Mechanochemistry in the preparation of advanced materials

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Abstract

Mechanochemistry is a branch of solid state chemistry which inquires into processes which proceed in solids due to the application of mechanical energy. At present, mechanochemistry appears to be a science with a sound theoretical foundation which exhibits a wide range of potential application. Amongst the potential viable processes we can mention the modification of properties of building materials, the new method of fertilizer production, the activity enhancement and regeneration of catalysts, the new method of modification of solubility and bioavailability of drugs in pharmacy, the control of reaction kinetics in the chemical technology and last but not least the recent achievements in the synthesis of advanced materials.

In this review paper, the definition of mechanochemistry and its history is given with the types of mills applied. Theoretical background for enhanced reactivity is given, several characterization methods and two examples of application in materials science and pharmacy are described.

Key words: *mechanochemistry, mill, reactivity, STM, AFM, TEM, nanocrystal, pharmacy, arsenic*

Introduction

Mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical transformations of substances in all states of aggregation produced by the effect of mechanical energy. This general definition has been formulated by Heinicke and is widely accepted nowadays (Heinicke, 1984). However, the origins of this science with many applications in extractive metallurgy go deep in the past. Takacs recently published a paper in which the tracks of mechanochemical treatment of cinnabar HgS might be dated to Aristotle era. In his book "On stones or de lapidus", Theophrastus of Eresus (371-286 B.C.), a student of Aristotle, describes a method to recover mercury from cinnabar by mechanical energy. The metal is obtained from native cinnabar after rubbing in a brass mortar with a brass pestle in the presence of vinegar (Takacs, 2000). At present, mechanochemistry appears to be a science with a sound theoretical foundation which exhibits a wide range of potential application. Its benefits include lower reaction temperatures, increased reaction rate, increased dissolution and the formation of water soluble compounds. As a consequence, further processing can be performed in simpler and less expensive reactors during shorter reaction times (Baláž, 2000a; Welham, 1997; Welham, 2000).

The key factor in mechanochemistry is the application of suitable mill which can work in different working regimes. In fact, there are various factors affecting the operation of milling process in mechanochemistry (Baláž, 2000a; Baláž, 2000b) and different types of mills are used (Fig. 1).
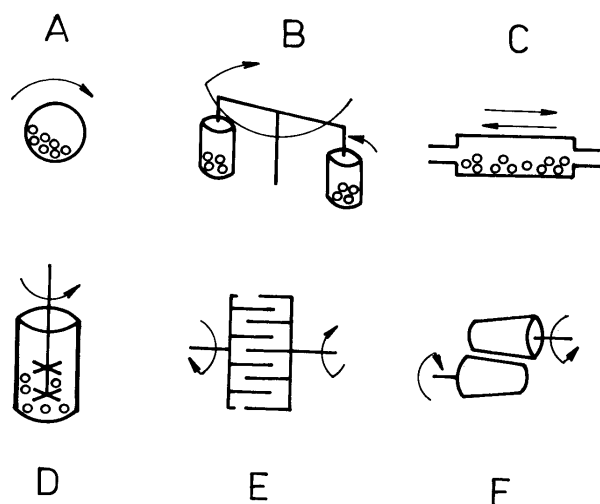

Fig. 1. *Types of mills applied on mechanochemistry; A – ball mill, B – planetary mill, C – vibratory mill, D – stirring ball mill (attritor), E – pin mill, F – rolling mill (Boldyrev, 1986).*

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Theoretical background

Generally, the mechanochemical treatment of solids leads to a positive influence on the solid – liquid kinetics (Baláž, 2000a; Baláž, 2003; Tkáčová, 1989). It has been documented by (Zelikman et al., 1975) that the breaking of bonds in the crystalline lattice of solids brings about a decrease (ΔE^*) in the activation energy and an increase in the rate of leaching

$$\Delta E^* = E - E^* \tag{1}$$

$$k^* = k \exp(\Delta E^* / RT) \tag{2}$$

where E is the apparent activation energy of the non-disordered solid, E* is the apparent activation energy of the disordered solid k, R and T stand for the rate constant of leaching for the non-disordered solid, (the pre-exponential factor) gas constant and reaction temperature, respectively; k* is the rate constant of leaching for the disordered solid.

If E > E*, then exp ($\Delta E^*/RT$) > 1 and thus it follows from eq. (2) that k* > k, i.e., the rate of leaching of a disordered solid is greater than that of an ordered mineral.

It was Senna who analysed the effect of surface area and the structural disordering on the leachability of mechanically activated solids (Senna, 1975). In order to solve the problem – whether the surface area or structural parameters are predominant for the reactivity - the rate constant of leaching was divided by the proper surface area and plotted against the applied energy by milling (Fig. 2).
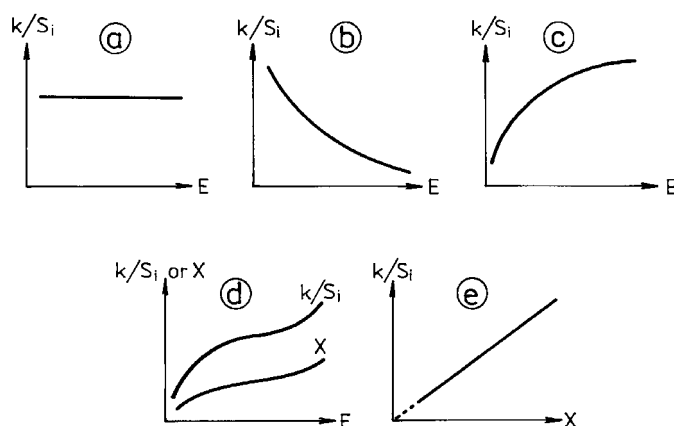

Fig. 2. The schematic diagrams representing the mutual dependence of physico – chemical characteristics and reactivity of mechanically activated solids: k *– the rate constant of leaching,* S_i *– surface area,* X *– structural imperfections,* E *– applied energy (Senna, 1975).*

For example, if the rate constant of leaching divided by the surface area remains constant with respect to the applied energy, as shown in Fig. 2a, then the measured surface area may be the effective surface area and at the same time, the reaction rate is insensitive to structural changes. If, on the other hand, the value k/S_i decreases with applied energy, as shown in Fig. 2b, then the surface area is probably not the effective surface area. In the third case where k/S_i increases with increasing applied energy, as shown in Fig. 2c, the surface area S_i, may be again the effective surface area, with an overlapping effect of the structural imperfection as a result of mechanical activation. Alternatively, when k/S_i and X vary parallel to each other with E, as shown in Fig. 2d, or the value k/S_i is proportional to X, as shown in Fig. 2e, it seems more appropriate to accept the chosen S_i as an effective surface area.

Selected identification methods

During the development of mechanochemistry, the number of applied identification methods gradually increased. At the beginning, the methods were directed to obtaining characteristics of mechanically activated solids, mostly in the integral form. At present, the number of methods applied in the investigation of mechanochemical phenomena comprises a few tens. Moreover, with the intergrowth of mechanochemistry into nanosciences, special techniques such as TEM, HRTEM, AFM, etc. have been applied.

Scanning tunneling microscopy (STM)

The scannig tunneling microscope, invented in 1981 by Binning and Rohrer (Nobel Prize in 1986), is the most powerful type of microscope ever built. In the STM method, which is non - optical one, a sharp metallic tip is brought to within a few nanometers of a conducting surface and a small potential difference (usually in the mV range) is applied between the tip and the sample. If the tip is biased positively relative

to the sample, electrons will flow from the sample to the tip. This process is called electron tunneling and produce a small, measurable current whose magnitude is exponentially dependent on the tip – surface separation, the larger the distance between the tip and the surface, the smaller the current.
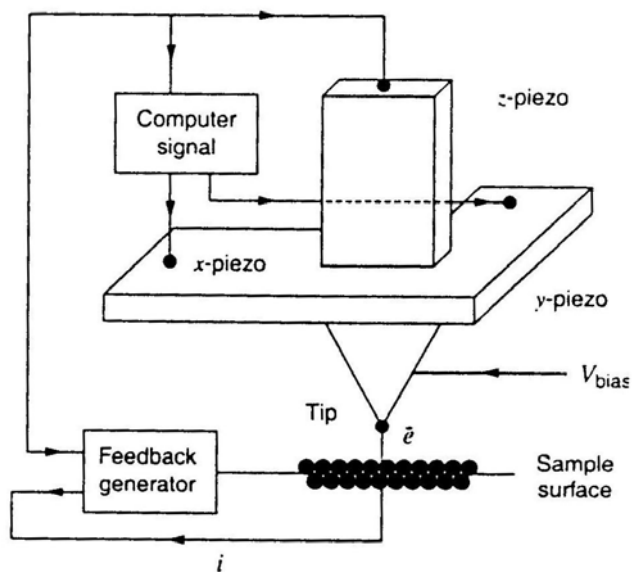
The topographic image of the surface by measuring the magnitude of the tunelling current can be obtained. In practice, this can be achieved by mounting a tip on a piezoelectric tube scanner. The experimental system (Fig. 3) gives the possibility of a high precision movement in the x, y, z directions, producing a 3 – dimensional image of the surface with a nanometer resolution (Wogelins and Vaughan, 2000). STM is particularly useful in nanoscale chemistry labs where the study of defects and physical structure of synthetic chemical compounds is of vital importance.

Fig. 3. The scheme of scanning tunneling microscope (Wogelins and Vaufghan, 2000).

STM images are sensitive to the chemisorptive bonding at surfaces. In semiconductors electronic wavefunctions (states) are localized on particular atoms and we should be able to distinguish between different atomic sites (Weimer et al., 1988). The symmetry of a surface unit cell of lead sulphide PbS (Fig. 4) is slightly distorted due to a drift but two different sites are distinguishable. The sites in the row labeled „A" are narrower than those in the row labeled „B". The surface cell is drawn so that the wider (B) sites occur at the cell corners and the narrower (A) sites occur at the cell edge midpoints. Based on the interpretation of this and other images, it was suggested that the B sites correspond to sulphur and the A sites correspond to lead (Eggleston and Hochella, 1990).

In nanotechnology, the scanning tunneling microscope can be used to alter the observed material by manipulating individual atoms, creating ions by removing individual electrons from atoms and then reverting them to atoms by replacing the electrons.
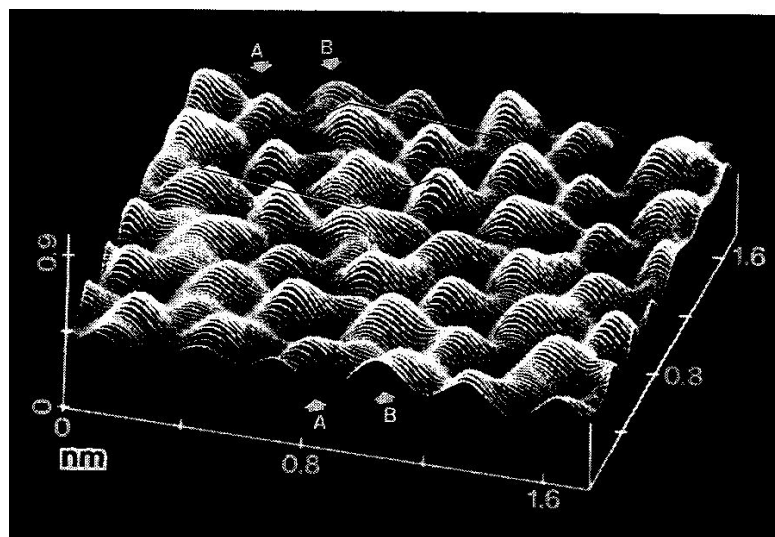
Fig. 4. STM image of PbS (Eggleston and Hochella, 1990).

Atomic force microscopy (AFM)

The atomic force microscope was invented by Binning, Quate and Gerber in 1986. This method involve using a piezoelectric scanner to move a tip across the surface of the sample (Fig. 5a). the tip is mounted on a cantilever with the force constant of between approximately 0,001 and 0,2 $N.m^{-1}$. When this tip is brought just into contact with the surface, it experiences a very small force (of the order of nanonewtons)

as a result of interaction with the surface atoms. In this kind of operation, the tip is scanned across the surface and the tip will be subject to varying attractive and repulsive forces of the kind associated with van der Waals bonds, and the movements of the tip will be registered by the deflection of the cantilever.
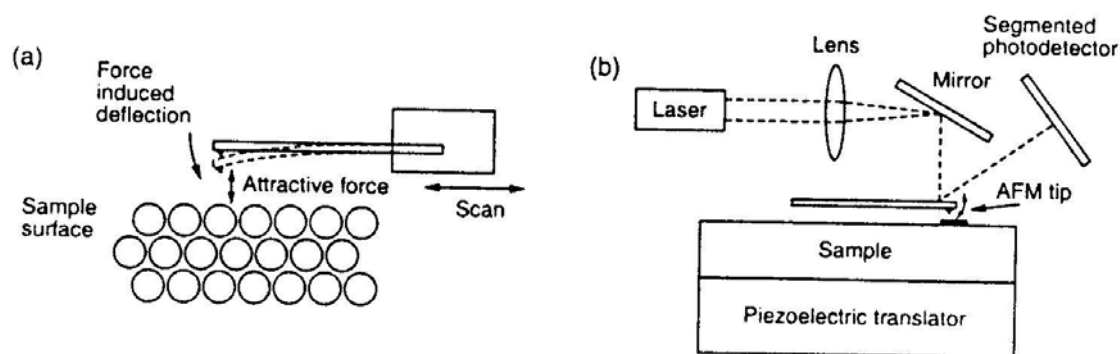

Fig. 5. The scheme of atomic force microscope: (a) the principle, (b) the experimental configuration (Wogelins and Vaufghan, 2000).

In a typical AFM instrument, the deflection of the cantilever is monitored by reflecting a laser beam from the back of the cantilever on to a segmented photodetector (Wogelins and Vaughan, 2000) (Fig. 5b). Unlike the electron microscope which provides a two – dimensional image of sample, the AFM provides a true three – dimensional surface profile (Fig. 6). While the electron microscope needs an expensive vacuum – environment for proper operation, the AFM can work perfectly well in an ambient or even liquid environment.

While STM method is suitable for studying of conducting and semiconducting materials, the AFM offers the same atomic resolution capabilities but also for insulating materials.
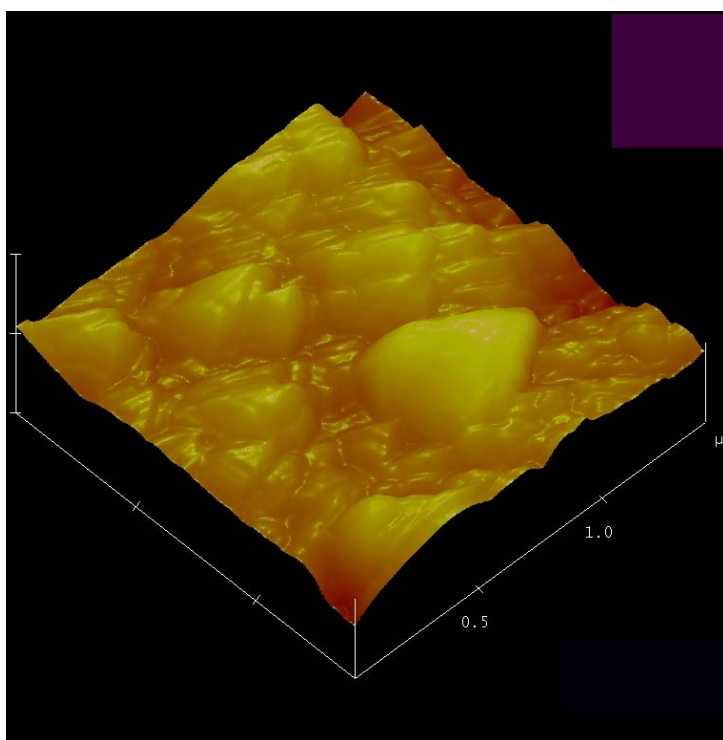

Fig. 6. AFM image of nanosized ZnS prepared by the mechanochemical synthesis.

Transmission electron microscopy (TEM)

Transmission electron microscopy is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film, or can be detected by a CCD camera. TEM is a powerful technique for a direct imaging the projected shapes of nanoparticles particularly when the particle size is small (Fig. 7).
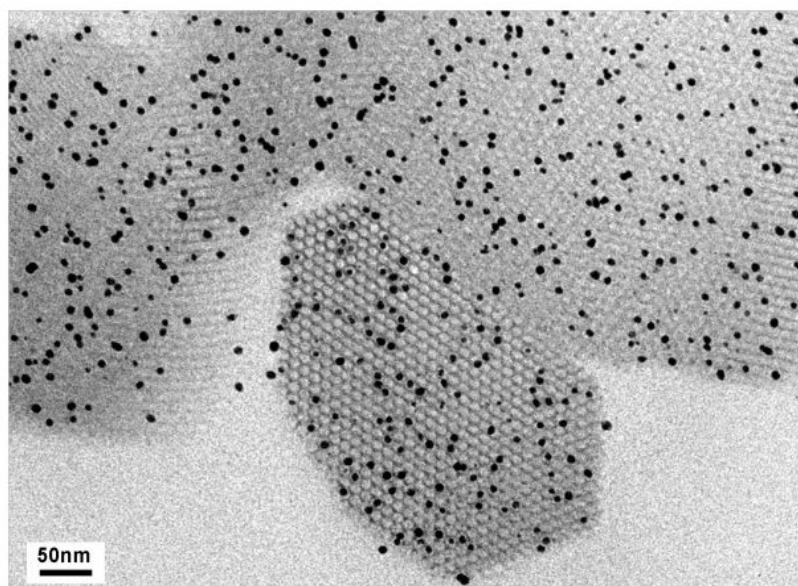
Fig. 7. TEM image of Ag – nanoparticles in the channels of zeolite (http://www.rz - berlin.mpg.de).

The whole measuring system of a modern transmission electron microscope is composed of a illumination system, a specimen stage, an objective lens system, the data recording system(s) and the chemical analysis system (Wang, 2000) (Fig. 8).

In the most powerful diffraction contrast TEM instruments it is possible to produce a diffraction pattern image which is directly analogous to the planes of atoms in a crystal. TEM is certainly the most direct method, providing real images of the particles. However, lack of contrast or overlap of particles frequently complicates the analysis of TEM images, because the particle boundaries cannot always be seen preciously. The degree of agglomeration is critical when bulk nanostructures or nanometer dispersions are desired.
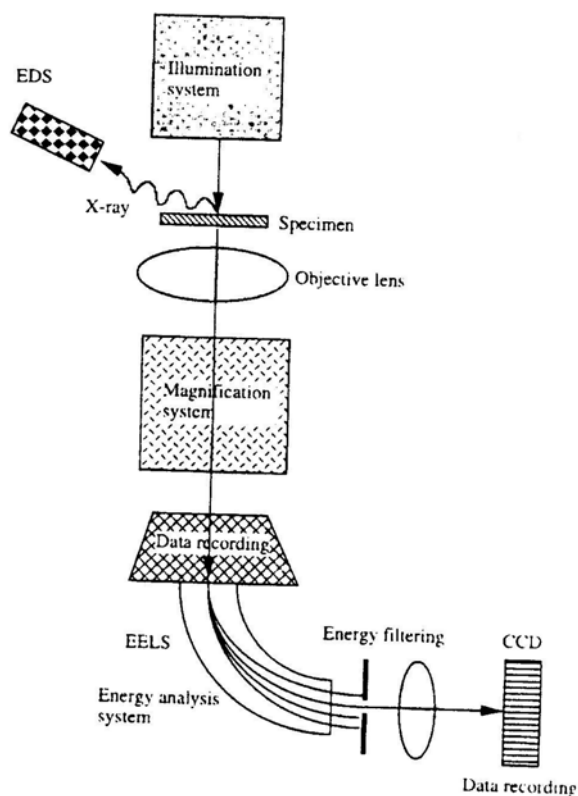

Fig. 8. The scheme of transmission electron microscope (Wang, 2000).

High – resolution transmission electron microscopy (HRTEM)

HRTEM is a technique to obtain interference patterns from very thin specimen (thickness smaller than 15 nm). To interpret the images in terms of atomic coordinates simulations are necessary. HRTEM is used on magnifications above 400 000 and is the common tool to image grain boundaries, interfaces, nanocrystals, and lattice defects at atomic scale (Fig. 9).
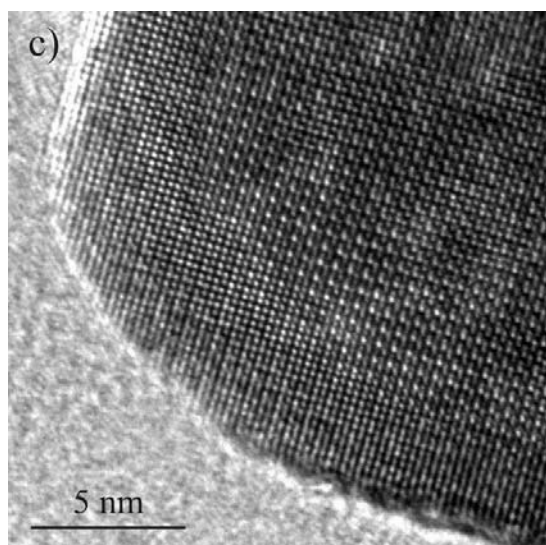
Fig. 9. HRTEM image of part of a cubic In2O3 nanocrystal (http:// www.pinna.cx/gallery/HRTEM).

Mechanochemistry in the preparation of nanosized metals (example 1)

Nanocrystalline antimony was prepared in a planetary mill under preventive atmosphere by the mechanochemical oxi – reduction reaction:

$$Sb_2S_3 + 3\,Fe \rightarrow 2\,Sb + 3\,FeS \qquad\qquad (1)$$

The phase analysis and kinetics of the reaction (1) was followed by X-ray diffractometry and magnetometry methods. Nanocrystalline antimony was obtained together with nanocrystalline iron sulphide.

The grain size of both phases were calculated from X–ray data as 19 nm and 10 nm, respectively. Antimony (JCPDS 05 – 0562) and pyrrhotite – 4H, FeS (JCPDS 22 – 1140) being the only solid state products (Fig.10) forming strongly agglomerated nanoparticles (Fig.11). The process kinetics as described by the XRD and magnetometry methods shows that more than 80 % of the reduction is over after 60 min of milling and the reaction is complete after 180 min of reaction time (Fig.12-13).
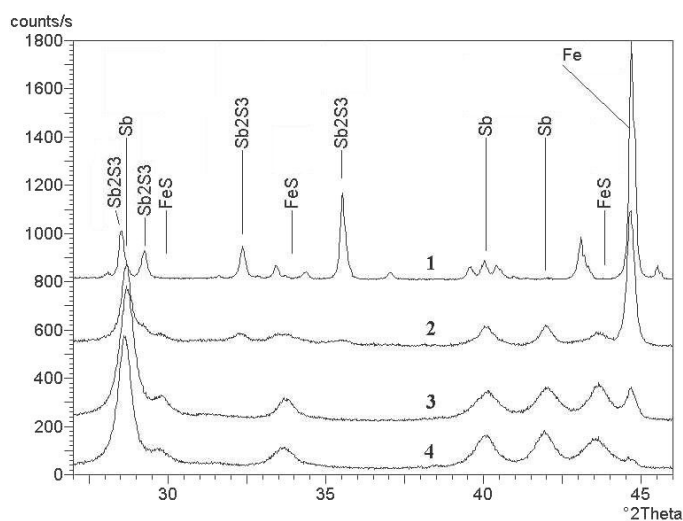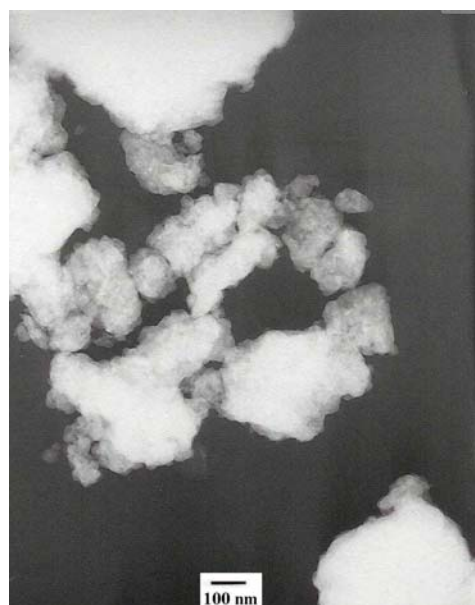

Fig. 10. XRD spectra for the reaction (1).
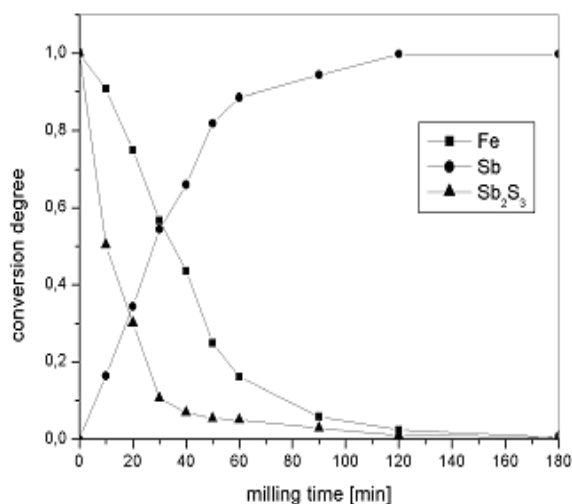

Fig. 11. TEM image for products of the reaction (1).

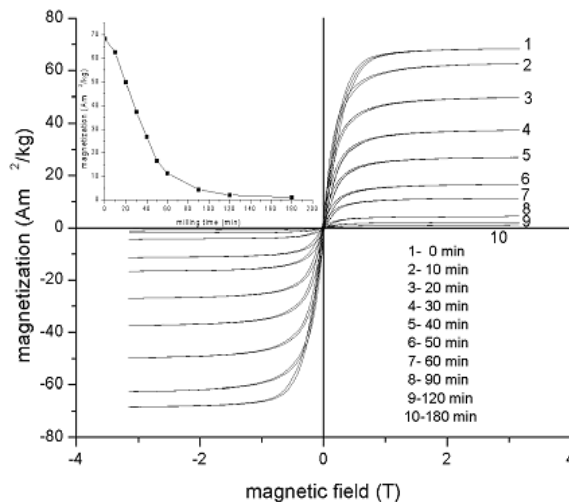*Fig. 12. The conversion degree for precursors (Sb_2S_3, Fe) and the product (Sb) for the reaction (1).*

Fig. 13. Magnetization as a function of external magnetic field for the reaction (1).

Mechanochemistry in the preparation of nanosized pharmaceutical drugs (example 2)

During a stay of one of the authors (P.B.) at the College of Pharmacy of Pusan National University was involved in the KOFST project "Mechanochemical preparation of nano – sized pharmaceutical drugs for the application in cancer therapy". The obtained results are good starting point for the future research activities. Arsenic sulphides belong to the very progressive compounds in pharmaceutical applications. In medicine, there is a great need for an effective treatment of cancer, particularly haematological cancer including leukaemia and lymphomas. Further, there is a great need for orally active anti - cancer agents. Drugs with arsenic sulphides as active components are good candidates for such demands. It is a hope of authors of this paper to continue in this research and to find the potential partners in the Korean pharmaceutical community.

Conclusions

1. The definition, several historical notes and mills as mechanochemical reactors are briefly described.
2. Theoretical background for understanding kinetics of solid – liquid reactions governed by mechanical treatment is given.
3. Scanning tunneling microscopy (STM), atomic force microscopy (AFM) and transmission electron microscopy (TEM) methods are introduced as advanced techniques for the characterization of nanosized particles synthesized by mechanochemical processes.
4. Mechanochemical reduction to prepare nanosize particles is illustrated and kinetically described.
5. The challenge for a cooperation in the field of arsenic sulphides as potential candidates for cancer therapy has been formulated.

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