Environmentally Protecting Reactive Milling

[1] H. Ren, [1, 3] H. Zoz, [2] G. Kaupp and [2] M. R. Naimi-Jamal
[1] Zoz GmbH, D-57482 Wenden, Germany
[2] University of Oldenburg, D-26111 Oldenburg, Germany
[3] ESIQIE, National Polytechnic Institute, Mexico City, DF 07300, Mexico

Abstract

Horizontal high energy ball-mills are known from academic as well as industrial applications in mechanical alloying (MA) [1-4], high energy milling (HEM) [5] and reactive milling (RM) [6]. They supply the highest relative velocity of grinding media, which leads to an intensive grinding effect, short process times and a lower contamination of the processed powders by the milling tools due to a process that is based more on the collision of the grinding media than on their shear and friction interaction. Since the grinding media are accelerated by a horizontally arranged rotor inside the grinding vessel, these devices have the additional advantage of not moving unnecessarily any large masses like e.g. the entire chamber/mill in the cases of vibration ball-mills. The systems are presently available at 0.5 to 400 L grinding chamber capacity [7] and larger volumes seem to be possible. Various existing applications for the environment include MA of different metals and/or ceramics [8], decontamination of dangerous residues by using the tribochemistry of milled sand (SiO_2) and waste-free organic chemical solid-state syntheses with 100% yield [9]. In particular these procedures are economically and ecologically favorable as in most cases they can be operated semi-automatically if they are combined with a continuous or semi-continuous (auto-batch) powder separation system. We report here on some applications of HEM/RM.

1. Equipment

Industrial mills of different types are in practical use. Vibration-mills have to move the mass of the milling chamber. This limits their sizes and they are hard to run in normal environments which is also valid for simple (drum-)ball-mills with a rotating vessel [10].

Figure 1: 2-L horizontal high energy ball-mill (Simoloyer® CM01-2l) with vacuum and inert-gas loading, operation and unloading.

Jet-mills use large streams of air or inert gas which limits their use in reactive milling. Bead-mills, horizontally or vertically, do not exhibit a significant kinetic impact, planetary ball-mills and shaker-mills [11] are limited to laboratory size [12]. The most suitable choice were horizontal rotor-mills that can be operated in dry processing at high relative velocity of the grinding media (up to 14 m s^{-1}) that cannot be reached by the other types (up to 5 m s^{-1}) under controlled condition like vacuum or inert gas [12].

Figure 2 shows a horizontal rotor mill with 2 L chamber volume, that can be run on a table next to the process controlling computer. It runs with water cooling at rotation frequencies up to 1800 rpm.

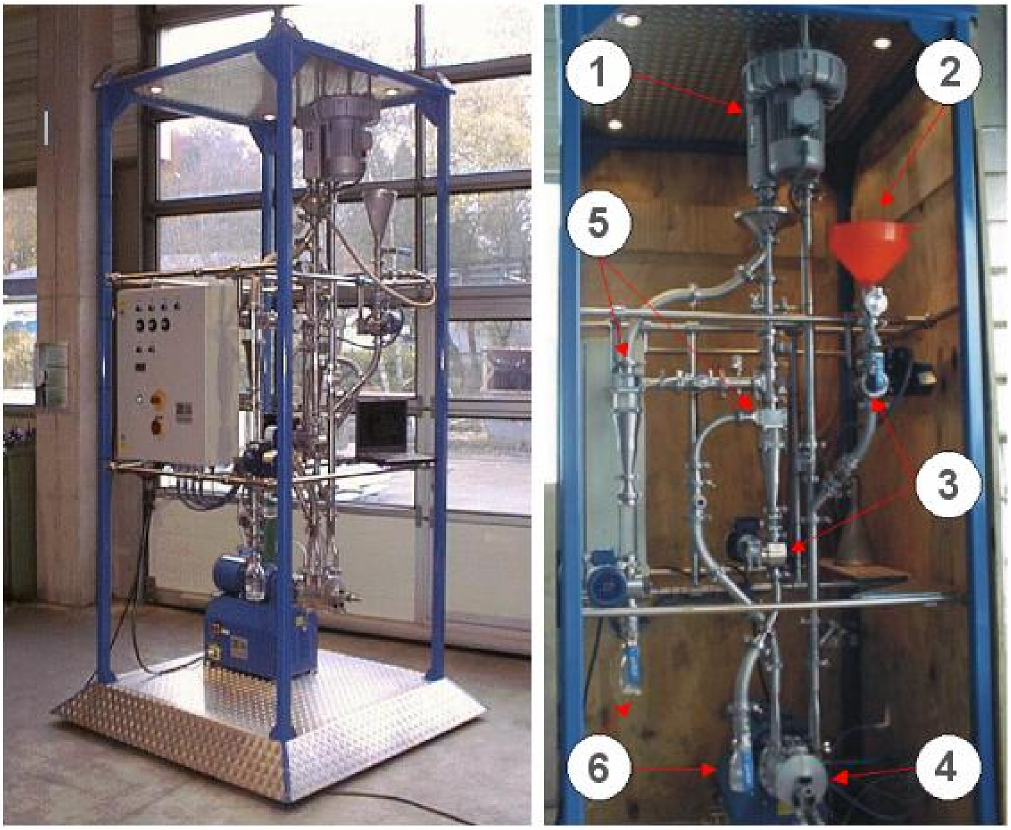


Figure 2: pilot-set-up of a high energy ball mill (Simoloyer® VS01a) with air/inert carrier gas-cycle and separation/classification system. 1. Side-Channel Turbine SKV; 2. Powder Charging; 3. Rotary-Vane Feeder ZS40; 4. High Energy Ball Mill Simoloyer® [CM01-2l 2s]; 5. Cyclon ZK70-L, 6. Powder Discharging.

An important criterium is the continuous collection of the produced powder. There must be no losses and no spoiling of the environment. Therefore, the collection occurs in a cyclone with an internal gas cycle if continuous or semi-continuous (auto-batch) operation [13-14] is desired for larger scale productions. Figure 2 shows a pilot setup and its principle of operation. This equipment allows for complete recovery of the milling product continuously or from various batches in a semi-continuous manner without charging it with impurities as will be important for synthesis and industrial production. Larger mills work equally well.

2. High Energy Milling, Mechanical Alloying and Reactive Milling

Mechanical alloying (MA) has been described as a process where powder particles are treated by repeated deformation, fracture and cold welding by highly energetic collisions of grinding media in a milling process. High energy milling (HEM) and reactive milling (RM) are performed by the same processing principle where the variation is in general based on the target of the processing, the transformation effect by the kinetic energy and the starting materials.

The various procedures can be described as high kinetic processing (HKP) where the collision of the grinding media is the main event of kinetic energy transfer from the milling tools into the powder [1-6, 15-16]. Fig. 3 shows the schematic of the collision. The basic equation describes the relation between the kinetic energy (Ekin) and the mass m and the velocity v of a ball:

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

It is clearly seen that the maximum relative velocity of the grinding media is the most determining factor contributing to the kinetic energy.

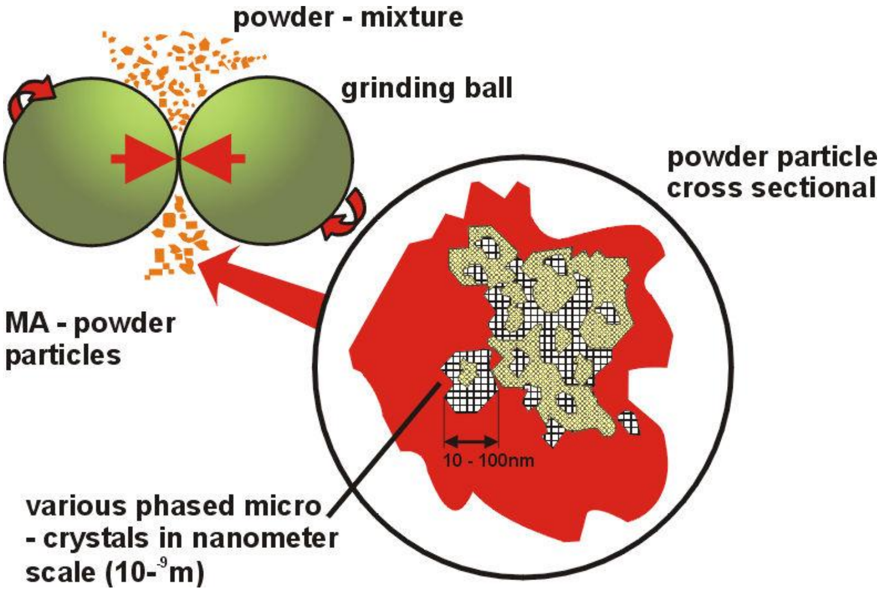


Figure 3: schematic of the collision as the main event of energy transfer

An interesting application field of this processing method is particle size reduction [17] and in particular particle deformation [5, 18] to receive a special particle geometry (e.g. flakes of ductile metals). As long as single-systems are regarded, this route is described as HEM.

The definition of RM is suitable if during milling a chemical reaction is wanted and observed. The advantage here can be an ultra-fine dispersion of transformed particles [19] in a matrix (e.g. Ag + SnO_2 where the starting powder is AgO_2 + Ag_3Sn) [6]. These processes are environmentally benign as they avoid wastes. Table 1 summarizes the most important applications of HKP.

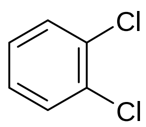
Applications of High Kinetic Processing (HKP)		
High Energy Milling	**Mechanical Alloying**	**Reactive Milling**
Surface, shape, particle size	Alloys (pseudo)	chemical reactions
flakes (particle deformed powder)	nanocrystalline materials	contact materials
Particle coating (LPS, S)	amorphous materials	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

Table 1: Applications and products of mechanical alloying, high energy milling and reactive milling

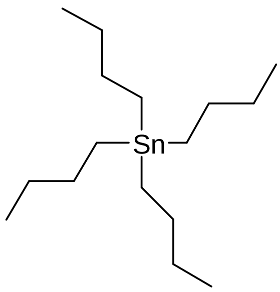
3. Tribochemistry with Oxides

Sand consists of quartz (SiO_2) which forms an infinite covalent crystal lattice. If it is split all Si-O bonds are broken that existed between the two fragments and the freshly cleaved faces are completely unsaturated with free ▒Si$^{\cdot}$ and $^{\cdot}$O-Si▒ surface radicals and other highly reactive species. They represent a local plasma. This plasma tends to be saturated immediately, a fact that has been used for more than 5000 years to ignite fire by hitting flint in air. Such tribochemistry should be also useful for the mineralization of dangerous environmental poisons such as chlorinated aromatics (PCBs, etc.) or tin alkyls etc., if milling with sand is performed. Such endeavour is much easier and more benign than the reductive removal of halogen from polyhalogenated aromatics by milling sea sand with large excesses of metallic sodium or magnesium (after thermal drying followed by drying with calcium oxide) and ethanol [20] in planetary ball mills (typically 5 h) or eccentric swing-mills (typically 90 min) to form the corresponding (aromatic) hydrocarbons.

In order to use benign tribochemistry we milled 0.8 g of *o*-dichlorobenzene (a polychlorinated aromatic) and 1 g of tetrabutyltin (a hazardous tinorganic) with 200 g of air-dry quartz sand (Sakret Trockenbaustoffe GmbH & Co KG; 0.1-0.5 mm; washed and dedusted) at 1300 rpm for 1 h in the 2 L Simoloyer® ball mill.



o-dichlorobenzene



tetrabutyltin

Figure 4: Tribochemistry with sand - the pollutants

Mass spectrometric analysis of the solid powder or ^{1}H NMR analyses of extracts (dichloromethane, ethyl acetate, or ether) did not exhibit the starting materials any more. At 1 g of *o*-dichlorobenzene and 200 g of sand, there were some traces of the starting material and of chlorobenzene still detectable in the mass spectrum, but benzene was not present if the milling was performed either in the presence of air or under an argon atmosphere. This points to mineralization of the hazardous compounds in the plasma of the freshly broken surfaces of the quartz sand. The final diameters of the quartz particles were 1 - 2 µm wide. These results show much promise for technical decontamination purposes (e.g. PCB, HCH, DDT, dioxines, $R_nSnX_{(4-n)}$) that are being developed.

4. Organic Solid-State Syntheses without Wastes

More than 1000 stoichiometric organic solid-state reactions proceed with 100% yield and do not require purifying workup, i.e. they are solvent-free and waste-free [21]. Some of these reactions have been successfully scaled-up with the Simoloyer® [9]. The scale-up is also possible for much more complicated quantitative solid-state cascade reactions. [22].

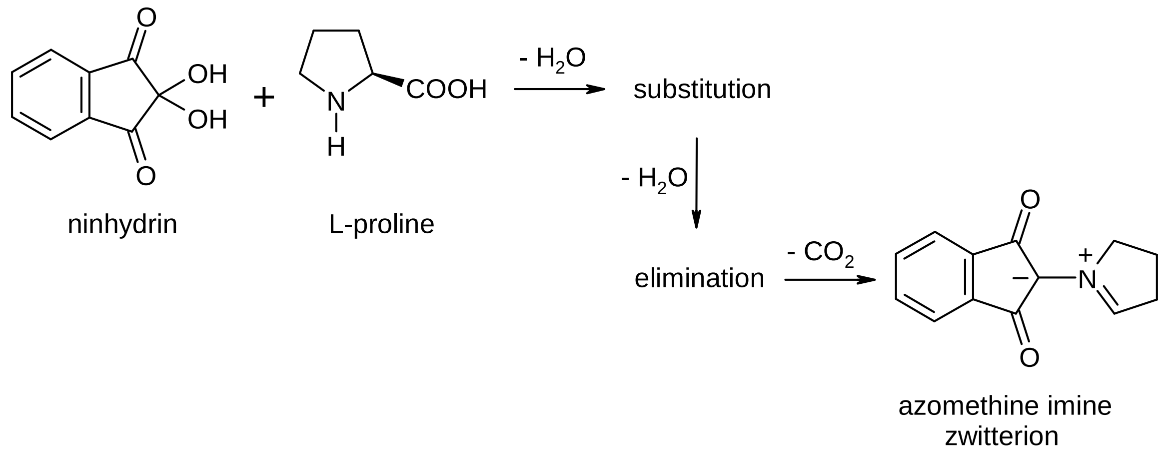


Figure 5: the solid-state reaction cascade

We checked the stoichiometric reaction of the widely used solid reagent ninhydrin with the solid amino acid *L*-proline that gives the versatile solid azomethine imine which is a zwitterion and has interesting properties and uses. Azomethine imines are hard to obtain in pure form. Here we use a solid state reaction cascade of 1.) substitution, 2.) elimination and 3.) decarboxylation at room temperature upon dry-milling and obtain 100% yield: 200 g of a stoichiometric 1 : 1-mixture of ninhydrin and *L*-proline was milled in the 2 L Simoloyer® charged with 2 kg of steel balls (100Cr6) with 5 mm diameter at 1100 rpm for 40 min when the liberation of carbon dioxide was terminated. The temperature varied from 15°C at the water cooled walls to a maximum of 21°C in the center. The power was 800 W. Quantitative reaction was secured by weight (146 g, 100%) and purity by spectroscopic techniques [22]. The zwitterion and the water of reaction formed a highly dispersed solid which did not form a lose powder but mostly a solid film on the balls and the walls of the mill. In this exceptional case, a different collection technique was applied: the product (its low solubility in water at 22°C is 0.20 g L^{-1}) was not separated in a cyclone (see Fig. 2) but easily milled out with 4 times 250 mL of water each, and the highly disperse (<1µm) pure azomethine imine product (m.p. 239°C) was obtained after centrifugation and drying in a vacuum. This is an economic, environmentally friendly and essentially waste-free synthesis of a highly interesting reagent, the only 'by-product' being 1 L of water containing 0.2 g of the zwitterion, that can, of course, also be isolated by evaporation of the water. The previous syntheses of this zwitterion in solution provided only a 82% yield with much wastes also from the purifying workup [23]. The solid-state technique is by far superior and fully benign.

5. Conclusions

High energy milling is an environmentally benign versatile technique that can be performed at the kg scale and can be scaled-up to technical importance. Applications are manifold in mechanical alloying, decontamination of dangerous residues by tribochemistry and waste-free organic solid-state syntheses. The size of horizontal high energy mills with carrier-gas operation may be increased to more than 400 L. Thus, the application to industrial production in the various fields that were treated in this survey will be only a matter of time, as environmentally friendly new processes are inevitable for the well-being of our environment.

6. References

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