Representative On-line Measurement of Comminution Results for Nanogrinding in Stirred Media Mills

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Introduction

The production of materials with higher homogeneity, solubility or strength and thus higher product quality requires the use of nanoparticles. Especially the chemical and pharmaceutical industry as well as the ceramic or the microelectronic industry demand more and more suspensions of materials with a high fineness and storage stability. One method to produce ultrafine particles is the grinding of coarse particles, which is called dispersion method or top-down process. For comminution processes down to the submicron particle size range high energy densities are required which can only be realized by wet comminution in stirred media mills. Stirred media mills are used in many different industries for the comminution of raw materials or the dispersion of products obtained from bottom-up processes.

A joint research project between the Technical University of Brunswick and the Technical University of Munich investigates the possibilities for the production of stable product suspensions in the particle size range smaller than 100 nm [i, ii]. The increasing particle-particle-interactions with increasing fineness are an essential problem during wet comminution in stirred media mills. These interactions have an influence on the stability of the product suspension towards agglomeration and on the rheology. If product particle sizes smaller than 1 µm are reached, these interactions can lead to an interrelation between agglomeration, desagglomeration and comminution, thus no further comminution progress can be obtained in spite of increasing energy input. To overcome this problem the milling suspension has to be stabilized by means of electrostatic, steric or electrosteric stabilization. Recent results for fused corundum have shown [i] that an electrostatic stabilization during the grinding process does not influence the grinding mechanism itself but determines the final dispersed state of the particles with median particle sizes far below 50 nm.

Another important task is the representative determination of the comminution results. In many cases sampling and a sample treatment is necessary for this task. If a dilution of the samples is required agglomeration effects can adulterate the results. Furthermore, measurements of real suspensions with different devices normally yield diverse results. Therefore, samples of real suspensions obtained from a grinding process were analyzed for comparison with different measurement devices.

Experimental set-up

For all experiments carried out at the Institute of Mechanical Process Engineering of the Technical University of Brunswick a laboratory stirred media mill of close to one liter content was used. The engine of the mill has a driving power of 3.3 kW. In order to reduce the amount of wear from the materials of the mill the grinding chamber was lined with ceramic walls (SiSiC) and the stirrer was supplied with 5 perforated discs of polyurethane (PU). The experimental set-up provides a circuit mode comminution of

the product (s. Figure 1). The suspension is pumped from the grinding chamber into a stirred vessel, from there directly into the measuring cell of the ultrasonic spectrometer DT 1200 (*Dispersion Technology*) and back to the grinding chamber.

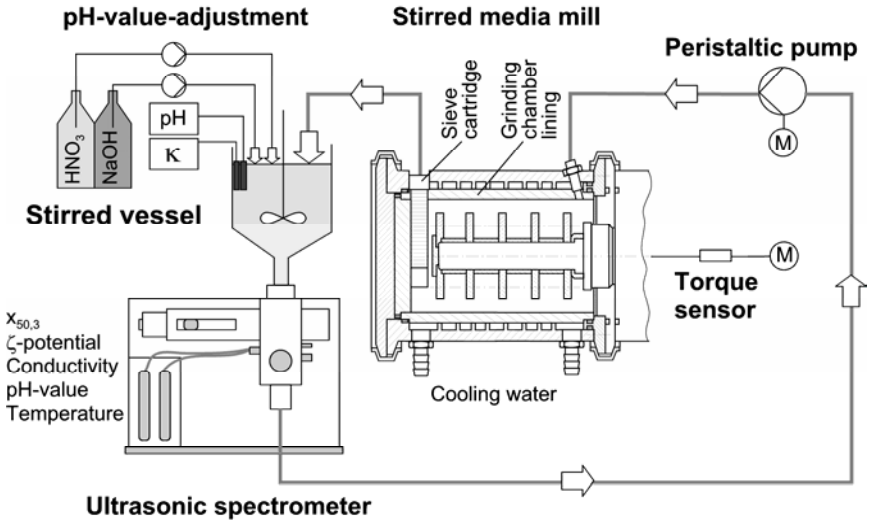

Figure 1: Experimental set-up

The ultrasonic spectrometer is specially developed for solid concentrations in a range of 1 – 50 vol. %. The device is equipped with different sensors which allow the simultaneous measurement of temperature, conductivity, pH-value, particle size distribution as well as ζ-potential. Before the product is pumped into the measuring cell, a suitable pH-value for the electrostatic stabilization is adjusted by addition of potential determining ions into the stirred vessel. The product suspension is pumped back into the mill behind the ultrasonic spectrometer. Torque and number of revolutions are measured by a torque sensor shaft which is installed in the stirred media mill. The pH-value and the conductivity of the product suspension were measured in-line by external measuring devices in the stirred vessel.

Grinding media

Grinding media differing in size, material and composition were used for the comminution experiments. The grinding media diameter, the density, the modulus of elasticity as well as the composition of the grinding media used are shown in Tab. 1 and Tab. 2.

Grinding media	Al_2O_3	ZrO_2
Grinding media diameter	900 bis 1300 µm	100 bis 1300 µm
Grinding media density	3300 kg/m³	6065 kg/m³
Modulus of elasticity	220 GPa	263 GPa

Tab. 1: Diameter, density and modulus of elasticity of the grinding media used

Grinding media	Al_2O_3	ZrO_2	Y_2O_3	SiO_2	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	other
ZrO_2		94.5	~5	-	-	-	-	-	-	-	0.5
Al_2O_3	86.5	-	-	10.5	0.29	0.15	0.57	0.12	0.26	1.5	-

Tab. 2: Percentage composition of the grinding media used

Tryout material

A highly pure fused corundum (Al_2O_3) is used as tryout material for all investigations. Tab. 3 shows the composition of the Al_2O_3. The physical properties of this material which is used for the production of polishing materials (corundum abrasive material) are shown in Tab. 4 and Tab. 5. The $x_{i,3}$ –values with i = 5, 10, 50, ... mean that i % of mass (respectively of the volume) of the whole particle collective have diameters smaller than $x_{i,3}$.

Al_2O_3	TiO_2	SiO_2	Fe_2O_3	MgO	CaO	Na_2O	Fe löslich
99.61 %	0.01 %	0.04 %	0.04 %	0.01 %	0.03 %	0.26 %	0.01 %

Tab. 3: Chemical composition of the tryout material

crystal structure	α-aluminium oxide, trigonometric, macrocrystalline
hardness (HV_{100})	22000 N/mm²
pure density	3930 kg/m³
melting point	2000 °C

Tab. 4: Chosen physical properties of the tryout material

$x_{5,3}$	$x_{10,3}$	$x_{50,3}$	$x_{90,3}$	$x_{95,3}$
5.49 µm	17.64 µm	33.63 µm	50.40 µm	57.00 µm

Tab. 5: Chosen particle size parameters of the tryout material

Fused corundum (Al_2O_3) was selected as the tryout material due to its very low solubility in water and a great flexibility for the formation of positive (pH 3) or negative (pH 11) surface charges and thus ζ-potentials. Figure 2 shows the results of titration experiments which were performed at the Institute of Particle Technology of the Technical University of Munich. The measured ζ-potentials of the SiO_2 and the Al_2O_3 suspensions (c_m = 20 % in distilled water) are depicted related to the pH-value. The pH-value of the suspensions was adjusted by the addition of nitric acid (HNO_3) and caustic soda (NaOH).

Comparison of results from particle size analysis with different devices

Besides the online particle size analysis further measurements were done offline by ultrasonic spectrometer with DT 1200, laser diffraction with the MasterSizer 2000 (Malvern) and dynamic light scattering with an ultrafine particle analyzer (UPA) (Leeds & Northrup) at the Institute of Particle Technology of the Technical University of Munich.

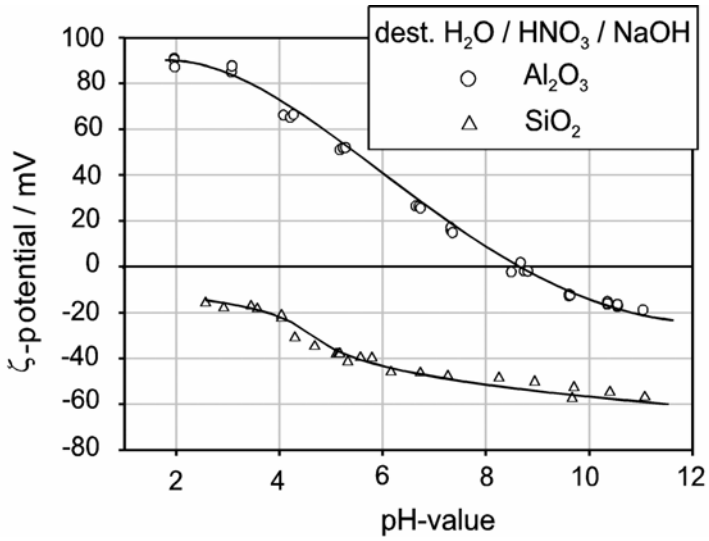

Figure 2: Development of the ζ-potential related to the pH-value

In Figure 3 the measured median particle sizes for the comminution of fused corundum are plotted versus the specific energy input, which is defined as the total energy input related to the mass of solid product. During the comminution of fused corundum Al_2O_3-grinding media show a significantly higher wear than ZrO_2-grinding media. Thus, the grinding media wear Δm_{GM} has to be considered for the calculation of the specific energy $E_{m,V}$ to allow comparisons when using different grinding media (Becker [iii], s. equation (1)). It is assumed that the grinding media wear increases proportionally to the power input N. Thus the mass of the product is extended by $0.5 \cdot \Delta m_{GM.}$

$$E_{m,V} = \frac{\int_0^t N(\tau)\,d\tau}{m_P + 0.5 \cdot \Delta m_{GM}} \qquad (1)$$

The stirrer tip speed was varied between 8 m/s and 12 m/s. Furthermore, in diverse experiments grinding media with diameters of 900 μm (bottom) and 1100 μm (top) of Al_2O_3 were used. Therefore no strong contamination of the suspension could be obtained and a stabilization of the suspension was not necessary.

For the analysis with laser diffraction and dynamic light scattering samples of 3 ml were diluted with 15 ml distilled water which had been adjusted to pH 3 by addition of nitric acid (HNO_3). Then the samples were sonicated at a constant pH-value (adjustment!) with a Bandelin ultrasonic disintegrator (200 W) minute by minute as long as no further desagglomeration progress could be obtained. The analysis with the ultrasonic spectrometer were done without any treatment of the sample.

For the analysis with the ultrasonic spectrometer with an increasing specific energy input an increasing comminution progress is obtained. In contrast, the measurement with the MasterSizer 2000 of Malvern Instruments (laser diffraction) leads to a plateau around 150 nm and the analysis with the Ultrafine Particle Analyser of Leeds & Northrup (dynamic light scattering) shows a plateau around 250 nm.

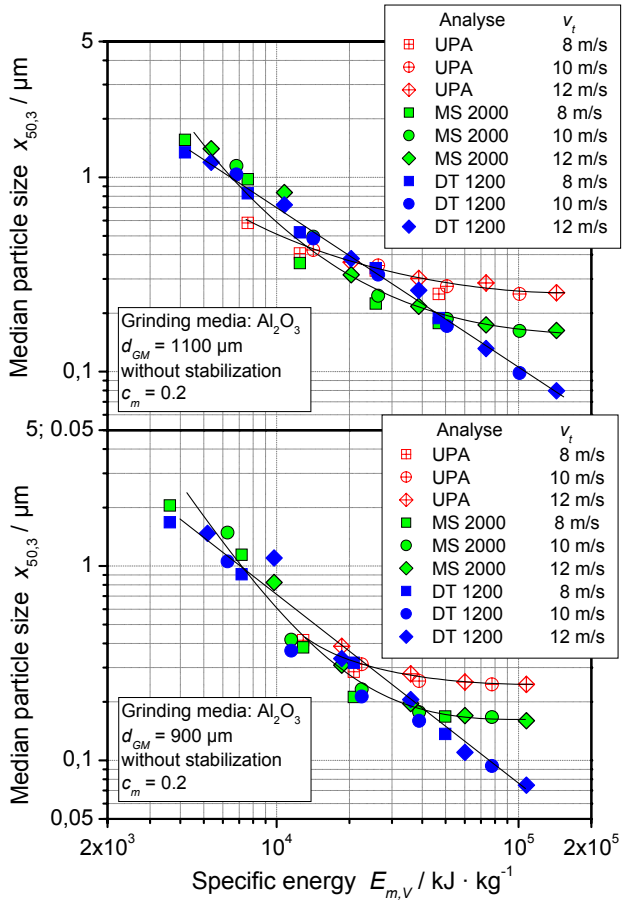

Figure 3: Comparison of diverse optical particle size analysis with ultrasonic spectroscopy

TEM analysis

Because of the different results obtained from the analysis described above samples from diverse product suspensions were prepared with two methods for analysis with a transmission electron microscope (TEM) additionally.

Figure 4 shows a TEM-image of a suspension from fused corundum which had been ground for 16 hours with ZrO_2-grinding media with a diameter of 800 µm and a stirrer tip speed of 12 m/s. During the comminution experiment the pH-value of the suspension was adjusted at pH 7 by the addition of nitric acid. With the ultrasonic spectrometer DT 1200 a median particle size of 53 nm and a ζ-potential of 27.5 mV were analyzed without any treatment of the sample.

For preparation the sample was frozen in original concentration (c_m = 23.4 %) and then broken under vacuum at -100 °C with the freeze-breaking-plant (Balzers BAF 400) at the Institute of Pharmaceutical Technology of the Technical University of Brunswick. The fragments were vaporized with a 2 nm-layer of platinum-carbon and further stabilized mechanically with a carbon layer. The so accrued replica were cleaned and dissected on a copper-net.

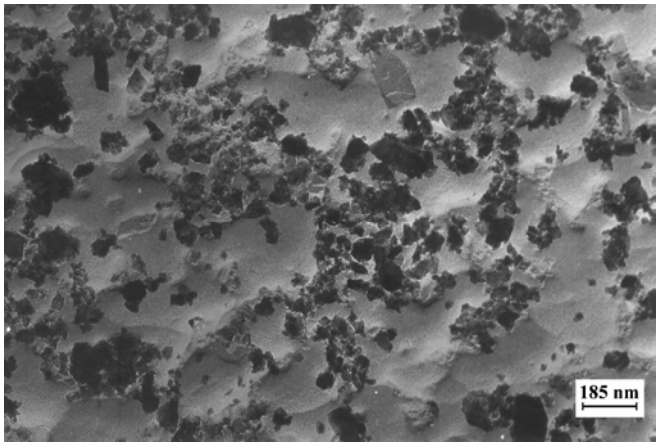

Figure 4: TEM-image, freeze-breaking-preparation, PHILIPS EM 300

The TEM-images seen in Figure 5 were established at the Institute of Electron Microscopy of the Technical University of Munich. For preparation the sample of the suspension was diluted and sonicated at a constant pH-value of pH 3. Afterwards the suspension was dropped on a carbon-grid and the excessive water was sucked up with an absorbent cloth before drying and vaporization.

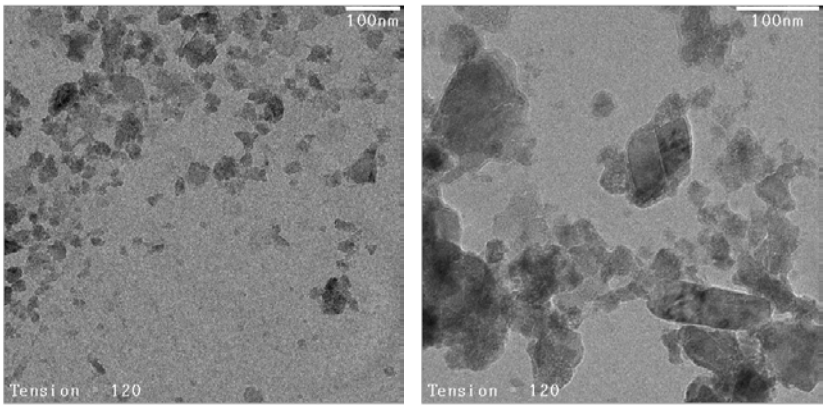

Figure 5: TEM-images, dilution-drying-preparation, JOEL 2010

Figure 5 shows two images of the same sample. For the comminution of this Al_2O_3-suspension a specific energy of about $214 \cdot 10^3$ kJ/kg was inserted in the mill. The suspension was stabilized electrostatically at pH 5. Besides the TEM-images the product suspension was analyzed with MasterSizer 2000, UPA and DT 1200.

Measurement device	Analyzed $x_{50,3}$
MasterSizer 2000	0,154 µm
UPA	0,115 µm
DT 1200	0,032 µm

Tab. 6: Results of particle size analyzes with diverse devices

As can be seen in Tab. 6 final particle sizes of about 154 nm were measured with the laser diffraction and 115 nm with the dynamic light scattering instrument whereas about 32 nm were detected with the ultrasonic spectrometer.

The TEM-images clearly show that there is a large amount of very fine particles (50 nm and smaller) already produced besides some larger partly agglomerated ones. The latter has a strong influence on the volume distribution, but less on the number distribution. Therefore the attenuation of ultrasound seems to be more sensitive to the primary particle size whereas the signal of the photon spectroscopy is influenced by a small amount of large particles. Nevertheless, the TEM-images prove that it is possible to grind fused corundum down to the nanometer size range.

Sedimentation analyzes

Figure 6 shows the particle size distribution $Q_3(x)$ measured by different analyses methods for a suspension which is comminuted with $ZrO_2(Y_2O_3)$-grinding media of 200 µm in diameter. During grinding the suspension was adjusted to pH 5 by the addition of nitric acid. Additional to the above discussed analyses methods sedimentation analyses were performed with the SediGraph 5100 of Micromeritics and a Brookhaven disc centrifuge after three comminution times steps.

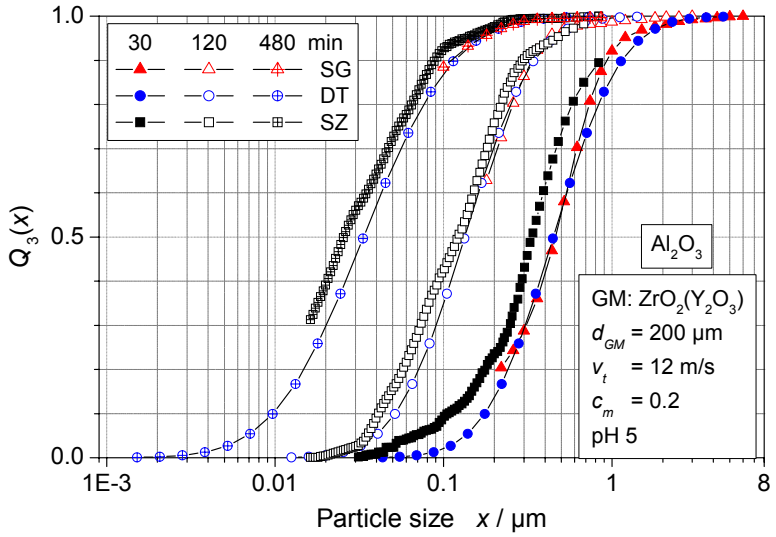

Figure 6: Comparison of different sedimentation particle size analyses with ultrasonic spectroscopy

With these devices strongly diluted samples are measured. For sample preparation of 10 ml of the product suspensions were diluted with 60 ml distilled water which had been adjusted to pH 3 by addition of nitric acid (HNO_3). Then the samples were sonicated at a constant pH-value (adjustment!) with a Bandelin ultrasonic disintegrator (200 W) minute by minute as long as no further desagglomeration progress can be obtained.