PARTICLE BREAKAGE IN THE NANOMETER RANGE

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Abstract

Comminution in stirred media mills enables the production of ultrafine particles down to the nanometer range. The grinding results are mainly determined by two contrary mechanisms: particle breakage and agglomeration of the so-created fragments. In this paper the breakage mechanism in the nanometer range and the existence of the overall limit of grinding will be discussed. By means of X-ray diffraction analysis microstructural changes during the grinding process are analyzed. One can observe that lattice imperfections are generated which enhance the total amount of stored energy in the particles. This energy is necessary to reach a breakage of the particles in the nanometer range. At a critical crystallite size defects cannot be stored in the lattice anymore and the limit of grinding is reached.

Introduction

Nanoparticles are increasingly used in many areas of chemical and pharmaceutical as well as in ceramic and microelectronic industry. Besides the direct synthesis of these materials by chemical methods, wet grinding in stirred media mills is a suitable technique for the production of nanoparticles in the liquid phase with high solid concentrations [1], [2]. The manufacturing of fine particles is influenced by particle breakage and interparticle interactions. The interactions become relevant especially for particles smaller than 1 µm because of an increasing collision rate of the particles due to their Brownian motion. In most grinding experiments a limit in particle size is reached where further energy input does apparently not lead to smaller particle sizes. Stenger et al [1] demonstrated that this observed limit is dependent on the stability of the suspension. By means of electrostatic, steric or electrosteric stabilization and shear stress this so called apparent grinding limit can be shifted to smaller particle sizes. Whereas the apparent grinding limit can be controlled by the interparticle interactions, the true grinding progress only refers to the actual breakage of particles. The existence of a true grinding limit as the minimal achievable particle size in grinding experiments, where no further particle breakage occurs even after excessive energy input, is an essential question in nanogrinding. By means of X-ray diffraction analysis the evolution of internal particle microstructural features such as the crystallite size (coherent domain size) and the lattice strain can be examined to understand the breakage mechanism in the nanometer range.

In this paper we present results of long term grinding experiments of different materials in a stirred media mill and discuss the influencing parameters on breakage kinetics and the grinding limit. With the knowledge about the breakage behavior in the nanometer range comminution processes in the field of wet ultrafine grinding can be controlled and optimized in order to avoid excessive energy input which in turn increases the efficiency of milling.

Experimental

Materials

Milling material

The materials used in milling experiments along with their initial particle sizes are summarized in Table 1.

Table 1: Particle size parameters of the inserted materials (measured with laser diffraction)

Material	Trade name	Manufacturer/ Supplier	$x_{10,3}$	$x_{50,3}$	$x_{90,3}$
SiO_2		Carl Roth GmbH & Co. KG	3.4 µm	14.3 µm	39.1 µm
Al_2O_3	CT 1200 SG	Almatis	1.2 µm	2.4 µm	4.4 µm
$CaCO_3$		Carl Roth GmbH & Co. KG	0.8 µm	7.0 µm	13.4 µm
SnO_2		Merck GmbH	0.2 µm	1.6 µm	5.2 µm
ZrO_2		Sigma Aldrich	1.0 µm	1.8 µm	3.3 µm

Solvents

Ethanol (96 % denatured with 1 % MEK, VWR, Germany) and distilled water were used as dispersants.

Grinding media

Wear resistant, commercially available yttrium stabilized zirconia (ZrO_2) milling beads in the size range of 0.4 – 0.63 mm (TOSOH, Japan) were used in the experiments. According to the manufacturer the grinding media has a density of 6065 kg/m³ and a chemical composition of 95 % ZrO_2 and 5.0 % Y_2O_3.

Experimental Set-up

All milling experiments in aqueous suspensions were carried out in a six disc stirred media mill with a content of 0.95 liter. The suspension flows axially through the mill and a sieving cartridge with gaps of 100 µm prevents milling beads from leaving the grinding chamber. The grinding chamber is lined for wear protection reasons with ceramic walls (SiSiC) and the stirrer is equipped with discs of polyurethane (PU). The experimental set-up provides a circuit mode comminution of the product. The suspension is pumped with a hose pump from the grinding chamber into a stirred vessel, where samples can be taken and stabilizers added. From the vessel the suspension flows back into the mill. Further details about the set-up and the construction of the mill are given elsewhere [1].

The commercial laboratory mill LabStar LS 1 (Netzsch, Germany) was used for the milling experiments in ethanol. The mill has an explosion-proof design and is equipped with a centrifugal separating system for the milling beads. This allows the use of small grinding beads down to 0.1 mm. The grinding chamber with a volume of 0.68 liter as well as the stirrer is lined with ZrO_2. The experimental set-up for this mill corresponds to the apparatus described above. Both grinding

chambers are equipped with a double wall for cooling, which is connected to an internal cooling water system.

Sample Characterization

Specific Surface Area (BET). BET (Brunauer-Emmett-Teller) measurements to determine the specific surface area of the particles were carried out on a Quantachrome NOVA 2000 gas sorption analyzer. The samples were degassed for 12 h at 150 °C under vacuum to remove adsorbed solvent molecules. The specific surface area was determined using a 7-point method with nitrogen as adsorption gas.

X-ray Diffraction (XRD). The XRD data was collected using a Siemens D 5000 powder diffractometer with graphite secondary monochromator using Cu K_α radiation ($\lambda = 0.15406$ nm). The XRD patterns of the samples were recorded with a step width of 0.02° and a counting time of 3.5 sec/step. A divergence silt and an anti-scatter slit of 0.5° as well as a detector slit of 0.2 mm were used. The samples were measured in a 2Θ range from $20° \leq 2\Theta \leq 80°$.

Results and Discussion

Long term grinding experiments of different materials have been carried out in a 20 wt% suspension in a stirred media mill. Samples were taken during the milling process and the dried powder was measured by the nitrogen adsorption method (BET) and X-ray diffraction. Micropore analysis of the feed materials and the final powders at low relative pressures were accomplished within the BET-measurements to exclude the existence of micropores in the materials which can distort the measured particle size.

Under the assumption that particle breakage occurs at the grain boundaries, i.e. the weakest points in a polycrystalline material, the development of the crystallite size can be used to explain the breakage process. Fig. 1 illustrates the X-ray diffraction patterns of zirconia particles of the initial state and after 50 h of stressing in a stirred media mill. One can clearly observe the loss in crystallinity with milling time. The peaks of the milled zirconia are significantly broadened which may be caused by either decreasing crystallite size and/ or enhanced strain in the lattice of the domains.

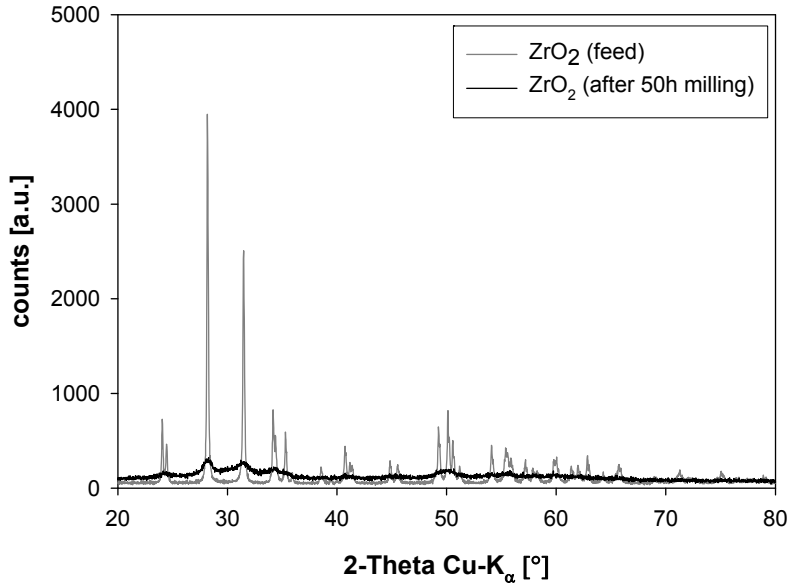

Fig. 1: Diffraction patterns of zirconia before and after 50 h milling

The crystallite sizes and the microstrains of the milled powders were determined from the X-ray patterns with a Rietveld refinement [3] using the commercial software package TOPAS (Bruker AXS). For modelling microstructural effects TOPAS is supported by the Double-Voigt Approach (e.g. Balzar, 1999 [4]). The possibility for a separate size-strain analysis is given by the effect that size broadening is angle independent, whereas strain broadening depends on the diffraction angle [4].

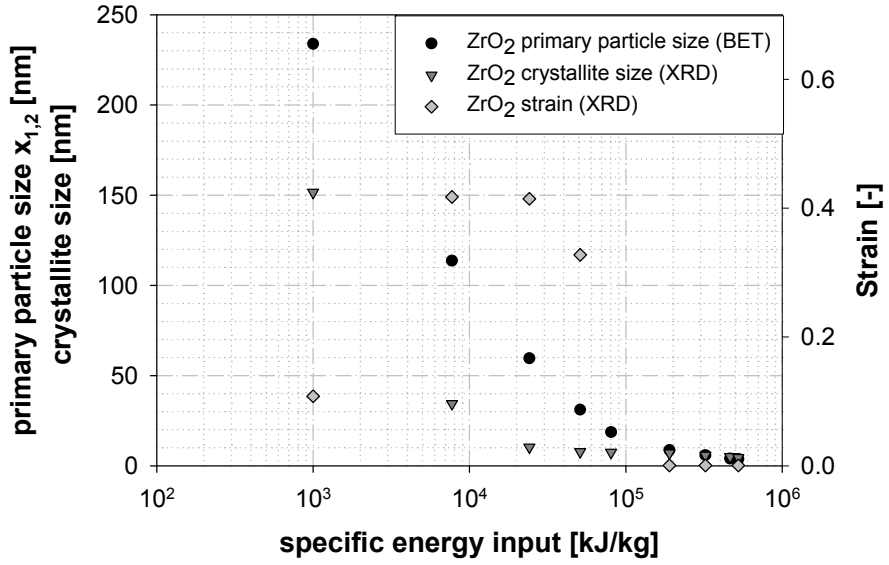

Fig. 2: Evolution of primary particle size, crystallite size and strain of zirconia with specific energy input

In Fig. 2 the evolution of the primary particle size, the crystallite size and the strain of zirconia particles over the specific energy input are shown. One can observe that the crystallite size decreases

until a plateau at a critical crystallite size (volume weighted) of about 4.5 nm and a primary particle size (area weighted) of approximately 4 nm are achieved. This plateau defined as true grinding limit is the minimal achievable particle size in grinding experiments and can be reached under stable milling conditions where the particle size is not influenced by an agglomeration process but only through real breakage of particles. Comparing the crystallite sizes with the primary particle sizes one can observe that above a certain energy input the initially polycrystalline zirconia particles become monocrystalline. From this point on particle breakage can only occur following a reduction of the crystallite size. The strain inside the crystallites increases at the beginning of the milling experiment until a maximal value is reached and afterwards decline to nearly zero. Due to the intensive stressing of the particles between the milling beads lattice imperfections are generated, enhancing the total amount of elastic stored energy in a crystallite. After reaching a critical crystallite size it is assumed the domains become so small that it is not possible to store further defects in the lattice [5]. As a result of this mechanism the strain decreases to a minimum. In Fig. 2 the disappearance of lattice strain corresponds to the point where no further reduction of the crystallite size occurs and the true grinding limit is reached. It is supposed that below a certain particle size the transferred stress intensity from the milling beads is no longer sufficient to achieve a brittle fracture with a single impact. Hence, further breakage can only occur if the elastic stored energy provided from lattice imperfections and external mechanical impact is sufficient to fulfill the integral energy balance and enable a fracture to traverse the entire particle [6]. This behavior of a fatigue fracture explains the reduced kinetics in the nanometer range where the available stress intensity becomes insufficient. Accordingly one can conclude that the generation of defects enables the breakage in the nanometer range whereas their absence below a critical size determines the grinding limit.

The kinetics of particle breakage as well as the grinding limit depend on a multitude of influencing variables. These influencing variables can be separated into three groups:

- Material parameters (material properties of the milling powder, properties of the solvent, stability conditions)
- Process parameters (rotational speed of the stirrer, milling bead size and material, etc.)
- Machine parameters (design of the mill, kind of stressing, etc.)

We have investigated the influence of different materials on the breakage behavior of particles in the nanometer range and their grinding limit. For this study five different materials (ZrO_2, Al_2O_3, SnO_2, SiO_2 and $CaCO_3$) were stressed in a stirred media mill. The milling experiments were carried out under the same following conditions: milling bead size 0.4 – 0.5 mm, filling ratio of the grinding chamber with milling beads 80 % and stirred tip speed 8 m/s. Whereas particles of SnO_2 and $CaCO_3$ were milled in water the other materials were milled in ethanol. However, as ethanol and water do not vary much in their viscosity, the influence of the different solvents can be neglected.

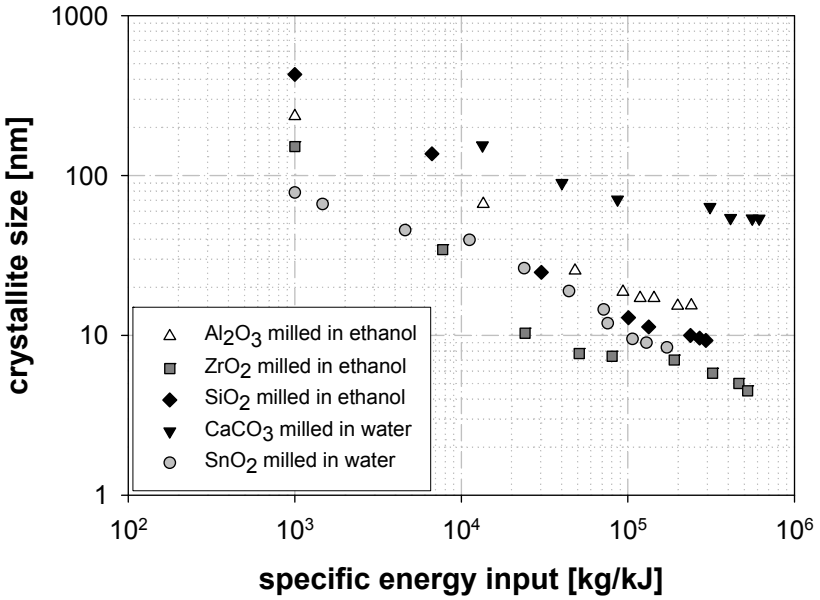

Fig. 3: Development of crystallite sizes for different materials with specific energy input

After stressing the particles for about 50 hours, most of the materials have reached their grinding limit. The continually decreasing final mean crystallite sizes of some materials may be caused by a crystallite size distribution which gets narrower as large crystallites break whilst the smaller ones have already reached their grinding limit. Additionally an amorphization of the particle surface due to intensive mechanical stressing can also lead to slightly smaller crystallite sizes without implying a breakage of the crystallites.

From Fig. 3 one can observe that each material shows a different breakage behavior expressed in different breakage kinetics as well as in a different grinding limit. In general the kinetics of crystallite breakage can be approximated by a power function:

$$x = a \cdot E_m^{-b} \tag{1}$$

where E_m is the mass specific energy input and a and b are parameters depending on material and process properties.

For ductile materials like calcium carbonate the smallest crystallite size reached in the milling experiment under the chosen conditions was about 55 nm whereas for very brittle materials like zirconia a grinding limit of less than 5 nm was observed. Ductile materials respond to mechanical stressing with distinct plastic deformation whereas in brittle materials the applied energy is mainly used for particle fracture. We have to point out that the grinding limits reached are not fixed values. It should become clear that under different milling conditions, for example by changing the rotational speed of the stirrer other stress intensities and therefore different values of the true grinding limit can be achieved.
A direct correlation of the minimal crystallite size with material properties is difficult for the time

being, because of a superposition of material and process parameters both influencing the breakage behavior. To correlate the material properties with the grinding limit and the breakage kinetics a separation of process und material parameters is necessary. Further investigations on this topic are in progress and will be presented in forthcoming papers.

Conclusions

The particle size in an agglomerate-free suspension is only determined by actual particle breakage. A grinding limit is observed in long term experiments for different materials and could be characterized by the crystallite size measured by X-ray diffraction. This true grinding limit is the minimal achievable particle size under the current milling conditions. It is assumed that the grinding limit is reached due to an insufficient intensity of stressing. During the grinding process lattice imperfections are generated which enhance the amount of elastic stored energy in a crystallite. Hence, the necessary energy transferred from the milling beads to reach a particle or crystallite breakage is reduced and can be bring up by the actual stress intensity for larger crystallite sizes. The procedure of generating defects in several stressing events until the stored energy combined with the constant 'external' energy are large enough to lead to a breakage event slows the breakage kinetics in the nanometer range. The grinding limit is reached when the crystallites become so small that nearly no defects can be stored in the lattice anymore. The total available energy below this critical crystallite size is insufficient and could not be increased by further milling. Accordingly the generation of defects enables nanogrinding by increasing the elastic stored energy, but determines with its disappearance below a critical size concurrently the overall limit of grinding.
The kinetics of particle breakage and the true grinding limit depend on material properties as well as on process parameters influencing the stress intensity. A correlation between those parameters and the actual primary particle size especially the critical particle size will to be determined by a separation of the material function and the machine function in future works.

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