Dry and

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.

eactive (dry) milling is still not widely used, even though mechanical al-Moying 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 be operated dry with the grinding media organic molecules cannot break covalent inert gas or in closed circuits. bonds by mechanical interaction (milling) unless very high forces are applied.

Milling techniques

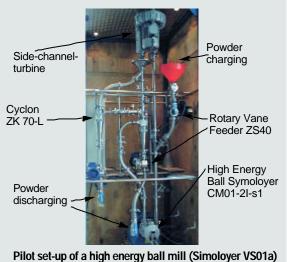
rently being used for a number of com-tive milling (RM) in both industry and acamercial applications. As vibration mills demia. These mills have the highest relahave to move the mass in the grinding tive velocity for grinding media, which in chamber, they are limited in respect of si- turn results in a high level of kinetic enerze and are difficult, if not impossible to ope-gy transfer, an intensive grinding action

rate 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

chemical reactions at low temperatures. moving at a high relative velocity (up to While there may be borderline cases bet- 14 m s⁻¹) that cannot be reached by other ween these various mechanisms with types of mill (up to 5 m s⁻¹) under controlsalts and metals, normal non-polymeric led conditions such as under vacuum or

Horizontal rotary ball-mill

Horizontal high-energy ball mills are known to be used for mechanical alloying Various types of industrial mill are cur- (MA), high energy milling (HEM) and reac-



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 I 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 environmentfriendly 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, particlesize 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 CM01-2Is1 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 Simologer 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 se-

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 ($E_{\rm kin}$) and the mass (m) and velocity (v) of a ball:

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

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 [I]	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		

pical example of practical importance that demonstrates the effects inherent in the figure on this page has been described in detail for the following system:

 $24 \text{ Ti} + \text{Al}_{11} \text{Nb R Ti}_{24} \text{Al}_{11} \text{Nb}$

The influence of the milling parameters has been evaluated and the processing route for the cyclical operation of CMBmaterials basically invented. The use of this method has made it possible to reduce significantly the tendency of Ti-Al-based material to agglomerate and stick during the dry milling process, which in turn led to an increase in powder yield from <4% to 80%. Similarly positive effects have been found in the Ti-Ni system and in the processing of various ductile metal flakes. In 1999, Kim et al. investigated the differences between cyclical and continuous operation in the Fe-Co system and found significant differences in particle-size and above all crystallite-size reduction.

If the processing method described is applied for particle- and/or crystallite-size reduction or for particle deformation (e.g. flakes) in single systems, then it can be described as HEM. The goal may be to obtain a specific particle geometry e.g. for the rapid and large-scale production of ductile metal flakes in dry processes using no solvents and very little energy, as is required for paint pigments, conductive pastes and anti-corrosives. Furthermore, the rapid particle-size reduction of brittle solids such as enamels or glass fluxes has recently opened up new areas of application.

The term RM can be used if, during milling, a chemical reaction is both intended and observed. This method can be used to obtain a dispersion of ultra-fine (nano-scale) crystals and/or a homogeneous dispersion of transformed phases in a matrix. One typical example of practical importance is that demonstrated in the Ag-Sn system.

 $Ag_3Sn + 2 Ag_2OR 7 Ag + SnO_2$

The CMB-behaviour of this ductile system necessitates a cyclical process. RM also has the advantage of being cheaper owing to its use of Ag₂O instead of Ag as a starting material. These RM processes are often environment-friendly as much as they do not produce any waste. A summary of some of the most important HKP applications and products is provided in the table on page 25.

Inorganic synthesis

Numerous binary high-melting insoluble salts are routinely synthesized at very high temperatures either by heating or melting the components or by precipitation from aqueous solutions. In many cases, inorganic synthesis can now be accomplished at room temperature or slightly higher temperatures, if the components

have first undergone high-energy reactive milling. Some examples of this new technique are presented here.

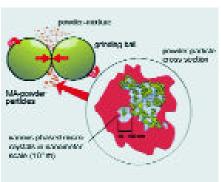
Copper powder and sulphur in a stoichiometric ratio of 2:1 are combined by HRM to produce copper(I)sulphide, which is a useful solid for the production of luminophors. Similarly, copper(II)sulphide can be obtained by using a stoichiometric ratio of 1:1. Both products are free of water. While x-ray powder diffraction shows the peaks of Cu₂S and CuS, respectively, most materials occur in x-ray amorphous form:

$$2 Cu + SR Cu2S$$

 $Cu + SR CuS$

Such waste-free, low-temperature synthesis may be useful and one could envisage many applications of sulphur for the synthesis of metal sulphides.

The copper-sulphur reactions were performed using ZrO₂ balls, because elementary sulphur has a corrosive effect on both iron and steel balls. Unlike the uniform reactions with copper, iron and sulphur in a stoichiometric ratio of 1:1 did in fact form iron(II) sulphide (FeS), some pyrite (FeS₂) and a material that has yet to be identified with unexpected *d*-spacings in the x-ray powder diffractogram at 3.8555, 3.4534, 3.337, 3.2235, 2.8475, 2.6203, 1.7254 Å. HRM may nevertheless be useful in this case, as FeS is a common source of hydrogen sulphide, when treated with



Schematic of the collision as the main event of energy transfer.

10% HCI (pyrite remains undissolved and stable under these conditions). Sulphur can be profitably reduced by dry milling as the $\rm ZrO_2$ balls, stainless steel housing and stellite rotor of the Simoloyer can all withstand this treatment more or less intact.

The co-milling of stoichiometric quantities of iron powder and sulphur up to 82% conversion of the sulphur produced 58% FeS, 26% FeS₂ and 16% unreacted Fe. The unknown product liberated H₂S and was thus added to the yield of FeS. This reaction is not clean, therefore, although it is

clear that HRM results in the formation of new phases. FeS is not an intermediate in pyrite formation, because FeS₂ cannot be obtained by co-milling FeS and S. Yet another phase is formed in this experiment. The x-ray powder diagram corresponds closely to the one reported for trigonal smythite (Fe_(1-x)S), except that there is a continuum. Furthermore, pyrite corrodes iron (powder or turnings) under HRM con-Aggregated sub-micrometer grains were formed that did not produce new peaks in the x-ray powder diagram on a strong continuum (some sharp residual pyrite signals were detected) and the application of 10% aqueous HCI did not liberate significant quantities of H₂S. The complexity of the important iron/sulphur system is therefore present in HRM as well and further phases may be created.

Gas/salt reactions

Inorganic reactions between gases and salts are also interesting. If a passivating cover is formed on the crystals, then milling will be needed to constantly create fresh surfaces. One example of this is the deoxygenation of nitrogen dioxide by sodium nitrite to produce nitrogen oxide. Performed in 200g batches (2.9 mol), this process also produced the more precious reactive gas in its pure form:

NO₂ + NaNO₂ R NO + NaNO₃

The Simoloyer was evacuated, filled with NO_2 (0.8 bar, 0.07 mol) and operated for 30 min. The colourless gas was transferred to a pressurized cylinder and the reaction allowed to continue with additional NO_2 until the sodium nitrate was used up.

The solid-state neutralization of acids may also be of technical importance, as many processing steps can be saved if solvents are avoided. The HRM of 200g batches of stoichiometric mixtures of L-(+)-tartaric acid and sodium carbonate, for example, liberated carbon dioxide at 1300 rpm in the water-cooled Simoloyer as well as producing clean sodium tartrate dihydrate in the form of a powder.

$$\begin{array}{c} \text{COONa} \\ \text{H} \stackrel{\bigcirc}{\longrightarrow} \text{OH} \\ \text{HO} \stackrel{\bigcirc}{\longrightarrow} \text{H} \\ \text{COOH} \\ \end{array} + \text{Na}_2\text{CO}_3 \longrightarrow \begin{array}{c} \text{COONa} \\ \text{H} \stackrel{\bigcirc}{\longrightarrow} \text{OH} \\ \text{HO} \stackrel{\bigcirc}{\longrightarrow} \text{H} \\ \text{COONa} \\ \end{array} + 2 \text{ H}_2\text{O} + 2 \text{ CO}_2$$

Sodium tartrate is a well known food additive (E 335). Similarly, sodium hydrogen tartrate hydrate is prepared by milling stoichiometric mixtures of L-(+)-tartaric acid and sodium bicarbonate. These crystals are used for the preparation of powders or tablets for refreshing drinks. The energy-consuming evaporation required by conventional, water-based methods can be dispensed with. No excessive heating was observed in this solid-state reaction and

the liberated CO_2 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 environmentfriendly 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 pro-

tion 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.

