


Peter Baláž



# Mechanochemistry in Nanoscience and Minerals Engineering

 Springer

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Mechanochemistry  
in Nanoscience and Minerals  
Engineering

 Springer

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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 large 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.

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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 tremendous 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

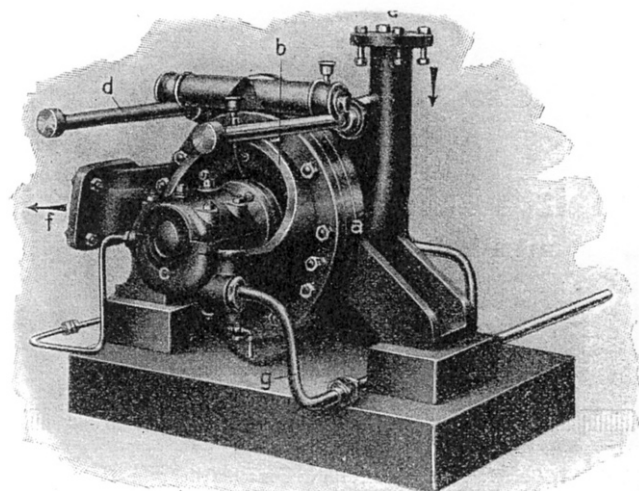
*Mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical changes of substances of all states of aggregation due to the influence of mechanical energy.*

#### 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 deflocculation by mechanical means, thereby bringing about so-called colloidal dispersions”.

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



**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; Baláz 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



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.

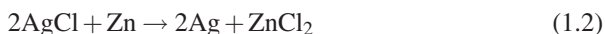
However, as published recently, examples of other mechanochemical reactions between 300 B.C. and the end of the 18th century can be also traced in medieval literature [Takacs 2000]. *Agricola* documented several examples of chemical reactions under influence of mechanical action which can be connected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



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-sustainability 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 read 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



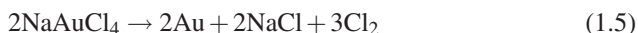
The reaction probably precedes through silver subchloride formation.

On the other hand, mercurous chloride  $\text{Hg}_2\text{Cl}_2$  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



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



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.

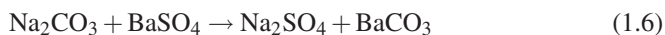
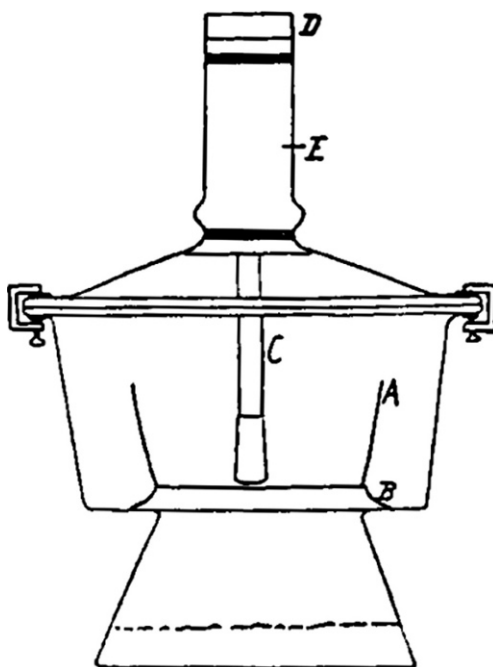
Lea has shown for the first time the parallelism between the action of electricity, heat, light, chemical action and mechanical force on the silver halides and allotropic silver. He experimentally proved the theoretical ideas of Ostwald's who in his textbooks on general chemistry understood the equivalency 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 criticized 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]



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

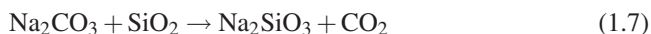
In several review papers on mechanochemistry [Boldyrev and Tkáčová 2000; Boldyrev 2002, 2006] the Russian scientist *Flavickij* is quoted frequently with his contributions in solid state reactions performed by milling [Flavickij 1903, 1909].



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]. *Tammann* 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 *Tammann* and his co-workers studied the powder reactions in oxide and carbonate systems. They observed that by mechanical contact of quartz ( $\text{SiO}_2$ ) with calcite ( $\text{CaCO}_3$ ) the monomolecular layer of  $\text{Na}_2\text{SiO}_3$  is formed



The old alchemist 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 *Tammann's* results [Hedvall 1938].

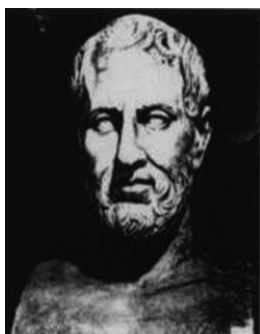
The other field of mechanochemistry has its traces in *Tammann's* time. In twenties, mechanochemistry of organic molecules was first elucidated. The first published papers [Wanetig 1921, 1922, 1927] were inspired by the needs of the pulp and paper industry. The beneficial effect of milling on cellulose solubility by the mechanical destruction of the macromolecule and creation of new hydrophilic groups in the place of disrupted 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; Simionescu 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  $700^{\circ}\text{C}$  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** Photogallery 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	Baláz 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  $1 \mu\text{m}^2$  can occur, and that these represent an 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]

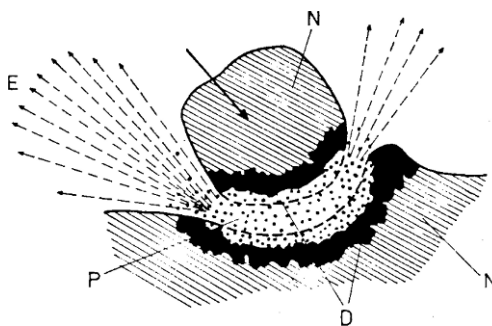
Material	Glass	Quartz	Sugar
Temperature (K)	3200	4700	2500

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]