# PROCESSING OF CERAMIC POWDER USING HIGH ENERGY MILLING

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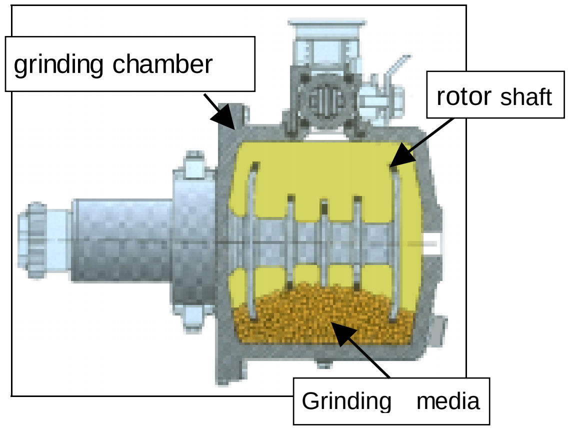
## 1. Introduction

High Energy Milling (HEM) is a well known and commercially used technique [1-3]. Today the applications are limited to the range of metal based materials, alloys and composites where the methods are described as Mechanical Alloying [3-5], HEM and Reactive Milling [5].
Since the high kinetic energy transfer represents the performance of these techniques [2-7], 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.
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.
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 characterized 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 ultrafine distribution of a ceramic hard-phase in a ceramic matrix in nanometer-scale [9-12].
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.

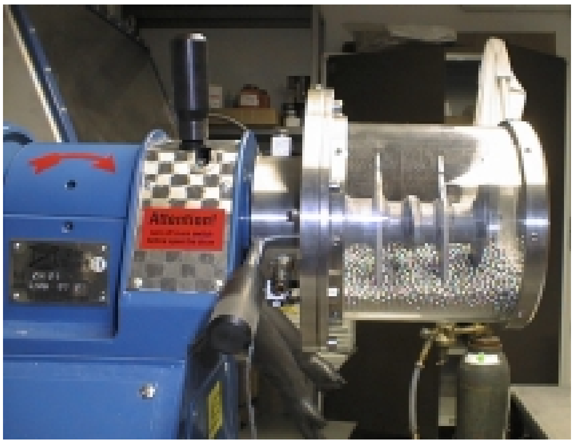
## 2. High Kinetic Processing Device

The principle of the High Energy Mill (Simoloyer) is based on a horizontally borne rotor which allows an energy transfer in a homogeneous and high efficient way from supplied power to kinetic energy of balls (grinding media). 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 is shown in Figure 1. 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).

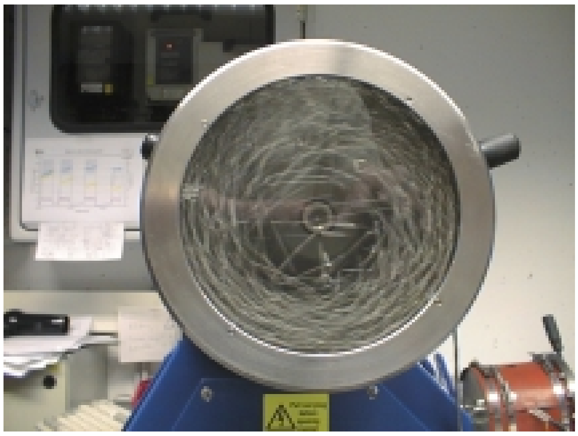
a) Simoloyer CM01-2l




b) static



c) static



d) dynamic

*Fig. 1: a) Simoloyer CM01-2l; b) Cross sectional view of the grinding unit with horizontal rotor shaft, milling balls and powder; c) Trial grinding unit made of glass; d) Dynamic moving of the milling balls by a rotary rate of 1650 rpm*

## 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 the table 1:

Table 1: Wear characterization, metal based

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

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 2 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.

Table 2: Three prototypes of the laboratory scaled grinding unit, Simoloyer CM01-2l

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

**Prototype 1**

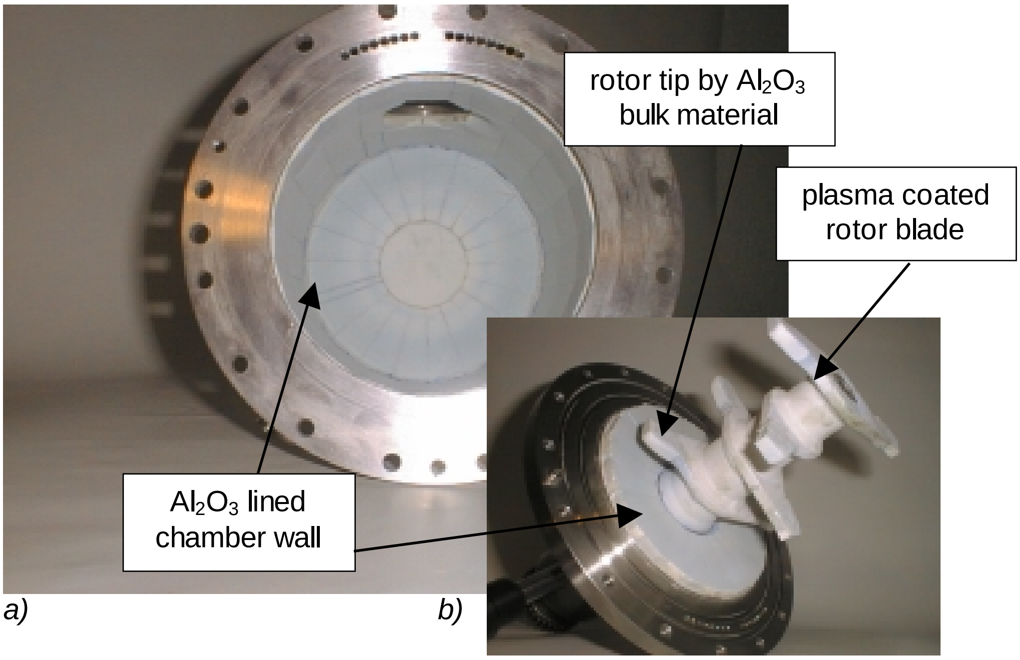



*Fig. 2: Grinding parts of prototype 1. a) chamber with $Al_2O_3$ lining;*
*b) rotor with $Al_2O_3$ full material rotor tips and plasma coated rotor blades*

**Prototype 2**

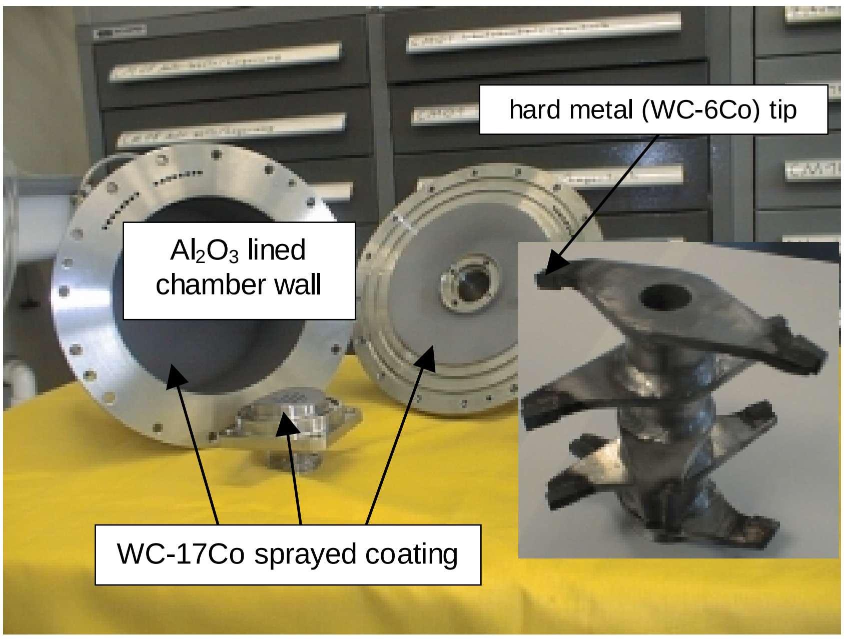



*Fig. 3: Grinding parts of prototype 2, WC-17Co coated chamber*

**Prototype 3**

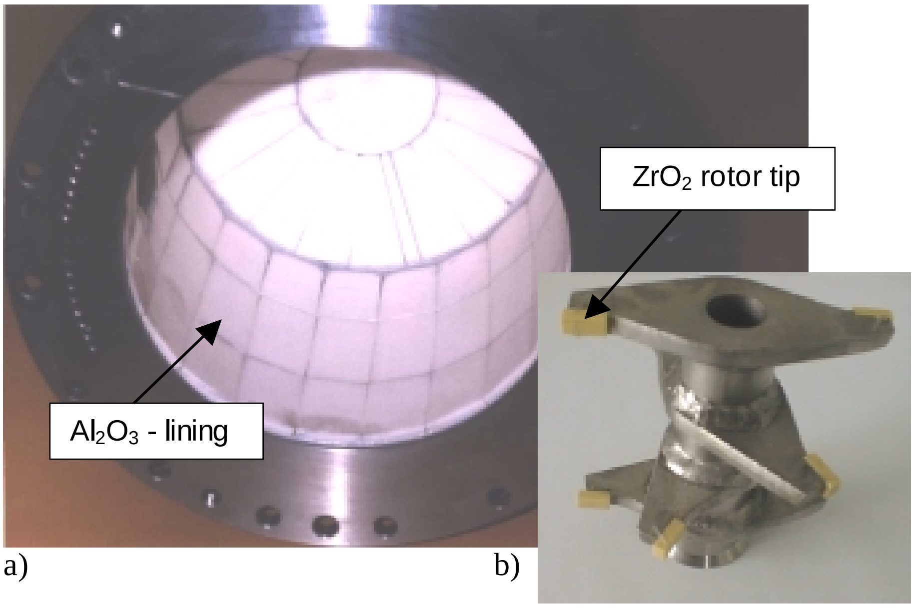



*Fig. 4: Grinding parts of prototype 3*
*a) chamber with $Al_2O_3$ lining, b) rotor with $ZrO_2$ bulk material rotor tips*

## 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 3.
In many cases cycle operation procedure [5-7] 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).

Table 3: Milling parameters for ceramic powder processing

| | |
|---|---|
| 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 |

The results with respect to the grinding units after wear test are shown in Figures 5-9. 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.

### 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 (Figures 5-6). 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. 5: Grinding chamber lined with $Al_2O_3$ after 5h: Hardly wear of the $Al_2O_3$ lining could be observed*


*Fig. 6: $Al_2O_3$ rotor after 3h milling The rotor tips were worn out.*

### 4.2 prototype 2

Well resistance against wear of the hard metal rotor tip were shown by the prototype 2 (Figures 7-8). After 20h hardly material loss could be observed (Figure 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 1500 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 Figure 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.

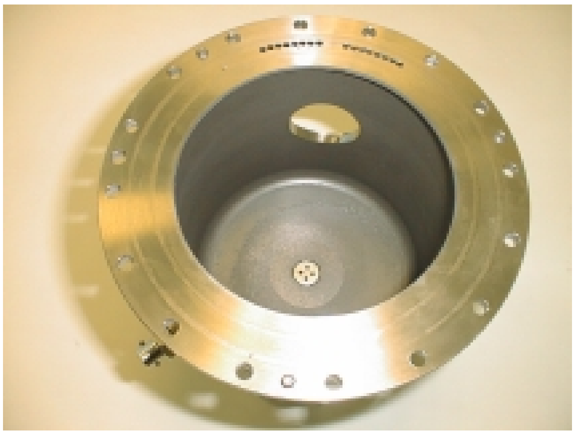


*Fig. 7: WC-17Co coated milling chamber after 3h test: The WC-17Co thermal spray coating remains*

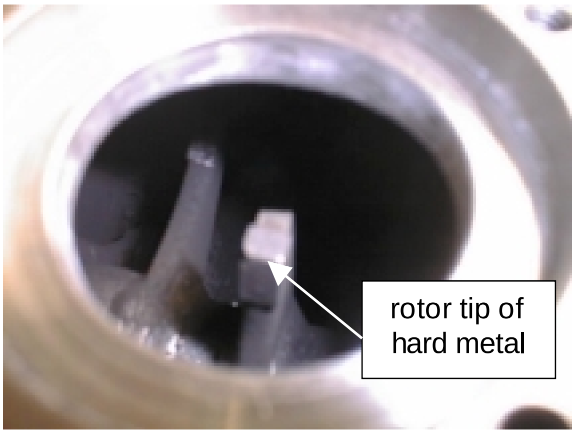



*Fig. 8: Hard metal rotor after 20h: Hardly wear of the rotor tips could be observed.*

### 4.3 prototype 3

The wear resistance of $ZrO_2$ plates on the rotor tip is not sufficient (Figure 9). 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.

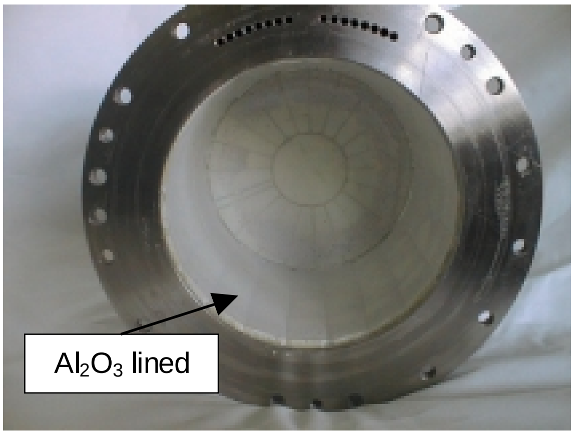



*Fig. 9a: Milling chamber after milling*

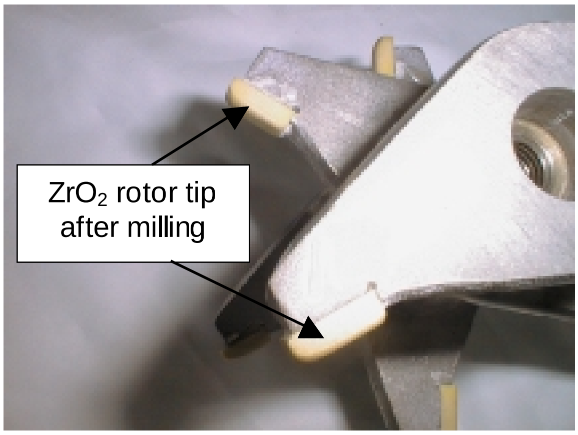



*Fig. 9b: ZrO2 rotor after 1h milling
The rotor tips were worn out.*

### 4.4 Grinding media, 100Cr6 (self) coated by $Al_2O_3$-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 (Figure 10) which might be adhered by van der Waals's binding [13-15]. This cold compacted "coating" did protect the steel surface from wear during the milling and prevents contamination from the iron.

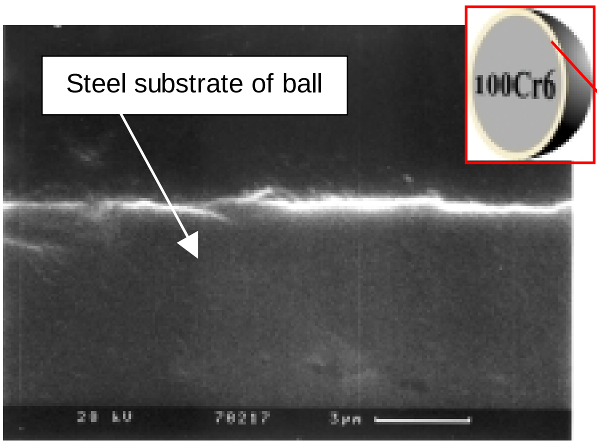



*Fig. 10a: cross section of a steel ball before milling
milling*

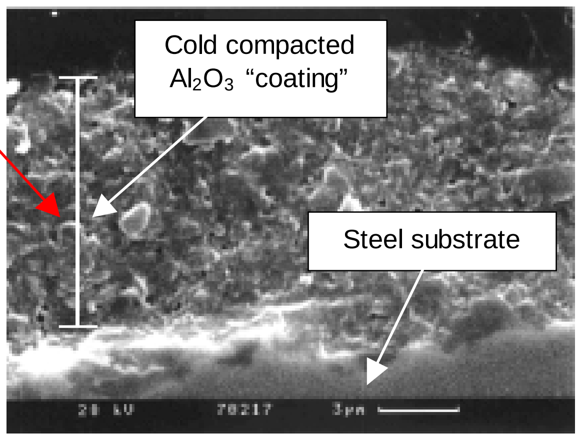



*Fig. 10b: Cross section of a ball with cold compacted "coated" $Al_2O_3$ layer after*

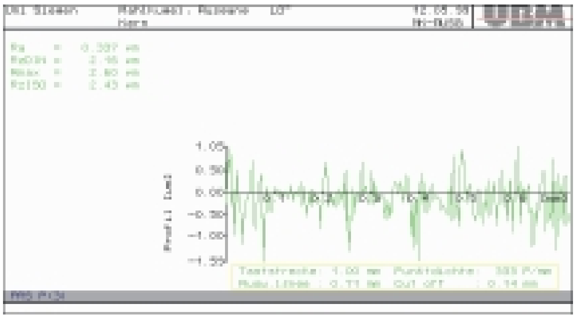


*Fig. 11a: Roughness measurement of a new ball*

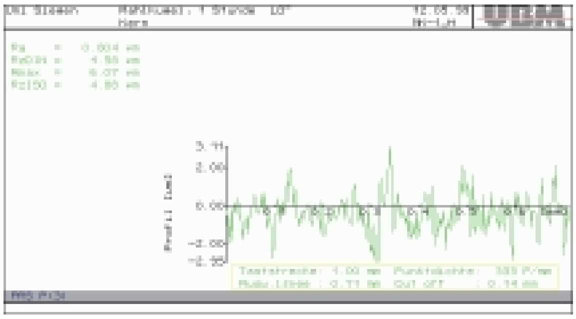


*Fig. 11b: Roughness measurement after 14h*

The variation of the surface roughness was determined (Figure 11). 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.

### 4.5 Grinding media, $ZrO_2$

Milling tests was carried out with $ZrO_2$ balls (Figure 12). 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. 12a: New $ZrO_2$ balls*

*Fig. 12b: $ZrO_2$ balls after 1 h milling*
*Many balls were broken up*

### 4.6 Grinding media, $ZrO_2$ yttria stabilized

Yttria stabilized $ZrO_2$ balls were tested under same condition presented in sub-chapter 4.5. The results shown in Figure 13. 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. 13a: New yttria stabilized $ZrO_2$ balls (Nagase & Co., LTD, Japan)*

*Fig. 13b: Yttria stabilized $ZrO_2$ 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.

## 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 (Figure 14a). After 10 min milling the particle size was reduced to < 15 µm (Figure 14b and 14c). The particle size was further reduced down to < 10µ after 60 min milling (Figure 14d). A part of the powder exhibits a size of 1-2 µm, which indicates a quick and efficient decreasing of the particle size.

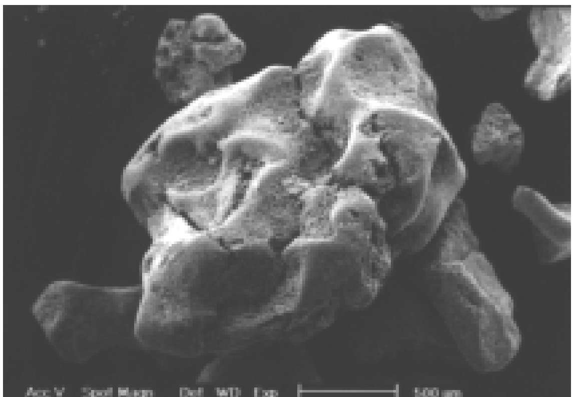


*Fig. 14a: Particle sizes of SiC starting powder*

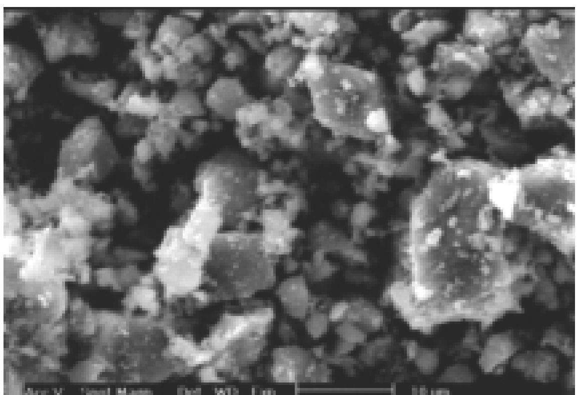


*Fig. 14b: Particle sizes of SiC powder after 10min*

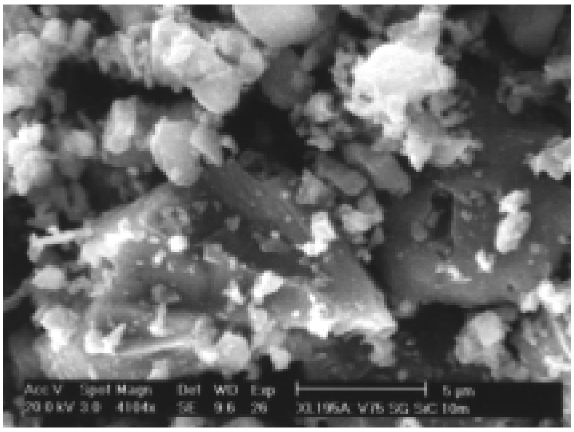


*Fig. 14c: Particle sizes of SiC powder after 10min processing*

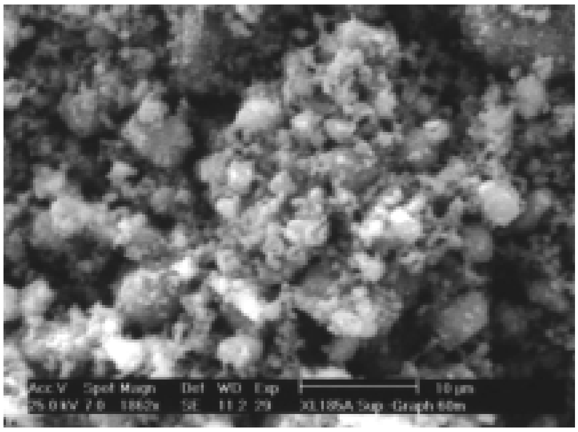


*Fig. 14d: Particle sizes of SiC powder after 60min processing*

Further examples of $Al_2O_3$ + 5% SiC powder are shown in Figure 15. 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.

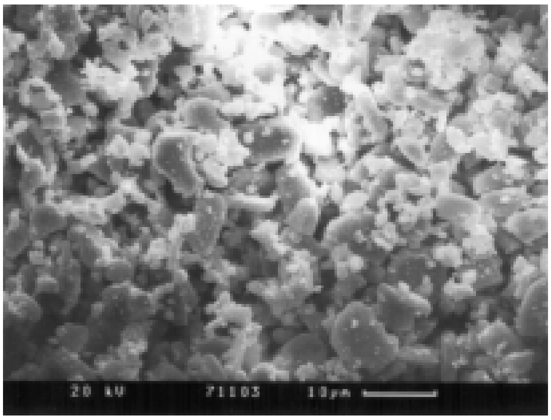


*Fig. 15a: Particle sizes of $Al_2O_3$ starting powder*

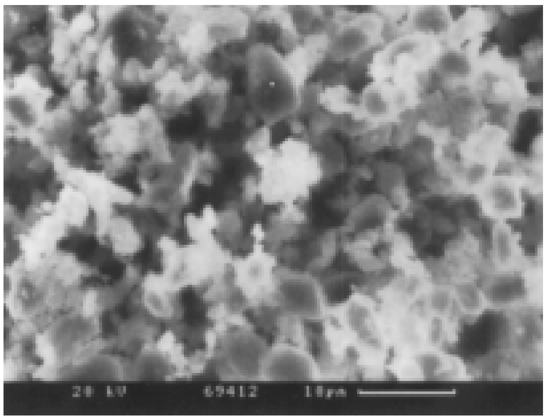


*Fig. 15b: Particle sizes of $Al_2O_3$-SiC powder after processing (SEM-backscatter electron)*

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 Figure 16. According to this REM investigation the particle size of quartz powder were evaluated to be < 1µm after 2h milling.

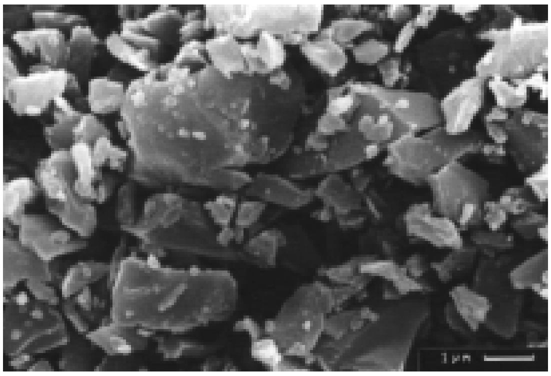


*Fig. 16a: Particle sizes of quartz starting powder*

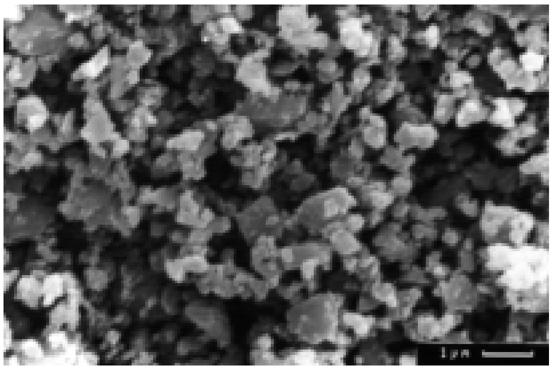


*Fig. 16b: Particle sizes of the quartz powder after 2h processing*

## 6. Conclusions

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.

## 7. Acknowledgment

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Cerasiv, Ebersbach, Germany
Nagase & Co., LTD., Tokyo, Japan
Morimura Bros., INC., Tokyo, Japan

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