

Dry and reactive

Reactive dry-milling for environmental protection

This article describes reactive dry milling technology by giving an overview of various devices and some examples of proven reactions. The goal is to protect the environment and save money by using optimized reaction methods.

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Production unit with a 100 liter chamber. The cross sections through the grinding chamber visualize the working principle. The rotor is the tool to transfer the kinetic energy into the grinding media and these transfer further into the powder materials.

Reactive (dry) milling is still not widely used, even though mechanical alloying has a long tradition and is known to permit waste-free inorganic or, more recently, organic synthesis. It therefore compares favourably with those contrast solution reactions that tend to be incomplete and result in subsidiary reactions. The purification required to get rid of the waste caused by these subsidiary reactions is often much more expensive than synthesis itself. Another alternative, that of very high temperature synthesis using inorganic solid or melt reactions, requires a lot of energy, which can be saved if reactive milling succeeds at ordinary temperatures. The nanoscopic nature of solid-state chemical reactions has recently been studied using supermicroscopic techniques such as atomic force microscopy (AFM), scanning near-field optical microscopy (SNOM) and nanoindentation/nanoscratching. A consistent mechanism has been found for non-tribochemical reactions with far-reaching molecular migration along "easy" paths within the crystal. While there is a three-step mechanism of phase rebuilding, phase transformation and crystal disintegration for molecular crystals, organic polymers or infinite inorganic covalent crystals undergo tribochemical reactions involving the mechanical breakage of covalent bonds. The extremely unsaturated fresh surfaces which occur upon cleavage of the crystals are lo-

cal plasmas which allow for all kinds of chemical reactions at low temperatures. While there may be borderline cases between these various mechanisms with salts and metals, normal non-polymeric organic molecules cannot break covalent bonds by mechanical interaction (milling) unless very high forces are applied.

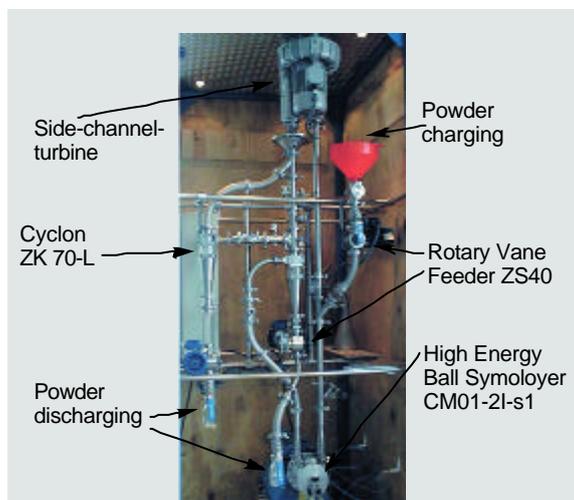
Milling techniques

Various types of industrial mill are currently being used for a number of commercial applications. As vibration mills have to move the mass in the grinding chamber, they are limited in respect of size and are difficult, if not impossible to operate under controlled atmospheric conditions or with a closed circuit. The same is true of simple (drum-)ball mills with a rotating vessel. Jet mills use large streams of air or inert gas which limits their use in reactive milling, while the absence of grinding media does not lead to significant kinetic effects. Bead mills, whether horizontal or vertical, do not have a significant kinetic impact, since there is no high-level relative acceleration of the grinding media. They produce shear and friction effects but not collision. Planetary ball mills and shaker mills are limited to laboratory size. The most suitable choice are horizontal rotary ball mills that can

be operated dry with the grinding media moving at a high relative velocity (up to 14 m s^{-1}) that cannot be reached by other types of mill (up to 5 m s^{-1}) under controlled conditions such as under vacuum or inert gas or in closed circuits.

Horizontal rotary ball-mill

Horizontal high-energy ball mills are known to be used for mechanical alloying (MA), high energy milling (HEM) and reactive milling (RM) in both industry and academia. These mills have the highest relative velocity for grinding media, which in turn results in a high level of kinetic energy transfer, an intensive grinding action



Pilot set-up of a high energy ball mill (Simoloyer VS01a) with air/inert carrier gas-cycle and powder separation/classification system.

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and short processing times. Contamination of the processed powders by the milling tools is naturally lower since the process is based on the collision of grinding media rather than on shear and frictional interaction, which usually leads to higher abrasion. Since the grinding media are accelerated by a horizontal rotor inside the grinding vessel, these devices do not have to move large masses as do vibration mills. The systems currently available have a grinding chamber capacity of between 0.5 and 400 l and larger volumes are likely to be possible too. The various environmental applications include the MA of various metals and/or ceramics, room temperature inorganic synthesis, waste-free organic chemical solid-state synthesis with 100% yield and the decontamination of dangerous residues using the tribochemical effect of milled sand (SiO₂). These procedures are both economical and environment-friendly as in most cases, they can be operated semi-automatically by being combined with a continuous or semi-continuous (auto-batch) powder separation system. Here, we will report on some typical applications of HEM/RM and – briefly – of HRM.

The most important criteria are the safe, continuous and complete collection of the powder produced. There must be no losses and no environmental damage.

Given these requirements, collection in a cyclone with a closed gas circuit is the method of choice, especially if continuous or semi-continuous (auto-batch) operation is desired for larger scale production. The experimental unit VS01a, which was originally designed and used for the controlled and continuous production of ductile metal flakes and for the rapid, particle-size reduction of brittle solids (such as enamels and glass fluxes) is therefore well suited to the job of reactive dry milling.

The figure on previous page shows a unit based on a closed, carrier-gas system, driven by a side-channel turbine adapted to a Simoloyer CM01-2ls1 and featuring 2 cyclones for separation/classification, some valves for circuit control, rotary vane feeders with airlocks, a filter, evacuation pump, computer and electrical controllers a special separation unit and other units. The system has two connected circuits – a primary circuit and secondary circuit. The secondary circuit is needed only for the processing of ductile metal flakes and is therefore closed by a valve installed between the two cyclones. If the first cyclone is used only for the separation of solids in the multiphase flow coming out of the HEM grinding chamber, the bypass between the rotary vane feeder and junction tube can be disconnected and used as the discharge route. If no inert atmosphere is needed, the airlock parts on the injection

side can be replaced by a simple plastic funnel.

This system can be operated successfully in auto-batch mode using the carrier gas to transfer the starting powder into the grinding chamber. After each batch has been processed, the carrier gas flow is again used to remove the milled powder from the vessel. The powder is then separated from the gas flow inside the cyclone. Since the carrier-gas circuit is a closed circuit, the gas is fully recycled and used again for the next operation. This also solves the problem of the relatively long time needed for discharging and so makes the mill even more efficient.

In continuous or semi-continuous operation, the starting powder is fed continuously into the unit, where it is transferred continuously by the carrier gas through the Simoloyer vessel and into the separation system. Up to now, this principle could also be applied to those batch operation processes that had processing times in the range of several minutes, such as the rapid particle-size reduction of enamels. The immediate and continuous removal of the fine particle fraction from the vessel means there is no sedimentation, which in turn improves the kinetics of the system tremendously. For these materials, therefore, we can achieve extremely short processing times in the range of just a few seconds.

For applications in chemical engineering, the complete recovery of the milling product without any significant contamination from the milling tools is paramount in both continuous and batch operation.

Short processing times are therefore of the essence, for both synthesis and industrial production. Larger mills and larger carrier-gas systems are expected to work equally well.

High energy milling

Mechanical alloying (MA) has been described as a process in which powder particles are subjected to repeated deformation, fracture and cold welding caused by the high-energy collisions of grinding media in the milling process. New materials with new properties that cannot be achieved conventionally can be obtained using this method. Furthermore, the physical state of the materials (e.g. nanocrystalline or amorphous) can be adjusted by structural design.

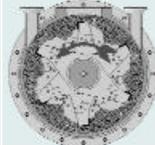
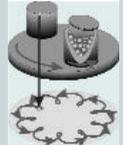
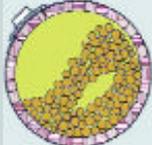
High energy milling (HEM) and reactive milling (RM) work on the same processing principle, which can be varied depending on the processing target, the transformation effects caused by kinetic energy and starting materials.

The various procedures can be described as High Kinetic Processing (HKP), it being above all the collisions of the grinding media that cause the transfer of kinetic energy from the milling tools into the powder (see also Figure on next page). The basic equation shown here describes the relationship between kinetic energy (E_{kin}) and the mass (m) and velocity (v) of a ball:

$$E_{kin} = \frac{1}{2} m v^2$$

The maximum relative velocity of the grinding media is the most important factor determining the kinetic energy. One ty-

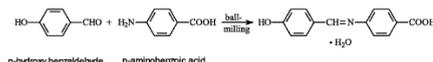
Comparison of most of the corresponding devices used for HKP

device	Simoloyer	Planetary Ball Mill	Attritor	Drum(ball)mill
max. diameter [m]	0.9	0.2	1	3
max. total volume [l]	400	8	1000	20000
max. rel. velocity [m/s]	14	5	4.5-5.1	<5
graphic (cross section)				

Important applications/products of HKP

Applications of High Kinetic Processing (HKP)		
High Energy Milling	Mechanical Alloying	Reactive Milling
surface, shape, particle size	alloys (pseudo)	chemical reactions
flakes (particle deformed powder)	nanocrystalline materials	contact materials
particle coating (LPS, S)	amorphous materials	nanocrystalline materials
nanocrystalline materials	oxide dispersion strengthened alloys	mechanochemistry
highly dispersed materials	iron and oxide based magnetic materials	solid state syntheses
soft magnets	bearing materials containing solid lubricants	hydrides - dehydrides
particle size reduction (e.g. enamel, ceramics)	ceramic-metal composites (MMC, CMC, MMC, CCC)	activation of catalysts

the liberated CO₂ was released by a safety-valve. The formation of covalent bonds is even more important in organic synthesis. Imines (Schiff's bases) are versatile building blocks that have been quantitatively synthesized by reactive milling. The scaling-up of *p*-hydroxybenzaldehyde condensation with *p*-aminobenzoic acid yielded 200g batches of the substituted solid, imine hydrate, which could be dried under vacuum and at a high temperature if desired.



Tribochemistry with oxides

Ball milling is very versatile. Another technique that uses the same equipment is tribochemical milling with the mechanochemical breakage of the covalent bonds of infinite covalent crystals, which are present in many oxides. Sand, for example, consists of quartz (SiO₂), which forms an infinite covalent crystal lattice. If the crystal is split, all the Si-O bonds are broken and the freshly cleaved faces are completely unsaturated with free -Si and O-Si- surface radicals and other high-

ly reactive species. These represent a local plasma, which tends to be saturated immediately, a fact that has been used for more than 5000 years to ignite fire by striking a flint stone. Such tribochemistry should also be useful for the mineralization of dangerous environmental poisons such as chlorinated aromatics (PCBs, etc.), tin alkyls and the like, which could be milled together with sand. Such a process would be much easier and safer than the reductive removal of halogen from polyhalogenated aromatics by milling sea sand with excessive quantities of metallic sodium or magnesium (after thermal drying, followed by drying with calcium oxide) and ethanol in planetary ball mills (typically 5 h) or eccentric swing mills (typically 90 min). This process produces not only the corresponding (aromatic) hydrocarbons, but also hazardous hydro-

gen that forms explosive mixtures with the air.

Conclusions

High energy milling is an environment-friendly and versatile method that can be performed on kg scale and scaled up as required. Its applications include mechanical alloying, waste-free inorganic room temperature synthesis, waste-free organic solid-state synthesis and the decontamination of dangerous residues by tribochemistry. Horizontal high energy mills that work with a carrier gas are now available with capacities in excess of 400 litres. Their application in industrial production and decontamination in the various fields mentioned in this survey is therefore only a matter of time, as environment-friendly new processes become increasingly vital to the long-term well-being of our environment.

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