Mechanochemical Technology: Application to Material Synthesis and to the Separation and Processing of Recyclable Materials from Wastes

Qiwu Zhang, Junya Kano and Fumio Saito
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University

1. Introduction

In mechanochemistry, an academic discipline with a long history, mechanical energy is used to drive chemical reactions, and the mechanisms of the resulting reactions, the changes in the characteristics of reaction products, and other phenomena are conceived from a materials science perspective in order to elucidate reaction phenomena. Its advantage is that instead of using heat to cause reactions, it changes the characteristics of substances by breaking bonds mechanically. For this reason the substances produced have a basically random structure while at the same time retaining their crystallinity, and therefore, in not a few cases they have characteristics differing considerably from those of perfectly crystalline substances. In other words, milling, ultrasound, and other mechanical energy sources engender stress that changes the state of the bonds in substances, and thus their physico-chemical properties. Because of this, substances exhibit chemical interactions with other substances (gases, liquids, solids) in their midst, and acquire characteristics different from those of the original substances. Changes induced have very unsteady states, and vary widely depending on the magnitude and extent of the stress acting on a substance, the length of time it affects the substance, and the time of release from that effect. In any event, the stress action process brings about frictional heat and other effects, but does not involve any active application of heat. Energy levels in mechanochemical processes are said to exceed thermochemical levels, [1] and many unusual phenomena have been reported. [2] In mechanical alloying, which is mechanochemistry applied to metals, unstable (active) intermediate substances are formed from mixing and diffusion achieved by the repeated deformation and folding of different types of metals, giving way to solid-state reactions that form alloys. This change differs from the route followed in heating and fusion methods. [3] Disrupting the ordered crystal structure of a substance by milling and activating it is known as mechanical activation, and reactions with nearby substances in that process are called mechanochemical reactions. In either case, physical manipulation can be achieved easily when performing subsequent chemical manipulation such as dissolution, or when heating. For example, recrystallization and pyrolysis can be achieved at low temperatures, and there are many other advantages. Milling and ultrasound exposure are simple and easy operations, but the phenomena they engender are chemical reactions that occur on the molecular and atomic levels.

As noted above, mechanochemistry research has a long history of work on both inorganic and organic substances. Recently people have undertaken to apply mechanochemistry in areas such as functional material synthesis, waste treatment, resource recycling, and global environmental conservation. And while mechanochemistry cannot do everything, it is comparatively simple to activate substances and create substances with random structures using milling, ultrasound exposure, and other processes, making it sometimes possible to express specific properties and accomplish solid-state synthesis that cannot be achieved by other methods. This suggests that mechanochemistry could in some cases make a contribution to separating substances, recycling, environmental conservation, and other areas.

The authors present some of their efforts on resource processing, functional material synthesis, new ways to recycle resources, and environmental conservation using mechanochemical phenomena, mechanical activation, and mechanochemical reactions brought about primarily with dry milling.

2. Milling Processes and Mechanochemical Phenomena

Fig. 1 shows the milling-induced change over time
in the surface area of a solid. In the initial milling phase, surface area increases with the passage of time, but the rate of increase gradually lessens and then declines after reaching a critical point. This surface area change during the milling process signifies the breaking of bonds on the new surfaces, and the increased numbers of surface atoms and molecules that have lost their joints. Disruption of the state of their bonds extends from the surface layer to the bulk, and the powdered solid is activated (by mechanical activation) and assumes a random structure. The above-mentioned decline in surface area due to long milling indicates agglomeration by fine particles caused by this mechanical activation. As a result, fine particle surfaces stabilize because their chemical potentials fall. In one form of this stabilization, milling of a single kind of solid may bring about polymorphic phase transition (mechanochemical (MC) phase transition). During MC phase transition one can observe crystal lattice strain, and the formation of amorphous phases, intermediate crystalline phases, and others. While the mechanism differs depending on the substance, the pressure, heat, and other forces that arise in the milling process bring about the accumulation of mechanical energy in the crystal lattice, and transition is promoted when that store of energy attains a level exceeding the activation energy of crystallization and transition. In not a few cases the effects of atmosphere contribute significantly to MC phase transition. For example, in the phase transition from calcite to aragonite by dry milling, the presence of even slight moisture in the atmosphere cannot be ignored. [4]

3. Solid-Phase Synthesis Without Heat

Sometimes composite compounds can be directly synthesized by wet or dry milling different kinds of substances together. In many instances a condition is that change in the free energy of formation be negative. In dry milling, the uniform mixing of different powders and the formation of mechanically activated powders proceed at the same time, and reactions occur due to the self-liberation of mechanical energy that has accumulated over the tolerance level.

Metals that readily undergo plastic deformation will become alloys when mutual diffusion occurs by mechanical alloying. Fig. 2 is the x-ray diffraction (XRD) patterns for the substance formed when mixing Mg and Ni and dry milling them in an Ar atmosphere. The pattern shows that without applying heat it is possible to synthesize the hydrogen storage alloy Mg$_2$Ni with dry milling. As the model illustrated in Fig. 3 shows, this process forms alloys through the mutual deformation (due to ductility) and repeated folding of different metal substances.

![Fig. 2 XRD patterns of the mixture of Mg and Ni milled for different periods of time](image)
When processing brittle materials the phenomenon is likely analogous, but it is hard to elucidate the mechanism of the phenomenon in detail owing to the difficulty of visualizing the alloying process as in the case of metals. But because there is little resultant plastic deformation, it seems likely that the materials undergo a solid-state reaction by turning into fine particles that mutually diffuse on the micro level as they enlarge their interfacial areas. For example, when CaO and TiO\(_2\) (rutile and anatase) were milled for a short time, small CaTiO\(_3\) crystals formed after the passage of adequate milling time, even though crystallization was insufficient. [5] When processing time was lengthened, crystal nuclei grew and good crystallization resulted. **Fig. 4** is a photomicrograph taken with a high-resolution transmission electron microscope after 5 h of milling when crystal nuclei had grown to a certain extent. Crystal particles are 20 to 30 nm large, and one can clearly distinguish particle boundaries and the spaces between lattice planes.

In wet milling as well, MC reactions will occur if the right conditions exist. For example, in the presence of water it is possible to directly synthesize a number of calcium silicate hydrates from silica and slaked lime. [6, 7] Although one can only speculate about the reaction mechanism, the possible explanation is that the localized high-pressure state of a high-concentration solid slurry squeezed between media resembles the conditions for hydrothermal treatment. [8]

**4. Material Synthesis that Combines Heating**

In ceramics processing it is known that if materials are mechanically activated by milling, and then molded and sintered while maintaining activation, the sintering temperature that yields a single phase is far lower than when milling is not involved. With kaolinite, for instance, the crystal structure is easily changed by milling it alone, and XRD produces a broad pattern that is amorphous. Normally the temperature at which kaolinite dehydrates by heating is about 800 K, but if its structure is first changed by milling, that temperature is low, and depends on the extent of milling. This means that kaolinite is easily broken down (made amorphous) by milling. It is known that aluminum hydroxides (Al(OH)\(_3\)) like
gibbsite also exhibit the same kind of changes. Therefore if kaolinite and gibbsite are mixed to assume the composition of mullite ($3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$), milled to change the crystal structure, and then heated, a mullite single phase will be obtained at a temperature that is far lower than that needed when milling is not used. [9] It is likely that in the milling process the composition becomes progressively more uniform on the micro scale as the kaolinite-gibbsite interaction brings about conversion into fine particles and the change of the crystal structure, thereby forming a mullite single phase at low temperature due to the interaction. Similar examples are seen in other kinds of ceramics processing. However, although activation by milling advantageously promotes sintering, reactions sometimes proceed quickly in heating processes because materials are activated, thus making optimum milling control necessary to obtain sintered products of fine texture.

5. Natural Resource Processing and Molecular Design

Milling is capable of mineral processing and molecular design of various kinds. As a representative example, we shall discuss the process in which the dry milling of gypsum dihydrate ($\text{CaSO}_4\cdot2\text{H}_2\text{O}$) and quick lime forms a powder containing hemihydrate gypsum, i.e., plaster. The powder formed by milling hardens when water is added because hemihydrate gypsum has formed. Because gypsum dihydrate is comparatively stable, usually a temperature of about 400 K is required to make plaster by heating, and milling in air cannot easily make gypsum dihydrate into hemihydrate gypsum. But when milling gypsum dihydrate after mixing with quick lime, as above, some of the gypsum’s water of crystallization (clustered water) is expended in digesting the quick lime, bringing about the following molecular design reaction and yielding hemihydrate gypsum and slaked lime.

$$2\text{CaSO}_4\cdot2\text{H}_2\text{O}+3\text{CaO} = 2\text{CaSO}_4\cdot0.5\text{H}_2\text{O}+3\text{Ca(OH)}_2$$

(1)

This quick lime-induced movement of clustered water in minerals is seen in other clay minerals as well. Here too is an example of how the simple operation of milling is capable of the molecular design of minerals on the micro scale.

Mechanochemical reactions can be used to change the valuable substances in minerals into an easy-to-extract form and recover them. For instance, to make and refine $\text{SrCO}_3$ from celestite (which is mainly $\text{SrSO}_4$), the current process entails transforming celestite into a sulfide by heating with coal, and then carbonating it. But according to Zhang, et al.: [10]

1) Perform dry mechanochemical processing of celestite and solid NaOH to form $\text{Sr(OH)}_2$.

$$\text{SrSO}_4+2\text{NaOH} = \text{Sr(OH)}_2+\text{Na}_2\text{SO}_4$$

(2)

2) Expose reaction product to air so $\text{Sr(OH)}_2$ becomes $\text{SrCO}_3$.

$$\text{Sr(OH)}_2+\text{CO}_2 = \text{SrCO}_3+\text{H}_2\text{O}$$

(3)

3) Recover $\text{SrCO}_3$ that is not water soluble (whose solubility is extremely low) by washing to remove the soluble substance ($\text{Na}_2\text{SO}_4$) from the reaction product (refining).

The carbonation process (step 2) is necessary because reverse reaction back to $\text{SrSO}_4$ occurs when washing the product of step 1 directly. In this process, therefore, both dry mechanochemical processing and carbonation have a major effect on the final $\text{SrCO}_3$ yield. The same mechanochemical processing using no heat, i.e., milling, carbonation, and washing, can be applied to make and refine $\text{BaCO}_3$ from barite (which is mainly $\text{BaSO}_4$), but care is needed in choosing the solvent used in the washing (extraction) stage, and one must keep the concept of solubility product in mind. [11] This process is also effective when making hydroxides from magnesite ($\text{MgCO}_3$), dolomite ($\text{CaMg(CO}_3\text{)}_2$), and other carbonate ores, and when obtaining and separating soluble tungsten from scheelite ($\text{Ca W}_4\text{O}_{12}$) and other tungstate ores. In these processes, however, the overall process can be simplified because step 2 above is unnecessary. [12, 13] This process is especially effective for reaction systems that cannot occur in the liquid phase.

6. Recycling Municipal Wastes and Recovering Recyclable Materials

(1) Disordering the Crystal Structure

(a) Recovery of rare earths from discarded fluorescent tubes [14]

Three-wavelength fluorescent tubes contain rare earths (Y, Eu, La, Ce, and Tb), and methods need to be developed to recover the rare earths from the many tubes that are discarded. The authors developed a method that combines dry MC processing and extraction with a weak acid to leach the aforementioned rare earths from waste fluorescent material.
without applying heat. Fig. 5 shows the XRD patterns for the products obtained by dry milling fluorescent material (three-wavelength type) with a planetary mill (Fritsch, Pulverisette-7). The fluorescent material comprises the blue phosphor BaMgAl_{10}O_{17}:Eu^{2+} (BAT), the two green phosphors LaPO_{4}:Ce^{3+}, Tb^{3+} (LAP) and CeMgAl_{10}O_{19}:Tb^{3+} (MAT), and the red phosphor Y_{2}O_{3}:Eu^{3+} (YOX). Overall, diffraction peak intensity decreases as milling proceeds, and the peak for YOX especially decreases. Fig. 6 shows the relationship between the yield (or leaching percentage) and milling time for each rare earth leached in 1 N hydrochloric acid. Despite the differences between rare earths in their leaching rates, yields are 80% or more when milling time is long. In research until now, rare earths have only been extractable from fluorescent material at 400 K and concentrated strong acids, but they can be extracted easily with preprocessing by milling because milling the phosphor fluorescent material makes the crystal structure of the rare earth compounds into disordered systems. Rare earth leaching rates can be calculated from \( E_N \), the specific collision kinetic energy of the ball media obtained from a ball mill simulation based on the particle element method (collision kinetic energy divided by sample weight; in this example only the normal component). By seeking \( E_N \) from any desired mill operation conditions in a simulation, one can predict rare earth leaching percentages under those conditions, making it possible to determine optimum milling conditions and to enlarge mill size. [15] A method for recovering rare metals from acid solutions in which they are dissolved has also been perfected.

(b) Other examples

There are a number of other examples of recyclable material recovery from municipal wastes through crystal structure change. Some of them are: recovery of Co and Li from lithium secondary battery positive electrode scrap and [16] recovery of In from ITO scrap. [17] For lack of space here, readers are encouraged to see the citations for details.

(2) Examples of Using Mechanochemical Reactions

(a) Vanadium recovery from EP dust [18]

The heavy oil combustion soot emitted by oil-fired thermal power plants contains much ammonium sulfate. Known as EP dust, its main constituents include about 62% ammonium sulfate and 28% carbon, and it also contains a small amount, about 1.5%, of vanadium. Due to the need for a way to efficiently recover the vanadium, the authors developed a method that can extract vanadium with water through the use of dry MC processing. Fig. 7 plots the relationship between V yield and milling time when leaching soluble V compounds with distilled water after dry milling EP dust with a planetary ball mill, a vibration ball mill,
and a tumbling ball mill. The V yield was over 90% after about 45 min of milling with the planetary mill, but decreased with further milling. Although there were differences in the milling time needed to obtain the same leaching percentage with the vibration and tumbling mills, the trends were the same. Soluble V compounds form through MC reactions between the V2O5 and ammonium sulfate in the EP dust, but wet processing offers no hope of raising the V yield. This is perhaps because in wet milling it is hard to apply enough mechanical energy to the EP dust, and because mechanical activation of solid surfaces is soon mitigated in a liquid phase. Fig. 8 [19] presents the results obtained when converting the milling time on the horizontal axis of Fig. 7 using the ball media specific collision energy obtained with the particle element method simulation (calculated from the resultant force of both the normal and shearing components). Although the curves for the three different mills were far apart in Fig. 7, here they nearly come together. This suggests that MC reactions are governed by the kinetic energy of the ball media, and shows that simulation-generated information is effective, for example, in predicting MC reaction yield, and in determining optimum operating conditions or the operating conditions for enlarged mills.

(b) Dechlorination of polyvinyl chloride (PVC) [20]

Because of its excellent chemical characteristics, low manufacturing cost, and other reasons, PVC is produced in large quantities and is used in a broad range of fields from industry, agriculture, pharmaceuticals, and other industrial applications to everyday goods. Discarded PVC is disposed by incineration or landfilling, but the former gives rise to concerns about dioxins, and the latter involves the difficulty of securing landfill space. And there are many other problems. The authors developed a process to dechlorinate PVC without heating by combining MC treatment with washing and filtration. In the MC stage, CaO or other dechlorination agents are added. The agent is determined by taking into account factors including reactivity with PVC, economy, ease of handling, and separation from the milled product. Fig. 9 shows the XRD patterns obtained when using CaO as the dechlorination agent, preparing an equimolar mixture with PVC, and MC processing. From this figure one can see that the longer the processing time, the more CaOHCl was formed. This is a radical reaction. Fig. 10 shows the relationship between the PVC dechlorination percentage and MC processing time for an equimolar mixture of CaO with PVC, and when CaO is mixed two-fold and four-fold in excess. The mixtures were MC processed, then washed and filtered, and chlorides separated from the product. The greater the amount of CaO, the larger (better) the dechlorination percentage and the faster the reaction rate. The chlorides formed by this reaction can be removed by washing, and the residue is a mixture of partly dechlorinated polymers and unreacted sub-
substances. To achieve 100% dechlorination it is essential to add the dechlorination agent to excess and perform MC processing to an appropriate degree. In addition to CaO, many other inorganic compounds, steel slag, and the like can be used as dechlorination agents. The dechlorination percentage can be estimated from the ball collision energy determined by a ball mill simulation.

7. Making a Contribution to Environmental Conservation

(a) Detoxification of PCBs (liquid) without heating [23]

PCBs have characteristics such as excellent electrical insulation, flame retardancy, and chemical stability, but they are highly toxic because they accumulate in the body. Their use is now prohibited, but there is still no effective disposal method, and they are stored along with contaminated oils in large quantities under strict conditions. Proposed PCB disposal methods include heating and chemical processing, but these are not necessarily adequate due to cost, safety, and other reasons. By contrast, there are expectations for mechanochemical methods because operational procedures are easy due to the lack of heating, and because they are safe. Fig. 11 shows the relationship between milling time and PCB breakdown (dechlorination) when milling a mixture of PCB and CaO. ESR analysis indicates that radicals form, and that they survive for the quite long time of several months.

(b) Detoxification of dioxin-contaminated soil [24]

Dioxins are hazardous substances found in incinerator ash and other places. Social concern is quickly rising over their dispersion into the soil and other parts of the environment. Methods of detoxifying dioxin-contaminated soil include the GeoMelt™ and catalytic methods, but just as with PCB disposal,
These methods involve problems of safety and economy, and have not been practicalized. For that reason there are increasing expectations for mechanochemical methods. The authors' group has performed detoxification tests on contaminated soil, and some of the results appear in Fig. 12, which indicates that it is possible for mechanochemical processing to reduce dioxin toxicity to zero (i.e., not detectable).

![Dioxin breakdown percentage according to milling time](image)

**Fig. 12** Dioxin breakdown percentage according to milling time

8. Conclusion

This paper has discussed results and methods pertaining to one use for mechanochemical technology involving the mechanical activation manifested by dry milling and the synthesis of materials using mechanochemical reactions, followed by the recovery of recyclable materials by extraction with solvents, thereby confirming the technology's effectiveness in resource recycling and environmental conservation. At the MC processing stage, mechanical activation and the driving force behind reactions are unsteady, and we lack a detailed understanding of the changes and reaction mechanism at that stage. Products are influenced by atmosphere, operating conditions, and other factors during processing, and work still remains to be done in this area. In the synthesis of materials it is necessary to avoid the problem of abrasion dust from the mill mixing into the product, but this avoidance is to an extent possible. This contamination problem can be ignored when processing wastes, and in fact contaminants sometimes effectively act as a milling assistant. MC processing can to an extent process large volumes, which has been considered difficult until now, and in some cases it has become practical. It will be necessary to show some actual examples (material or process development) of MC processing as a means for synthesizing materials, processing wastes, and recycling resources, and one good way of doing this is combining MC processing with subsequent chemical processing (such as heating, dissolving, or leaching). Important to facilitating practicalization will be not only demonstrating the method's effectiveness on a variety of wastes, but also taking factors such as the economy of processes into account. While anticipating even greater future contributions by mechanochemistry to material synthesis, resource recycling, and environmental conservation, we intend to actively move ahead with seminal and pacesetting basic and practical research that will lead to the technologies of the future.

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14 KONA No.19 (2001)
Qiwu Zhang

Qiwu Zhang received the degrees of BS and MSc in Mineral Processing from Wuhan University of Technology, China in 1984 and 1987, respectively. He has worked at Zhengzhou Institute of Multipurpose Utilization of Mineral Resources, China from 1987 to 1992. He joined Prof. Saito's group in 1992 and took his Ph.D. degree at Tohoku University, Japan under the supervision of Prof. F. Saito in 1997. He has started to work as a Research Associate at Institute for Advanced Materials Processing (IAMP), Tohoku University since 1997 to the present time, although the Institute has grown to be created a new one named Institute of Multidisciplinary Research for Advanced Materials (IMRAM), which became the biggest Institute in Tohoku University in April of 2001. He has been assigned to research work on mechanochemistry of different kinds of materials, aiming its engineering applications.

Junya Kano

Junya KANO received the degrees of BS in Chemical Engineering and MSc in Industrial Chemistry at Doshisha University in 1990 and 1992, respectively, and received his Ph.D. from the same university in 1997 in the area of Chemical Engineering. His main research work on his Ph.D course was computational simulation based on the DEM, in connection with monitoring and visualization of the flow of particles in different types of powder storage bins, tanks and a like. He has started to work with Prof. F. Saito as a Research Associate at IAMP (now, IMRAM (2001-)), Tohoku University since 1995. One of his research works focuses on development of computational simulation technique enabling to simulate particles flow in powder handling devices such as mills, hoppers and tanks. The second of his works is aimed on the optimum design of powder handling devices by a theoretical approach based on the simulation work. The final part of his works covers powder processing, looking at energy and environmental conservation. This brings him to estimate powder behavior and mechanochemical phenomena by harmonizing his simulation works with the experimental ones, leading to establishment of scaling-up law for the devices.

Fumio Saito

Fumio Saito received the degrees of BS and MSc in Chemical Engineering from Yamagata University, Japan in 1970 and 1972, respectively. He got his Ph.D. in Mining and Minerals Engineering at Tohoku University, Japan in 1982. He had moved his working place at Yokohama National University, Japan, and worked for about 8-years as a lecturer and an Associate professor. During his stay at Yokohama, he got a chance to collaborate with Prof. A.W. Nienow at the University of Birmingham, UK as a research fellow supported by British Council for more than one year. After his back to Japan, he was promoted as a full-time professor at Institute of Mineral Dressing and Metallurgy (now, IMRAM), Tohoku University in 1993. He has been working as a Visiting Professor at Ecole des Mines d’Albi-Carmaux, France supported by French Government since April to December, 2001. His main interests cover mechanochemical engineering for human life, molecular design by grinding, nano-technology in comminution and nano-structural control by an arc-plasma method.