Mechanical Alloying - Principle, Development & Current Activities -
(Part I-VII)

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Abstract
During the last decades the mechanical alloying technique (MA) [1,2] has been found to be very effective in producing powders with interesting properties. By this means it is possible to synthesize alloys or composite materials with highly dispersed components [3] far away from thermal equilibrium state like amorphous or nanocrystalline materials. Furthermore, the powder route is a way to combine elemental or pre-alloyed components to materials which are generally not receivable by conventional processing techniques due to e.g. the immiscibility of their components.
Another interesting application field of the same processing method is particle size reduction and in particular particle deformation [4] to receive a special particle geometry (e.g. flakes of ductile metals). As long as here no composite or alloy, just single-systems are regarded, this route is described as high energy milling (HEM).
The definition of Reactive Milling (RM) is suitable if during milling a chemical reaction is wanted and observed. The advantage here can be an ultra-fine dispersion of particles in a matrix (e.g. Ag-SnO_2 where the starting powder is AgO_2 + Ag_3Sn) [5].

The present paper gives a survey on the principle of HEM / MA / RM, on general applications and technological aspects.
The important keys regarding the processing equipment like kinetic energy transfer [1,6], controlled atmosphere and temperature [7] as well as non-existence of dead-zones [8,9] are explained. With respect to an economical production by HEM / MA / RM, the requirements regarding the processing procedure like reproducibility, direct scalability, cycle operation procedure [10,11] and protection are discussed.
Potential procedures in order to realize a reproducible, safe and economical industrial production (energy balance, semi-continuous processing) are reported.
One of the first existing industrial application with tons of product (ductile metal flakes [4,12,13]) and its' future development is described.
A given survey of currently operated projects promises products like Contactors [5], Piston-Rings, CFRE-products for paper-making industry [14], wear-parts [15], bearing-bushes for steel-industry [16] as well as decorative, conductive, anticorrosive and wear-resistible coatings [17-21] for automotive, building and construction industry as well as household appliances [22] made by and with HEM, MA and RM.
The general aim of the development here is to make the in principle cheap techniques of MA, HEM and RM available for commercialization in a large scale. The major arguments are: safety, producing cost, environment, impossibility of other producing method.

Part I Introduction HEM / MA / RM, Technological Aspects
During the last decades the mechanical alloying technique (MA) [1], [2] has been found to be very effective in producing powders with interesting properties. By this means it is possible to synthesize alloys or composite materials with highly dispersed components [3] far away from thermal equilibrium state like amorphous or nanocrystalline materials. Furthermore, the powder route is a way to combine elemental or pre-alloyed components to materials which are generally not receivable by conventional processing techniques due to e.g. the immiscibility of their components.

I-1 Applications and Products
Mechanical alloying leads to modification of the crystalline structure of substances and finer and more homogenous phase distribution by materials with more than two phases. The Gibbs´ free energy is increased to higher levels during milling and results in reactions which under conventional condition can not been taken place. Atomic dislocations, a high defect structure of the lattice, the immense magnification of the boundary surface and a high diffusion rate leads to low activation energies for those reactions. The interaction between milling balls and powder particles can be characterized by processes like cold-welding, plastic deformation and further fragmentation of the particles.

The definition of Reactive Milling (RM) is suitable if during milling a chemical reaction is occurred. The advantage here can be an ultra-fine dispersion of particles in a matrix (e.g. Ag-SnO_2 where the starting powder is AgO_2 + Ag_3Sn) [5].
Another interesting application field of the same processing method is particle size reduction and in particular particle deformation [4] to receive a special particle geometry (e.g. flakes of ductile metals). As long as here no composite, just single-systems are regarded, this route is described as high energy ball milling (HEM).
The following Table I-1 gives most important applications of High Energy Milling, Mechanical Alloying and Reactive Milling in survey:

HEM / MA / RM Applications, Products		
Surface, Shape, Particle Size (geometry)	**Alloy (pseudo)**	**Reactive Milling**
• Flakes (Particle Deformed Powder)	• Nanocrystalline Materials	• Contact Material
• Particle Coating (LPS, S)	• Amorphous Materials	• Nanocrystalline Materials
• Nanocrystalline Materials	• Oxide Dispersion Strengthened Alloys	• Mechanochemistry
• Highly Dispersed Phased Materials	• Iron and Oxide based Magnetic Materials	• Solid state synthesis
• Soft Magnetics	• Bearing Materials containing Solid Lubricants	• Hydride - Dehydride
• Particle Size Reduction (e.g. enamel)	• Ceramic Metal Composites (MMC, CMC, MMC, CCC)	• Activation (Catalysts)

Table I-1: applications & products of Mechanical Alloying, High Energy Milling and Reactive Milling

I-2 The Principle of HEM / MA / RM

The various procedures can be described as high kinetic processing where the collision of grinding media is the main event of kinetic energy transfer from the milling tools into the powder [6],[7]. Fig. I-1 shows the schematic of the collision. The basic equation for the kinetic energy in dependency of mass and velocity:

$$\mathbf{E_{kin} = ½\ m\ v^2} \quad (1)$$

leads to the conclusion that the maximum relative velocity of grinding media is the most determining factor is the in the process.

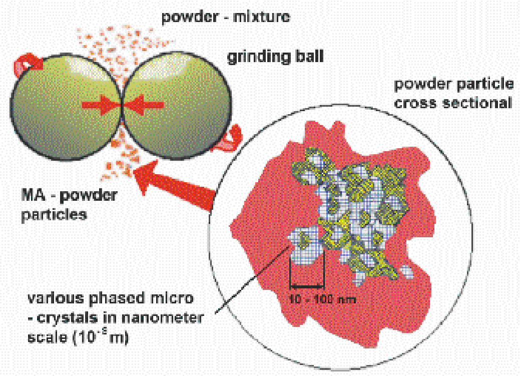


Fig. I-1: schematic of the collision as the main event of energy transfer

I-3 Devices in use: Shaker Mill, Simoloyer®, Planetary Ball Mill, Attritor®, Drum / BallMill

For the high kinetic processing techniques a various number of milling devices have been applied during the last years. The well-known planetary ball mill, the shaker mill or the vertical attritor are often used devices to produce e.g. mechanical alloyed powders for laboratory purpose. The Simoloyer® (horizontal rotary ball mill) is a modern and advanced device for the processing of HEM/MA/RM and allows the advantage of a direct-scaling-up for means of an industrial purpose.
Table I-2 is a survey and comparison of the most frequently used devices referring to previous work of several authors [1],[6],[7],[8],[10],[11],[12].
To be able to compare the most determining factor, the maximum relative velocity of grinding media, in case of the drum(ball)mill, the diameter was limited to 3 meters. In this case this most simple device, where a simplicity an advantage, allows a maximum velocity of x-5 m/s calculated by the free-fall principle. The expression x-5 m/s covers the gravity dependency of this principle.

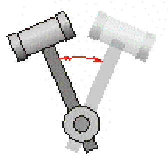
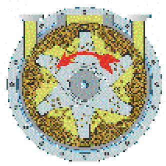
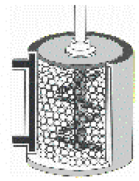
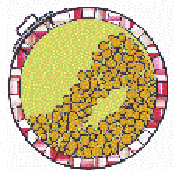
Device properties / brand	Shaker Mill (spex)	Simoloyer® (zoz)	Planetary Ball Mill (various)	Attritor® (union process)	Drum/Ball-Mill (various)
energy impact relation	10	08	05	04	01
friction / sheer relation	low	low	medium	medium - high	high
collision relation	high	high	medium	low – medium	low
kinetic, processing	very fast	fast	medium	medium	slow
influence of gravity	little	very little	little	difficult	Needed !
max. diameter [m]	0.08	0.9	0.2	1	3
max. total volume [l]	0.2	400	8	1000	20000
max. relat. velocity [m/s]	19	14	5	4.5 - 5.1	x - 5
specific energy [kW /l]	--	0.55 (- 3)	--	0.1 (- 0.75)	0.01 - 0.03
continuous process (dry)	impossible	yes, semi	impossible	difficult	impossible*
scaling up	no	yes	No	yes	yes
max. batch [kg]	0.2	250	2	250	12000
contamination	low	low - high	low	low - high	low
vacuum	possible	- 10^{-4} hPa	possible	poor	poor
discharging	very difficult	easy	very difficult	medium	easy
airlock	impossible	yes	impossible	difficult**	impossible***
temperature control	very difficult	possible	difficult	possible	possible
investment (costs)	low	very high	low	high	low
operation (costs)	very high	high	low	high	very low
***exception tube-mill** ****due to gravity** *****exception BMxx-zoz**					

Table I-2: devices used to perform Mechanical Alloying, High Energy Milling and Reactive Milling

Compared to the (vertical) attritors (4.5-5.1 m/s) and to the planetary ball mill (5 m/s), the Simoloyer® reaches up to 14 m/s [9]. Only the shaker mill goes higher up to 19 m/s [10], however this extremely high kinetic device due to direct change of motion cannot be scaled up at all for the same reason.

I-4 Demands of successful processing and economical production

In the laboratory stage, the main criteria is the successful processing. Small quantities of product mostly received by batch modes are suitable.
To perform a successful process, a high and homogeneous kinetic energy of ball impacts is necessary. To monitor the influence of the processing onto the product, often a controlled atmosphere as well as a controlled temperature is needed. Temperature control is critical as the transfer of heat from the spherical milling media into a cooling system of the grinding chamber is naturally poor.
The level of contamination is of major importance. In principle, any kind of the here discussed processing without impurities from the milling tools is not possible. Whit respect to this, the contamination must be acceptable either by quality or by quantity.
In case of an industrial application, several additional demands must be obeyed:
Most important is the reproducibility of the processing that must lead to a homogeneous product. A homogeneous product can only be guaranteed if there are no dead-zones in the process where a dead-zone is described as an area where powder can be located but the milling tools have no access. The worst-case effect would be that the processed product would be polluted with non- or not completely processed starting material.
Very important is the scalability of the process where it is naturally preferable to scale up proportional based on laboratory testing. With respect to this, the device itself should be scalable which means availability of large industrial systems based on the same principle than small laboratory units.
Due to the fact that the high kinetic processing leads to high (large) and active surfaces, the oxidation reaction is of an extremely high kinetic. Often materials are treated, that in principle exhibit a high affinity to oxygen and nitrogen. Therefore the processing but also charging and discharging which means loading and unloading the material must be done under vacuum or inert gas condition. This leads to a necessary availability of air-lock systems and gas/vacuum-tight devices in many cases.

The product costs shall be as low as possible which, regarding the producing costs refers to a short processing time, to a high degree of automatic, to a low proportion of workforce as well as to low investment, operation and maintenance costs. The protection of human and nature is of major importance. The final goal can be summarized as a 100 % process-control. Table I-3 gives the main demands in key-words:

HEM / MA / RM Applications, Products	
demands for a successful processing	**additional demands for an economical production**
• high and homogeneous kinetic energy of ball impacts	• reproducibility
	• homogeneous product
• controlled atmosphere	• no dead zones
	• direct Scaling up
• controlled temperature	• charging and Discharging under controlled condition and automatically
	• good relationship operation : maintenance
• acceptable contamination, quality and quantity	• low costs (investment and operation)
	• safe process: protection of human, environment, equipment and product

Table I-3: demands for a successful processing and an economical production

I-5 Evaluation of the Process: MALTOZ® software and high speed cinematography

Today, Mechanical Alloying ,High Energy Milling and Reactive Milling are well-known techniques but rarely used in powder metallurgy industry. Still the main processing principle is the energy transfer into the powder by highly kinetic ball collisions, however there are only a few applications that have really 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. The main questions to be answered for the extremely high-leveled goal of a 100 % process control are:

- How to understand the process ?
- Understanding of parameters ?
- How to record parameters ?

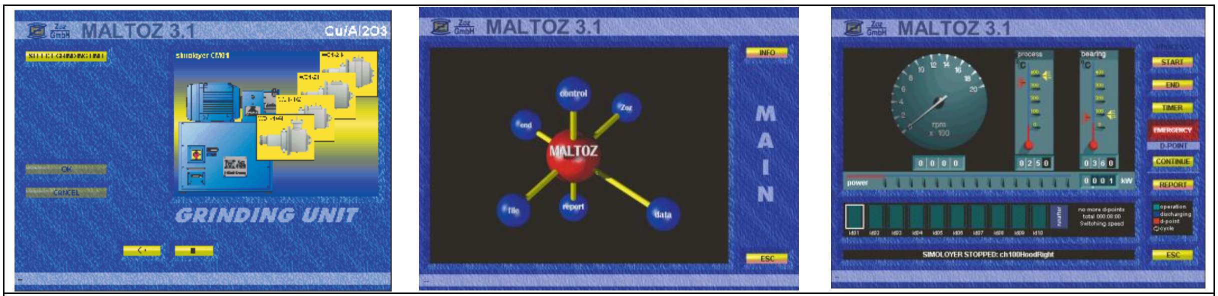


Fig. I-2: examples of Maltoz®-software-screens, a: detection of device, b: survey, c: control of drive

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

Since the Cycle Operation Procedure (see part IV) 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 up to now mostly is given, partly not.

Maltoz®-Simoloyer® Operating System			
processing	**process control**	**record (1 per second)**	**safety functions**
time - speed function	rotor velocity	rotor velocity and torque	mechanical protections
sampling	power consumption	power consumption	electrical protections
cycle operation	process temperature*	process temperature*	temperature limits
time - power function**	pre-seal units temperatures	pre-seal unit temperature	power limit
	bearing temperatures	drive shaft cooling temp.	product protection***
	drive shaft cooling temp. (in/out)****	bearing temperatures	equipment protection***
scaling betw. Simoloyer®	sampling	sampling	human protection
discharging violent cycle	discharging	discharging	productivity protection
grinding unit angle	violent cycle operation	errors	rotor velocity guarantee

timer start	cycle operation	manually program stepping	drive shaft cooling flow control ****
	broken-wire indicator (thermometers)		power on self check
	grinding unit lock indicator		
	flow control ****		
	coupling switch indicator ****		
*temperature of the inner surface of the vessel	**not possible with version 3.*	***run-after sequence	
**** only CM100 and CM400			

Table I-4: control, record and functions of the Maltoz®-operating-software

To support the evaluation of processing, in particular to explain the kinetic model of motion in order to prove that the right parameters do lead to the wanted collision effect, high speed cinematography is applied.

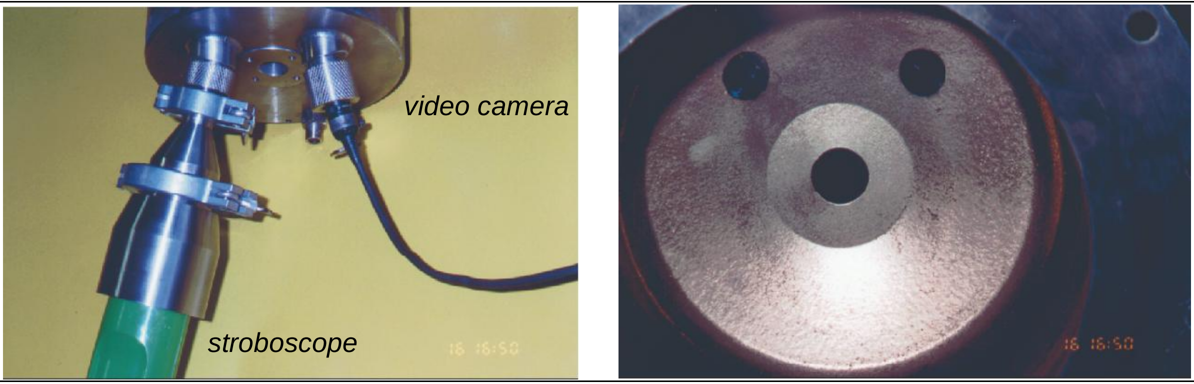


Fig. I-3: grinding unit with video equipment, outside & inside view

Fig. I-3 shows the outside configuration investigation of the process by a video-equipped grinding unit of the laboratory-scale Simoloyer® CM01-2l with a grinding chamber volume of 2 liters. A small size video camera as well as a stroboscope have been connected to the grinding chamber in a dedicated angel, in order to film trough the rotor circle at the theoretical contact-point of stroboscope and camera. The equipment is prevented by glass-sheets and is fitted gas-tight to the system.

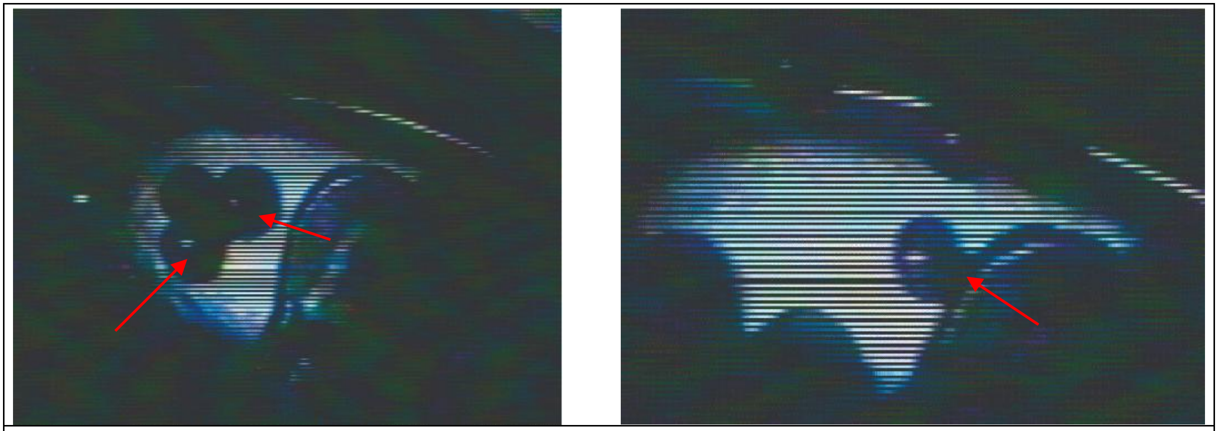


Fig. I-4: colliding balls during high kinetic processing, visual analysis

The two photos at Fig. I-4 each show a real image to inside the chamber during high kinetic processing. On the left picture, a group of in minimum 3 balls can be seen, probably before being hit by the fast blades, coming from the right hand side. The picture on the right shows in minimum 3 balls but distributed all over the small monitored area.

The very important and determining message is that the rotor inside the vessel is not moving a compact package of grinding media in the area of the outer rotor circle. The balls do have enough free space for free movement in order to pick up a velocity close to the maximum velocity !

I-6 Conclusions (Part I)

HEM/MA and Reactive Milling are interesting techniques to synthesize new and advanced materials with interesting properties.

The principle demands for a successful processing of this powder-processing-technique have been explained. A comparison-attempt between the most well known devices in use has been made.

As the technique is on the step out of the laboratory-use into the industrial application with commercial products, the availability of a device not only for a successful processing but additionally and most important, for an economical production is of major interest.

The therefore main additional demands have been discussed.

The goal has been defined as the total process control which is not available up to now.

An important tool to understand and qualify as well as to control and perform the process is the MALTOZ® software. It operates the equipment and partially controls the process.

High speed cinematography has been used to understand the kinetic in the process where not only a high energy impact leads to the alloy-, reaction-, surface- or particle shape effect, most important is the mode of transfer.

Without a high kinetic, consequently without a high relative velocity, the process will often not be performed.

Part II Optimized Charging and Discharging in the HEM / MA / RM - Process

In part I of the present paper, the non-existence of *dead-zones* in high kinetic processing has been defined as a major need to be able to produce a homogeneous product in larger quantities under reproducible conditions. Next to this it is often necessary to perform the processing and charging and discharging of the powder material under vacuum or inert gas condition.
With respect to both demands, the draingrating of the Simoloyer®, as the most specialized device for high kinetic processing, the unit that opens and closes the grinding chamber and has to transfer the powder but to block the grinding media is one of the most critical sections.
Part III describes an application and design route for an advanced draingrating system as the key-unit of the Simoloyer®-air-locks.

II-1 Difficulties Concerning Agglomeration and Adhesion Tendency of the Powders

As a matter of fact most nonstructural powders exhibit a high oxidation tendency due to increased boundary surfaces and lattice dislocations. Therefore the processed powders have to be discharged under controlled atmosphere (argon or vacuum). Furthermore, often another difficulty appears during Simoloyer® processing: because of the high adhesion and agglomeration tendency of many powders, mainly in the beginning of the mechanical alloying process it occurs that the powders block up the screen-grating at the charging and discharging port of the Simoloyer®. Un-milled powder could stick at that position and cause a sensitive change of the original powder concentration on the one hand and hinder the discharging procedure on the other hand [3]. In the worst case, the un-milled powder would pollute the processed powder during discharging. Consequently sophisticated equipment is necessary.

II-2 Advantages of the Simoloyer®

The most special device for High Energy Milling is the Simoloyer® [27]. Fig. II-1 shows a Simoloyer® model CM01 fitted with a cylindrical grinding unit W01-2l having a capacity of 2 liters. The cross section Fig. II-2 shows the grinding unit W01-2lk, also of 2 liters capacity but having a bi-conical grinding space and a cylindrical unit of CM01-Simoloyer®.

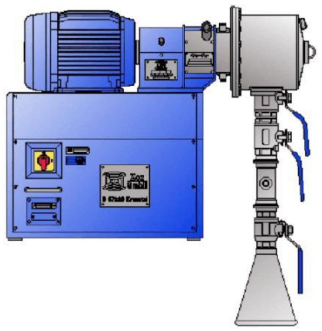


Fig. II-1: Simoloyer®CM01 with draingrating & air-lock system

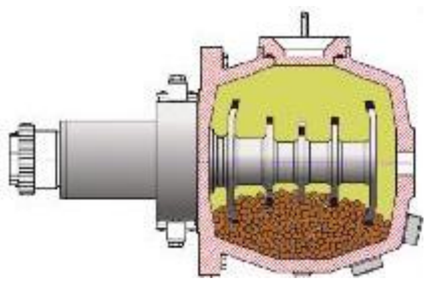


Fig. II-2: grinding unit W01-2ll, cross section

Typically, the CM-Simoloyer® is a rotary ball mill with a horizontal borne rotor, intended for dry-operation. Important characteristics of this unit are the strong rotor with broad blades, the air-lock-connection, an adjustable pre-seal unit, a decompression chamber and the rotary seal. As in case of all horizontal systems, the effect of gravity on the milling media is overlaid by the impact of the rotor and, due to its strong design, the Simoloyer® can be operated at a 2 up to 3 times higher rotational speed than conventional vertical rotary ball mills [7]. Consequently the CM01 Simoloyer® reaches a much higher kinetic energy impact.
The principle and design of the Simoloyer® leads to the possibility of an extremely high energy impact and avoids dead zones as well as different powder densities due to gravity in the process. The Simoloyer® can be experimented at laboratory level using small volume chamber-units with a volume of 0.5 or 2 l and, for industrial production, using larger volume units up to 400 l (Fig. II-3) based on the same conceptual design. This possibility of a subsequent scaling up for larger production allows a good scalability as the principle of processing is kept.

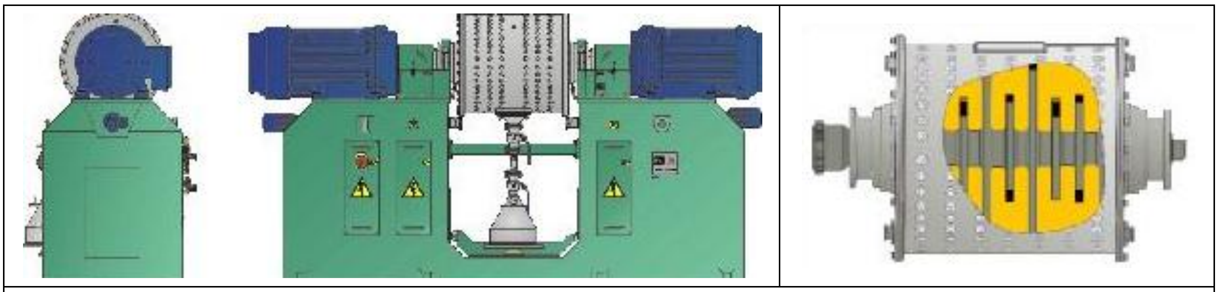


Fig. II-3: industrial Simoloyer® CM 400 and partly cross section of grinding unit

II-3 Charging and Discharging - previous solution and difficulties

A characteristic of major importance concerning the *horizontal technology* is the possibility of charging and discharging the chamber without opening the system.
Up to now, this has been possible by means of a draingrating system with an air-lock. Two different procedures could have been chosen where always one disadvantage had to be accepted:

The first, but rarely used procedure, is the process operating with a covering (Fig. II-4). The grinding chamber is fully closed in this case, and regarding the lid, a geometric optimum concerning the milling dynamics is reached. This possibility is therefore used rarely, as for charging and discharging, the lid has to be replaced by the draingrating. During this replacement, it cannot be avoided, that the material inside the drum is exposed to the outside atmosphere for a short time. Because of the grain size reduction during the process with the following surface-extension, the kinetic of the oxidation is increased and so, many materials can get unusable.

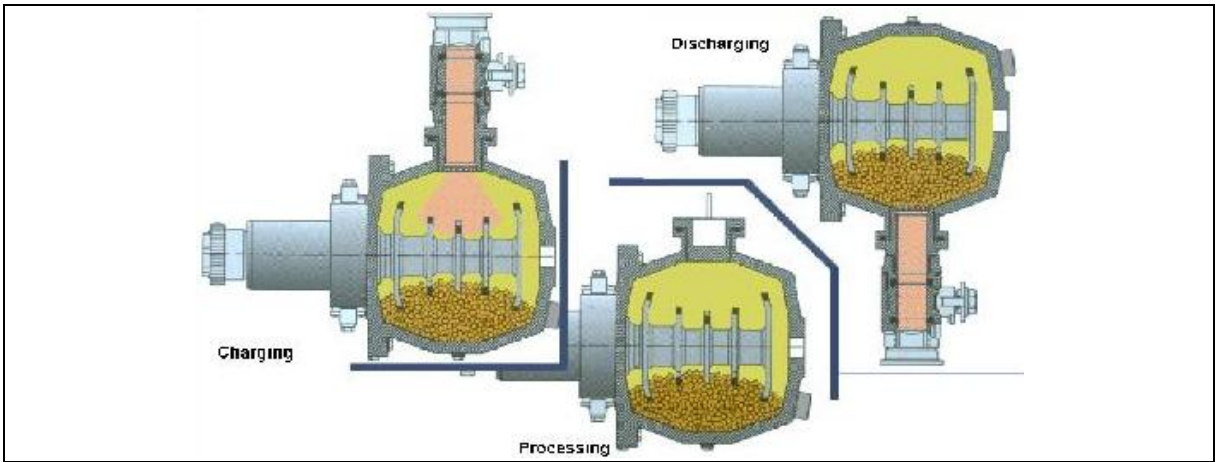


Fig. II-4: operating with a covering

The second, regularly applied variant is the processing with the draingrating, that is closed by a following ball valve (Fig. II-5). By means of this principle and by using an air-lock, it can be guaranteed, to work with powder, that never will be exposed to outside during the whole process. Certainly a real problem in particular in case of processing powders with agglomeration and adhesion tendency is the danger of blocking up of the screen-grating during the process. Then in the discharging operation, the material will not drain out and the full charge could be lost.

The second and essential difficulty concerning the milling with the draingrating is the problem, that the draingrating itself contains a *dead-zone* between the screen-grating and the closed ball-valve. Dust of powder can pass the screen-grating, can remain in this space up to discharging or fall back into the process. In any case it will not be treated for the full time. And one strong demand is to have the same powder quality in one charge.

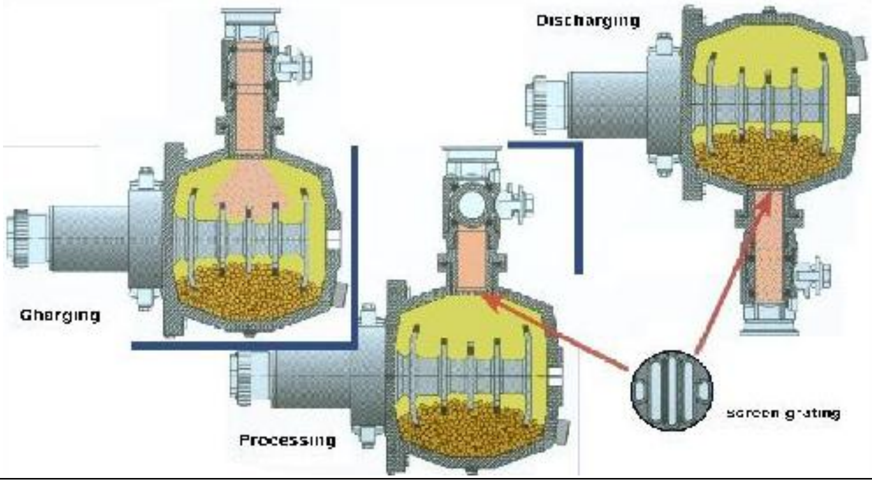


Fig. II-5: operating with the draingrating

II-4 New solution (1st step)

Every discontinuous process is described by at least three stages, charging, processing and discharging.
To avoid the disadvantages as described per 3.a) +b), the opening itself as well as the *dead-zone*, a unit is needed, that can be passed by the powder, but not by the balls in the 1st and the 3rd stage. In the second stage it must close the grinding chamber. Setting must be possible without destroying the inert atmosphere or the vacuum.
To achieve this, an ordinary ball-valve was redesigned and the screen-grating was placed right at the end of the valve-balls´ hole (Fig. II-6).
As the screen-grating and the blocking face describe almost the same radius on the same axis when turning, no gap and consequently no *dead-zone* exists. In comparison to 3.a) + b), the kinetic is disadvantageous, but can be ignored, as the dynamics here are overlaid by the main kinetic impact direction. This can be seen on (Fig. II-7). It shows the pilot unit before and after testing for 140 h:

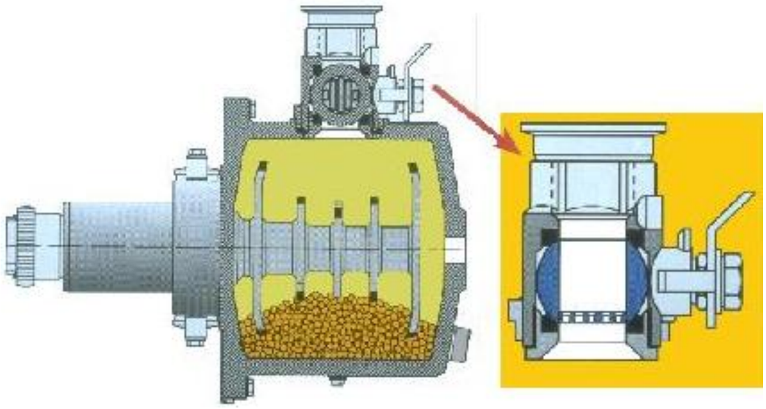


Fig. II-6: combination of a conventional ball-valve with the screen-grating

Fig. II-7: pilot unit before and after testing for 140 h

Laboratory	ENEA, M. Magini, Italy
Simoloyer®	C01-2l (2 liters)
Grinding Balls	3 kg, ø 5 mm, 100Cr6
Powder weight in	300 g, Fe_3Al
Drive-Speed	900 - 920 rpm
Operating time (Interval)	20 - 25 h
Operating time (Total)	140 h

Table II-1: the 5 main test conditions of the pilot unit

There are no substantial damages neither on the connecting flange nor on the casing.

II-5 Resultant difficulties

Fig. II-7 shows also, that as expected, the blocking face of the valve-ball is either coated with powder or damaged or both by the process. When setting the valve again, this coated or damaged blocking face of the ball has to pass the seal (Fig. II-6) and makes it useless concerning inert atmosphere or vacuum by its rough surface, but **not** concerning the blocking of the material. Although the second seal on top is useless for gas-tightness, as the free play between the seals is getting bigger. Finally a valve that works only for 1 up to 5 times is not an acceptable solution.

II-6 Resultant solution (2nd step)

As a solution here, a resistible seal or a material for the ball, that could avoid a coating or the possibility to un-coat the ball by a cutting tool in front of the seal might be considered. However, as most of the Simoloyer® today are used in science and development, the treated materials are of a high variety and consequently the same goes for the coating concerning thickness and quality. With respect to this, these are no potential possibilities.
What has been found as a suitable and simple solution is to accept the malfunction concerning gas-tightness and to solve the resultant problematic by a second ball-valve following the first redesigned one (Fig. II-8).

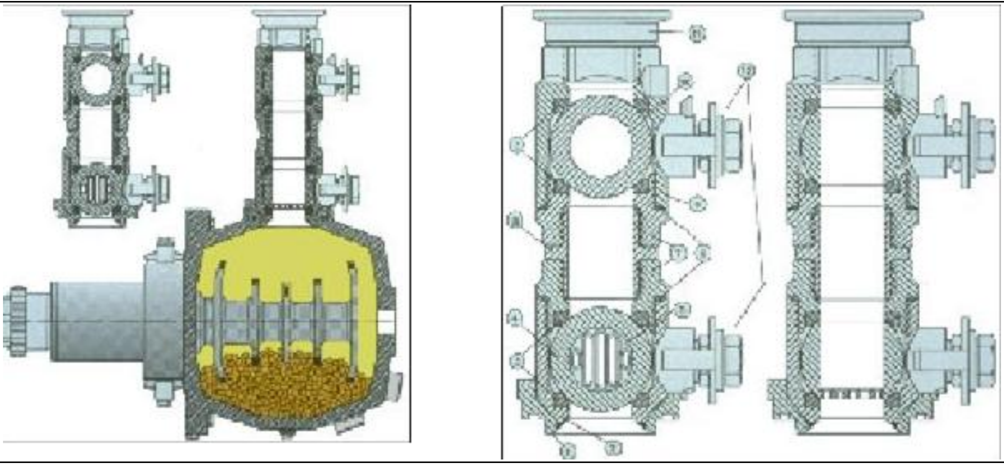


Fig. II-8: Ask-draingrating system

Pos. 1	connection flange	Pos. 7	stuffing box
Pos. 2	casing	Pos. 8	fitting
Pos. 3	seal	Pos. 9	casing
Pos. 4	valve-ball	Pos. 10	valve-ball
Pos. 5	screen-grating	Pos. 11	connection flange
Pos. 6	seal	Pos. 12	set-unit

Table II-2: part-list and explanation of the Ask-draingrating system

The here developed system **-Ask-** does avoid all difficulties as described under chapter 4 and 6 as it is totally closed in the 2nd stage (operating). The material, but not the grinding media can pass the Ask-draingrating in the 1st and the 3rd stage (charging and discharging). The screen-grating is not exposed to the grinding chamber during processing and can consequently neither be damaged by the grinding media nor blocked up by the powder or both. There is no longer a *dead-zone*.

II-7 Conclusions Part II

The important advantages of the Simoloyer® (Horizontal Rotary Ball Mill) have been shown. On the one hand caused by the horizontal borne rotor, on the other hand due to a strong design as well as available air -lock systems.

The subsequent scaling up keeping the device- and processing principle allows a good scalability for larger production.

The tremendous disadvantages of dead-zones in the process (zones of passive processing) regarding laboratory purpose as well as regarding industrial production have been discussed.

Consequently no dead-zone in the process is acceptable. This must be valid for charging and discharging, too.

It has been explained how a critical dead-zone in the draingrating / main port is avoided and powder processing and powder handling is performed under controlled condition without any dead-zone.

Part III Milling Parameters, Scaling up, Physical limits

In part II of the present paper, the maximum relative velocity of grinding media has been defined as the most determining factor in high kinetic processing. The future goal for any industrial application of HEM, MA and Reactive Milling has been described as a 100 % process control.
With respect to these demands, it is of major importance, once to be able to calculate, not only to try the needed parameters for the processing device.
Up to now, there has been no model available for the horizontal high kinetic process which would allow to calculate the milling parameters in order to optimize the processing. Therefore the reproducibility and the optimization of milling parameters is done by trial - and - error.
Part IV is a first attempt to desire a model for the milling process in the horizontal Simoloyer®.

III-1 Analysis of the milling parameters in the horizontal Simoloyer®

It has been shown by several scientists, that the primary event for the energy transfer to the processed powder is the collision itself [8], [27]. Consequently the most important parameter in the high kinetic processing is the kinetic energy of the impacts.
The kinetic energy is described by the well known formula:

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

where ***m*** is the mass of the ball and ***v*** is the relative velocity of the balls.
In case of the Simoloyer®, the ball velocity is expressed in terms of the rotational speed of the rotor and an effective diameter for the center of gravity of a theoretical slide of the forced ball packet.
Fig. III-1 shows the simplified schematic cross section of the grinding chamber of the Simoloyer® model CM01-2l. The main dimensions are:

diameter of the vessel	dv =	146 mm,
diameter of the rotor	dr =	116 mm,
length of the vessel	lv =	135 mm,
rotational speed (max)	nr	= 1200 rpm

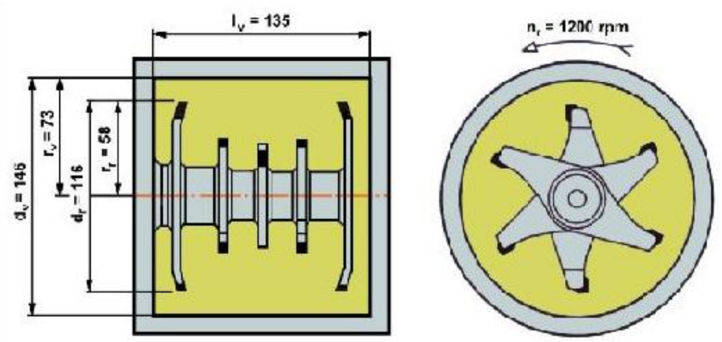


Fig. III-1:CM01, simplified cross section of the grinding unit W01-2l

In case of a uniform rotational speed, highest velocity will be transferred to the balls located near the end of the rotor blades. This is calculated by:

$$v_{b\max} = \pi\, n_r d_r \qquad (2)$$

For the case of the rotational speed of 1200 rpm, the result for the CM01 Simoloyer® is:

$$v_{b\max} = \pi \ \ 1200 \frac{1}{\text{min}} \ \ 0.116\text{m} = 437.09 \frac{\text{m}}{\text{min}} = 7.28 \frac{\text{m}}{\text{s}}$$

This is the maximum velocity that is transferred by a 90° impact of the rotor blade onto a ball located near the end of the blade. This ball will attain this velocity for a short time. Following this collision, the ball will lose velocity by collisions with other balls. To reach a similar ball velocity during free fall under vacuum (Fig. III-2Fig. III-), the ball should be dropped from a height:

$$s = \frac{v_b^2}{2g_e} = \frac{(7.28 \frac{m}{s})^2}{2 \times 9.81 \frac{m}{s^2}} = 2.7m \tag{3}$$

For high kinetic processing in drum(ball)mills, the angular velocity is adjusted to achieve the transition of cascade to cataract mode (Fig. III-3) [28]. In that case the free fall height is approximately 55 % of the diameter of the vessel (drum). Consequently the drum-mill diameter would need to be:

$$d_d = \frac{2.7m}{0.55} = 4.9m \tag{4}$$

This simple calculation demonstrates one of the main advantages of the horizontal Simoloyer®.

free fall	cascade mode	cataract mode

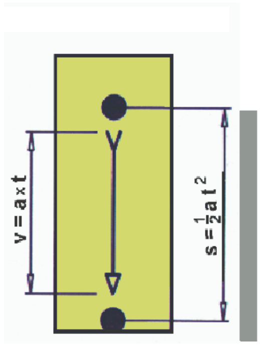
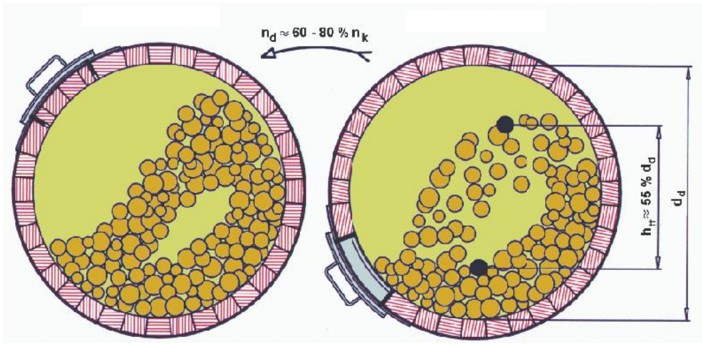

	

Fig. III-2: free fall experiment	Fig. III-3: schematic cross section of a drum-mill	

III-2 Determination of the optimum ball size and filling ratio

In the Simoloyer® (Fig. III-4), the free play or tolerance between the rotor and the inner vessel surface is:

$$d_v - d_r \tag{5}$$

To avoid the blocking of the system, it is very important to obey the relation:

$$d_v - d_r \geq 5\ d_b \tag{6}$$

As the kinetic energy is proportional to the mass, the balls have to be as large (heavy) as possible. As a matter of fact, the inner vessel surface and the balls are often coated during high kinetic processing. Therefore the advice for the CM01 Simoloyer® is:

$$d_v - d_r = 6\ d_b \tag{7}$$

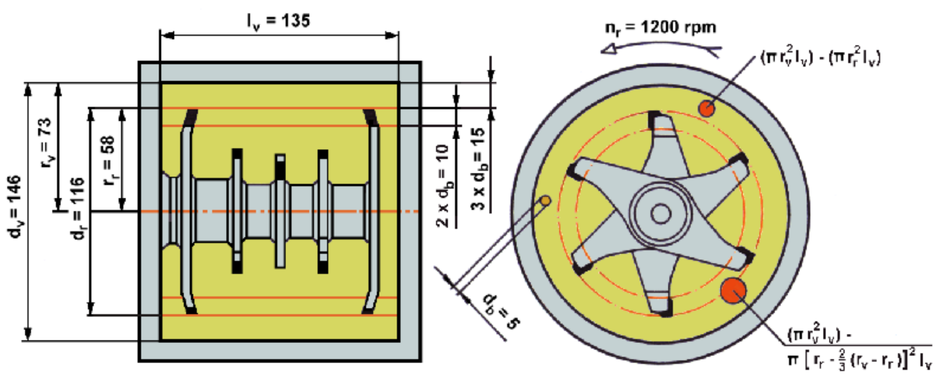


Fig. III-4: CM01, simplified cross section of the grinding unit W01-2l

Consequently for the present examination of Simoloyer® CM01-2l, the optimum diameter of the grinding media is 5 mm.

The vessel volume that needs to be filled up with balls in order to guarantee that all the balls will impact the rotor blades at the same time can be expressed by the hypothesis:

$$V_{\mathbf{b}} \geq (\pi\, r_{\mathbf{v}}^2\, l_{\mathbf{v}}) - \pi\, [r_{\mathbf{r}} - 2/3\, (r_{\mathbf{v}} - r_{\mathbf{r}})]^2\, l_{\mathbf{v}} \times \mathbf{k_d} \times \mathbf{v_b} \tag{8}$$

where $\mathbf{k_d}$ represents the density of the ball packet when accelerated, and
$\mathbf{v_b}$ is the velocity of the balls

It shall be noticed that if the velocity goes to zero, the chamber has to be filled up to 100 % in order to balance Eq (8). To allow a high degree of free space for free movement of the balls and a high kinetic impact per collision, the vessel should not be filled up more than necessary. Experience has shown that the best filling ratio is:

$$V_{\mathbf{exp}} = (\pi\, r_{\mathbf{v}}^2\, l_{\mathbf{v}}) - (\pi\, r_{\mathbf{r}}^2\, l_{\mathbf{v}}) \tag{9}$$

This is the volume between rotor and chamber circle of the Simoloyer® (Fig. III-4), which for the Simoloyer® model CM01-2l is 0.83 dm^3. In order to reach this result, the product $\mathbf{k_d} \times \mathbf{v_b}$ in Eq (8) is taken as **0.65**. This result is valid for all known Simoloyer® sizes. The formula for the volume of grinding media becomes:

$$V_{\mathbf{b}} = (\pi\, r_{\mathbf{v}}^2\, l_{\mathbf{v}}) - \pi\, [r_{\mathbf{r}} - 2/3\, (r_{\mathbf{v}} - r_{\mathbf{r}})]^2\, l_{\mathbf{v}} \times 0.65 \tag{10}$$

For the grinding chamber of the CM01-2l Simoloyer®, the result is:

$$\mathbf{V_b = [\pi\, (0.73dm)^2\, 1.35\ dm] - \pi\, [0.58\ dm - (0.73\ dm - 0.58\ dm)]^2\, 1.35\ dm \times 0.65}$$

$$\mathbf{V_b = 0.83\ dm^3} \tag{11}$$

For the case of the 5 mm steel-balls, 0.83 dm^3 correspond to a mass of 4 kg.

III-3 Conclusions Part III

To perform HEM, MA and / or Reactive Milling, a high kinetic energy impact is necessary, as the collision is regarded as the main event for the energy transfer.

Consequently not the mass of single grinding balls but the velocity (relative velocity) is of major importance.

It has been shown that a common drum (ball) mill working on the effect of gravity needs to have a 33 times (42 times / 1500 rpm, today) larger diameter than the Simoloyer®, to pick up the same velocity value.

The maximum velocity can only be reached if the grinding media has enough space for free movement. Therefore a calculation attempt for the minima filling ratio has been explained.

The maximum ball size has been determined.

Up to this point it is an attempt of the model that has to be completed.

Part IV Cycle Operation, a new way to synthesize CMB-Materials

A lot of the mechanically alloyed advanced materials show a critical milling behavior due to their ductility.
Often ductile powder components are combined with brittle components. In most cases a combination of those powders is critical due to the inherent adhesion tendency of the powder sticking to the grinding unit and the grinding media.
To be able to process these kind of powders nevertheless, milling agents or / and deep temperature milling have been applied in the past. Today these difficulties and limits are solved by the cycle operation procedure using the so called Operation Cycle and Discharging Cycle for the processing.
Part IV will focus on the results of several experiments on titanium, nickel, silver and aluminum based Materials. This is investigated by chemical analysis, by scanning electron microscopy and X-ray diffraction.

IV-1 CMB-Materials - Challenge and Difficulties

Materials with CMB, which means ductile materials like titanium, nickel, silver and aluminum based powders are of high interest for industrial applications, e.g. in aerospace, electrical components, metallic paints, etc. and are increasingly produced on the powder metallurgical route. Being processed in conventional ball milling devices those powders exhibit difficult properties: In most cases the powder yield after processing is very low because of the high adhesion tendency of the powders.
This is due to the fact that the powders stick to the grinding media, the grinding chamber and other parts of the milling device. The first consequence is that a large amount of powder is stored in layers, where no further processing can take place.

The second consequence is a sensitive change of the component concentration of the remaining powder rest which is processed. In the end of the mechanical alloying process only a low powder yield can be obtained, as a large amount of powder remains in the milling device. Furthermore, if the use of milling agents would pollute the material, the only way to achieve an acceptable powder yield is to use a suitable milling device and to apply a special milling process which also allows a scaling-up to an industrial application with an efficient powder yield, short processing times and low contamination rates.

IV-2 Processing

To perform Mechanical Alloying which is regarded as a repeated deformation, fracture and welding by highly energetic ball collisions, a high and homogeneous kinetic energy impact is necessary. To achieve this aim, a high rotational speed of the rotor of the rotary ball mill is needed. The availability of free space for free movement of the milling balls after any impact is performed by a total filling ratio of 40 % and below. However, the needed high degree of deformation and welding causes tremendous difficulties as the powder coats the milling tools and the vessel in dead layers.
These layers have a similar bad influence as dead zones. They can be avoided by frequently interruption of the impact. The idea is to break the balance between deformation, fracture and welding in the process. The procedure is described as Cycle Operation.
Since the here discussed powders mostly have to be clean powders, the processing and the powder handling, this means milling and charging and discharging have to be performed under defined conditions like vacuum or inert gas atmosphere to avoid reactions of the processed powder with oxygen and nitrogen. This is realized by the use of an air-lock with an advanced draingrating system.
Most frequently the temperature of the grinding chamber unit has to be controlled by a cooling system as the high energy impact causes an increasing powder temperature that has to be compensated by the device. In some cases even an external increase of the temperature is necessary, e.g. to favor a chemical reaction.
The milling experiments were performed in a *Simoloyer® CM01* with a chamber volume of 0.5 liters.

IV-3 The Materials Ti-24Al-11Nb and Ti-50Ni

IV-3.1 Starting powders

Several milling experiments have been carried out with titanium based alloys, especially Ti-24Al-11Nb and Ti-50Ni powders which are very difficult being processed by ball milling due to CMB. The starting powders and the evolution of the milling process were investigated by a scanning electron microscope (SEM) *Cambridge CamScan 24*. The X-ray diffraction patterns were resolved by a *Seifert PTS 3000* diffractometer (XRD) using monochromatic CuK$_\alpha$ radiation.
The starting powder Ti-24Al-11Nb (at%) was a powder blend of elemental Ti-powder and prealloyed Al-Nb powder. Fig. IV-1 and Fig. IV-2 show the particle shape of elemental Ti and Al-11Nb starting powder.

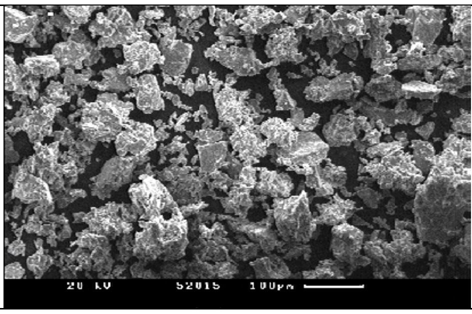


Fig. IV-1: Ti starting powder

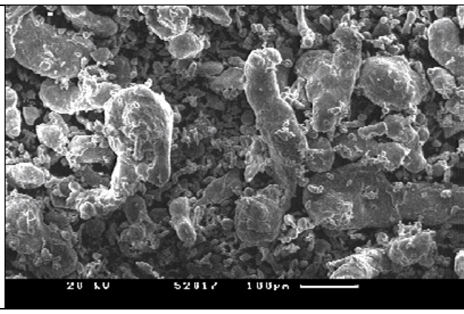


Fig. IV-2: Al-11Nb starting powder

It can be seen that both starting powders are characterized by broad particle size distributions. In the case of Ti the sizes vary from low sizes of a few microns up to sizes of 100 microns. The particle shape is fissured and irregular. The Al-11Nb starting powder exhibits particle sizes from also a few microns up to 300 microns of the largest particles. Their geometry are of spherical and cylindrical shape. The X-ray diffraction pattern in Fig. IV-3 proves the presence of crystalline phases.

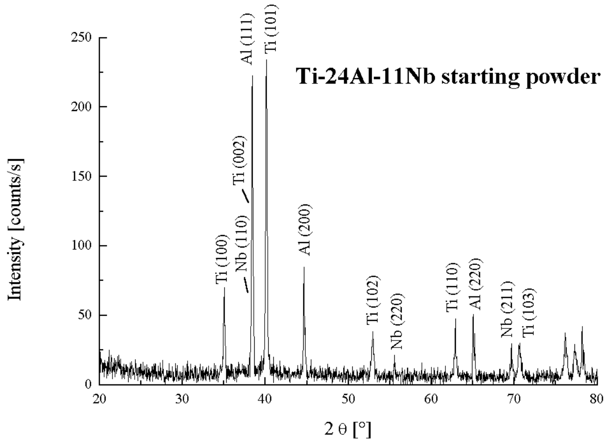


Fig. IV-3: X-ray diffraction pattern of the Ti-24Al-11Nb starting powder blend

The Ti-50Ni starting powder was a powder blend of elemental Ti-powder and elemental Ni-powder. The SEM-micrograph in Fig. IV-4 and Fig. IV-5 show the particle shape of the elemental Ti and Ni starting powder.

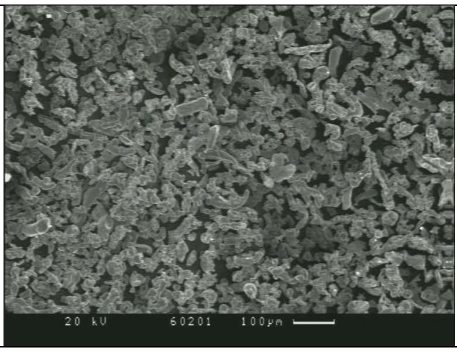


Fig. IV-4: Ti starting powder

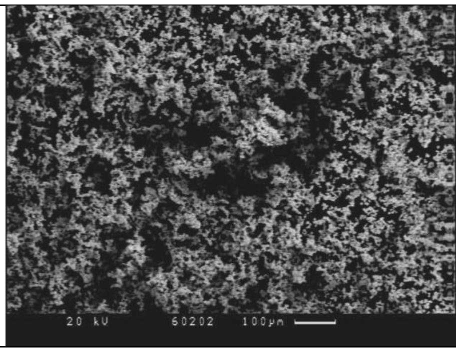


Fig. IV-5: Ni starting powder

The sizes of the Ti particles vary from 40 microns up to sizes of 100 microns and in case of the Ni starting powder particle sizes with regular shape about 10 microns can be observed. It can also be seen by the X-ray diffraction pattern in Fig. IV-6 that crystalline phases are present.

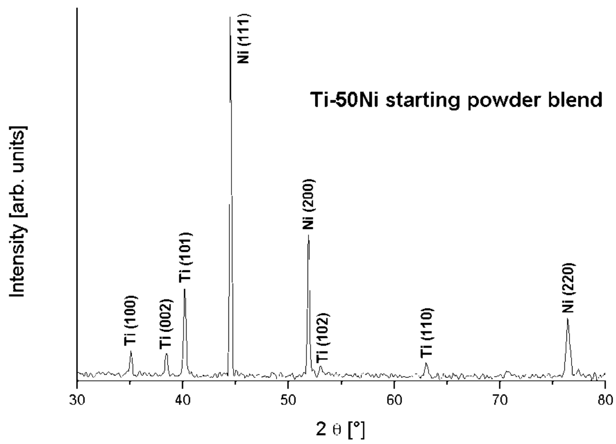


Fig. IV-6: X-ray diffraction pattern of the Ti-50Ni starting powder blend

IV-3.2 Milling Parameters

To avoid reactions with oxygen all powders were handled and processed under inert gas atmosphere (argon). The powder to ball weight ratio for all powders was chosen as 1:10 and the used conventional steel balls (100Cr6) had an average diameter of 5.1 mm.

For the Ti-24Al-11Nb alloying system milling intervals from 20 min up to 15 hours were carried out and the resulting powders were investigated by SEM and XRD. Since the tests from the time interval from 20 min up to 5 hours were followed by a constant rotational speed of 1300 revolutions per minute, the two last tests (10 h and 15 hours) were prepared by Cycle Operation (see Table IV-1).
After 10 hours of processing time 5 g of the resulting powder were extracted for investigation. The final powder discharging procedure was carried out by a special discharging cycle to receive a high yield.

Simoloyer®:	CM01-1/2 l
Milling balls:	material steel (100Cr6), diameter: 5.1 mm, total weight: 1300 g
Weight of powder charge:	130 g
Powder/ball-weight ratio:	1:10
Rotational speed:	1300 / 900 min^{-1} (cycle)
Milling atmosphere:	Argon

Table IV-1: milling parameters of the Ti-24Al-11Nb experiments for the time intervals of 10 and 15 h

The Ti and Ni starting powders were premixed in the composition of Ti-50Ni (at%) and an amount of 100 g of premixed powder was processed for each test (see Table IV-2). Several milling intervals from 1 to 10 hours were carried out and the resulting powders were investigated by SEM and XRD afterwards. Since the Ti-50Ni powder also show a CMB due to its high ductility, the procedure of Cycle Operation was to be applied. Thus, being used for Operation and Discharging allowed the alloying process as well as an acceptable high powder yield.

Simoloyer®:	CM01-1/2 l
Milling balls:	material steel (100Cr6), total weight: 1000 g, diameter: 5.1 mm
Weight of powder charge:	100 g
Powder/ball-weight ratio:	1:10
Rotational speed:	Cycle Operation, 1500 / 900 min^{-1}, 4 / 1 min (see chapter 3.)
Milling atmosphere:	Argon

Table IV-2: milling parameters of the Ti-50Ni experiments for all processing durations

IV-3.3 Operation and Discharging Cycles

Cycle Operation Procedure means to apply cyclic varied rotational speeds in order to break the balance of deformation, fracture and welding in the process.
In Fig. IV-7 and Fig. IV-8, the aplied operation and discharging cycles of the Ti-50Ni experiments can be seen. The shown operation cycle was applied on the milling experiments after the 10 h processing time in case of the Ti-50Ni powder.
An operation cycle in this case is characterized by a time interval of 4 min at 1500 min^{-1} followed by 1 min at 900 min^{-1}. Having passed the last milling interval at 10 h, a final discharging cycle was added. Such discharging cycle was composed by an interval of 4 min at a rotational speed of 900 min^{-1} and an interval of 1 min^{-1} at 1500 min.

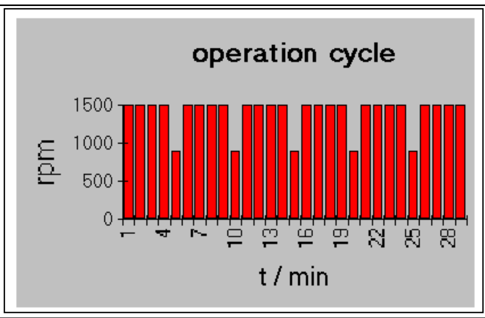


Fig. IV-7: operation cycle Ti-50Ni

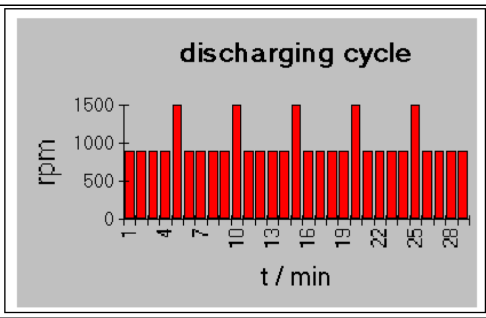


Fig. IV-8: discharging cycle Ti-50Ni

The following results were achieved by this route:

IV-3.4 Processed Powders

The results for the experiments of the processed Ti-24Al-11Nb and Ti-50Ni can be seen as follows by SEM and XRD. After a short duration of milling the particle shape of both investigated powders has completely changed compared to those of the starting powders.

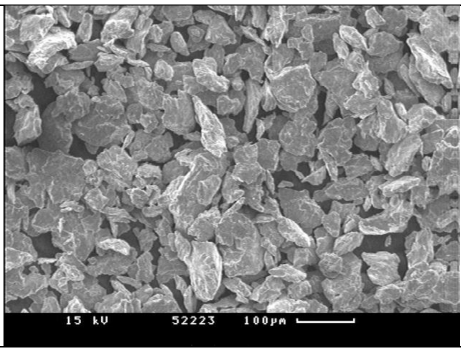


Fig. IV-9: Ti-24Al-11Nb: powder after 15 h

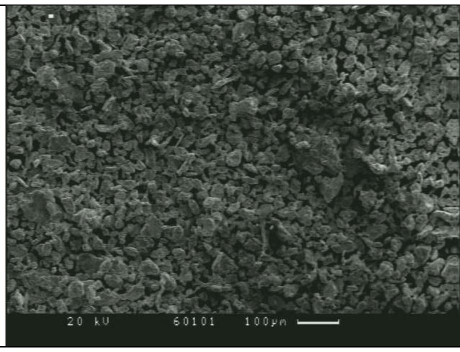


Fig. IV-10: powder after 10 h

In the case of the Ti-24Al-11Nb the particle size has been reduced to an average value of 30 microns after a total milling time of 15 h. The SEM micrograph of the final Ti-50Ni powder extraction after 10 hours shows particle sizes of 20 microns and lower. Both results indicate the beginning of the final alloying process and a homogenization of the phases. This is also represented by the XRD patterns (Fig. IV-11 and Fig. IV-12).

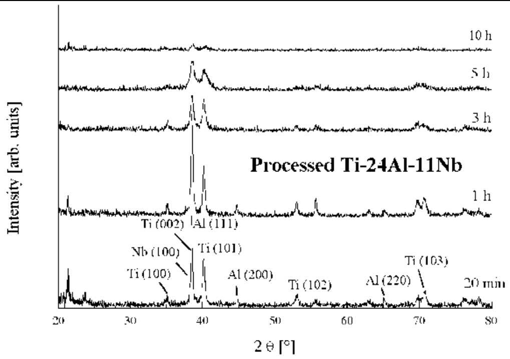


Fig. IV-11: X-ray diffraction patterns of the processed Ti-24Al-11Nb powder

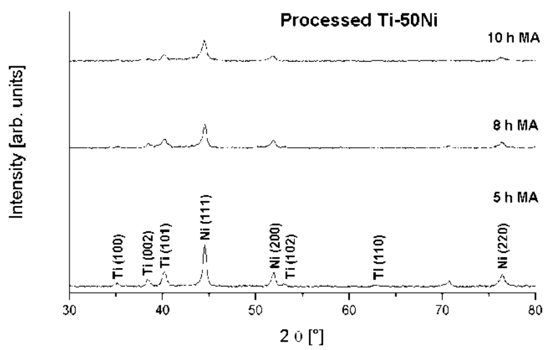


Fig. IV-12: X-ray diffraction patterns of the processed Ti-50Ni powder

IV-3.5 Powder Yield and Chemical Analysis

The achieved powder yields of these problematic alloying systems which are represented by the following diagrams (Fig. IV-13 and Fig. IV-14) are of high interest:

Although showing a critical milling behavior (CMB) and being processed for a large time interval, large amounts of processed Ti-24Al-11Nb and Ti-50Ni powder have been received following the special discharging procedure. As a successful result of a yield of 80 % powder was reached for the Ti-24Al-11Nb after 64 minutes of discharging and a yield of 70 % for the Ti-50Ni after 50 minutes approx. has been achieved. This fact proves that the milling parameters can sensitively influence the milling behavior and consequently the milling results.

The chemical analysis of the Ti-24Al-11Nb powder shows that the oxygen respectively nitrogen pickup during processing with average values of 0.279 wt.% respectively 0.058 wt.% was very low since the initial powder had values of about 0.067 wt.% oxygen and 0.0050 wt.% nitrogen. This is a remarkable result especially because Ti powders with small particle sizes usually show high reaction rates with oxygen due to their affinity.

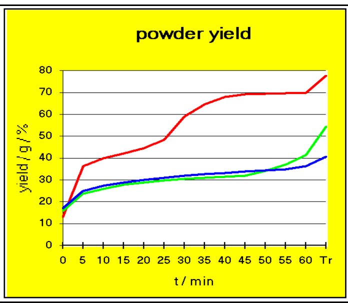


Fig. IV-13: powder yield Ti-24Al-11Nb, 15 h of processing

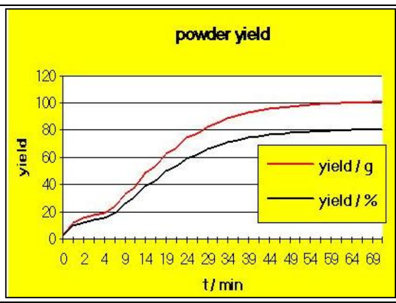


Fig. IV-14: powder yield Ti-50Ni

For the Ti-50Ni composition, these results are not yet available. The powder yield in case of Ti-Ni composition is similar.

IV-4 High Temperature Applications: Reactive Milling of Ag3Sn + Ag2O

Further investigations have been done on the system Ag_3Sn / Ag_2O which is very interesting for industrial application in electrical components (contact material). During the milling process in the Simoloyer®, a chemical reaction is started that leads to a highly dispersed tin oxide phase in a silver matrix (see Fig. IV-15). The reaction kinetic depends on the temperature and the kinetic of the milling process. This powder extremely exhibits CMB. Without Cycle Operation Procedure, no useable results can be obtained. After optimization of the milling parameters and applying Cycle Operation, however, it is possible to achieve a very high powder yield of nearly 95 % of the processed powder. Only very short milling times are necessary and consequently the contamination is not problematic.

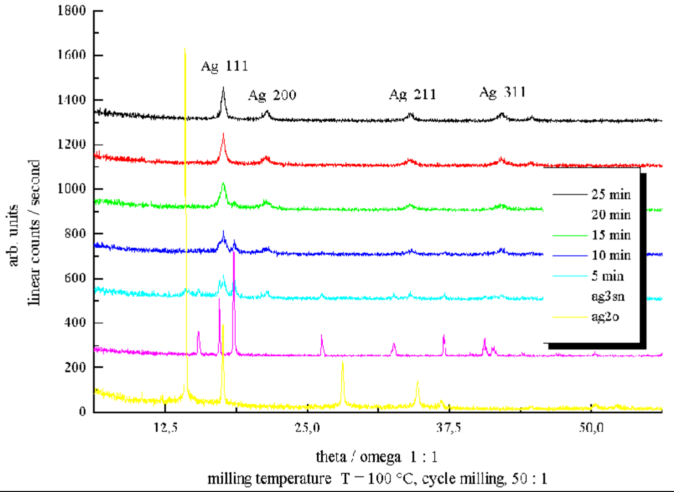


Fig. IV-15: X-ray diffraction pattern of the processed Ag3Sn/Ag2O powder

Fig. IV-16: grinding chamber after constant operation

Fig. IV-17: grinding chamber after cycle operation

Various experiments have been carried out under different temperature conditions to optimize the reaction and the powder yield [24][8]. Previous tests [21], [22] have shown that a high milling temperature favors the reaction kinetic and shortens the milling process.

During these experiments an unexpected behavior of the powder occurred: during a trial almost all of the powder stuck to the milling tools and the vessel at a dedicated time. Somehow later in the process this adhesion behavior disappeared until it appeared again later on. This effect occurred repeatedly and is not explained up to now.

IV-5 Conclusions Part IV

The HEM / MA and Reactive Milling technique applied for ductile materials opens an interesting window for prospective industrial applications, e.g. in aerospace, electrical components, metallic paints, etc.

As these materials show a Critical Milling Behavior (CBM) due to their ductility, a standard ball milling procedure does not lead to suitable results.

Using the examples of Ti-24Al-11Nb and Ti-50Ni compositions, the enormous influence of the Cycle Operation Procedure on the achievable powder yield as well as on the process itself has been shown.

HEM / MA can be used efficiently and can lead to clean powders.

In case of the Ti-24Al-11Nb, the achieved powder yield has been 80% after 60 min of discharging, the oxygen pickup has been about 0.2 wt% and the nitrogen pickup has been about 0.05 wt% after processing times of 15h, which are in particular regarding the affinity of titanium remarkable results.

In case of the contact material Ag-$Sn0_2$ where the kinetic of the chemical reaction depends on the milling temperature, it has been shown that usable results are not achievable without Cycle Operation.

This possibility of processing ductile materials (by cylce operation) in larger quantities with a sufficient powder yield gave an important push to the processing technique in general so that MA, HEM and RM is approaching many industrial fields today, like the production of ductile metal flakes [15], of electrical contact materials [5] and hydrogen storage materials [16].

Part V Energy Balance during Mechanical Alloying

0 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.

V-1 Theoretical approach

V-1.1 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:

$$P=M\,n \tag{1}$$

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).

$$E_{in} = P\,t = M\,n\,t \tag{2}$$

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

V-1.2 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) [9].

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:

$$v_{ball} = d_{rotor}\,\pi\,n \tag{3}$$

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.

Fig. V-1: grinding unit, cross section

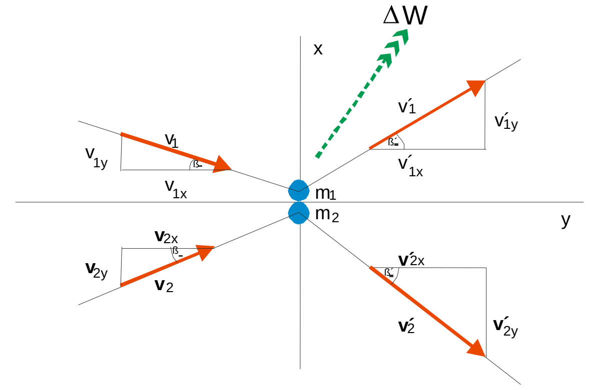


Fig. V-2: collision of grinding media

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 by several other authors. 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:

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

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.

$$\Delta W = \Delta W_{heat} + \Delta E_{powder} + \Delta E_{noise} + \Delta E_{unknown} \tag{5}$$

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

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 its 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.

V-1.3 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.

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

Further the system is losing energy in form of noise etc. (ΔE_{noise} + $\Delta E_{unknown}$), see equation Noxx.

V-1.4 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.

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

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:

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

V-1.5 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.

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

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.

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

As a result the milling chamber should be scaleable.

V-2 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.

V-2.1 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 energy.

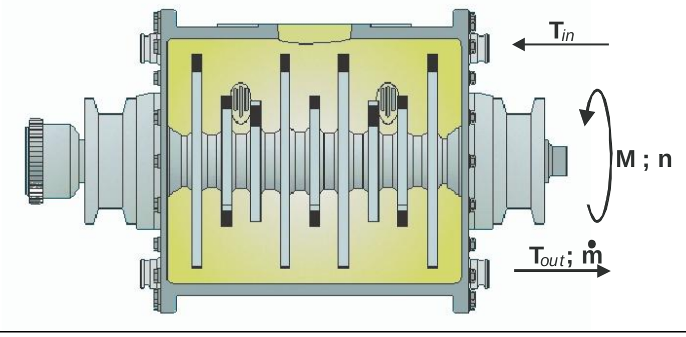


Fig. V-3: energy balance with mill CM01

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.

Simoloyer®	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
grinding media 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 V-1: milling parameters for energy balance

V-2.1.1 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.

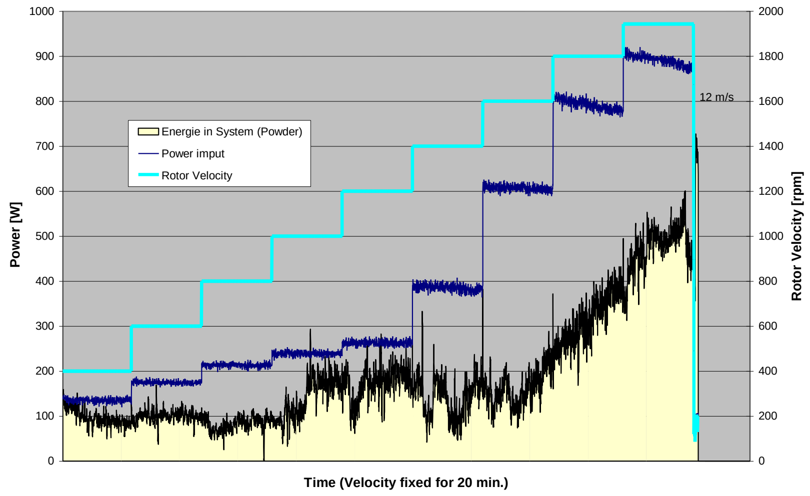


Fig. V-4: measured "powder energy

The rotor velocity, measured power consumption of the motor and the calculated energy input are shown in Fig. V-4**Fehler! Verweisquelle konnte nicht gefunden werden.**. 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.

V-2.2 Further experiment to understand the kinetic motion in the process

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.

V-2.2.1 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.

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 recognize 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.

V-2.2.2 Observations

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

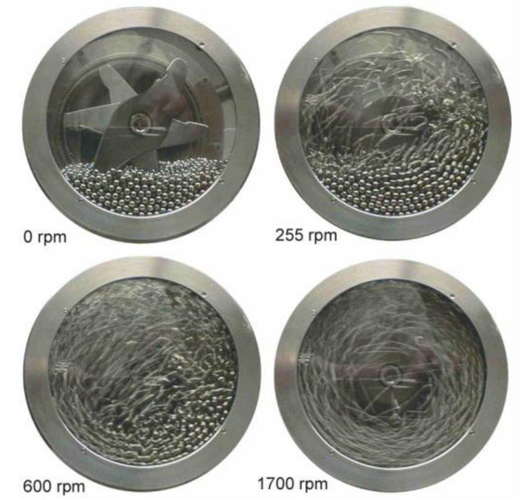


Fig. V-6: grinding media motion while operation at 0, 255, 600 and 1700rpm

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.

V-2.3 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.

Simoloyer®	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	
grinding media 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 V-2: milling parameters for scale up

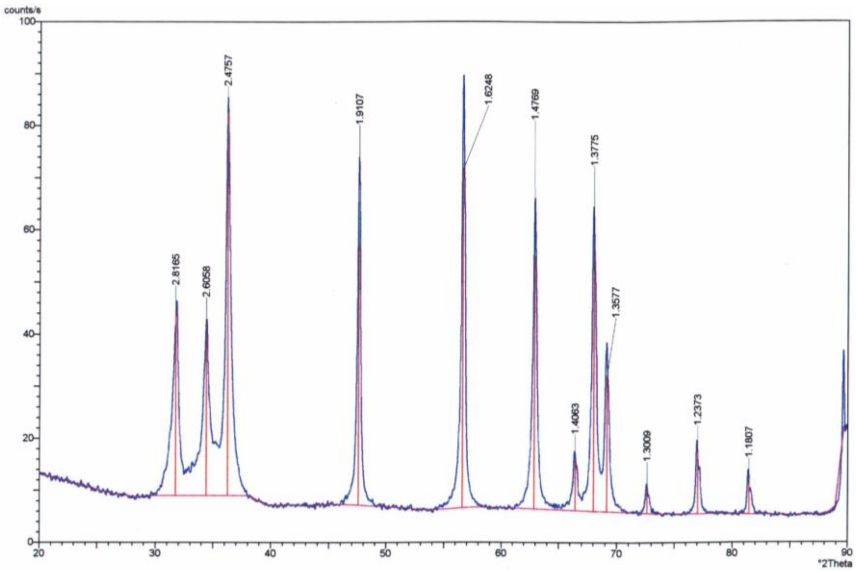
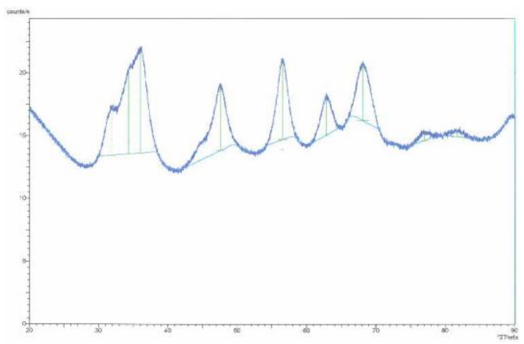
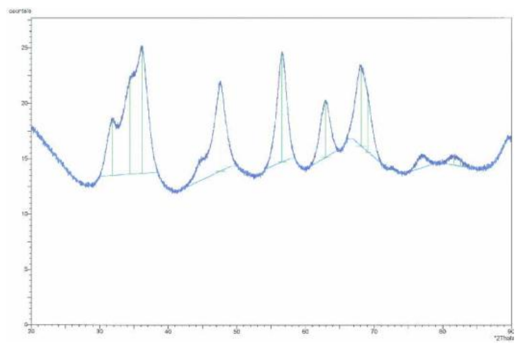


Fig. V-7: XRD-analysis of ZnO, starting powder

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

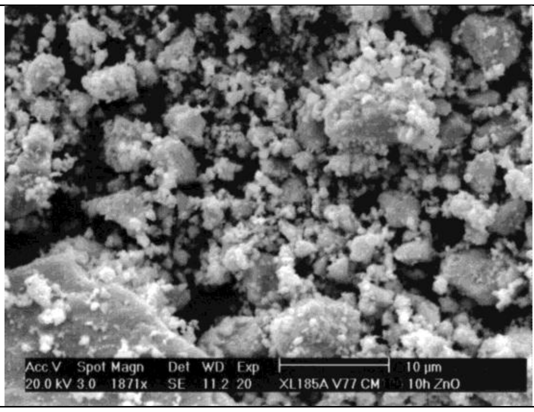
The XRD-analysis shows a slightly difference between the milling using the CM01 and the CM100 concerning the intensity of the peaks. Noticeable is the peak-intensity at about 37,5° (middle one), which was not reduced after processing with the CM01 even after longer milling time.

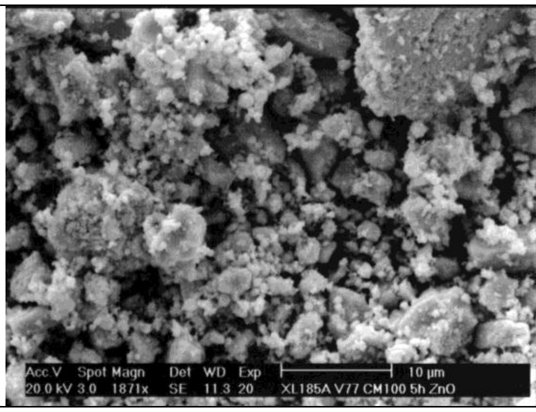
The Philips X'Pert-Organiser calculated crystallite-sizes, which are shown in table. It should be mentioned, that the necessary background, which is able to be seen in the graphs (e.g. green line in Fig. VI-8) is not the relevant one. For calculation the *full width at half-maximum* (fwhm), the background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

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

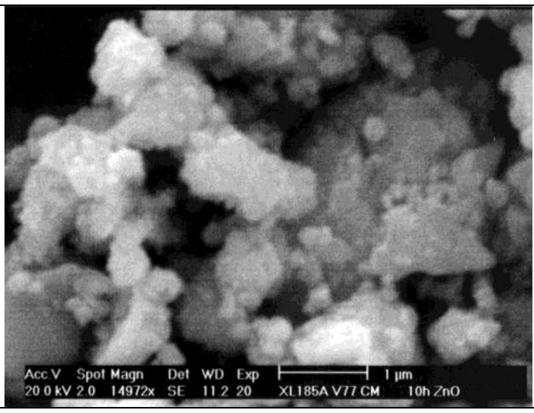
Table V-3: Philips X'Pert-Organiser calculated crystallite-sizes

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.





CM01	**CM100**



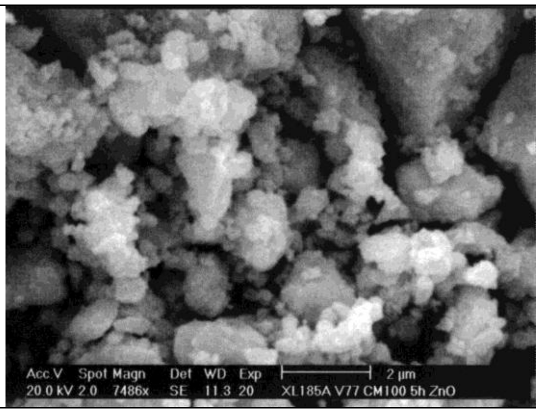


Fig.V-9: SEM-pictures after 5h milling

V-3 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 characterized as mixing. The rotor blades are moving through 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 to 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 cannot 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.

V-4 Conclusions Part V

The theoretical base for the kinetic in a horizontal rotary ball mill has been derived, the energy balance for this system has been established.

A second model, the kinetic attempt has been introduced.

The practical prove of the theoretic attempts has been given.

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.

The dependency of rotor velocity and kinetic mode in a horizontal rotary ball mill has been explained.

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.

Part VI Semi-continuously processing of Ductile Metal Flakes, Industrial Application

VI-1 Introduction

The possibility of processing ductile materials (by cycle operation) in larger quantities with a sufficient powder yield gave an important push to the processing technique in general so that MA, HEM and RM is approaching many industrial fields today, like the production of ductile metal flakes [15], of electrical contact materials [6] and hydrogen storage materials [16].

In particular the ductile metal flakes are of a high interest as they are produced by thousands of tons every year on a conventional route.

Flakes are used as metallic paints and as electrical conductive material. This leads from decoration purposes mostly based on Au, Cu and Au-Ag-Cu-alloys up to paint-pigments in automotive (Al-flakes) as well as from soldering material for micro-electronics up to printable flake-pastes (Ag-flakes and composites) for every computer-keyboard and most of the screen-heating in automotive [17].

Flakes can be used in the liquid phase sintering technique (LPS) as a suitable starting geometry for coating the to be sintered component as well as in soft magnetic materials, where the coating, the incapsulation of a magnetic [18] by a nonmagnetic can be obtained by adding nonmagnetic and ductile flakes to spherical and less ductile magnetic powder in a correspondingly tuned milling process.

The today conventional processing route is described by a low kinetic milling process in (drum)ball mills either in wet condition often using alcohol or in dry condition using stearic acid or other organic PCA`s. This leads to milling times in the range of 5 hours up to several days.

By the HEM method, the high kinetic energy transfer in the process [15], [14] is used to deform powder particles to the flaky geometry under a minimum number of collisions for the single flake where a ratio of thickness and diameter up to 1000 can be reached and a processing time of only 3 – 60 minutes is needed. A thickness far below 1µ can be reached.
The aim of the here described work is to replace a common and cost-intensive powder production procedure by a modern and high efficient processing technology.
In the first part of this work [9], the initial testing, the possibility of reaching the product-standard of quality with the high energy milling technique [1], [2] using a laboratory-scale Simoloyer® CM01-1/2 l (capacity 0.5 liters) has been proved with satisfying results regarding quality where at the same time the necessary processing time has been reduced to the surprising range of several minutes.
The following step is the scaling up of the laboratory-experience to the industrial application. Therefore the Simoloyer® CM100s (capacity 100 liters) for batch and semi-continuous powder processing has been designed and manufactured. The testing of the batch operation procedure with this system was done in Germany in Oktober 1997, to verify principle and function and in particular to prove the reproducibility of processing compared to the laboratory scale.
Due to a high demand for powder production in time, the first chosen principle for the testing of the continuous operation has been the depression method (based on suction and separation using cyclones) as the therefore necessary equipment had already been available.
The current paper describes the testing of different production principles. The results including energy consumption and total costs are discussed and compared.

VI-2 Milling Experiments - Industrial Scale

The industrial scale Simoloyer® CM100s in which the experiments were carried out is shown in Fig. VI-1.

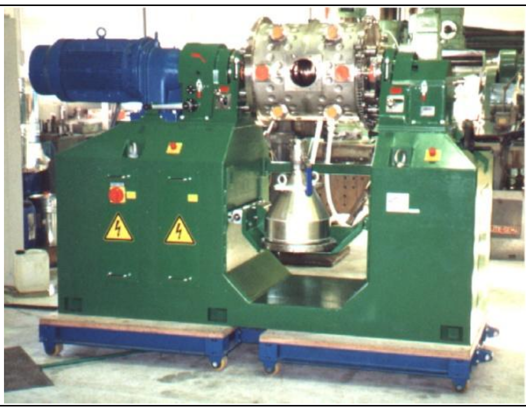


Fig. VI-1: Simoloyer® CM100s, 100 l capacity for batch

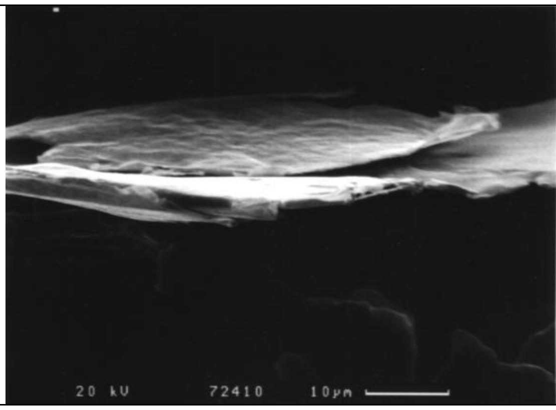


Fig. VI-2: lamellar thin Cu-particle, vertical oriented and semi-continuous powder processing (SEM-micrograph)

This system is based on the same principle as the laboratory-scale Simoloyer® that has been used for the initial testing [9]. Additionally this mill has been designed to be used in different semi-continuous processing methods. The cycle operation procedure that is known to be very useful and partly necessary for the processing of ductile powders / CMB-materials [8] can be applied as well as an air-lock system with the through diameter of 100 mm (DN100).
The constant drive power of the CM100s is pointed with 30 kW at a maximum rotational speed of 430 rpm. This refers to the maximum relative velocity [10] of grinding media in the system of 10 m/s approx. The maximum drive power is shifted to 45 kW by the frequency converter of the engine.
A part of the kinetic energy of the grinding media is transferred into the as atomized starting powder by the innumerable ball impacts [12], [13] and leads to a high deformation rate of the particles and the final product: a lamellar particle shape (flake) with an approximately diameter-to-thickness proportion of 200:1 (see Fig. VI-2).
The specific energy of the system of 0.45 kW/l in maximum is lower than the value being applied for MA (0.55 kW/l) [11], but suitable for the here needed deformation-part of mechanical alloying that is correctly described as high energy milling (HEM).
In case of the production of Cu-flakes, the processing under inert gas or vacuum is not necessary and not wanted. Only because of that, next to the well known batch operation, two different principles of a semi-continuous processing route are relevant:
One is the continuous transportation of the powder particles (product) through the impact zone (grinding chamber) using a high pressured carrier gas that is fed with powder particles outside the chamber. This carrier gas can be inert gas, but obviously not vacuum !

The second possibility is based on a vice versa principle: depression can be used to constantly discharge deformed particles due to their reduced apparent density and increased surface where the starting powder is constantly fed into the grinding chamber.
In both cases, the main criteria are the control of the transportation: in particular the remaining time of the particles in the process as well as the separation of processed, not processed and not ready processed particles. In case of batch operation these questions must not be answered because the process success can easily be checked by initial sampling and determination of the milling parameters.
In the following, these three different modes are discussed.

VI-2.1 Batch Operation

For the batch operation experiments, the 100 liter grinding chamber of the milling device was filled with 200 kg of 4.76 mm chromium steel balls (100Cr6) which refers to a total filling ratio of 41 %. The Cu-powder charge was 20 kg which refers to a filling ratio of 268 % of the gap-space of grinding media between rotor-circle and chamber-circle and to a ratio of 12 % regarding the total grinding media volume [10]. Finally the powder-to-ball-mass ratio can be calculated to 1:10.

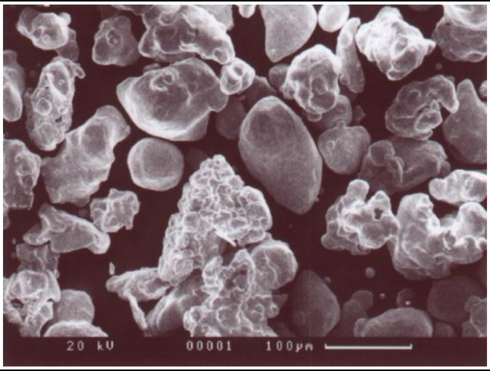


Fig. VI-3: Cu starting powder (SEM-micrograph)

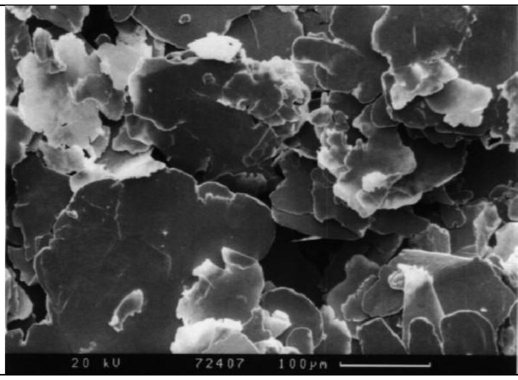


Fig. VI-4: deformed Cu-powder after 15 min of processing (SEM-micrograph)

The Cu-starting powder (see Fig. VI-3) had a mean particle size distribution of 100 µm and different particle geometry. The particles exhibit spherical but also very fissured shapes which are due to the starting powder processing of water atomization. To minimize the cold-welding process between the Cu-particles and to enforce their plastic deformation by the high energy ball impacts, an addition of 0.5 wt.% of stearic acid was used. Furthermore, as a critical oxidation reaction of the Cu-powder is not expected, the high energy milling was carried out under air. The 20 kg-powder charge was processed for a duration of 3 minutes under a rotational speed of 430 rpm which refers to a total power consumption of 45 kW. The resulting Cu-flakes of a 15 min batch can be seen in Fig. VI-4. During processing the grinding unit, the rotor shaft, the pre-seal-units as well as the bearing-units were permanently water-cooled to avoid an over-heating of the powder and a damage of the machine parts. The temperature measurement is guaranteed by the Maltoz®-control-software which allows a permanent and complete control of the milling device.

VI-2.1.1 Discharging after Batch Operation

To discharge the product after batch operation under air, the blind-lid of the main port P01 is replaced by a draingrating that retains only the grinding media from passing but not the product.
The grinding unit is turned around 180º to get the main port P01 into the discharging position. Typically, without rotor motion almost no powder comes out due to the blocking effect of the grinding media and the powder itself (poor flowability of the powder).
Therefore the Simoloyer® is usually set into (discharging-) operation, which is a constant rotation or in particular in case of ductile materials a discharging cycle [24].
In this case of lamellar particles, even the standard discharging cycle procedure is not successful.
We found for discharging the whole powder stock, another special procedure being necessary. Several tests have shown, that during discharging most of the powder particles float on the surface of the grinding media level due to their large surface area and their lamellar geometry. This is caused by the effect that the particles which have a specific low density are displaced by the milling balls with a higher density value. The result is that the flaky powder cannot pass the gaps between the balls and therefore is forced to move into the opposite direction onto the top of the grinding media.
The solution to get the powder out of the grinding unit was to apply a cyclic discharging procedure with extremely high peaks (violent-cycle). One discharging cycle here can be characterized by a time range of 3 sec at a rotational speed at 350 rpm followed by a duration of 13 sec at 65 rpm. Due to the inertia of the system and the initial ramp of the converter, the change of rotational speed cannot be imagined rapidly.

The so called violent cycle had to be applied for 5 minutes to get the powder out.

The principle what happens with the powder particles during the violent cycle can be explained by Fig. VI-5. At 350 rpm the Cu-powder particles and the grinding media are completely distributed in the grinding chamber ("powder" and "grinding media gas"). In this state of the cycle, mainly the powder particles are concentrated close to the inner container wall. Now the rotational speed is reduced to 65 rpm and the gravity is getting active.

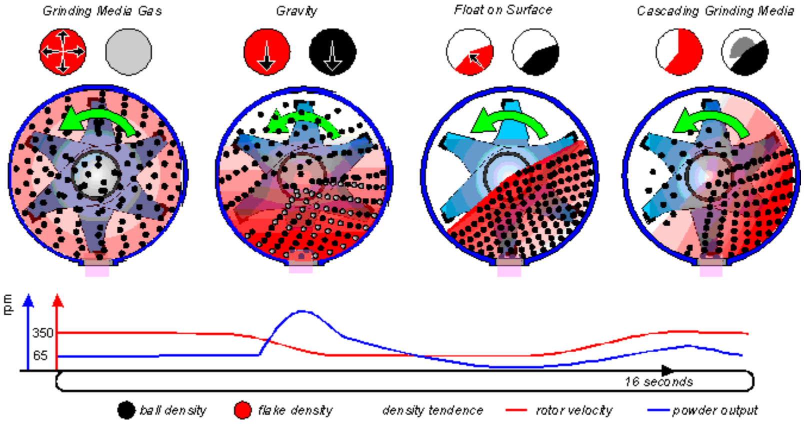


Fig. VI-5: principle of the violent discharging cycle

The result are pulsed high powder outputs for a short sequence each. However, the fact that the grinding media also drops under the influence of gravity and cover the discharging port, leads to the effect that the powder is blocked again. A second effect is that the low density flakes float on the surface of the grinding media so that again only a little powder comes out. As the rotational speed is increased to 350 rpm again, the grinding media starts cascading which leads to a limited higher powder output. After a short instant the powder output is decreasing again. Now the principle of the violent cycle is to get the short but very high powder output described at the beginning as often and as fast as possible. This works very effective and here discharges the 20 kg within 5 minutes.

If the position of the discharging port is inclined as shown in (Fig. VI-6), a higher powder output can be achieved, too. However the efficiency is much lower as in case of the here described batch of 20 kg, 15 minutes are needed for complete discharging.

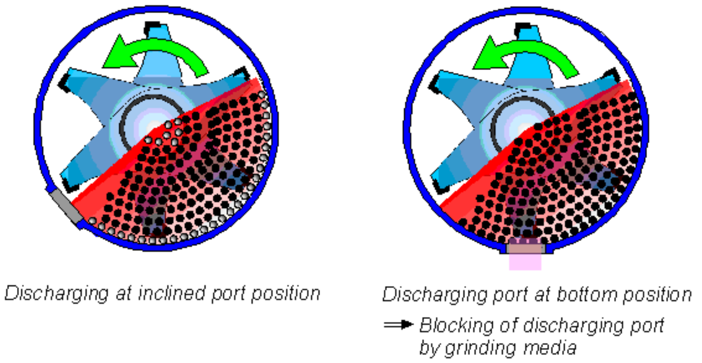


Fig. VI-6: scheme of the inclined grinding unit during discharging

VI-2.2 Semi-continuously Operation

One general goal of any industrial application or production is to receive the best possible product or often not more than the necessary quality but for the lowest possible price. As labor cost and time are very important cost-factors, a continuous processing method is in general expected to be more efficient than a batch process at least regarding the production of large quantities.

The continuous mode saves expensive labor-times for charging and discharging if this cannot be done automatically. The non-existence of interruptions in the process should safe time, too and should make the total process faster.

As far as we understand a continuous process being a process where 100 % starting material is transferred in a system to 100 % ready product and as it is not expected that the here discussed methods will reach this optimum stage, we describe the processing as a semi-continuous one.

We do expect a continuous flow of material as well as a constant operation of the processing plant, but we do not believe that the here discussed production will be possible without any classification, separation and return of *not ready product* into the process.
In case of the production of Cu-flakes two different principles of a semi-continuous processing route are relevant:
The compression-method where a high pressured carrier gas is needed and the depression-method where the principle of suction is used. In the following, these two different modes are explained:

VI-2.2.1 Principle: using Compression

The scheme in Fig. VI-7 shows the principle of semi-continuous operation inside the grinding chamber using *compression*. The additional ports M01-M07 designed for semi-continuously processing using *depression* are not shown as they are not necessary here.

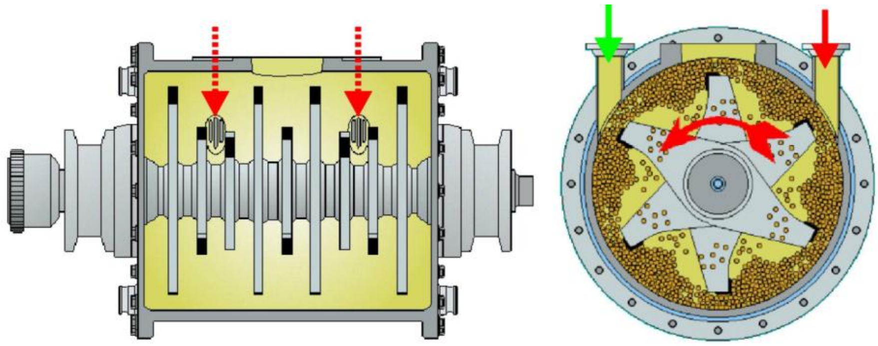


Fig. VI-7: principle of powder flow during processing

The tangential ports Z01-Z04 (see Fig. VI-8 and Fig. VI-9) are intended for a powder transportation by means of a high pressured inert gas flow (carrier gas) into and out of the grinding chamber. For this configuration the main port P01 designed for batch operation is only necessary to get an easier access to inside of the grinding chamber e.g. for loading and unloading the grinding media.
The tangential ports Z01 and Z02 respectively Z03 and Z04 can pairly be used either for powder and gas flow inlet or outlet. In this situation the powder is forced on a tangential path into the grinding chamber and is injected either with the same direction or against the direction of the grinding media. The direction of the ball motion is important for the remaining time of the powder in the grinding chamber and the influence of the process on the powder particles.
Due to the pressure gradient at those ports, the tangential accelerated powder particles are expected to be classified into light-weight/large-surface particles and heavy-weight/small-surface particles. This allows a first classification in the grinding chamber. The remaining time of the powder in the process is depending on the velocity of the rotor, the filling ratio of the grinding media, the powder content of the carrier gas, the carrier-gas pressure and the direction of gas/powder input.
Good results are expected to be obtained in case of a high rotational speed and or a high filling ratio when the input direction is chosen parallel to the rotation. In case of a low rotational speed and or a low filling ratio, the direction of input shall be in opposite direction to the rotation. A strong dependency to the accelerated mass of the balls is expected.
However, experiments concerning this configuration that is the most prospective possibility are not yet finished and are a main future task.

VI-2.2.2 Principle: using Depression, testing

The second relevant possibility for the semi-continuous operation is the operation under depression. Concerning this configuration several experiments with the Simoloyer® CM100s have been carried out. The general idea is to charge and discharge the milling system continuously with powder in that way that always the same mass of powder is in the grinding unit. The transportation of the powder is done by depression.
Therefore this grinding unit is fitted with 7 additional ports in order to find out the optimum configuration by experience.
Regarding the filling-parameters, the same mass, size and quality of grinding media (200 kg of 4.76 mm chromium steel balls) as in case of the batch operation procedure was loaded into the grinding chamber. In several tests, the rotational speed has been varied from 250 to 340 rpm and the constant powder stock in the grinding unit has been varied from 5, 10 to 15 kg.

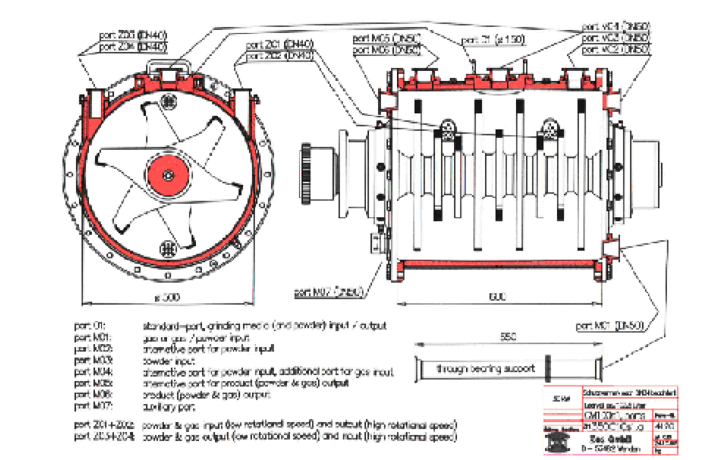


Fig. VI-8: scheme of the grinding unit, ports

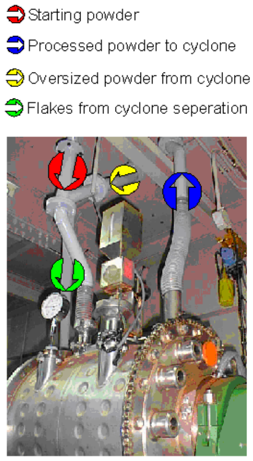


Fig. VI-9: piping-configuration (depression)

The best results have been found with the following (piping) configuration:
The ports M03, M04 and M05 are connected to a first cyclone which manages the powder classification. The whole system including the grinding chamber is depressed by a fan installed outside of the system. The starting powder is fed into the grinding chamber by a cross-connection in the pipe between the port M04 and the first cyclone. A load cell measures the total weight of the machine and the amount of the powder in the process which is kept at a constant value of 10 kg by an electronic control system with an automatic feeder at the cross-connection. If the powder is varying from the constant value, the corresponding amount of starting powder is automatically reduced or added.
Because of their reduced density and their increased surface area the powder particles are sucked out of the ports M03 and M05 and classified by the first cyclone. Heavy particles are returned through port M04, lighter ones are led through a pipe to a second cyclone were the particles are classified again. As a narrow distribution is needed, now to light particles are separated and the final product is deposited in a container which is positioned on a second load cell in order to measure the amount of produced powder.
A defined amount of stearic acid (PCA) is added at a tangential port directly into the grinding chamber by another automatic feeder that is connected to the control-system. For the definition of the amount, the dependency to the power-consumption of the system is used. This is possible as this PCA has a lubricate-function and consequently influences the power-consumption where the filling parameters are constant. A necessity here are sensitive measurement systems that cannot further be described here. Another tangential port is equipped with depression-measurement.

VI-3 Productivity

As for any industrial process the productivity - the relationship between input and output - is of major importance, several tests have been carried out in order to determine economical parameters regarding filling ratio (grinding media and powder), time and energy consumption.

VI-3.1 Productivity of Batch Operation

By the described batch operation procedure it is possible to produce a powder batch of 20 kg in a satisfying quality within a processing time of 3 minutes. To discharge the powder, the described violent cycle has to be applied for 5 minutes. Fixing the necessary time for charging the powder and handling the system to another 10 minutes, the total time for 1 trial is 20 minutes all together. This leads to a production-capability of 60 kg per hour (the theoretic process-capability refers to 400 kg/h). The needed total power had a value of 45 kW during processing and an average of 20 kW approximately during discharging by means of the violent cycle.

VI-3.2 Productivity of Semi-continuous Operation using Depression

By the described semi-continuous operation procedure using *depression*, the most prospective results were achieved with 10 kg copper powder being constantly in the grinding unit.
Figure 10 describes the powder yield (received mass of ready product per hour), the measured apparent density of this product, the power consumption of the system as well as the calculated specific energy consumption per ton of powder yield for 5 tests with different rotational speeds (250 - 340 rpm). Additionally, on the right hand side of the graph, the corresponding data of the production-capability (not the process-capability !) of the described batch operation procedure is given.
The measured parameters show that at a rotational speed of 320 rpm a yield of 80 kg per hour with an apparent density of 1.07 g/cm^3 could be achieved at a minimum of an energy consumption of 263 kWh/ton.

Keeping in mind that the amount of powder and grinding media being in the process is constant, it can be explained that the apparent density is vice versa proportionate to the rotational speed of the rotor that is under these conditions proportionate to the maximum relative velocity of - and consequently proportionate to the kinetic energy transfer by - the ball impacts (collisions) in the chamber.
The comparison between batch operation and the depression-mode of semi-continuous operation regarding the production-capability shows that the result in case of the semi-continuous procedure is 25 % higher (60 kg/h : 80 kg/h). However also the total energy consumption is higher. This is explained by the much higher theoretic process-capability of 400 kg/h in case of the batch operation procedure.

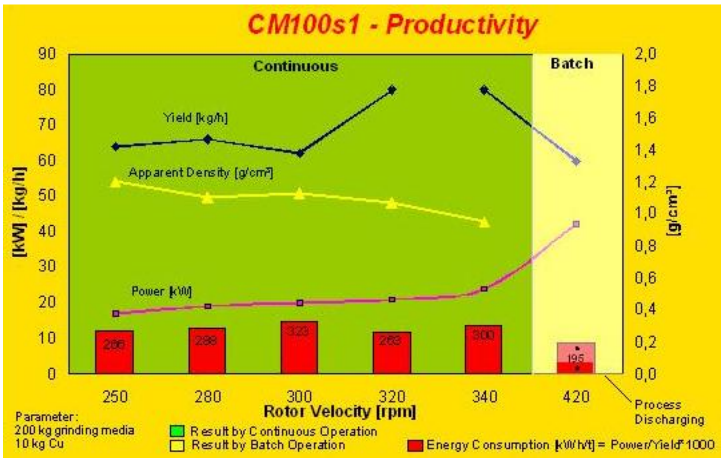


Fig. VI-10: CM100s - productivity

VI-4 Processing costs

The following table describes the calculation attempt of the total processing costs. The results there are of major importance for the decision if a process can be economically applied, which kind of process has to be chosen and where in the world this has to be.

	CM100s1 Continuous	CM100s1 Batch
Grinding Unit	185,000 DM	125,000 DM
Load Cell	100,000 DM	-
Air Lock, etc.	-	20,000 DM
Cyclone	50,000 DM	-
Basis Simoloyer®	300,000 DM	
Total Investment	635,000 DM	445,000 DM
Investment / Yield	567 DM / t	530 DM / t
Calculated Life Time	14000 h	
Yield	0,08 t/h	0,06 t /h
Life Time Yield	1120 t	840 t
Energy Consumption	263 kWh/t	195 kWh/t
Energy Costs	0.35 DM / kWh	
Energy	92 DM / t	86 DM / t
Labor costs Germany: China:	80 DM / h 3 DM / h	
Supervising time	6 min / h	
Handling time	-	30 min / h
Labor costs / operation hour Germany: China:	8 DM / op-h 0.30 DM / op-h	40 DM / op-h 1.50 DM / op-h
German Labor costs / t Germany: China:	100 DM / t 4 DM / t	667 DM / t 25 DM / t
Total Processing Costs Germany: China:	**759 DM / t** **663 DM / t**	**1.283 DM / t** **641 DM / t**

Table VI-1: production costs

The following graph explains that the main varying factor is the part of labor costs:

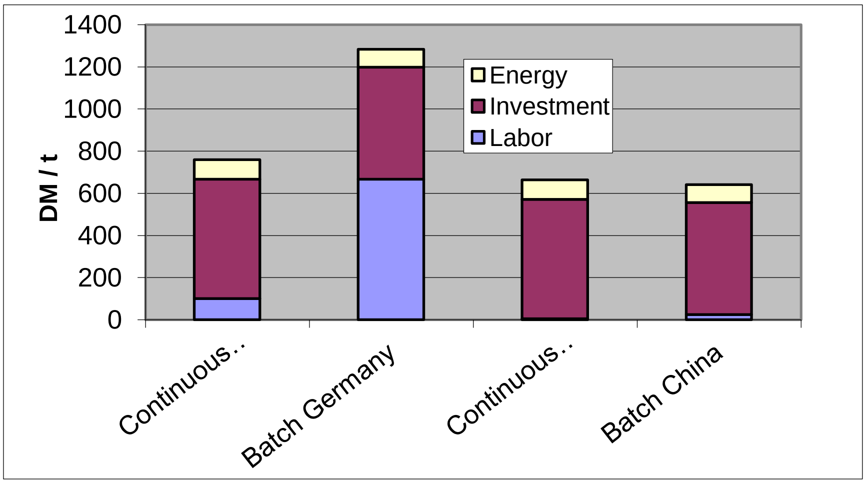


Fig. VI-11: production costs (Germany/China – Batch/Conti.)

Furthermore labor-intensity describes the main difference between batch- and continuous operation: 1 hour and 15 minutes of labor per 1 ton of continuous production is to be compared with 8 hours and 20 minutes of labor per 1 ton of batch production. This is a factor of 6.6 and explains the surprising situation, that e.g. in Germany, where the labor-costs are very high, the continuous operation procedure is much more economically and e.g. in China, where the labor costs are very low, the batch operation procedure is the cheaper one.
At this point it can be seen, that it has been the right decision, to operate the Simoloyer® with a control-software (Maltoz®) based on multimedia [24] where an important aim is easy using.
At this point the market-access (transportation and storage costs to meet the customer) is not regarded.

VI-5 Conclusions Part VI

A very interesting and already existing industrial application of particle deformed powders (ductile metal flakes) has been described.

It has been explained that a part of Mechanical Alloying, the deformation-part can be used with a much higher efficiency than any other common method to achieve the wanted goal.

It has been shown that the batch operation procedure of the tested CM100s1 leads to a high productivity of 60 kg/h.

However, neither constant discharging nor the discharging cycle procedure could be successfully used to unload the powder (due to *float on surface*). Therefore a new discharging procedure (Violent Cycle) was described and introduced into the Maltoz®-control-software.

The two relevant principles (depression and compression) of semi-continuous processing were discussed.

The productivity of the depression method (80 kg/h) was found to be 25% higher than the productivity of batch operation. The total energy consumption was 26% higher (263 kWh/t : 195 kWh/t).

The possibility of highest potential, the semi-continuous processing using compression has not been tested yet.

The attempt of total processing cost-calculation has shown that based on conditions in Germany, the tested continuous processing (DM 759,00/t) is 46 % cheaper than the batch operation (DM 1.399,00 / t).

As the main difference of costs between continuous and batch operation is caused by labor costs, this model is almost turned around when going e.g. to China. Here the batch operation with a value of DM 641,00 / t is 3 % cheaper than the continuous method (DM 663,00/t).

Part VII Processing of Ceramic Powder using HEM

VII-1 Introduction

High Energy Milling (HEM) is a well known and commercially used technique [1], [2], [12]. Today the applications are limited to the range of metal based materials, alloys and composites where the methods are described as Mechanical Alloying [4], [12], [30], HEM and Reactive Milling [30].
Since the high kinetic energy transfer represents the performance of these techniques [2], [4], [12], [30], [15], [31], up to now it has not been possible to apply them for pure ceramic materials. This is simply caused by the contamination problem, as milling tools e.g. made by ceramic usually do either not show a suitable shock-resistibility or hardness.

Part VII is the report of a study and development of suitable milling tools to be used in the well known Simoloyer®-mill or in other high kinetic systems.
The goal is to be able to use the high kinetic processing technique and approach the existing range of ceramics processing. Most important is the high potential of new materials, composites and applications.
The majority of today's applications are the production of fine powders, thus the main route is described as particle size reduction.
The traditional milling-devices used for this are the drum-ball-mills which are characterised as low energetic systems with a specific energy of 0.01-0.03 kW/l [9].
The terminal size in dry milling condition refers to a diameter d = 15-20 µm, in wet milling condition d = 10 µm.
Usually a long duration of the milling procedure of up to a few days is required, a real continuously processing is not considerable.
As e.g. the consolidation behavior of metallic and ceramic powders is considerably influenced by their particle size, there is a high potential for fine ceramic powders with a particle size of a few microns or less one micron which is required to improve the mechanical properties [10] of products and/or facilitate following processing, e.g. a better fluidity of the powder by injection and thermal spray or a better sintering activity due to their large free surface with an elevated particle contact density.
Another very interesting application is the ultra fine distribution of a ceramic hard-phase in a ceramic matrix in nanometer-scale [31], [14], [35], [36]
Always a dry milling process is in principle to be preferred as any fluid process control agent (PCA), such as water or alcohol, is required to brake the milling intensity unnecessarily.

VII-2 High Kinetic Processing Device

Using the high kinetic processing device (Simoloyer® CM01-2l, figure VII-1a), the milling balls are accelerated by the rotating rotor and collide with each other at a relative velocity up to 14 m/s. A section view of the grinding unit W01-2l is shown in Figure VII-1b. Due to a high kinetic energy transfer with a specific energy of 0.55 - 3 kW/l, the processing is also for ceramic materials expected to be tremendously more efficient than achievable by the conventional systems (mills).
High Energy Milling (HEM) is a well known and commercially used technique [1], [2], [12]. Today the applications are limited to the range of metal based materials, alloys and composites where the methods are described as Mechanical Alloying [4], [12], [30], HEM and Reactive Milling [30].
Since the high kinetic energy transfer represents the performance of these techniques [2], [4], [12], [30], [6], [7], up to now it has not been possible to apply them for pure ceramic materials. This is simply caused by the contamination problem, as milling tools e.g. made by ceramic usually do either not show a suitable shock-resistibility or hardness.

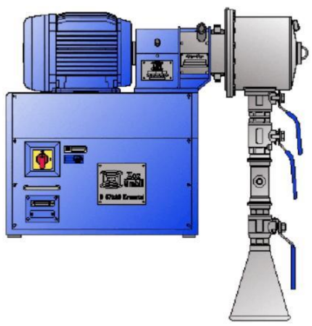


Fig. VII-1 (a) Simoloyer® CM01-2l

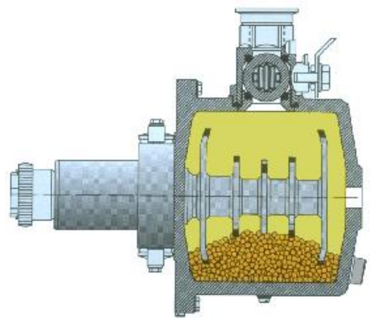


Fig. VII-1 (b) cross sectional view of the grinding unit

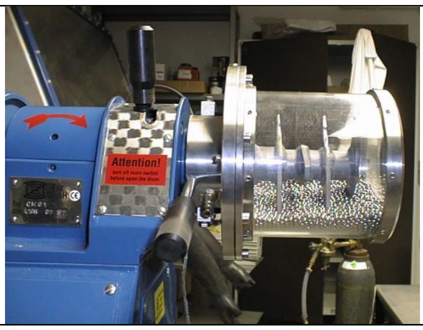


Fig. VII-1 (c) trial grinding unit made of glass

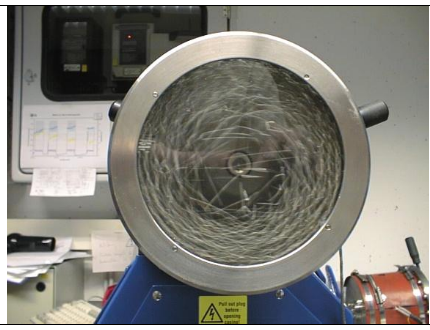


Fig. VII-1 (d) dynamic moving at 1650 rpm

Part VII of the present paper is the report of a study and development of suitable milling tools to be used in the well known Simoloyer®-mill or in other high kinetic systems.
The goal is to be able to use the high kinetic processing technique and approach the existing range of ceramics processing. Most important is the high potential of new materials, composites and applications.
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The traditional milling-devices used for this are the drum-ball-mills which are characterized as low energetic systems with a specific energy of 0.01-0.03 kW/l [9].
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Another very interesting application is the ultra fine distribution of a ceramic hard-phase in a ceramic matrix in nanometer-scale [9], [10], [11], [12].
Always a dry milling process is in principle to be preferred as any fluid process control agent (PCA), such as water or alcohol, is required to brake the milling intensity unnecessarily.

VII-3 New milling tools

The demand of ceramic powders on the grinding unit is extremely high due to the high hardness of these materials. Following long-term experience with the application of the HEM-mill and assuming that the principle of wear-behavior of this system for the use of ceramic powders will be similar to the principle in case of metal-based materials, the characteristic of the main components of the milling tools, the grinding chamber, the rotor and the grinding media are differently exposed to the kinetic and have estimated values regarding contamination as given in Table VII-1:

component	value of contamination	surface in contact	kinetic impact
grinding chamber	< 5 %	large	low
rotor	< 5 %	small	high
grinding media	> 90 %	very large	high

Table VII-1: wear characterization, metal based

Rotor and grinding media do show a high degree of interaction due to the equal and high kinetic impact here. The most stressed parts of the rotor are the tips (blade ends) where bulk wear-parts transfer the energy impact. These parts must be chosen according the grinding media. With respect to the by experience given knowledge, that the grinding media in general causes more than 90 % of the contamination by weight, the quality of grinding media must be chosen with respect to acceptability as a contamination impurity in the product or/and the contamination value must be acceptable low.

In the theoretic attempt, the high kinetic process here shows an advantage over the low kinetic one, as HEM is mainly based on collision, not on friction and shear. If the grinding media does not break during its collisions, the single grinding balls transfer a high degree of kinetic energy and are more exposed to plastic deformation than to wear. The same is valid for the partners rotor and grinding media.

The rotor and the grinding media are the most critical components regarding the application in ceramics as they are highly exposed to shock-load in the process which is a critical aspect of ceramic material. The shock-resistibility or toughness has a strong dependency to the hardness where the hardness of the grinding media is a determining factor for the impurities into the product due to its large surface being in contact with the product during processing. Components must be found that are hard and though enough to allow an acceptable contamination rate and quality without fall out.

In order to enhance the wear resistance of the rotor and to prevent the powder from contamination of iron, the rotors are made by different materials, such as full ceramic rotor of Al_2O_3, ZrO_2 and hard metals. The inside wall of the chamber is either built by Al_2O_3 slabs (lining) or coated by Co-WC-based hard coatings.

The three main designs of tested grinding units for the laboratory scale mill (Simoloyer® CM01-2l), are described in Table and shown in Figures 2-4. A further wear experiment with Si_3N_4 rotor tips will be done. The background of the choice of Si_3N_4 bulk material as rotor tip is based on his high hardness and well toughness in comparison with other ceramic materials. However a test with this material could not be successfully performed yet.

prototype	description of the test unit	
prototype 1	rotor tip: rotor blade: chamber:	Al_2O_3 ceramic bulk material Al_2O_3 plasma coated steel rotor wing Al_2O_3 lining
prototype 2	rotor tip: rotor blade: chamber:	hard metal from WC + 6% Co binding method: brazed without coating thermal coated by WC + 17% Co
prototype 3	rotor tip: rotor blade: chamber:	ZrO_2 – ceramic full material binding method: glued without coating Al_2O_3 lining

Table VII-2: three prototypes of the laboratory scaled grinding unit, Simoloyer® CM01-2l

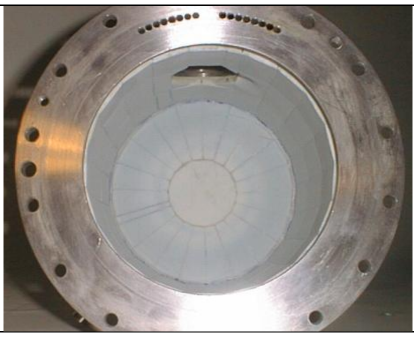
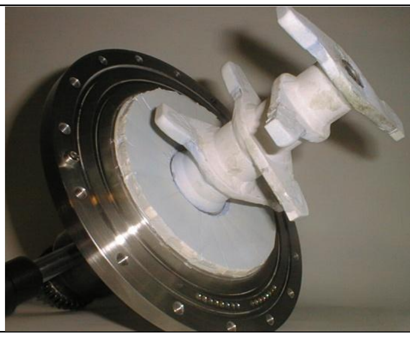


Fig. VII-2 (a) prototype 1: chamber with Al2O3 lining



(b) Al2O3 bulk rotor tips and plasma coated rotor blades

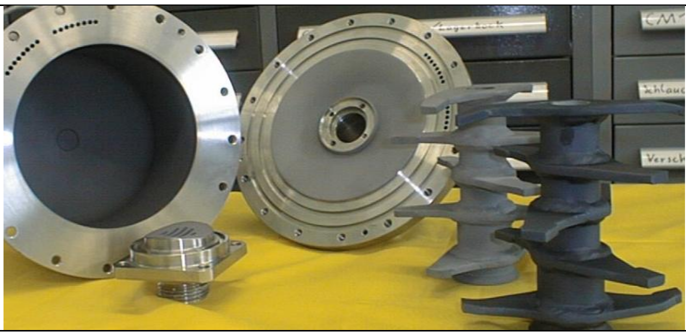
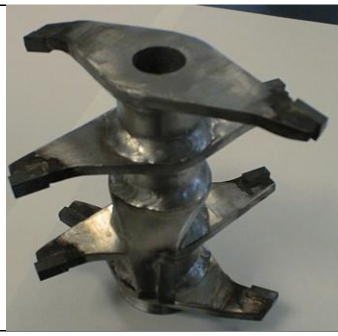


Fig. VII-3 (a) prototype 2: chamber with WC-17Co sprayed coating



(b) WC-6Co (hard metal) bulk rotor tips before spray coating

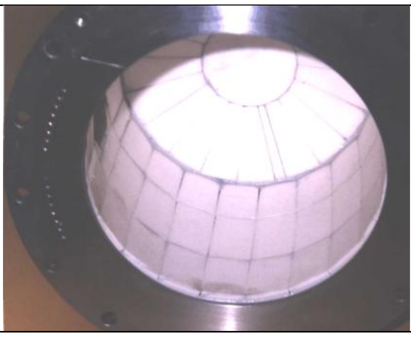


Fig. VII-4 (a) prototype 3: chamber with Al2O3 lining

(b) ZrO_2 bulk rotor tips

VII-4 Wear Testing

Milling tests in the prototype-grinding units (two liter total volume) were carried out with different ceramic and/or intermetallic powders, such as Al_2O_3, SiC, Quartz, $ZrSiO_4$, TiC, NiAl. Small samples of powder were extracted from the grinding chamber for SEM investigation. The remaining powder stock was processed continuously and followed by a final and complete powder discharging. A typical combination of milling parameters is shown in Table VII-3.

In many cases cycle operation procedure [30], [6], [7] for the processing is chosen in order to achieve a high powder yield (>90%), by preventing agglomeration and adhesion. Materials such as steel (100Cr6), ZrO_2 and ZrO_2 (Yttria stabilized) were used as grinding media (milling balls).

Simoloyer®	CM01-2 l
grinding media	steel (100Cr6), ZrO_2, ZrO_2 (Yttria stabilized), diameter:4.8mm
weight of one powder charge	100-200g
powder/ball-mass ratio	1:50-1:10
rotational speed	1000-2000min^{-1}
process atmosphere	Argon or air
cooling	water
duration of milling process	0.5 – a few hours

Table VII-3: milling parameters for ceramic powder processing

The results with respect to the grinding units after wear test are shown in Fig. VII-5 to Fig. VII-10. It could be observed that the materials loss of the components of the grinding unit, the rotor, the chamber and the balls, were differently, which means that they suffer under various intensity of ball impact and wear during the milling process.

VII-4.1 prototype 1

In case of prototype 1, the Al_2O_3 rotor tip has a clear wear after 3h milling with ceramic powder. The surface of Al_2O_3 lined inner wall of the chamber was optical not changed. Slight wear of the rotor wing could be seen (Fig. VII-5 and Fig. VII-6). The application of Al_2O_3 ceramic for the inner wall of the chamber is possible, but for the rotor tip is not to be recommended.

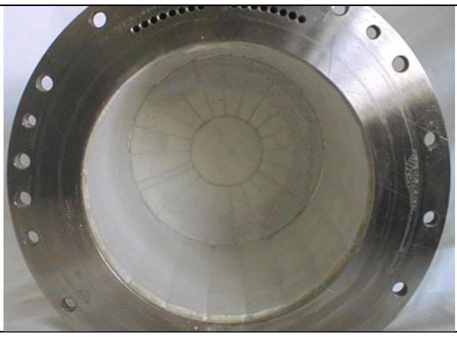


Fig. VII-5: grinding chamber lined with Al2O3 after 5h, hardly wear of the Al2O3 lining could be observed

Fig. VII-6: Al2O3 rotor after 3h milling, the rotor tips were worn out

VII-4.2 prototype 2

Well resistance against wear of the hard metal rotor tip were shown by the prototype 2 (Fig. VII-7 and Fig. VII-8). After 20h hardly material loss could be observed (Fig. VII-8, only the sharp edges of the plate were broken up after short time). Over 200 h milling time of this rotor was carried out under extreme abrasive conditions with ceramic powders. Furthermore, an increase of the rotary speed from 1300 rpm to 2000 rpm was realized, which refers to an increase of the kinetic energy of around 79%, so that a more efficient milling process could be expected. The adhesion of the thermal spayed WC+17Co coating is very important for the application. After a few hours processing a small area of the coating on the bottom of the chamber was removed (see Fig. VII-7). Due to the impact of balls during the milling process a press loading was charged on the wall, which could lead to an embedding of the hard coating into the steel matrix of the chamber.

Fig. VII-7: WC-17Co coated milling chamber after

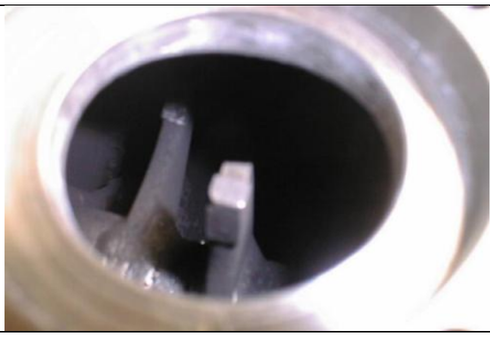


Fig. VII-8: Hard metal rotor after 20h, hardly wear of the rotor tips, thermal spray coating remains

VII-4.3 prototype 3

The wear resistance of ZrO_2 plates on the rotor tip is not sufficient (Fig. VII-9 and Fig. VII-10). Even though no breaking of the ZrO_2 pieces was observed, the rotor tips shown strong material loss after 1 h. A further testing with other ceramic materials, e.g. Si_3N_4, will be continued. A prime work to bind the Si_3N_4 onto the rotor tips by brazing appeared not successful, because a strong thermal stress was built after the brazing by a temperature of 1000°C which leads to an increasing of the brittleness of the Si_3N_4 plates. An improvement of the binding method should be developed.

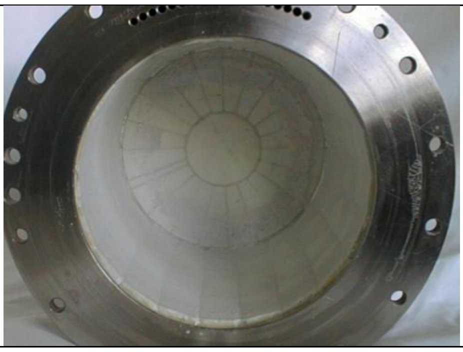


Fig. VII-9: chamber after milling

Fig. VII-10: ZrO2 rotor after 1h, the rotor tips worn out

VII-4.4 Grinding media, 100Cr6 (self) coated by Al2O3-5SiC

The milling tests of chromium steel balls with Al_2O_3 + SiC (5%) powder showed that the wear of the steel balls is surprisingly slight, even though the balls were used for the processing of high abrasive material. The microscopic investigation reveals that the steel balls were coated after a short milling time by the powder, so that a further wear of the balls could be avoided. The “coating” consisted of Al_2O_3 and has an average thickness of 5 microns (Fig. VII-12) which might be adhered by van der Waals’s binding [13], [37], [38]. This cold compacted “coating” did protect the steel surface from wear during the milling and prevents contamination from the iron.

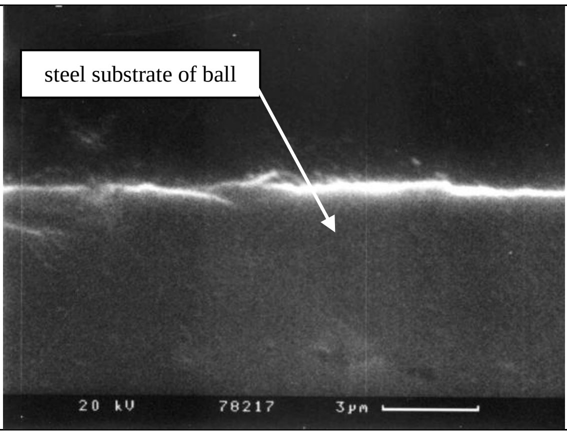


Fig. VII-11: cross section of a steel ball before milling

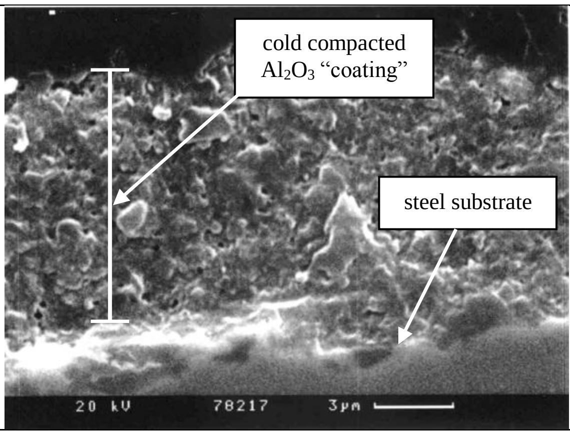


Fig. VII-12: cross section of a ball with cold compacted “coated” Al2O3 layer

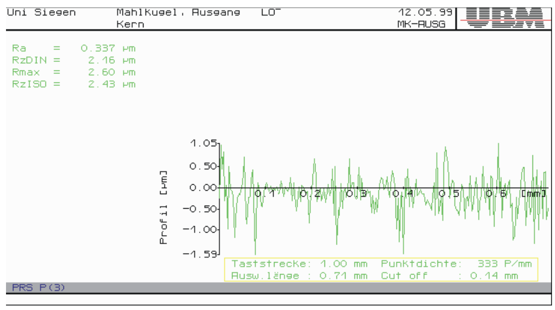


Fig. VII-13: roughness measurement of a new ball

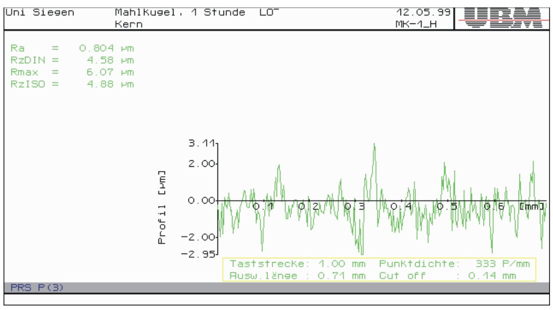


Fig. VII-14: roughness measurement after 14h

The variation of the surface roughness was determined (Fig. VII-13 and Fig. VII-14). The average value of Ra was 0.4 microns before the milling and 0.8 microns after 14h. Although the roughness of ball surface was increased after short milling time, the measurement of the values of Ra reveals that they kept constant with the time of processing.

VII-4.5 Grinding media, ZrO2

Milling tests was carried out with ZrO_2 balls (Fig. VII-15 and Fig. VII-16). Milling unit was a laboratory scaled machine with tow liter milling volume, by a rotary speed of 1300 rpm and with Al_2O_3 powder. After 1h the milling balls shown a strong wear and a part of the ball were broken.

	
Fig. VII-15: new ZrO2 balls	Fig. VII-16: ZrO2 balls after 1 h milling. Many balls were broken up

VII-4.6 Grinding media, ZrO2 yttria stabilized

Yttria stabilized ZrO_2 balls were tested under same condition presented in sub-chapter 4.5. The results shown in Fig. VII-17 and Fig. VII-18. A comparison of wear behavior of two kinds of the ZrO_2 balls are clearly to be seen. The yttria stabilized ZrO_2 balls present a much higher wear resistance and a higher toughness than that the above tested ZrO_2 balls. No broken balls were observed after the milling tests.

	
Fig. VII-17: new yttria stabilized ZrO2 balls (Nagase & Co., LTD, Japan)	Fig. VII-18: Yttria stabilized ZrO2 balls after 1h milling; Hardly wear of the balls could be observed

According to the results of the wear tests it could be summarized that the rotor, especially the rotor tip, suffers from the strongest abrasive wear. High wear resistance and well toughness of the materials are required. The main nature of load of the grinding media is the collision. A high toughness is more important than the hardness in order to avoid the break of the balls. On the surface of chamber wall a press loading was put on and the wear is the slightest in comparison with the rotor and balls.

A optimum combination of the grinding unit is then a rotor with hard metal tip which possess a high wear resistance. Yttria stabilized ZrO_2 balls show a sufficient roughness and well wear resistance and could be used as milling media. The choice of chamber materials is large. Both materials and techniques, lined Al_2O_3 and thermal coated WC-17Co are usable for the chamber wall.

VII-5 Characterization of tested ceramic powders

Figure 14 shows the scanning electron microscopy (SEM) images of SiC powder samples before and after processing with one of above mentioned prototypes 2. The SiC starting powder has a particle size of 850 µm (Fig. VII-19Fig.). After 10 min milling the particle size was reduced to < 15 µm (Fig. VII-20 and Fig. VII-21). The particle size was further reduced down to < 10µ after 60 min milling (Fig. VII-22). A part of the powder exhibits a size of 1-2 µm, which indicates a quick and efficient decreasing of the particle size.

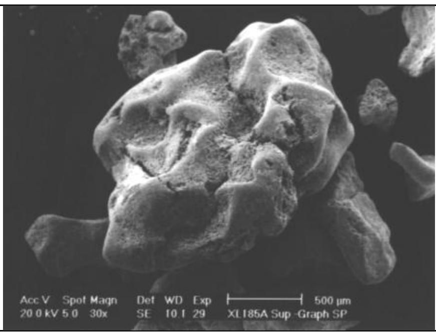


Fig. VII-19: SiC starting powder

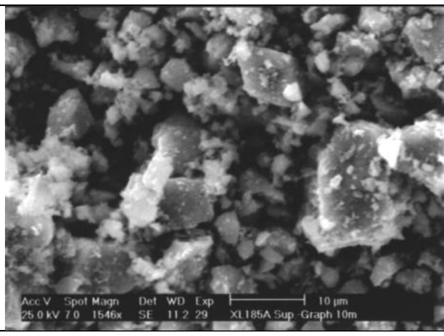


Fig. VII-20: SiC powder after 10min processing

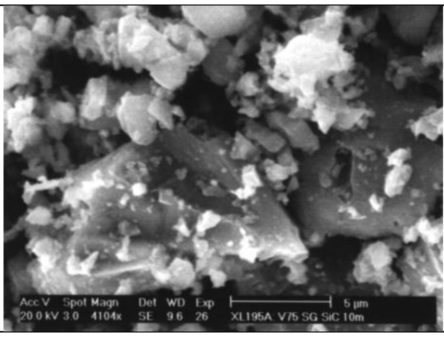


Fig. VII-21: SiC powder after 10min processing

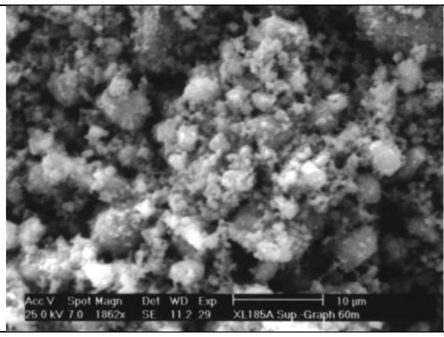


Fig. VII-22: SiC powder after 60min processing

Further examples of Al_2O_3 + 5% SiC powder are shown in Fig. VII-23 and Fig. VII-24. Characterization of as-milled Al_2O_3-SiC5% powder were carried out by SEM. The investigations reveal that, fine powder with particle size d < 5 µm after a few hours milling time could be obtained under dry milling conditions by the use of the High Energy Ball Mill.

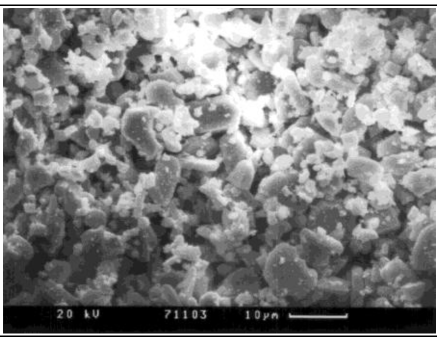


Fig. VII-23: particle sizes of Al2O3 starting powder

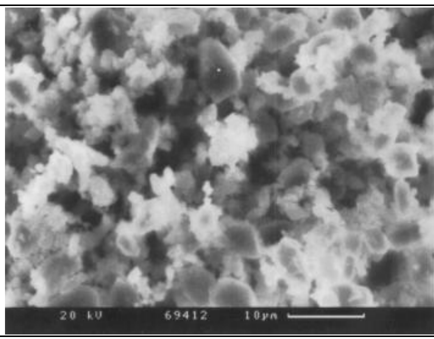


Fig. VII-24: particle sizes of Al2O3-SiC powder after processing (SEM-backscatter electron)

Further examples of quartz powder were performed by company Cerdec AG in Germany with Al_2O_3 balls. Although the Al_2O_3 balls were broken quickly after a short milling time, a reducing of the particle size was still reached. The results are shown in Fig. VII-25 and Fig. VII-26. According to this REM investigation the particle size of quartz powder were evaluated to be < 1µm after 2h milling.

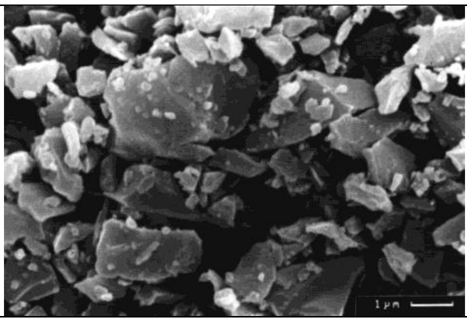


Fig. VII-25: particle sizes of quartz starting powder

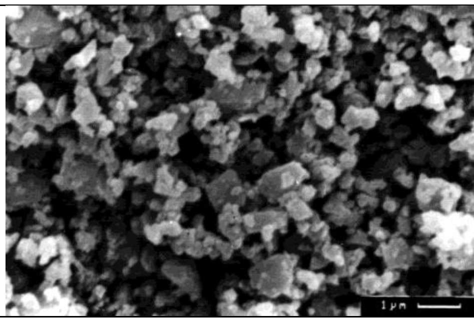


Fig. VII-26: particle sizes of the quartz powder after 2h processing

VII-5.1 Conclusions Part VII

New milling tools have been designed and tested with respect to HEM processing of ceramic powder.

Most critical is the dependency of shock-resistibility / toughness and hardness of the tool-material under high kinetic and high abrasive condition.

The most critical components are the rotor and the grinding media, not the vessel.

Rotors have been made using ceramic bulk- and coating material, rotors with hard metal plates show the best performance (wear resistance).

Yttria stabilized ZrO_2 balls were found to be the suitable grinding media for HEM in ceramics-processing.

Next to this it has been shown, that e.g. in case of processing alumina / SiC composite, standard chromium steel balls can be used as these balls are immediately coated with a thin but steady coating of alumina which prevents contamination of iron.

The vessel can easily be lined with ceramic plates or coated with WC-17Co to achieve suitable results.

With these tools, the production of fine ceramic and intermetallic powder can be realized by High Energy (ball)Milling.

In case of given examples SiC, alumina/SiC and SiO_2, a dramatic reduction of particle size from hundreds of microns to a few microns within 10 min processing was realized.

Within 60 min processing time, partly diameters of as-milled powder smaller than 1,5 - 2µm were obtained.

High Energy Milling shows a potential in processing of ceramic powders.

General Conclusions (Part I-VII)

HEM, MA and Reactive Milling have been described as interesting processing techniques used in powder metallurgy and powder technology.

Important improvements regarding the ***processing equipment*** (draingrating, air-lock, kinetic) have been explained.

Important improvements regarding the ***processing procedure*** (kinetic model, cycle operation, high temperature operation) have been shown.

Potential procedures in order to realize a ***reproducible, safe and economical industrial production*** (energy balance, semi-continuous processing) have been reported.

The first existing industrial application with ***large scale product*** (ductile metal flakes) has been described.

The attempt of transferring the capability of high kinetic processing into ***ceramic-systems*** has been shown.

HEM, MA and Reactive Milling do show a high potential in process engineering and will play an important role in PM-Technology in the future.

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