from this determine the thermodynamic state [Heegn 1989].

The new definition of activated solid state has been postulated [Hüttig 1943]. Hüttig defined this state as a thermodynamically and structurally unstable arrangement at temperatures exceeding the melting point. He characterized the activated state of solid by "residual" Gibbs energy ΔG

$$\Delta G = G^*_T - G_T \tag{1.13}$$

where $G_T{}^*$, G_T and T are the free enthalpy of activated solid, free enthalpy of this substance in non-activated state and temperature, respectively.

The Gibbs energy ΔG was analyzed by several authors and a simplified term was derived

$$\Delta G = \Delta G^*_1 + \Delta G^*_2 \tag{1.14}$$

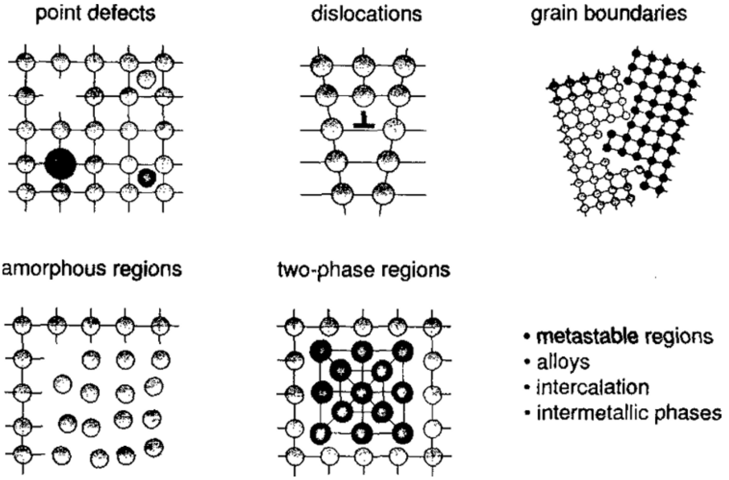

Fig. 1.10 Defects created by mechanical activation of solids [Hoffmann et al. 2005]

where $\Delta G_1{}^*$ is the residual surface energy and $\Delta G_2{}^*$ is the energy of lattice defects formation [Zelikman et al. 1975].

It holds for the surface energy in thermodynamics

$$\Delta G_1 = \sigma \Delta S \tag{1.15}$$

where σ is specific surface energy and ΔS in the change of overall surface of a solid. It was estimated for mechanical activation of ionic crystals that the surface energy ΔG_1 corresponds approximatelly to 10% of overall Gibbs energy ΔG [Schrader and Hoffmann 1973].

Schrader estimated the dependence of calcite milling efficiency η on milling time (Fig. 1.11). Based on presented plots one can obtain the maximum values $\eta = 0.19\%$ (1) and 0.006% (2), respectively (1-total milling efficiency, 2-milling efficiency consumed for increase of surface area). By comparison of these values, only 3% of total energy is consumed for increase of surface area of $CaCO_3$.

However, it has been found that there are reactions, for which the equilibrium thermodynamics does not afford favourable conditions and in spite of it they successfully proceed. The oxidation of gold is governed by reaction

$$4Au + 3CO_2 \rightarrow 2Au_2O_3 + 3C \tag{1.16}$$

From the point of view the equilibrium thermodynamics the reaction (1.16) has to be only hypothetic because of positive ΔG values (Table 1.4).

But the reaction proceeds by milling and from the mechanochemical point of view gold is not so much noble as we know from its chemistry [Thiessen et al. 1970]. In such cases the relationships of irreversible thermodynamics seemed to be more suitable [Heinicke and Sigrist 1971].

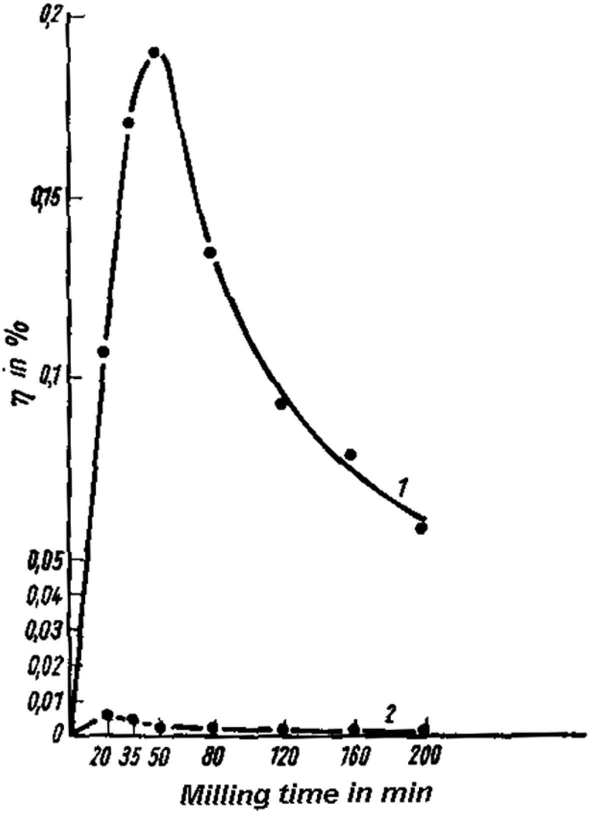

Fig. 1.11 Efficiency of calcite $CaCO_3$ milling, η in dependence on milling time [Schrader and Hoffmann 1973]

Table 1.4 The value of ΔG for reaction (1.16) [Heinicke 1984]

T (K)	ΔG (kJ mol^{-1})
298	377
1000	477
2000	615

1.1.5 Kinetics of Mechanochemical Reactions

1.1.5.1 Mechanochemical Pecularities

The general idea of a mechanochemical reaction course under effect of mechanical energy on reacting system can be illustrated by Fig. 1.12.

The reaction occurring before the beginning of the mechanical treatment (phase 1) is determined by the thermal excitation and is therefore a function of the reaction

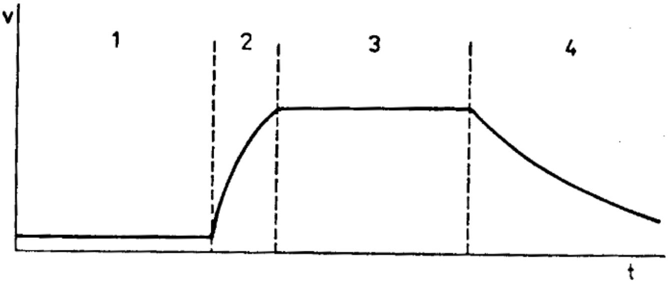

Fig. 1.12 General diagram of a mechanochemical reaction course, v – reaction velocity, t – reaction time, 1 – reaction on untreated solid, 2 – rising reaction, 3 – steady-state reaction, 4 – decaying reaction [Heinicke 1984]

temperature. However, at room temperature most solid state reactions proceed immeasurably slowly. The application of mechanical energy generally results in a significant increase of the reaction velocity (phase 2). After having passed through the rising phase a constant reaction velocity appears under external constant conditions (phase 3). After the interuption of the treatment, the decay phase comes into the existence (phase 4) [Heinicke 1984]. It was shown later that the mechanochemical reaction course described by Fig. 1.12 had a general character. However, the course of reaction is not only determined by the type of reaction but also by the kind and the intensity of applied mechanical energy, since these factors also determine the formation of the defects mainly responsible for the solid state reactions.

Probably, the first experimental observation of a change in reactivity caused by the introduction of defects in crystalline solids was that of Faraday who noticed that certain hydrated salts, dehydrated spontaneously when scratched with a pin [Faraday 1834]. Since then numerous reports have appeared on the correlation of dislocation generation and bulk and surface reactivity [Tompkins 1963]. As stated later, much of this work suffers from the drawback that insufficient attention has been paid to the research for a direct one to one correlation between change in reactivity and dislocation density. For example it is usually not sufficient to observe that a change in reactivity occurs when the solid is subjected to some treatment which is assumed to change the concentration of defects, unless it can be shown that no other accompanying change can explain the observed effect [Fox 1975].

However, even after more than 30 years the situation is sometimes the same. 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 reactivity”, which is rather meaningless and worthless [Boldyrev 2006].

1.1.5.2 Kinetic Description

In literature, several attempts have been described to apply principles of solid state heterogeneous kinetics for the mechanochemical systems [see e.g. Avvakumov