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Influence of Process Parameters on Breakage Kinetics and Grinding Limit at the Nanoscale

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In long-term milling experiments, in a stirred media mill, a grinding limit where no further particle breakage occurs was identified. During mechanical stressing of the particles, defects are generated in the crystalline lattice, which allows real fracture of nanoparticles. Below a critical size, defects cannot be stored or generated in the crystallites and the overall limit of grinding is reached. This limit is strongly influenced by material properties and hardly affected by most of the process conditions. However, the breakage kinetics strongly depend on the process parameters and suspension conditions as long as the grinding limit is not reached. Based on these findings, two mechanisms of nanoparticle breakage are proposed. Proper choice of process parameters saves not only up to 90% of the energy input to reach the grinding limit but also leads to a higher product quality in terms of crystallinity and less milling bead wear. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1751–1758, 2011
Keywords: ultrafine grinding, stirred media mill, grinding limit, microstructure

Introduction

Nanoparticles are increasingly used in many areas of industry. Besides the direct synthesis of these materials by chemical methods, wet grinding in stirred media mills is a suitable and efficient technique for the production of nanoparticles in the liquid phase with high solid concentrations.[1,2] Recently, Knieke et al.[3] did show that graphite, a layered material with strongly anisotropic binding forces, can be delaminated down to even single graphene layers. The manufacturing of fine particles is influenced by particle breakage and interparticle interactions. These interactions become relevant especially for particles smaller than 1 μm because of an increasing collision rate of the particles due to their Brownian motion and smaller interparticle distances. Thus, the particles have to be stabilized against agglomeration to advance the grinding progress. Whereas different stabilization mechanisms have been a subject of much research, the breakage behavior of particles in the nanometer range is not well understood for the time being.

Knieke et al.[4] and Armstrong et al.[5] published data on micromechanical changes of tin oxide nanoparticles within comminution processes. In their experimental investigations, a grinding limit was identified in the lower nanometer range where no further breakage of the particles occurs. It could be shown that the evolution of the internal microstructure of the particles determines the breakage behavior in the nanometer range. Especially, the grinding limit seems to be strongly influenced by the stability of lattice imperfections. By means of high-resolution transmission electron microscopy (HRTEM), the generated defects in SnO_2 were identified as shear bands and crystal twins, which could also be observed in molecular dynamics (MD) simulations. Beside the comminution of tin oxide, Knieke et al.[4] investigated the microstructural changes of several other inorganic materials in wet grinding processes. A grinding limit in the lower nanometer range was observed for most of these materials. The grinding limit and breakage kinetics strongly depend on material properties. Forssberg and coworkers[6,7] analyzed microstructural changes of hematite particles in stirred media

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Table 1. Product Specifications of the Initial Tin Oxide Powders

Manufacturer	Specific Surface Area	Crystallite Size
Merck	8.2 m^2/g	65 nm
Keeling & Walker	4.0 m^2/g	81 nm
Thermox VS	4.1 m^2/g	52 nm

mills. In their experiments, a grinding limit was not reached. In earlier studies, Schönert and coworkers[8,9] already defined a material-dependent grinding limit based on theoretical considerations, in which the minimum particle size is determined by the size of a plastic fracture zone surrounding the crack tip.

In this article, we present results of long-term grinding experiments of tin oxide particles in a stirred media mill under various process conditions. The influence of different process parameters and suspension conditions on the breakage behavior of nanoparticles, i.e., breakage kinetics and grinding limit, is investigated. Especially, the question of the necessary energy input to reach the grinding limit and its influencing factors are of great interest to make ultrafine grinding processes more energy efficient.

Materials and Methods

Materials

Tin (IV) oxide powder in the modification cassiterite was purchased from three different manufacturers to investigate the influence of the feed material. Unless otherwise noted, tin oxide powder with a purity of 99% from Merck GmbH was used in the experiments. The other powders were obtained from Keeling & Walker and Thermox Zinnoxide GmbH. The product specifications concerning specific surface area and crystallite size are summarized in Table 1. The specific surface area was measured by nitrogen gas adsorption [Brunauer–Emmett–Teller (BET)] and the crystallite size could be determined from X-ray diffraction (XRD) patterns using the Scherrer equation.[10,11]

As solvent, deionized water and denatured ethanol (95 vol.%) obtained from VWR were used in the experiments. Wear resistant, commercially available yttrium stabilized zirconia milling beads in the size range of 0.3–1.25 mm (TOSOH, Japan) were used. According to the manufacturer, the grinding media has a density of 6065 kg/m^2 and a chemical composition of 95% ZrO_2 and 5% Y_2O_3.

Experimental setup

The experimental setup 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. From the vessel, the suspension flows back into the mill. A schematic diagram of the experimental setup is given in Figure 1.

The commercial laboratory mill LabStar LS 1 (Netzsch Feinmahltechnik GmbH, Selb, Germany) was used for the milling experiments. The mill has an explosion-proof design and is equipped with a centrifugal separating system for the grinding media. This allows the use of small milling beads down to 0.1 mm. The grinding chamber with a volume of 0.68 dm^3 as well as the stirrer is lined with ZrO_2 for wear protecting reasons. The grinding chamber is equipped with a double wall for cooling, which is connected to an external cooling system. To measure the power input into the grinding chamber, the consumed motor power $P(t)$ was measured. The mass-specific energy is calculated according to Eq. 1 using the product particle mass m_p and the no-load power P_0.

$$E_m = \frac{\int (P(t) - P_0) d\tau}{m_p} \tag{1}$$

Characterization methods

Specific Surface Area (BET). BET 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 at least 2 h at 250°C under vacuum to remove adsorbed solvent molecules. The specific surface area was determined using a 7-point method with nitrogen as adsorption gas. As micropores could not be detected, the mass-specific surface area, S_m, was used to calculate the primary particle size, $x_{1,2}$, under the assumption of spherical and monodisperse particles with a bulk density, ρ_p, by Eq. 2.

$$x_{1,2} = \frac{6}{\rho_p S_m} \tag{2}$$

X-Ray Diffraction. The XRD data were collected using a Bruker AXS D8 Advance powder diffractometer equipped with a VÅNTEC-1 detector and Ni filter. Cu K_α radiation with a wavelength of $\lambda = 0.15406$ nm was used to measure the ground powders at different milling states. The X-ray patterns were recorded in a range from $20° \leq 2\Theta \leq 80°$ with a step width of 0.014° per step and a counting time per step of 1.0 s. To determine the microstrain within the samples, a Rietveld refinement was performed using the Bruker AXS TOPAS software (Version 3).[11]

Rheology. Rheological measurements were carried out on a Physica USD 200 universal dynamic spectrometer (Paar Physica GmbH, Austria) with double-gap geometry. The instrument is cooled with an external thermostat to keep the temperature constant during the measurements. The shear

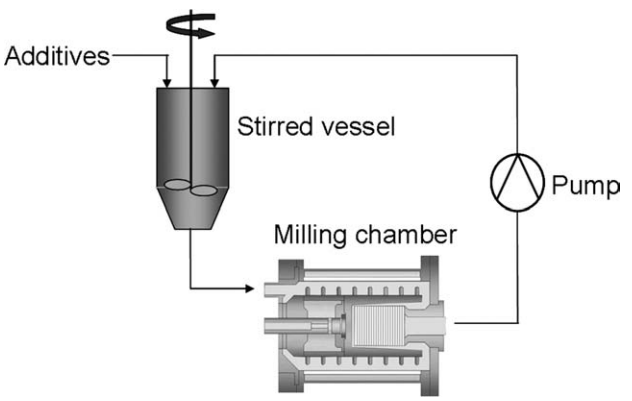

Figure 1. Experimental setup.

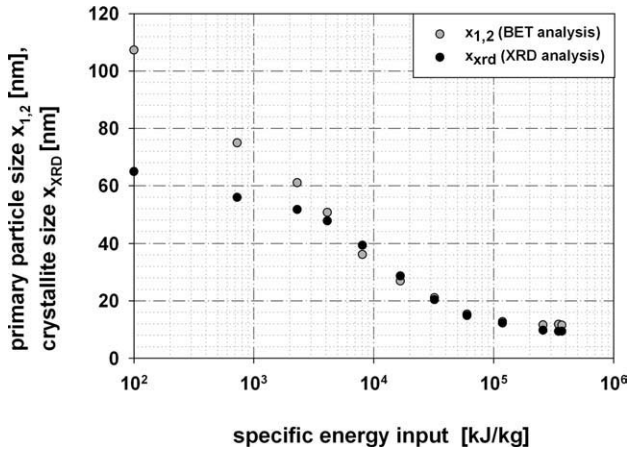

Figure 2. Development of primary particle size and crystallite size during comminution of tin oxide.

rate was varied during the measurements from 0.1 s^{-1} to 1000 s^{-1}.

Results and Discussion

Microstructural evolution of tin oxide during mechanical stressing

XRD analysis was used to determine microstructural changes inside the particles during the milling process. As particle breakage occurs preferred at the domain interfaces for being the weakest areas in a crystalline material, the development of the crystallite size can be used together with the evolution of particle size for investigating the breakage process. In Figure 2, the typical evolution of primary particle size, $x_{1,2}$, and crystallite size, x_{XRD}, of tin oxide dispersed in ethanol are presented. The primary particle size provides information about the real breakage of the particles and is not superposed by agglomeration effects.

The initially polycrystalline particles become monocrystalline during the milling process because the breakage kinetics is faster than the size reduction of the crystalline domains. The feed particles break preferred at the weak domain interfaces where less energy is required for fracture than for a size reduction of the stronger crystallites. With increasing energy input, fracture of monocrystals occurs. After a certain energy input is exceeded, no further fracture of the tin oxide occurs and the grinding limit is reached at a particle size of about 10 nm. According to Knieke et al.,[4] defects are generated during mechanical stressing, which enhance the elastically stored energy in the particles and weaken the material. Thus, real breakage becomes possible even in the nanometer range. The fracture mechanism can be regarded as a fatigue fracture as an accumulation of defects is necessary to fulfill the energy balance allowing the crack to propagate throughout the entire particle. Below a critical crystallite size, the defects become unstable and simultaneously the grinding limit is reached indicating that the transferred energy from the grinding media is no longer sufficient to allow fracture of the strong defect-free particles for the given stressing conditions.

In the following, the influence of process parameters including milling bead size, revolution speed of the stirrer, temperature, suspension stability, and viscosity will be discussed. Unless otherwise mentioned, the following standard milling conditions apply: tin oxide powder purchased from Merck, filling ratio of milling beads: 80%, solid content: 10 wt %, solvent: ethanol, milling bead size: 450 μm, rotational speed of the stirrer: 2000 rpm, which corresponds to a stirrer tip speed of 8 m/s and suspension temperature: 25°C.

Influence of feed material/initial microstructure

To prove if the presented development in Figure 2 is influenced by the initial microstructure of the particles, the milling behavior of tin oxide from three manufacturers with different initial mean particle and crystallite sizes was studied. The results are presented in Figure 3.

The powders from Keeling & Walker ($x_{1,2}$ = 216 nm and x_{XRD} = 81 nm) and Thermox ($x_{1,2}$ = 211 nm and x_{XRD} = 52 nm) have nearly the same initial primary particle size but different crystallite sizes. The powder with the finer microstructure (Thermox) shows slightly faster breakage kinetics than the Keeling & Walker powder. This can be ascribed to the different number of grain boundaries where particle fracture occurs more easily. Finally, all three powders end up at the same particle and crystallite size indicating that the grinding limit is not affected by the initial microstructure or differences in purity.

Influence of stress energy

In Figure 4, the influence of stress energy on the breakage behavior of nanoparticles is presented. The stress energy of the grinding media, SE_{GM}, is a measure for the energy of the milling beads and can be expressed according to Kwade and coworkers[12,13] by

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

where d_{GM} is the diameter of the grinding media with the density ρ_{GM} and v_t is the tip speed of the stirrer. SE_{GM} defines an upper limit for the energy transferred from the stirrer to the

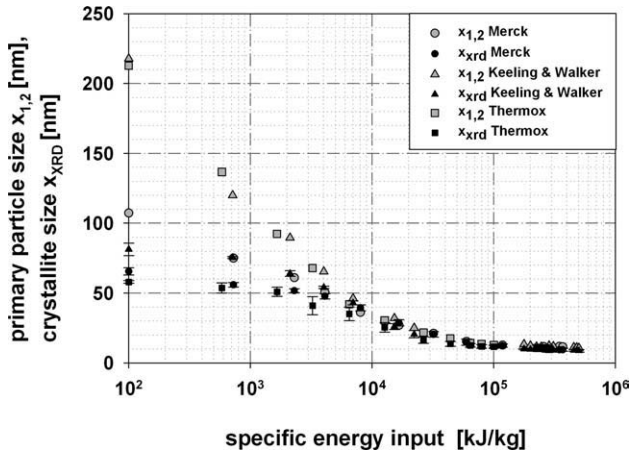

Figure 3. Influence of the feed material on the breakage behavior of tin oxide.

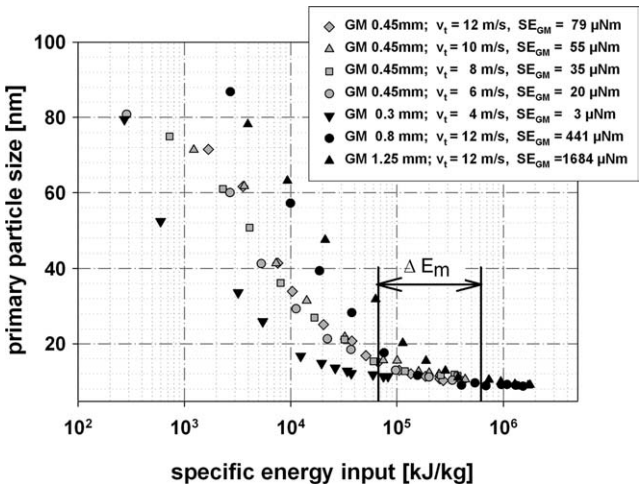

Figure 4. Influence of stress energy on the grinding behavior of tin oxide.

beads and prooved extremely helpful for the interpretation of experimental data. This simple scaling argument is, of course, only a rough measure of the true grinding speed velocity distribution and the related energy for stressing the particles. Currently, research is being pursued to simulate the bead motion in the mill by a coupling of computational fluid dynamics and discrete element methods (CFD-DEM). [14] For the time being, however, the true stress distribution in the mill is unknown. In the following, the stress energy was varied by changing the tip speed of the stirrer and the grinding media size.

In all experiments, the primary particle sizes decrease with increasing specific energy input until a plateau in particle size—the grinding limit—is reached. Changing the revolution speed of the stirrer does not lead to significant changes in the evolution of particle size. As the stress energy has a cubic dependency on the milling bead size, the latter influences the breakage kinetics more strongly. Smaller milling bead sizes (0.3 mm) lead to a faster reduction of the particle size related to the energy input. A comparison to larger beads (0.8 mm) yields that the grinding limit can be reached with only 10% of the energy input. At a constant filling ratio of grinding media, a higher number of beads can be inserted in the milling chamber if smaller beads are used. Hence, a larger stress number, which is a measure for the total number of grinding media impacts, can be achieved. Referring to the concept of stress energy and stress number developed by Kwade et al.,[15] where an optimum in stress energy exists for a constant energy input, the stress energy chosen for the standard experiment seems to be too large. Reducing the stress energy will shift the value toward the optimum at lower stress energies and the grinding process will thus become more energy efficient. In the case of Figure 4, about 90% of the used energy can be saved by a proper choice of the process parameters.

To analyze the influence of stress energy on the grinding limit, a closer look at the milling results in the double-logarithmic scale is necessary (see Figure 5).

Although there are huge differences in the stress energies, only a slight shift in the grinding limit could be observed. With a SE_{GM} of about 3 μNm, a limiting particle size of 11 $\pm$ 0.20 nm could be achieved, whereas in the case of SE_{GM} = 441 μNm, the grinding limit is decreased to about 9 $\pm$ 0.20 nm. In the experiment with the largest stress energy, the grinding limit was not reached at the end of the milling procedure.

Influence of overstressing

To study the influence of an unnecessarily high energy input on the quality of the product, the suspensions ground with an SE_{GM} of about 3 μNm and SE_{GM} of about 1684 μNm were analyzed for crystallinity and the amount of grinding media wear. The amorphous content in the final powder rose to a value of 51 $\pm$ 2 wt % for the high stress energy, whereas a significantly lower amount of 27 $\pm$ 2 wt % was found for the low stress energy. A similar trend could be found for grinding media wear: a zirconia content of 3.8 wt % was measured in the milled powder at low stress energy. For the high stress energy, a content of 5.1 wt % wear was observed. By autogeneous grinding, i.e., by using beads of the same material as the product particles, undesired impurities can be avoided.

Influence of suspension viscosity

Higher suspension viscosities can lead to a dampening of the milling bead motion so that smaller stress intensities are transferred to the product particles.[16] Frances and Laguerie[17] already examined the influence of the viscosity on the grinding behavior of micro-sized alumina hydrate particles in a media mill. They observed a fall in the grinding performance with increasing viscosity of the slurry.

To investigate if those findings are valid for nanoparticle breakage as well and if the suspension viscosity also affects the grinding limit, tin oxide was milled in ethanol (η = 1.18 mPa s at 20°C) and ethylene glycol (η = 21.3 mPa s at 20°C) under standard conditions. The grinding results are presented in Figure 6.

Obviously, the breakage kinetics of tin oxide milled in ethylene glycol is strongly reduced. However, again the

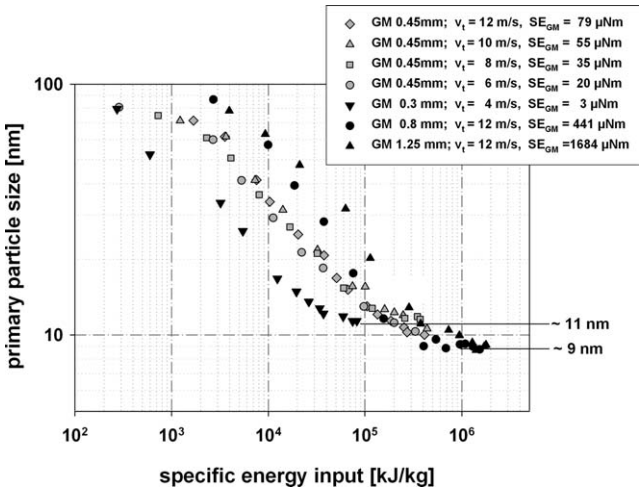

Figure 5. Influence of stress energy on the grinding limit of tin oxide.

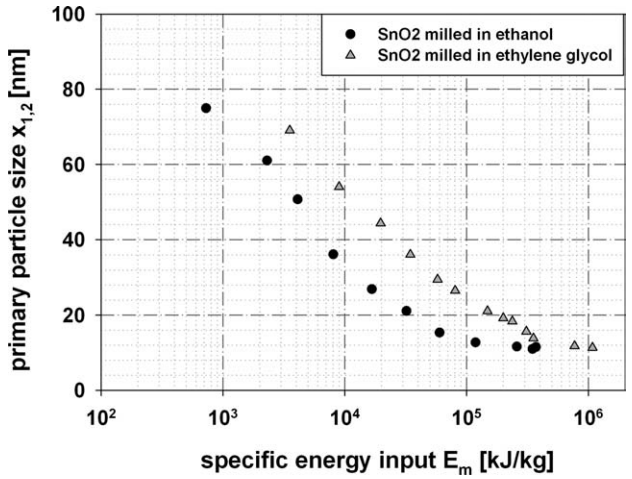

Figure 6. Influence of viscosity on the breakage behavior of tin oxide.

same grinding limit could be achieved for both suspensions. To get an impression of the viscosity differences, rheology measurements have been carried out of the final milling suspensions and are presented in Figure 7. It can be seen that the suspension based on ethylene glycol shows nearly Newtonian behavior over the whole shear rate range, whereas the ethanolic suspension follows a shear thinning behavior. At high shear rates, which are present in the milling chamber, the viscosities of the ethylene glycol suspension are much higher than those of the ethanolic suspension. This leads to a dampening of the grinding media velocity and therewith less energy can be transferred to the product particles. Hence, the grinding performance becomes worse with increasing suspension viscosity, resulting in reduced breakage kinetics. As already shown in the previous sections, the grinding limit is fairly insensitive concerning changes in the transferred stress energies, i.e., the overall grinding limit is not affected by the viscosity differences.

Although the grinding limit itself is seemingly not altered by the suspension viscosity, the possibility to reach this limit is not necessarily given: it was shown by Stenger et al.[18,19] that a strong increase in viscosity and yield stress due to a higher solid content or more pronounced particle-particle interactions can lead to an early stop of the experiment as the suspension cannot be pumped anymore. Thus, both a suitable temporal evolution of the viscosity and the related yield stress are necessary preconditions to reach the true grinding limit.

Influence of suspension stability

In Figure 8, the influence of suspension stability on particle breakage is demonstrated. The evolution of the primary particle size and the crystallite size are given for a grinding experiment under stable conditions in water at pH 11 (adjusted by addition of NaOH) and under unstable conditions in ethanol.

Comparing the milling results in water (pH 11) and ethanol, it becomes clear that the formation of agglomerates in the ethanolic suspension does not influence the breakage behavior. Both crystallite size and primary particle size show nearly the same evolution in water and ethanol, respectively, and finally, the same plateau of about 10 nm is reached. Additionally, viscosity measurements have been carried out because the suspension stability also influences the rheological behavior. In the case of the two milling suspensions, no significant changes in viscosity could be observed in the high shear rate range. Therefore, the stressing conditions are comparable resulting in the same breakage behavior.

Influence of temperature

Finally, the influence of temperature has been investigated. Hence, the tin oxide particles were ground in ethanol at −5 and 45°C, so that a total temperature variation of 50°C could be realized with the experimental setup. To reach a temperature of −5°C inside the milling chamber, the tip speed of the stirrer was slightly decreased to 6 m/s. Such small decrease of stirrer tip speed does not influence the grinding behavior as shown in Figure 5. The evolution of primary particle sizes is presented in Figure 9.

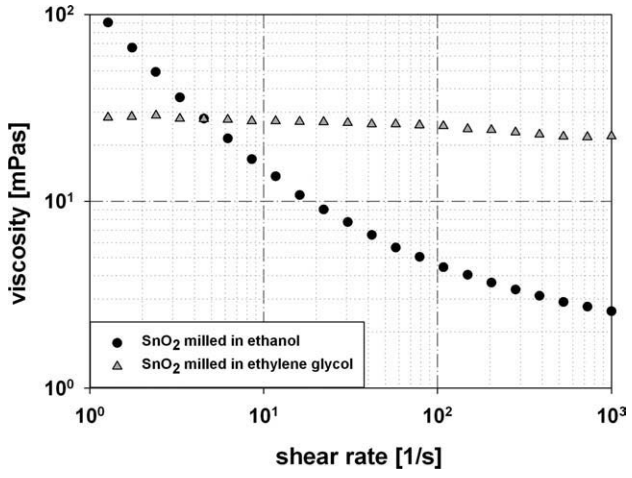

Figure 7. Comparison between the viscosities of tin oxide milled in ethylene glycol and ethanol.

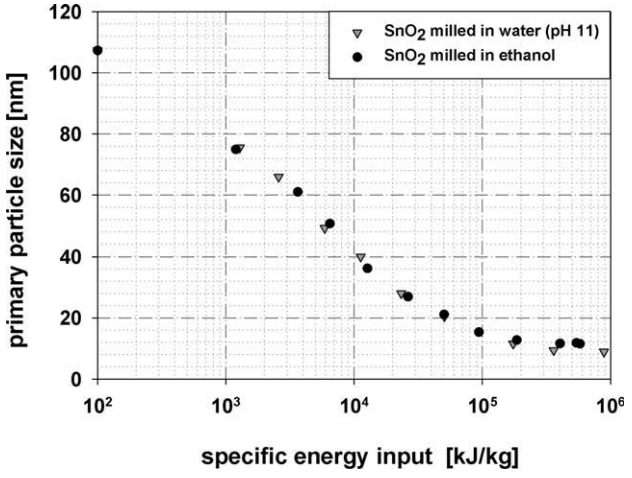

Figure 8. Influence of suspension stability on the breakage behavior of tin oxide.

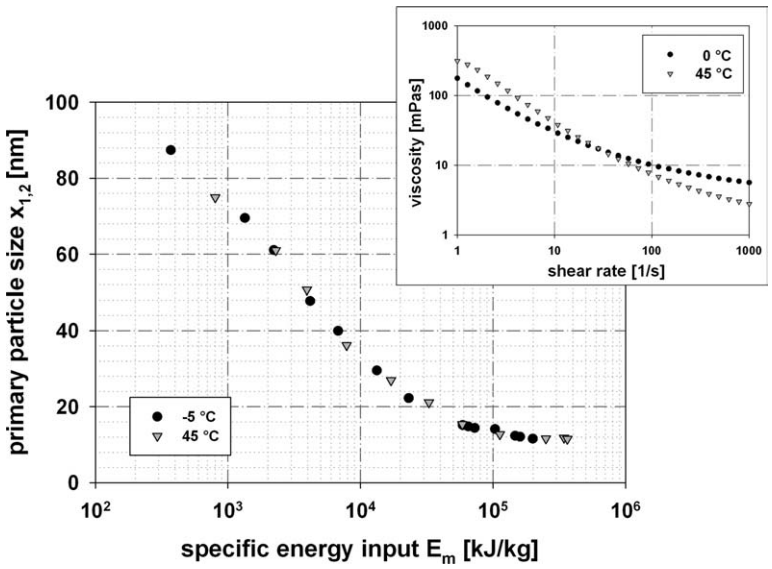

Figure 9. Influence of temperature on the grinding behavior of tin oxide.

Reducing the temperature from 45 to −5°C does not influence the grinding behavior of the tin oxide particles. Both the breakage kinetics and the grinding limit are not affected by the temperature variation in the analyzed range. As oxide particles are innately very brittle materials, a decrease in temperature of 50°C will hardly change their material properties. Changes are expected for materials which behave more plastically such as organic materials.[20]

Beside breakage and stability, the temperature can also influence the suspension viscosity, which itself can affect the breakage by dampening of the grinding media as already shown above. As it was not possible to measure viscosities at temperatures below 0°C with the available rheometer, the viscosity at 0°C for the suspension is given. As can be seen in the inset of Figure 9, the changes in viscosity are not significant. At a shear rate of 1000 s^{-1}, the suspension viscosity at 45°C is about 5.6 mPa s, whereas at 0°C, the viscosity yields a value of about 2.8 mPa s. Hence, comparable stressing conditions can be assumed resulting in a similar breakage behavior. For low shear rates, higher viscosities are achieved for higher temperatures indicating stronger interparticle interactions.

Breakage mechanisms

From the experimental data presented here and elsewhere,[4,5] at least two different fracture mechanisms for nanoparticles can be derived. Figure 10 shows the development of the averaged number of crystallites per primary particle, derived from the ratio of primary particle volume to crystallite volume, accompanied by preliminary microstrain measurements for SnO_2 and ZrO_2. To highlight the

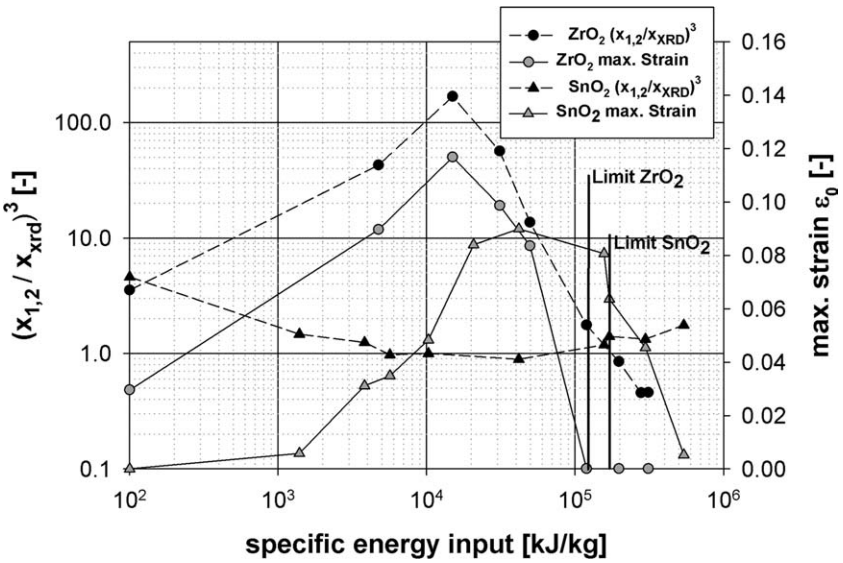

Figure 10. Breakage characteristics for SnO_2 and ZrO_2.

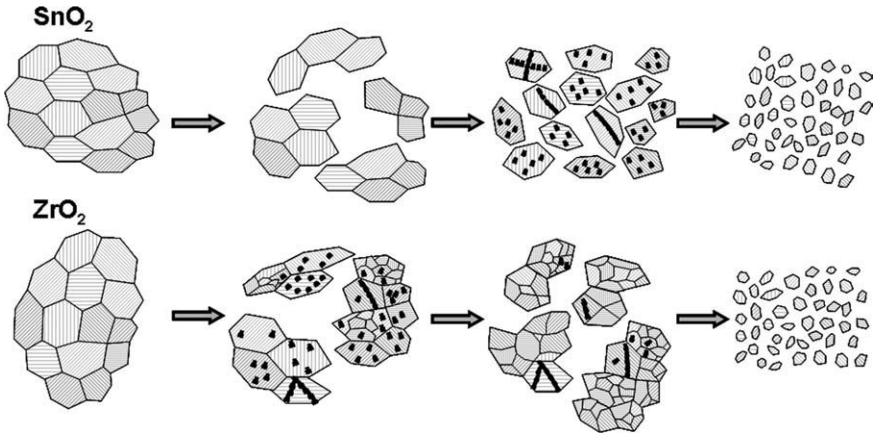

Figure 11. Schematic representation of SnO_2 and ZrO_2 breakage mechanisms.

difference in breakage even further, a schematic drawing of the mechanisms is given in Figure 11.

For tin oxide, breakage occurs in the beginning predominantly along weak grain boundaries: the averaged number of crystallites per primary particle starts at a value of about 5 and drops rapidly to a value of 1: as breakage along grain boundaries is much faster than grain refinement, the particles become monocrystalline before the grinding limit is reached. As soon as the monocrystalline stage is reached, the strain within the particles increases quickly. This indicates defect formation and multiplication within the particles. Nevertheless, the average number of crystallites per primary particle is not increased again and stays constant until the grinding limit is reached: the generated defects lead to a breakage of the primary particles before new domains can be formed. As soon as the grinding limit is reached, compared with Figure 2, the microstrain drops to a value close to 0. The absence of microstrain indicates that the defect (i.e., dislocation) density within the particles must be low: either defects cannot be created anymore or newly formed defects are not stable within the particles and are driven to the surfaces.[21,22] For high energy inputs, the ratio of primary particle size to crystallite size is apparently increasing again, which can be attributed to an ongoing amorphization of the tin oxide particles.

In case of ZrO_2, the behavior is different: only when the grinding limit is reached, ZrO_2 becomes monocrystalline; in the beginning, both the number of crystallites per primary particle and the microstrain increase until a maximum is reached. It seems that defects are stored within the particles and lead to a refinement of the grain structure. The maxima of the microstrain and the averaged number of crystallites per primary particle coincide. This means that the grain boundaries are either comparable in strength to the bulk material and are not preferably broken or the kinetics of the involved generation processes are much faster than the rate of the comminution kinetics. As soon as the density of defects exceeds a maximum value and the domains are weakened, the microstrain is relieved by breakage along grain boundaries and through grains. The average number of crystallites per particle drops rapidly to 1, and thus monocrystalline particles, not capable of storing any defects, are obtained. It can be seen in Figure 2 that the ratio $x_{1,2}/x_{XRD}$ for the zirconia particles reaches values below 1. This can be explained by the fact that differently related mean particle sizes are compared. Whereas the $x_{1,2}$ is surface-weighted, the x_{XRD} is a volume-weighted value. As a consequence, x_{XRD} can take larger values than the $x_{1,2}$.

Further investigations are ongoing to elucidate the mechanisms of defect formation and defect stability, which are thought to be critical for the understanding of fracture at the nanoscale.

Conclusions

Ultrafine wet grinding in stirred media mills is limited at a critical size in the lower nanometer range where no further fracture of the particles occurs. This grinding limit of about 10 nm in the case of tin oxide and zirconia oxide is hardly influenced by the investigated process parameters and suspension properties (at least if sufficient flowability is guaranteed). Neither the initial microstructure of the powder nor the suspension stability, temperature, and viscosity influence the value of the overall limit of grinding in the analyzed range. Only huge variations of the stress energies by changing the grinding media size lead to a slight shift of the grinding limit. This suggests that the grinding limit is mainly influenced by material properties.

In contrast to the grinding limit, the breakage kinetics varies strongly with most of the analyzed process conditions. Thus, by adjusting the process parameters properly, the grinding limit is reached with a reduced energy input of 1 order of magnitude. With the knowledge of such dependencies, large energy savings can be realized in ultrafine grinding applications, a very topical issue in the current discussions on energy savings. Furthermore, an unnecessarily high energy input leads to an undesired loss of crystallinity and an increased contamination by grinding media wear.

Additionally, fracture mechanisms are proposed, shedding light on breakage and defect formation at the nanoscale and allowing a classification of the grinding behavior of the investigated materials zirconia and tin oxide.

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