Energy Balance during Mechanical Alloying, Measurement and Calculation Method supported by the MALTOZ®-software

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Abstract

Mechanical Alloying [1,2], High Energy Milling [3] and Reactive Milling [4] are well-known techniques used in powder metallurgy. The main processing principle is the energy transfer into the powder by highly kinetic ball collisions [5,6]. However there are only a few applications that have been commercialized in the past. One important limit is always the difficulty of determining the influence of the various parameters in the process. Most of the work there is still done by trial and error.

Since the Cycle Operation Procedure [7,8,9] has been introduced for the processing of ductile materials, the MALTOZ®-software became an indispensable requirement to control the processing. The process itself is not under control today, only but important parts are, so that an acceptable reproducibility is given.

Since MA, HEM and RM is approaching many industrial fields today, like the production of metal flakes [3], of electrical contact materials [4] and hydrogen storage materials [10], there is a high demand of determination the energy input not only into the system (total energy consumption), it is of major interest to quantify the part of energy that is transferred into the powder.

To increase the understanding of processing, the number of single parameters that can be controlled must be increased. If a parameter can not be controlled, the attempt is to record the corresponding data in order to find a solution to control it in the future.

Following this philosophy, a module to calculate the energy balance during processing [3] is implemented to the MALTOZ®-software which is controlling the equipment for the powder production.

To quantify the transmitted energy from the milling device into the powder, which is mainly plastic deformation and surface energy, it is necessary to determine the heat transfer due to friction effects in the process (grinding media) as well as in the machine (bearing, seals, etc.). Other unknown energy factors are noise as well as heat of powder due to powder reactions.

Measurement equipment for the process temperature, the grinding unit and is cooling system as well as the power and speed of the motor of the milling-system is used.

The difference between the energy balance of a milling test with and without powder eliminates the process independent energy consumption. The result is the energy consumption of the powder as a function of milling speed and milling time.

An application for this energy balance is a MA-process with milling times of hours or days, because the system is able to calculate the power consumption of the powder. In future milling devices equipped with the energy balance system are able to stop themselves when the energy transfer from the milling device to the powder ended.

1 Introduction

The present paper is a macroscopic research of the energy and kinetic model in a milling system. The goal here is a better understanding of processing in mechanical process engineering in order to determine optimized parameters for economically and scalable results.

In a milling system, energy is transferred from a drive into a product, where the device and the milling tools are the transfer-medium.

In the past, several authors presented works regarding the energy consumption during Mechanical Alloying (MA). Here the used and consequently discussed devices have been the planetary ball mill, the shaker-mill (Spex) and the ball(drum)mill.

However to be able to take advantage for an industrial application of modeling, it is necessary that the results are scalable. With respect to this, a system (device) is to be preferred, that can be scaled up by itself (due to its' design).

Very important is the availability not of a fully modeled algorithm, but of a partly modeled one. With this an insitu-calculation is expected to be realized which is an important step away from trial and error.

2 Theoretical approach

2.1 Energy transfer by the drive (total power consumption)

The asynchrony threephase A.C. motor represents the energy source of the here discussed system. The Torque (M) and the velocity (n - equal to the rotor blades) of the motor can be measured with the MALTOZ®-control-software of the mill.

The power is calculated as: $P=M\,n$ (1)

where the torque can be understood as a resistance to the rotation of the rotor blades. The balls and the powder inside are the resistance to the rotation, similar to the brakes of a car. Because the threephase A.C. motor has got a constant torque in dependency of the speed, in opposite to a combustion engine, the increase of the torque is interpreted as a higher resistance of the grinding media.

The energy which is transferred into the system is a function of the power (P) and the time (t).

$$E_{in} = P\,t = M\,n\,t \qquad (2)$$

The longer the system (mill) is operating, the more energy will be transferred into the grinding chamber and consequently into the powder.

2.2 Energy transfer by grinding media

In this section, the energy transfer from the grinding media in the mill into the processed powder is derived. Furthermore the energy balance regarding power input and power output as well as the difference between operation with and without powder is described.

Inside the grinding chamber, the rotor blades (diameter d_{rotor} ; rotor velocity n) transfer kinetic energy into the grinding media (diameter d_{ball} ; mass m_{ball}), where the collision of the grinding media itself is regarded as the main event for the energy transfer into the powder (product).

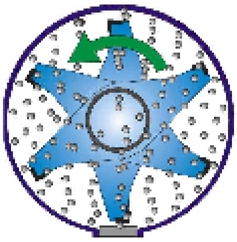


Fig. 1 Grinding Unit, cross section

The circumferential velocity of the tips of the rotor blades is useful in the description of the kinetics of the grinding media inside the mill. The maximum relative velocity of a single ball is described as:

$$v_{ball} = d_{rotor}\, \pi\, n \qquad (3)$$

During the milling process the ball-to-ball impacts in most cases induce material deformation of the affected powder particles which leads to highly disordered crystalline structures (ZnO). The interactions between milling balls and powder particles can be characterized by processes like cold-welding, plastic deformation and further fragmentation as well as embrittlement due to an increasing number of atomic dislocations and stacking faults. Next to that, the surface energy is increased.

The forces exerted on a single ball in the milling chamber are the forces from the rotor blades, the friction resulting from the interactions between the balls, the powder and the milling chamber, and the gravity. The influence of the gravity can be neglected, because of the less forces and the horizontal construction of the grinding chamber. This hypothesis is valid in the first approximation since the gravity represents only a small percentage of the acceleration of the mill as operated with high velocity. Furthermore the influence of gravity would be eliminated by the subtraction of the two energy measurements (with and without powder) later in this work.

The energy caused by low forces, e.g. atmosphere resistance to the balls or the Coriolis-force, are neglected and mentioned in this theoretic approach as $E_{unknown}$.

In another modeling of ball mills, similar hypotheses were made.

The single ball is considered as a point of mass represented by the movement (vector) and rotation of its center of gravity.

The maximum kinetic energy of one ball (E_{ball}) is described as:

$$E_{ball} = \frac{1}{2} m_{ball} v_{ball}^2 = \frac{1}{2} m_{ball} \left(d_{rotor} \pi\, n\right)^2 \qquad (4)$$

The ball-to-ball impact can be described as an combination of an elastic and plastic collision. While collision some of the energy (ΔW) will be transformed to heat and plastic deformation of the balls, furthermore the energy transfer from the balls to the powder and the noise of the mill is also included in this energy.

$$\Delta W = \Delta W_{heat} + \Delta E_{powder} + \Delta E_{noise} + \Delta E_{unknown} \qquad (5)$$

$$\frac{1}{2}m_{ball}\vec{v}_{ball1}^{\,2}+\frac{1}{2}m_{ball}\vec{v}_{ball2}^{\,2}=\frac{1}{2}m_{ball}\left(\vec{v}_{ball1}^{\,\prime 2}+\vec{v}_{ball2}^{\,\prime 2}\right)+\Delta W$$

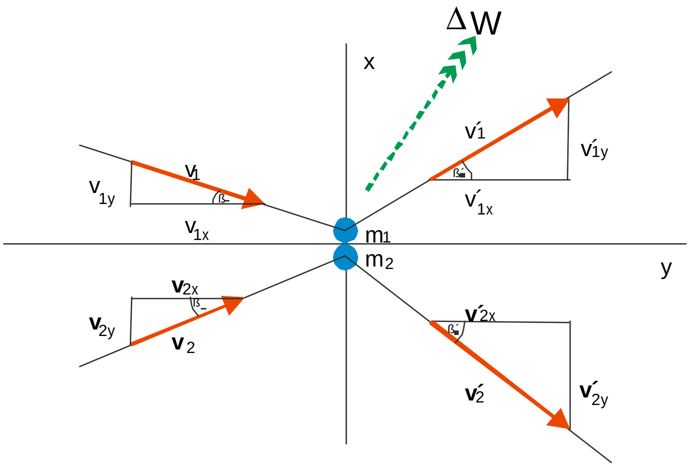


Fig. 2: Collision of grinding media

The movement of the ball starts from the collision with the rotor blades as a free movement orientated in tangential way towards the exterior of the milling chamber. Until the ball is in contact with the milling chamber it reduces it's speed caused by collision (energy transfer to the powder) and then it moves onto the surface of the milling chamber (friction). Once the ball leaves the surface of the milling chamber it is hit and accelerated again by the rotors blades or other balls.

2.3 Energy diversion by the cooling system

The grinding chamber is cooled by a water cooling system. The heat of the grinding media and the powder is carried off by the water.

In order to calculate the carried off energy (W_{heat}) of the system, it is necessary to know the inlet temperature (T_{in}), the outlet temperature (T_{out}) and the mass flow ($\dot{m}$) of the water. The specific thermal capacity of the water ($\bar{c}$) is supposed as constant.

$$W_{heat} = \dot{m}\,\bar{c}\,(T_{in} - T_{out}) \qquad (6)$$

Further the system is loosing energy in form of noise etc. ($\Delta E_{noise} + \Delta E_{unknown}$).

2.4 Energy balance (energy transfer into the powder)

The energy balance of the grinding unit is derivable from the energy which is going into the system and the energy which is going out of the system.

$$E_{1/2} = E_{in}\text{-}E_{out} = M\,n\,t - (\dot{m}\,\bar{c}\,(T_{in} - T_{out}) + \Delta E_{noise} + E_{unknown}) - \Delta E_{powder} \qquad (7)$$

In order to determine the energy increase of the powder and to eliminate constant energy loss, two energy balances are needed. At first is it important to now the energy of the system with grinding media but **without powder** (E_1). After that it is necessary to measure the energy with exactly the same parameters (speed, time, ball mass etc.), but **with powder** (E_2). To operate with the same parameters the MALTOZ®-Software is used.

The energy variation of the milled powder is the result of the subtraction of the test with and the test without powder:

$$\Delta E = E_1 - E_2 = \Delta E_{powder} \qquad (8)$$

2.5 Kinetic attempt (kinetic transfer into the system)

As shown above it is possible to calculate/measure the energy increase of the milled powder.

Supposed, that the main event in processing powder is to transfer energy into the powder in a specific range, this is expected to be independent from the time of this energy transfer.

$$E_{powder}\ (const) \equiv P_1\, t_1 = P_2\, t_2 \equiv \frac{P_1}{P_2} = \frac{t_2}{t_1} \qquad (9)$$

In other words: Milling the powder a shorter time but with higher velocity shut bring the same result with a longer milling time but with lower velocity.

Because the kinetic energy of the grinding media (E_{ball}) is only caused be the collision with the rotor blades, it also should not matter how big the diameter of the rotor blades is – in a specific range, of course. To get the same kinetic energy of the balls with a larger rotor, the velocity of the rotor shall be slowed down.

$$E_{ball}\ (const) \equiv \frac{1}{2} m_{ball} \left(d_{rotor1} \pi\, n_1\right)^2 = \frac{1}{2} m_{ball} \left(d_{rotor2} \pi\, n_2\right)^2 \equiv \frac{d_{rotor1}}{d_{rotor2}} = \frac{n_2}{n_1} \qquad (10)$$

As a result the milling chamber should be scaleable.

3 Experiments

For the qualitative and quantitative evaluation of the energy balances, three different experiment series have been considered. The testing powder has been Zinc-Oxide (ZnO). This material has been chosen as it is not necessary to process this material under inert gas. Also the milling of Zinc-Oxide is more or less an academic problem and it has been proven that its amorphization caused by energy transfer into the powder can be shown by X-ray-diffraction.

For the experiments horizontal High Energy Mills (HEM) have been chosen, because this principle is available in several sizes in opposite to Planetary Ball Mills or Spex Mills.

The principle of this mill is based on a horizontally rotor blades fixed on a drive shaft. By rotating the rotor blades accelerating the grinding media (steel balls) which are transferring its kinetic energy by collision to the powder.

3.1 Experiment based on Energy balance

The laboratory scale mill (Simoloyer® CM01, 1.5kW power) has been operated only with grinding media. A prototype has been modified regarding the maximum rotor velocity, it has been increased from 1500 rpm to 2000 rpm which results in a maximum grinding media velocity of 12,1 m/s.

Furthermore a hard metal rotor [25] has been used to prevent higher abrasion caused by the higher velocity.

For Temperature measurement of the cooling water PT100 thermometers and a flow-meter have been added to enable the calculation of the carried of energy.

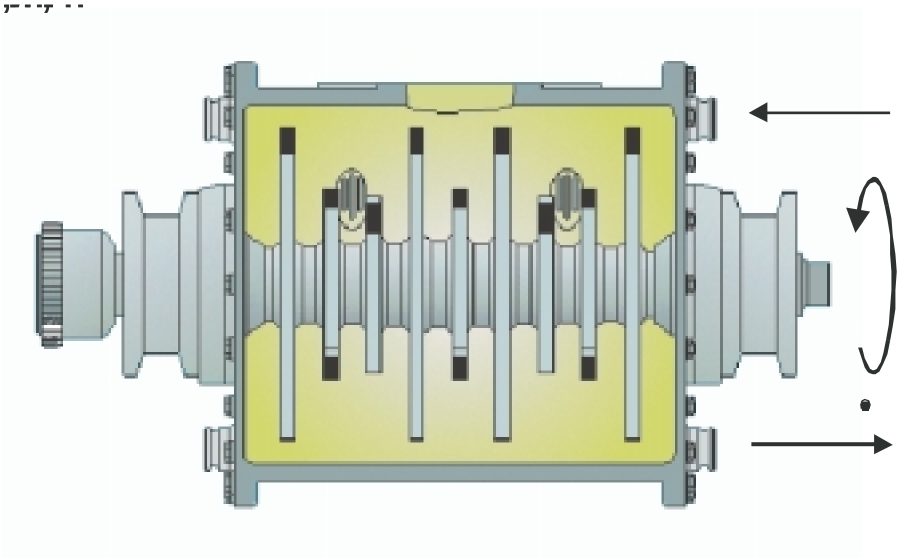


Fig. 3: Energy balance with mill CM01

2 kg of 100Cr6 steel balls (5mm diameter) in a 2 liter stainless steel grinding unit have been uses as grinding media.

The rotor velocity has been increased in a range from 200 rpm to 2000 rpm by steps of 200 rpm. The milling time has been 20 minutes per step.

While milling, the torque, rotor velocity, process temperature, bearing temperature, the water cooling systems inlet and outlet temperature as well as the water flow has been recorded by MALTOZ®-Software twice per second.

The experiments have been repeated three times to calculate the standard distribution and the average with 200g Zinc-Oxide (ball to powder ratio 1:10). All the other milling parameters (time, speed) have been the same as the milling without powder.

Milling device	CM01
Max Power	1.5 kW
Volume	2 l
Rotor diameter	116 mm
Rotor velocity	200...2000 rpm step 200
velocity	Max 12.1 m/s
Ball mass	2 kg
ZnO powder	200 g
Grinding media diameter	5 mm
Grinding media / powder ratio	1:10
Milling time	20 min per step

Table 1: Milling parameters for energy balance

3.1.1 Results (Energy Balance)

To calculate the energy increase of the powder the average of the two series has been used to calculate the energy of the two series. The subtraction if the two energies represents the energy increase of the powder.

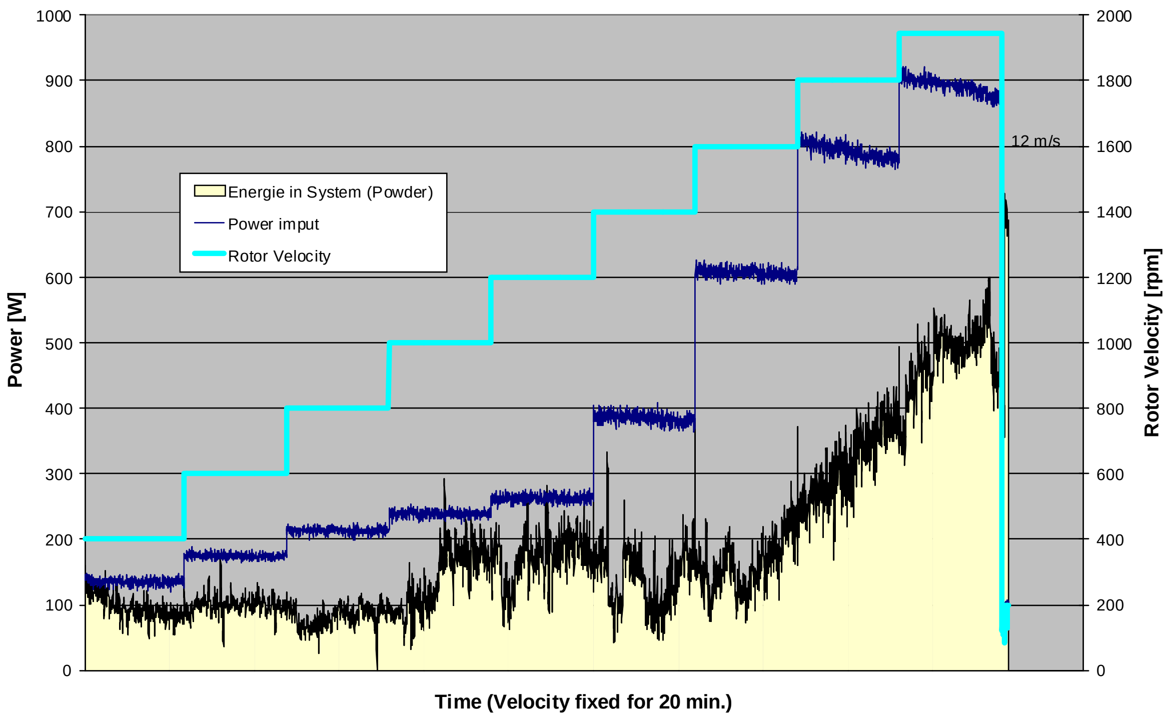


Fig. 4: Measured Powder Energy

The rotor velocity, measured power consumption of the motor and the calculated energy input are shown in figure 3.

The marked area under the powder-power line is the energy increase of the powder. To determine the exact quantity energy input of the powder, the power absorption over the time has to integrated.

3.2 Further experiment to understand the kinetic motion in the process with respect to 3.1.1.

To understand the kinetic inside the grinding chamber a transparent 2 liter grinding chamber was developed to simulate the standard grinding chamber's milling properties.

3.2.1 Experiment with transparent vessel

The grinding chambers design has been simplified to its grinding function. In opposite to a commercial grinding chamber the transparent grinding chamber is not able to keep vacuum, it has got no port for the air-lock (powder in- and outlet) and the inner surface is not conical. Furthermore is has got no cooling system, so its operating time is restricted.

The rotor blades have been taken from a standard grinding unit, the grinding media, too.

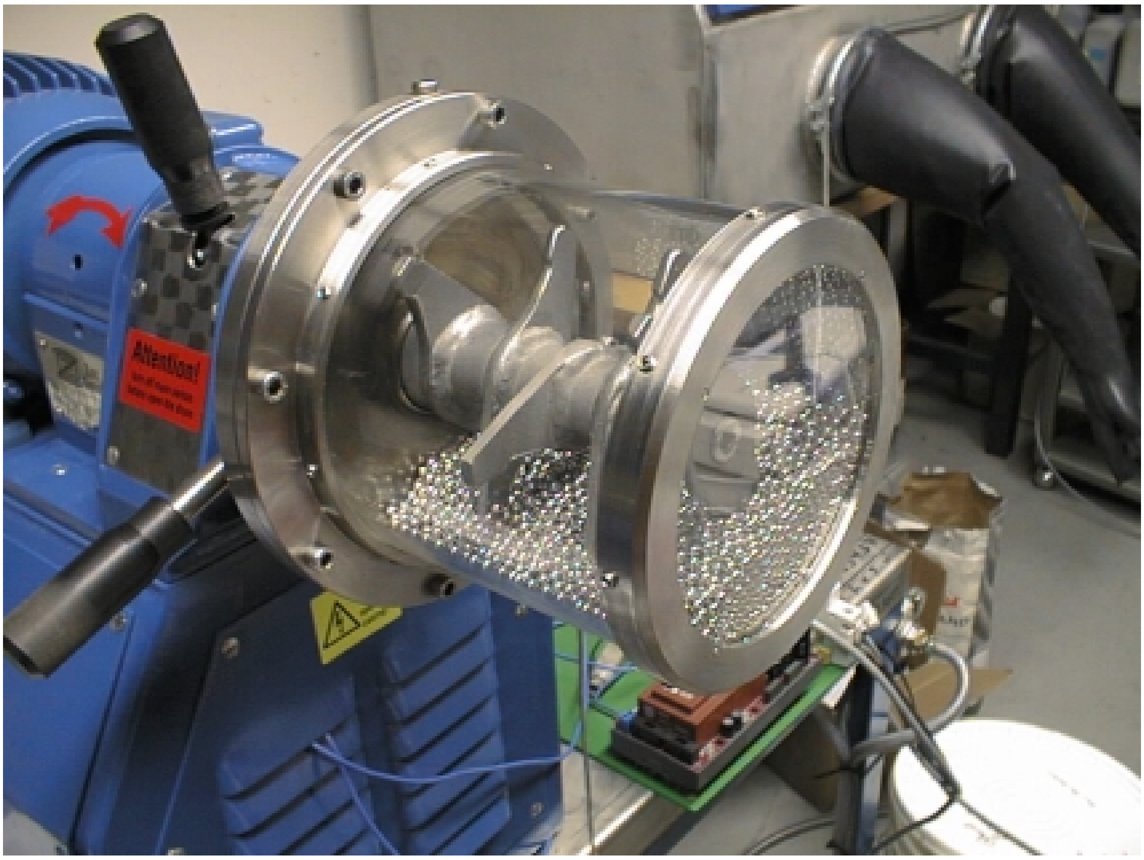


Fig. 5: Transparent 2 liter grinding unit connected to laboratory scale mill Simoloyer® CM01

The transparent grinding chamber has been operated with new grinding material (100Cr6 steel balls) and without powder to keep all windows clean. It is an assumption, that the motion of the ball are similar to the operation with powder.

While operation two recording techniques have been used. By photography with a digital camera and by video camera, front view and side view pictures have been taken. The digital camera pictures contain the location of the grinding media while operating (milling-simulation).

The given pictures are typical for the different operation modes and have been taken by the digital camera with longer exposure time, because the grinding media's motion and direction is clear to see. Using a shorter exposure time produces sharper pictures and is better to recognise the grinding media's distribution, but these pictures do not have any information about the velocity distribution.

A mathematical model of the grinding media movement will be presented separately.

3.2.2 Observations

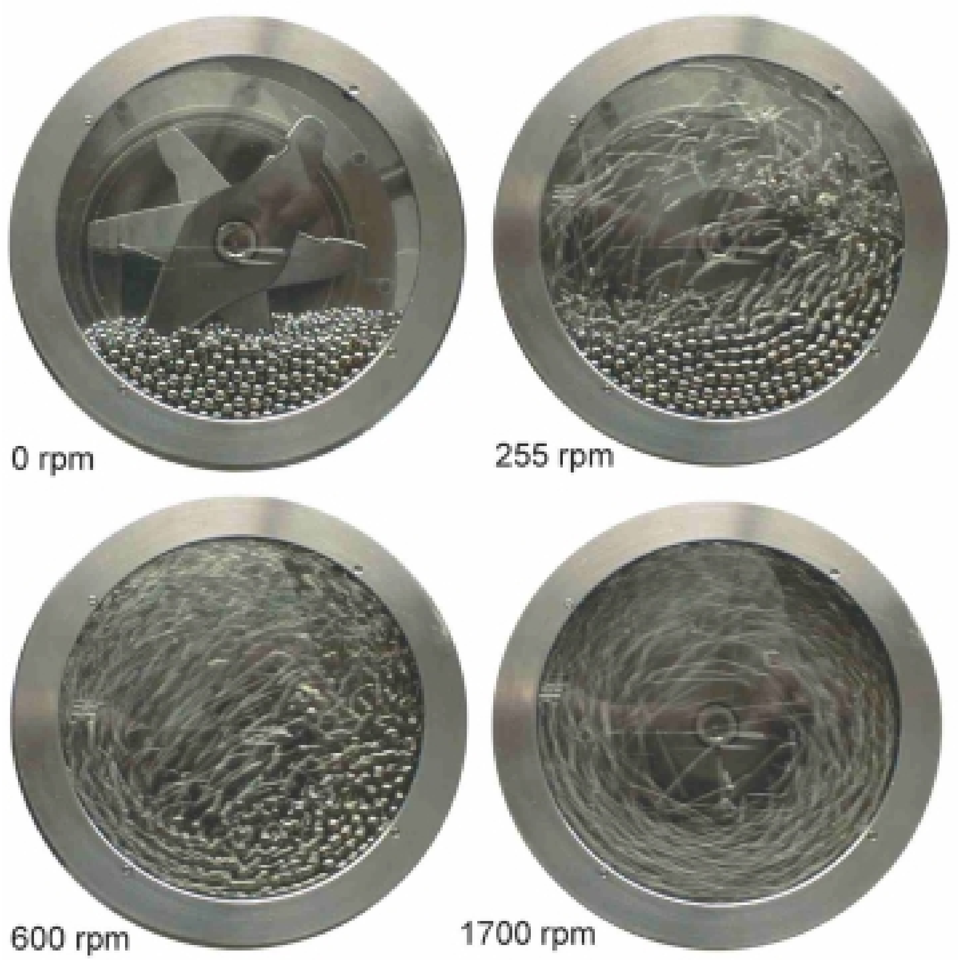


Fig. 6: Grinding media motion while operation

While visual observation the grinding media's motion, it has been found that up to 200 rpm the rotor blades are moving through the grinding media nearly without any kinetic effect. Over 250 rpm more and more balls are skidded against the wall an over the drive shaft. By increasing the speed a turbulence over the packed balls at the bottom of the grinding chamber can be observed. This turbulence is moving towards the centre by continuing increasing the speed, while the ball package at the bottom becomes less and less.

Above 1500 rpm the grinding media is located nearly homogeneously at the outer 60% of the grinding chambers diameter. The influence of gravity to the grinding media's location is as good as zero, and it's motion is similar to the collisions of gas particles.

The pictures are proving that the steel balls have got a free way to fly and that the milling technique is more based on collision than on friction the higher the rotor velocity is.

3.3 Experiment based on Kinetic Attempt

The laboratory mill CM01 and the up scaled industrial mill (Simoloyer® CM100s2, 60kW power, 100 liter volume) have been operated with zinc-oxide. Both mills have been operated at the same circumferential velocity for 5h under air.

Milling device	CM01	CM100
Max Power	1.5 kW	60 kW
Volume	2 l	100 l
Rotor diameter	116 mm	440 mm
Rotor velocity	2000 rpm	530 rpm
velocity	12,1 m/s	
Ball mass	2 kg	150 kg
ZnO powder	200 g	15 kg
Grinding media diameter	5 mm	
Grinding media / powder ratio	1:10	
Milling time	5 h	

Table 2: Milling parameters for scale up

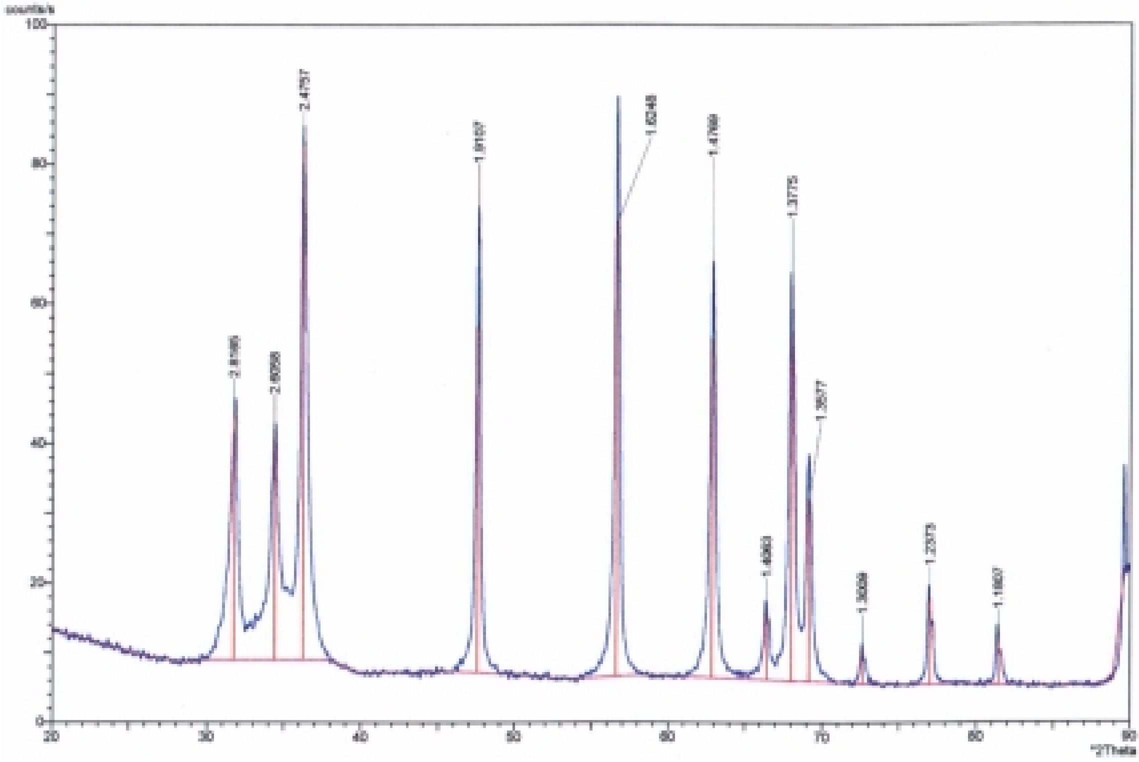


Fig. 7: XRD-analysis of ZnO, starting powder

After milling, samples have been taken and were characterized by SEM and X-ray diffraction to compare the milling of zinc-oxide in a lab scale and industrial scale mill.

In comparison with the starting powders x-ray diffraction, the main peaks have been reduced. The powder became highly amorphous, but for detailed quantification by Rietveld-calculation analysis - a mathematical method for calculating the crystallite-size - the intensity of the background relative to the powder peaks is to high.

A rough estimation of the crystallite-size shows values in the range of 4nm after treatment of the ZnO with maximum rotary-speed.

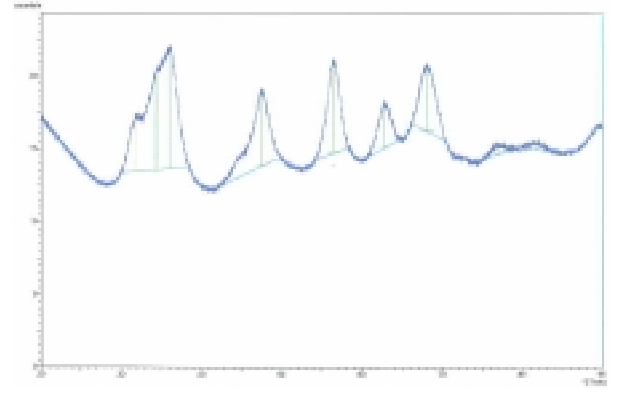
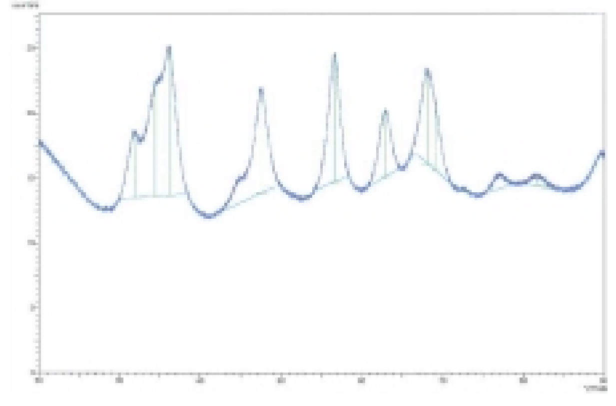
	
CM100; 530 rpm; 5 h	CM 01; 2000 rpm; 5 h

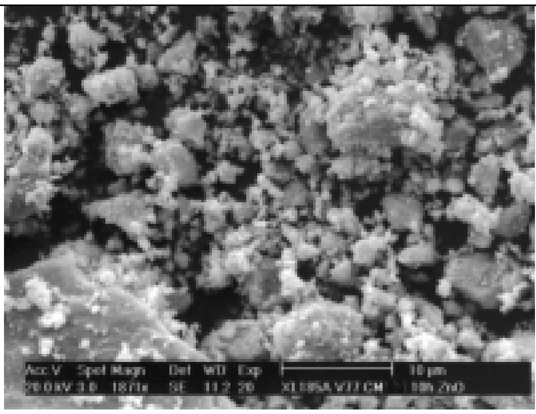
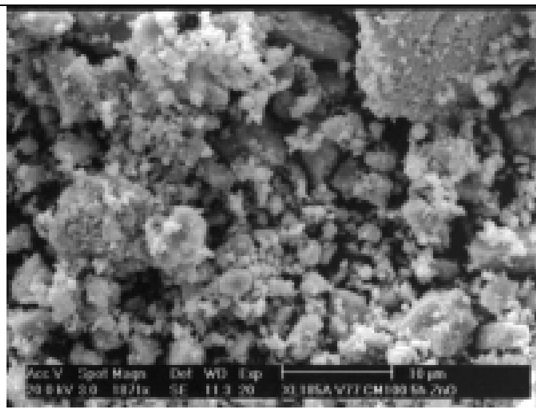
Fig. 8: XRD-analysis of ZnO, milled 5h, 12.1 m/s

The XRD-analysis shows a slightly difference between the milling using the CM01 and the CM100 concerning the intensity of the peaks. Noticeable is the peak-intensity at about 37,5° (middle one), which was not reduced after processing with the CM01 even after longer milling time.

The Philips X'Pert-Organiser calculated crystallite-sizes, which are shown in table. It should be mentioned, that the necessary background, which is able to be seen in the graphs (e.g. green line in Fig. 8) is not the relevant one. For calculation the *full width at half-maximum* (fwhm) the background was set manually.

crystallite-size	CM01	CM100 5h
[nm]	6,2	4,2

Table 3: Philips X'Pert-Organiser calculated crystallite-sizes

CM01	**CM100**
	

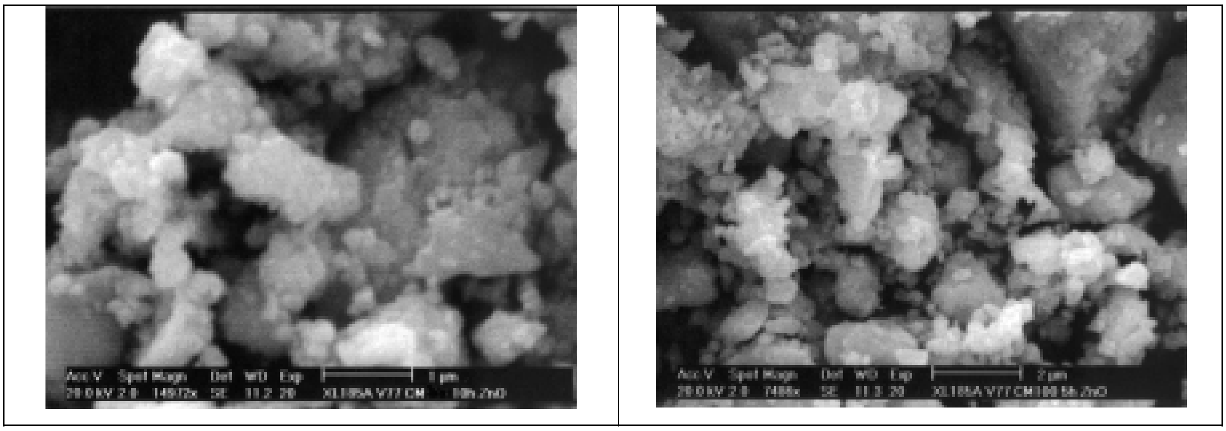


Fig. 9: SEM-pictures after 5h milling

By comparison of the SEM-pictures of the two experiments it is difficult to see the differences between the milled powders in opposite to the X-ray diffraction pattern.

4 Discussion

The results obtained in the theoretical approach and their applicability to the high energy milling process are discussed.

The energy distribution of the milling process (system) has been calculated in dependence of the rotor velocity. Milling-operations with equal process parameters have been carried out with and without powder and have been used for the energy calculation.

The trajectories of the balls have been observed by video-analysis with the assumption that the trajectory is independent of powder presence.

The main result of the energy calculation is the distinction of three modes of operation of a horizontal mill. Similarly to conventional ball mills and planetary ball mills, a critical speed exists below which a reduced grinding action is expected. This quantification of the critical speed measured and calculated here is in accordance to the visual observation of ball movement.

Under a rotor velocity of 200 rpm the kinetic of the grinding media can be characterised as mixing. The rotor blades are moving trough the grinding media with nearly no resistance. Consequently the cooling water is not heated and therefore not shown.

The second mode is in the interval between 250 rpm and 1500 rpm the milling process is a combination of both friction and collision, which tends to collision with higher speed. In this range the heating of the cooling water leads to a calculable energy increase of the milled powder.

The third mode is observable over 1500 rpm. All grinding media is in collision with each other, the rotor and the inner grinding chamber. The high kinetic energy leads to elastic collision between the grinding chamber and the grinding media and to plastic deformation and crystallite size reduction of the powder (ZnO). Because a high part of the kinetic energy is consumed by the powder, less energy is converted to heat and carried off by the cooling water. At the maximum velocity of 2000 rpm over 50% of the energy inlet has been consumed by the powder.

All these observation relate to the 2 liter horizontal laboratory scale mill.

Furthermore the scalability of the horizontal milling process has been derived by the kinetic energy of the grinding media. The ball-powder interactions have been simplified to collision. Thus has been valid in mode three caused to less friction being present.

For comparison of two rotor diameters an industrial and a lab scale mill have been operated with the same circumferential velocity and the same filling ratio.

In the experiments on zinc-oxide the main point has been to reduce the particle size. SEM-pictures identify that the particle size of the milled power of the lab scale mill is similar the these of the industrial scale mill.

By comparison of the two X-Ray diffraction patterns of both milled powders, the industrial scale milled powder tend to have a lower particle size. Because of the amorphous like powder and the very high presents of the background a detailed analysis of the powder has not been possible with our x-ray diffraction.

Here it might be assumed, that a kind of texture is present. The origin of this difference can not be explained at this stage.

For statements concerning the crystallite-size, the Rietveld-calculation based on x-ray diffraction data received with another detector should be done. A first and rough estimation is given the calculation by the Phillips-X'Pert Organiser, where a tremendous reduction of the crystallite-size up to 4nm could be obtained after 5h-milling-time of ZnO. A further indicator for this statement is the high level of the amorphous signal.

The differences of the two milling results are based on the large scale differences between the two milling-systems and the fact that a full scaling up of an milling process is more complicated. Never the less the two results are highly comparable, so that a lab scale mill can be used for the prototyping of new materials to be produced in industrial scale milling devices.

All the work presented here is related to high speed milling conditions, which are the typical milling conditions of a commercial horizontal ball mill and which are also the milling conditions of the most published work regarding horizontal mills.

It has indeed been shown with a prototype lab scale mill that there is a limiting critical rotational velocity above which collisions are dominating the friction effect. This leads to a energy transfer from the grinding media to the powder up to 50% and has been shown by partly amorphization of zinc-oxide.

5 Conclusions

1. The theoretical base for the kinetic in a horizontal rotary ball mill has been derived, the energy balance for this system has been established.
2. A second model, the kinetic attempt has been introduced.
3. The practical prove of the theoretic attempts has been given.
4. The example of the laboratory Simoloyer® CM01-2l did show that up to 50 % of the total power consumption is directly transferred into the powder.
5. The dependency of rotor velocity and kinetic mode in a horizontal rotary ball mill has been explained.
6. The scalability from the laboratory size (2 liter) to the industrial scale (here 100 liter) has been successfully shown by the example of amorphisation of ZnO.

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