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Production of sub-micron particles by wet comminution in stirred media mills

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A joined research project between the Technical University of Braunschweig and the Technical University of München investigates the possibilities for the production of stable product suspensions in a particle size range smaller than 100 nm. In this paper results for comminution of fused corundum showing the influence of the electrostatic stabilization at different pH-values on the grinding progress and the grinding media wear are presented. Furthermore, by means of experimental results the influence of the grinding media diameter and the stirrer tip speed is discussed.

1. Introduction

The fabrication of products 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 demands more and more suspensions of materials with a high fineness and storage stability. One way to produce such suspensions is wet comminution in stirred media mills.

First comprehensive investigations about grinding in stirred media mills were done by Stehr [1] and Weit [2]. These investigations show that the comminution progress mainly depends on the specific energy input E_m, which is the total energy supplied to the grinding chamber related to the product mass. Further studies published (among others Joost [3], Thiel [4], Bunge [5], Mankosa *et al.* [6], Stadler *et al.* [7] and Roelofsen [8]) show that besides the specific energy input the grinding media size has a great influence on the comminution result. The specific energy consumption can be reduced considerably by accommodating the grinding media size to the comminution problem. In a product particle size range down to 1 μm the comminution behavior of stirred media mills can essentially be described by the parameters specific energy E_m, stress number SN and stress energy SE (see Kwade [9]).

In the sub-micron particle size range the behavior of the product suspensions is more and more influenced by increasing particle-particle-interactions. Due to these interactions often spontaneous agglomeration of product particles occurs and the viscosity of the product suspension increases [10]. 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 results in spite of increasing energy input. Fundamental theoretical and experimental investigations about grinding and crack formation in solids have been undertaken by Schönert [11]. Based on this work he estimates the possible minimum particle size for breakage to be in a range of 10 to 100 nm depending on the physical properties of the material.

Investigations of the comminution of fused corundum (Al_2O_3) should answer the question whether and in which particle size range a limit of the grindability exists. Therefore, reagglomeration phenomena as well as problematic changes of the rheological behavior of the product suspension were prevented by the fast electrostatic stabilization.

Besides size reduction materials can be mechanochemically modified in stirred media mills. The tremendous stresses acting on the particle's

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surface lead to a mechanically activated, highly energetic surface that may react with the surrounding environment in various ways. As a result, phase transformations and amorphization can occur thus creating particles with totally different properties, e.g., higher solubility and reactivity or better catalytic performance. Stenger *et al.* [12, 13] show that grinding of alumina particles in stirred media mills leads to the formation of an alumina hydroxide layer around the particles which in turn influences the grinding behavior.

2. Experimental set-up

In Mende *et al.* [10] the experimental set-up is shown which allows the measurement of the most important electrochemical properties and the analysis of the particle size distribution of the product suspension as well as an adjustment of the pH-value for stabilization during the comminution process.

3. Influence of the electrostatic stabilization

It should be discussed whether reagglomeration of product particles during wet comminution in a stirred media mill can be prevented by an additional electrostatic stabilization and whether an influence of electrostatic stabilization on the comminution result exists.

For the comminution of fused corundum (Al_2O_3) with Yttrium-stabilized ZrO_2-grinding media with a diameter of 800 μm in Fig. 1 the development of the pH-values, the ζ-potential and the median particle sizes $x_{50,3}$ are plotted versus the specific energy input $E_{m,V}$ according to Equation 1.

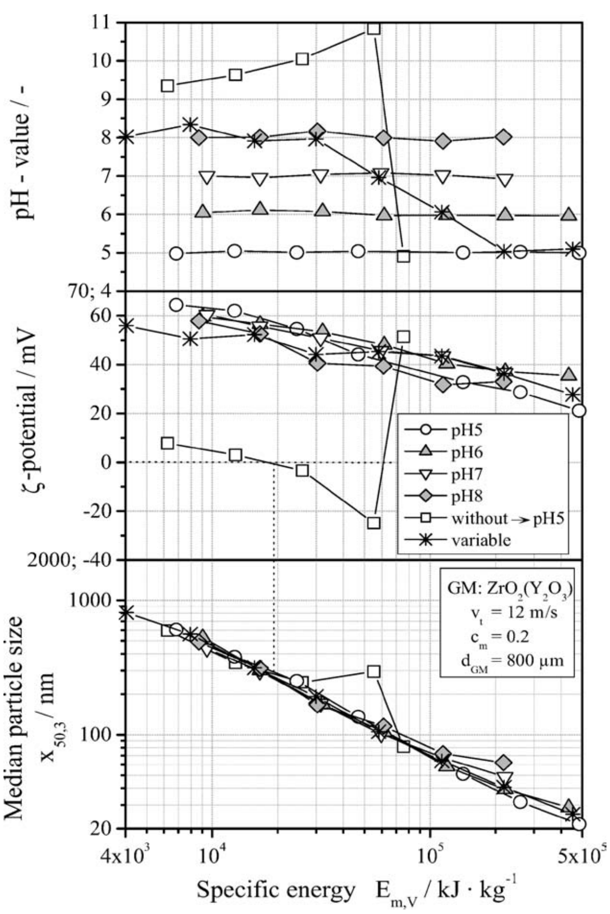

Figure 1 Influence of the electrostatic stabilization.

$$E_{m,V} = \frac{\int_0^t (N(\tau) - N_0) d\tau}{m_p + 0.5 \cdot \Delta m_{GM}} \tag{1}$$

Here, m_P is the mass of the product solid, $N(\tau)$ is the power at the time τ and N_0 is the no-load power. It is assumed that the grinding media wear increases proportional to the power input N. Thus the mass of the product is extended by $0.5 \cdot \Delta m_{GM}$, with Δm_{GM} as the grinding media wear at the end t of the grinding process.

In all experiments the results of which are shown in Fig. 1 the mass concentration was $c_m = 0.2$ and the stirrer tip speed v_t was 12 m/s. The first experiment was started without stabilization (□). The ζ-potential starts at a small positive value, crosses the isoelectric point and goes down to negative values around −20 mV. After the isoelectric point is reached no further comminution progress can be obtained. After a specific energy of about 54.000 kJ · kg^{-1} was reached the pH-value of the product suspension was adjusted to pH 5 by the addition of nitric acid (HNO_3). As soon as the addition of potential determining ions was started, the ζ-potential increased to values up to 56 mV. As a result, the median particle size $x_{50,3}$ decreased abruptly from 300 nm down to values smaller than 100 nm.

In addition, investigations with stabilization of the product suspension at pH 5 from start of the experiment were done (○). These investigations show that the time of the start of the pH-adjustment is irrelevant for the final comminution result. If an Al_2O_3-suspension is comminuted with the same grinding media and operating parameters the same ζ-potential and median particle size results at the same specific energy input at identical pH-values regardless of the time of pH-adjustment.

According to Joost [3] a dimensionless value of the grinding media wear is obtained by relating the loss of grinding media Δm_{GM} to the mass of grinding media at the start of the comminution experiment m_{GM} (see Equation 2).

$$\frac{\Delta m_{GM}}{m_{GM}} \tag{2}$$

From earlier experiments it is known, that with increasing grinding chamber volume the grinding media wear decreases. Therefore, the dimensionless wear value is related to the total energy input E_{tot} divided by the grinding chamber volume V_{GC} (see Equation 3).

$$E_{V,GC} = \frac{E_{tot}}{V_{GC}} = \frac{\int_o^t N(\tau) d\tau}{V_{GC}} \tag{3}$$

In Fig. 2 the grinding media wear is plotted versus the energy input related to the grinding chamber volume. The highest grinding media wear is obtained for a comminution at pH 5 and the lowest for a comminution at pH 8. For energy inputs larger than 10^4 J · cm^{-3} the grinding media wear at pH 5 is about 50% higher

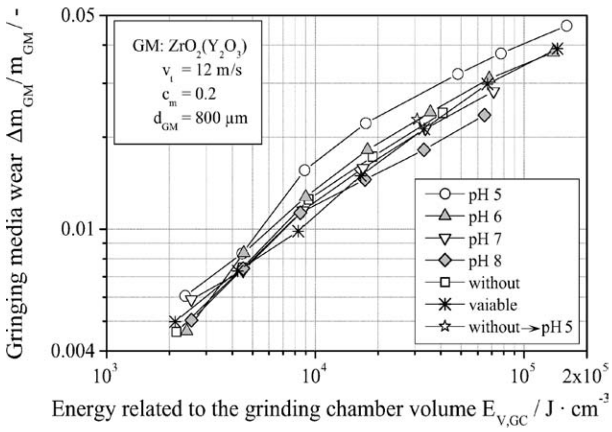

Figure 2 Influence of the pH-value on the grinding media wear.

compared to the value at pH 8. The grinding media wear for a comminution of a non stabilized product suspension is significantly higher than for a comminution at pH 8 but lower than for a comminution at pH 5. The reason can be found by looking at the influence of the pH-value on the viscosity of the product suspension. In [14, 15] the rheological behavior of the product suspension is examined depending on grinding progress and suspension stability.

These investigations show a strong increase in the shear stress and the yield stress with increasing pH-value in the lower shear rate range. The lower the viscosity of the product suspension is, the more intensive are the impacts of the grinding media and thus the grinding media wear. An increase of the suspension viscosity leads to an increase of the concentration of the grinding media at the mill exit (sieve cartridge) and may lead to a compression of the grinding media. This also leads to an increasing grinding media wear. Therefore, with respect to the grinding media wear an optimum of the suspension viscosity and thus of the adjusted pH-value exists. On the other hand the lowest suspension viscosity leads to the highest grinding media wear.

4. Influence of the grinding media diameter

To investigate the influence of the grinding media size Y_2O_3-stabilized ZrO_2-grinding media of different diameters between 200 and 1300 μm were used in experiments with different specific energy inputs. In Fig. 3 the developments of the ζ-potential and the median particle size are plotted versus the specific energy input $E_{m,V}$. In all experiments the results of which are shown in Fig. 3 the suspension was stabilized at a constant pH value of pH 5, the mass concentration was $c_m = 0.2$ and the stirrer tip speed was 12 m/s.

It can be seen that there is a continuous decrease in the ζ-potential, but it always stays above the line of zero charge. It clearly can be seen that with increasing specific energy input and decreasing grinding media diameter a finer product can be achieved at identical specific energies (Fig. 3).

The stress number SN is the total number of stress events and the stress energy SE is the energy transferred to a product particle during one stress event. From earlier investigations at the Institute of Mechanical Process Engineering—mainly Kwade [9], Becker [16] and others—it is known that the specific energy $E_{m,V}$ can be regarded as being proportional to the product of the number of stress events SN and the stress energy of the grinding media SE_{GM}. Identical comminution results occur if two of the three parameters specific energy, number of stress events and stress energy, are equal.

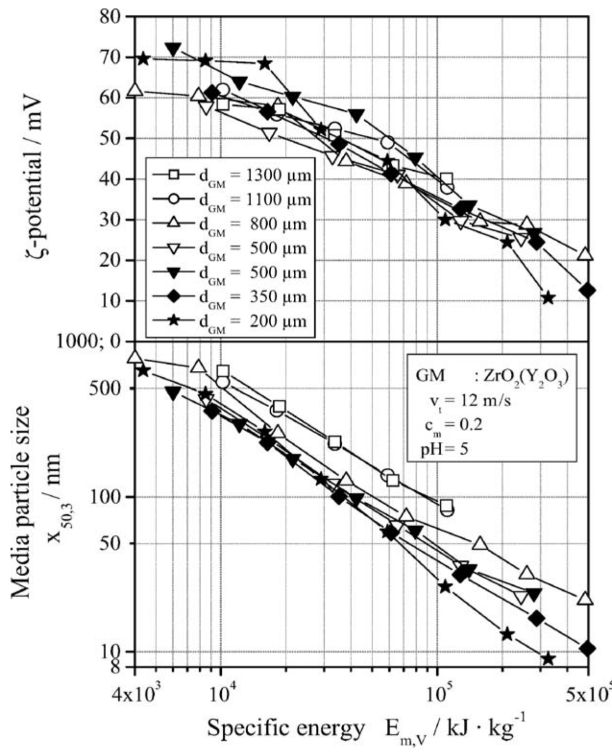

Figure 3 Influence of the grinding media diameter on the ζ-potential and the grinding progress.

The stress energy of the grinding media is the maximum energy which can be transferred from two colliding grinding media to the feed particle being caught by the media. The stress energy of the grinding media is defined as the product of the grinding media diameter to the power of three, the grinding media density and the stirrer tip speed to the power of two (see Equation 4).

$$SE_{GM} = d_{GM}^3 \cdot \rho_{GM} \cdot v_t^2 \tag{4}$$

From earlier experiments with limestone and other test materials it is known, that an optimum value of the

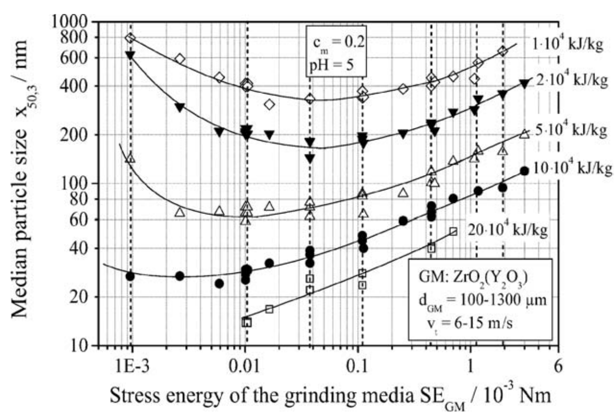

Figure 4 Comminution result versus the stress energy of the grinding media.

stress energy of the grinding media SE_{GM} exists for a given specific energy $E_{m,V}$, at which the finest product is obtained. In Fig. 4 the median particle size is plotted versus the stress energy of the grinding media for different values of the specific energy input. The figure contains results of experiments with different stirrer tip speeds v_t between 6 and 15 m/s and grinding media diameters down to 100 μm. It clearly can be seen that a lower optimum value of stress energy of the grinding media exists the higher the specific energy input and therefore the finer the product is.

5. Conclusions

The investigations show that the production of particles with a median particle size lower than 10 nm is possible by wet grinding in a stirred media mill. Furthermore, no influence of stabilization on the comminution progress itself was found. If an Al_2O_3-suspension is comminuted with the same operating parameters the same ζ-potential and median particle size seem to result at the same specific energy input at identical pH-values regardless of the time of pH-adjustment. On the other hand the stabilization influences the grinding media wear. With respect to the grinding media wear an optimum of the suspension viscosity and thus of the adjusted pH-value exists.

Investigations with grinding media of different diameters show that a finer product can be achieved with increasing specific energy input and decreasing grinding media diameter. Optimum values of the stress energy of the grinding media at which the finest product is obtained also exist for the data of this project in the sub-micron particle size range.

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