1. Introduction

Nanoparticles are widely used in many industrial fields such as the ceramic, pharmaceutical, chemical or microelectronic industry. Caused by the extraordinary high ratio of surface area to volume, nanoparticles can yield totally new properties compared to the bulk material. Additionally, nanoparticles can be used as building blocks to create larger structures with tailored properties. For nanoparticle production, two distinctly different fabrication routes exist. Bottom-up processes are based on a direct arrangement of molecules to particulate clusters, whereas the top-down approach describes the production of nanoparticles by fragmentation of coarser feed materials. Top-down processes can be realized for example in wet operated stirred media mills, which can supply the high specific energies necessary for nanoparticle production. Stirred media milling allows the production of highly concentrated suspensions with high throughputs in an industrially well established process. In general the production of nanoparticles requires two preconditions. The first one is the fracture of the particles as a result of a sufficiently high stress field inside the particles, which has to build-up during the impact between the grinding media. The second condition demands the stabilization of the created fragments against agglomeration. Below sizes of about 1 μm, particles tend to agglomerate because of an increased Brownian motion and smaller interparticle distances, both enhancing the collision rate of the particles. As a consequence a steady state between breakage and agglomeration appears in the milling process, which strongly affects the grinding result. In the last few years many research activities have been carried out in the field of stabilization to control the agglomeration behavior in wet grinding processes by an adjustment of the interparticle interactions [Sten 05a], [Mend 04b].

To this day the breakage mechanisms of nanoparticles are still poorly understood. In contradiction to earlier theories that predict a grinding limit for

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brittle oxide materials in the lower micrometer range [Scho 71], [Kend 78], [Haga 79], particle sizes down to 10 nm can nowadays be observed by real breakage. Approaches to explain the observed discrepancy between the postulated grinding limits and the experimentally achieved particle sizes are still missing. Therefore, the main objective of this work is to gain deeper understanding about the breakage mechanisms at the nanoscale. In general three questions can be defined, which display the focus of this thesis:

1. How does particle breakage become possible in the nanometer range?
2. Does there exist a true limit of grinding?
3. If yes, which parameters affect the limit of grinding?

To answer these questions a closer look into the particles' microstructure is necessary. Microstructural changes in terms of crystallite size and microstrain evolutions under mechanical stressing are investigated under different process conditions in stirred media milling. Beside the breakage behavior of brittle ceramic particles, the size reduction characteristic of graphite particles as a typical example of a layered material with a strong anisotropy in the bond forces is presented in this work.

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2. State of the Art

2.1. Ultrafine grinding in stirred media mills

The top-down approach for the production of ultra fine particles can be reasonably realized in stirred media mills since they can provide the necessary high specific energies for fracturing fine particles. Stirred media mills are the most frequently used milling machines in many fields of industry. A consideral amount of research investigations on the operation performance of stirred media mills has been carried out at the Institute of Mechanical Process Engineering (today: Institute for Particle Technology) in Braunschweig, Germany. Fundamental results of their research activities are summarized in section 3.1.

Recently, it was shown by Stenger and Mende that even nanoparticles can be produced by stirred media milling [Sten 05c], [Mend 03]. The authors figured out that an appropriate stabilization is necessary to avoid agglomeration of the created fragments to improve the grinding results. Below particle sizes of about 1 μm the collision rate of the particles increases because the particles show an enhanced Brownian motion and the interparticle distances decrease at a constant solid content. Hence, the overall grinding result in the submicrometer range depends on both, breakage and stabilization. Since many important suspension properties such as the rheological behavior [Sten 05b] or optical properties are affected by the degree of agglomeration, Stenger and Mende focused on the stabilization of inorganic oxide particles in aqueous media by a pH adjustment.

Later on, Sommer and Breitung-Faes extended the work of Stenger and Mende to non-aqueous media and the use of polymers as dispersing agents [Somm 07], [Brei 09]. Sommer showed for polyethylene oxide that large polymers can break under high shear forces during the milling process. Furthermore, he discovered a dampening effect of the polymer leading to

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reduced breakage kinetics. Based on the work of Stenger and Mende several other groups extended their research investigations to the submicrometer size range [Wang 06], [Vita 08], [Henn 10]. Nano-sized organic pigment particles have been produced via wet milling and stabilizing in the group of Scarlett [Bilg 06]. Particle sizes down to 10 nm could be produced with polymeric grinding media of about 20 μm in size.

Microstructural changes of hematite during wet and dry grinding in different kinds of media mills were investigated in the group of Forssberg [Pour 08], [Pour 07]. By means of X-ray diffraction the evolution of crystallite size and lattice strain was detected with milling time. A decrease of crystallite size and an increase of dislocation density were observed. Simultaneously the amorphous content of the product powders rises caused by highly energetic impacts of the grinding media. A limit of grinding was not observed in their investigations.

2.2. The limit of grinding

Throughout the history there are many discussions about a size limit in comminution processes. In general, the grinding limit can be the result of a

- machine limitation: problem of transferring energy from the milling machine to the product particles. In media milling this, for instance, can be the case if no trapping of particles between the grinding media or a strong dampening of the bead motion in a highly viscous media occurs.
- material limitation:
  a) agglomeration or welding (relevant in dry grinding applications, where high temperatures or high local stresses are present)
  b) no further breakage of the particles below a certain size.

Whereas the machine limitation can be overcome by an optimization of the milling device or an adjustment of process parameters, the material limitation determines the minimal particle size which could theoretically be achieved in grinding processes. The existence of this minimal particle size was predicted by several authors. First of all, Schönert presented in 1971 an

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experimental study about single particle compression experiments of quartz and limestone. He claims that a limiting particle size in grinding operations is reached if plastic flow of the particles takes place exclusively instead of breakage. An almost breakage-free deformation of the investigated particles was achieved for sizes below 2 μm and 4 μm for quartz and limestone, respectively [Scho 71]. Later on, Schönert published a theoretical approach to estimate the smallest specimen size in milling experiments based on considerations from Dugdale [Dugd 60]. This size depends on the size of the plastic zone δ which is formed around the crack tip, if the local stress at the notch root exceeded the yield stress of the material [Scho 88]. Schönert's equation (Eq. 2.1) is valid, if the length of the fracture zone is much smaller than the length of the crack.

$$\delta \approx 0.4 \left(\frac{RY}{\sigma_y^2} \right) \tag{2.1}$$

Schönert specified values for δ between 1 nm and 10 nm for brittle minerals. This length determines the minimum separation between fractures and, therewith the size of the smallest fragments (ca. 5 - 10 δ). The material data used for this estimation are not mentioned in the publication of Schönert. From today's perspective, an exact calculation of the plastic zone size is difficult because of the lacking of reliable material data especially for ceramic particles and in particular for nano-sized ceramic particles as they are known to yield different properties as their bulk materials [Gerb 06]. Additionally, the crack resistance R depends on the notch depth as well as the fracture history, which is usually visualized in so-called R-curves [Evan 84], [Kneh 82].

Replacing the crack resistance R and the Young's modulus Y by the fracture toughness (mode 1: crack opening under a normal tensile stress perpendicular to the crack) K_{1c} with the relation $K_{1c} = \sqrt{RY}$, gives the following expression for the minimal particle size:

$$d_{crit,S} = 2...4 \left(\frac{K_{1c}}{\sigma_y} \right)^2 \tag{2.2}$$

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In 1978 Kendall [Kend 78] published a paper about the *"The impossibility of comminuting small particles by compression"*. For a special geometry based on the Griffith energy criterion for fracture, he derived an expression for a critical particle size, below which crack propagation is impossible under compressive force (Eq. 2.3). Kendall postulated that bodies smaller than d_{crit} appear ductile and are pressed flat under loading. d_{crit} is therewith equal to the size of brittle-to-ductile transition.

$$d_{crit,K} = 10.7 \left(\frac{K_{1c}}{\sigma_y} \right)^2 \tag{2.3}$$

Kendall confirmed his theory by single compression experiments of polystyrene specimens. He observed that the brittle-to-ductile transition size was in good agreement with the theoretical predictions from Eq. 2.3.

One year later, Hagen described that crack nucleation is the limiting factor for fracture rather than crack propagation as assumed by Kendall. Beside a critical load, the presence of initial flaws with a minimal length inside the material is another condition for crack nucleation. The size of the critical flaw length and therewith the minimal grain size can be estimated with Eq. 2.4 [Haga 79].

$$d_{crit,H} = 29.5 \left(\frac{K_{1c}}{H} \right)^2 \tag{2.4}$$

For Al_2O_3 particles, a critical size of 3.3 μm and 1.1 μm for SiO_2 was determined from Hagan's equation. If the hardness H is replaced by the expression $H = 3\sigma_y$ [Tabo 70], the critical size can be written in the following form:

$$d_{crit,H} = 3.3 \left(\frac{K_{1c}}{\sigma_y} \right)^2 \tag{2.5}$$

The independent approaches from Schönert, Kendall and Hagan show the same dependence of the critical particle size. Only the constants differ resulting from different adopted body geometries.

Several authors have compared their grinding results with the predicted limits. Ghadiri, for instance, investigated the milling behavior of α-lactose

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monohydrate and microcrystalline cellulose in an oscillatory single ball mill. Particle sizes well below the predicted limits of Kendall and Hagan were achieved [Kwan 04]. Also, the grinding results of Stenger and Mende cannot be explained by the dominating theories of Schönert, Kendall and Hagan. The main reason for this discrepancy might be the different loading cases in the investigations. In the experiments of Schönert and Kendall the bodies were compressed under static loading with high load forces, while the media milling experiments of Ghadiri and Stenger were carried out under cyclic loading, where the applied forces are much smaller. However, breakage must be possible below the size of brittle-to-ductile transition by other breakage mechanisms, which cannot be described with the above equations.

The grinding limit in wet media milling

In 1992 Jimbo [Jimb 92] presented results of milled alumina suspensions in a stirred media mill. He distinguished between a minimal particle size that was measured with scattering methods and a much smaller particle size that was calculated from the mass specific surface area of the ground powders (S_m). Jimbo also claimed that sizes determined from S_m reach a certain value for long grinding times which is independent of the mechanical grinding conditions and the feed particle size. Cho et al. also carried out investigations of the grinding limit in stirred media milling for quartz particles dispersed in water [Cho 96]. A grinding limit at a size of about 30 nm was found by means of dynamic light scattering, TEM, and gas adsorption measurements. A physical explanation for the observed limit is not given in the publication of Cho.

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The grinding limit in dry media milling

Dry grinding applications, typically realized in planetary ball mills, are widely used in the field of mechanical alloying or for grain refinement of metals to improve selected properties. In contrast to wet media milling, the grinding limit in dry operated high-energy mills is determined by an equilibrium between size reduction and growth processes. Caused by strong welding phenomena, the particles typically remain polycrystalline during the milling procedure so that it has to be distinguished between a minimal particle and a minimal crystallite (i.e. grain) size. The minimal particle size is determined by an equilibrium between fracture, agglomeration and possible welding processes. Since agglomeration effects cannot be avoided as in the case of wet milling by the addition of grinding aids, much larger particle sizes are obtained in dry grinding experiments. Due to the missing surrounding medium, heat can hardly be dissipated and the grinding media impacts are much more intensive, which often results in welding of the particles. The minimal crystallite size is determined by an equilibrium between grain refinement through a severe plastic deformation and the recovery by thermal processes (splitting and coalescence/recrystallization of grains) [Kara 03].

Eckert and later on Koch investigated such equilibrium conditions for various metal particles [Ecke 92], [Koch 97]. Eckert showed that a steady state grain size is reached when the refinement rate equals the recovery rate. Both rates depend on intrinsic material properties as well as on process conditions like impact intensities [Ecke 95]. Since the recovery rate scales inversely with the melting temperature of the materials, high-melting-point materials yield the smallest grain sizes. If no recovery takes place, the smallest achievable size by milling would be determined by the minimum grain size that can sustain a dislocation pile-up. This minimum grain size is only determined by intrinsic material properties so that the material itself provides a limit for further grain refinement. Nieh et al. estimated this limit as the equilibrium separation distance between two edge dislocations by [Nieh 91]

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$$L = \frac{3Gb}{\pi(1-\nu)H} \tag{2.6}$$

with the shear modulus G, Burgers vector b, Poisson's ratio ν, and hardness H of the material. Applying this relation to ball-milled metal powders shows that the achieved minimum grain sizes are larger than the sizes obtained from Eq. 2.6. The reason is the simultaneous recovery that dominates at small grain sizes and prevents further size reduction.

The theory of an equilibrium between grain refinement and recovery in dry milling applications was confirmed by the group of Boldyrev [Bokh 95] who used smaller initial crystallites than the steady state size as feed material in the grinding experiments. A growth of the hematite crystals from 10 nm to about 50 nm in size was observed after 2 minutes of high energy milling in a planetary ball mill. Additionally, the crystals were almost spherical in shape. Milling of 5 nm γ-alumina also leads to an increase in the crystallite size to 20 nm accompanied by a phase transition to α-alumina, which is for larger grain sizes the thermodynamically most stable modification [Chen 02].

Planetary ball mills can also be used as mechano-reactors for chemical reactions or mechanical alloying, since they provide the necessary high energy densities. In the group of McCormick, mechano-chemical synthesis reaction are carried out in planetary mills. Therefore, the solid precursor mixture is embedded within a salt matix (e.g. LiCl or NaCl). After reaction, which is caused by impact between the grinding media, the generated nanocrystalline product particles can be recovered by removing the salt through a simple washing procedure. The salt matrix as an inert dilute phase surrounding the reactants allows the formation of finest particles by a reduction of the reaction rate. Particle sizes down to 5 nm for various material systems ranging from pure metals to oxide, carbonate, and sulphite matrials are obtained by this method [Dodd 02], [Tsuz 04].

Moreover, media mills are not only suitable for size reduction and synthesis reactions, but also for delamination processes. If a material holds

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a strong anisotropy in its bond forces, a selective size reduction can occur during mechanical stressing. This knowlegde is used to investigate the delamination behavior of graphite particles stressed in a stirred media mill. Especially the question of the smallest possible sheet thickness is in the focus of this work.

2.3. Graphene - properties and production methods

Since the discovery of the 1-dimensional carbon nanotubes (CNTs) by Iijima in 1991 [Iiji 91] and the 2-dimensional graphene sheets by Novoselov and Geim in 2004 [Novo 04], there arised an enormous interest in new carbon nanomaterials having unique electrical, thermal, and mechanical properties. In 2010 Geim and Novoselov were awarded the Noble Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene". An overview about the existing carbon allotropes is given in Fig. 2.1.

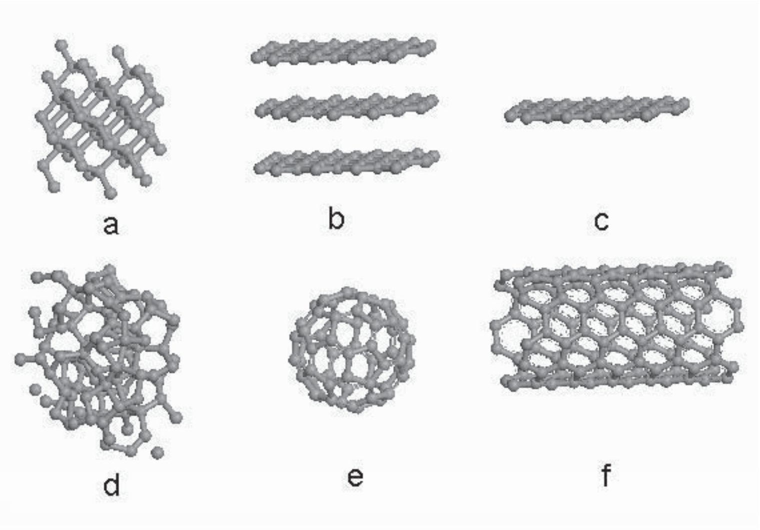

Figure 2.1.: Allotropes of carbon: a) diamond, b) graphite, c) graphene, d) amorphous carbon, e) C_{60} (Buckminsterfullerene or buckyball), f) carbon nanotube [Sun 10]

Beside the 3D modifications diamond, graphite, and amorphous carbon, there exist the 2D allotrope graphene, the 1D carbon nanotubes, and the 0D fullerenes. Graphene is a one-atom-thick planar sheet of sp^2-bonded carbon

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atoms that are arranged in a hexagonal lattice. In contradiction to the former state of the art manifested by Landau and Peierls, that 2D crystals are thermodynamically unstable, free-standing graphene monolayers can be produced nowadays [Stan 06a]. Meyer et al. showed by TEM studies that the suspended graphene sheets are not perfectly flat, but exhibit an intrinsic roughness, which is assumed to stabilize the 2D structure at finite temperatures [Meye 07]. The first graphene monolayer was proven by the group of Novoselov and Geim at the University of Manchester with a simple Scotch tape method [Novo 04]. Single graphene sheets were cleaved from a highly oriented pyrolytic graphite (HOPG) plate with an adhesive tape and pressed onto a silicon wafer with a defined thickness of SiO_2. Due to interference effects with the Si-SiO_2-substrate, even graphene monolayers become visible in an optical microscope [Blak 07]. Common techniques to detect single graphene layers are Raman spectroscopy, scanning probe, and transmission electron microscopy.

The remarkable properties of graphene are summarized in a publication of Ruoff [Park 09]. So far, high values of the Young's modulus (~ 1 TPa, [Lee 08]), fracture strength (130 GPa, [Lee 08]), thermal conductivity ($\sim$5000 $Wm^{-1}K^{-1}$, [Bala 08]), and electron mobility ($>$ 200000 $cm^2V^{-1}s^{-1}$, [Bolo 08]) have been reported, accompanied by an enormous specific surface area of 2630 m^2g^{-1}. Additionally, a single graphene layer shows an optical adsorption of only 2.3 % in the visible [Nair 08] and NIR [Mak 08] range and yield fascinating transport phenomena such as the quantum Hall effect [Zhan 05]. This makes graphene a promising candidate for applications in many technological fields such as sensors, composites, supercapacitors, transparent conductive films, or solar cells [Geim 07], [Stan 06a], [Stol 08], [Wang 07]. Graphene is known to be a zero-gap semiconductor. Recently, it was demonstrated that the band-gap is tuneable by an adsorption of specific molecules or tailoring its geometry to nanoribbons [Balo 10], [Han 07].

In the graphite crystal, graphene layers are stacked parallel with an interatomic distance of 0.335 nm. Whereas the carbon atoms within a graphene sheet are covalently bound, only weak van der Waals forces are acting between the sheets. As a consequence of this structure, a strong anisotropy of the material properties such as thermal and electrical conductivity or

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mechanical strength results. The latter enables the production of graphene layers by cleavage from thicker graphite specimens and is utilized in many fabrication routes. Although there has been intensive research on the preparation of graphene monolayers in the last few years, a large-scale and low-cost production of the new 2D carbon material still remains challenging. The existing production routes can be separated into chemical intercalation methods, growth methods, and mechanical exfoliation methods.

Chemical intercalation and subsequent exfoliation

Most of the described methods to fabricate graphene sheets are based on the intercalation of oxygen or other intervening atoms or molecules between the graphite layers and subsequent thermal or mechanical treatment. Usually, graphite is oxidized to graphite oxide (GO) in the presence of strong acids such as sulfuric or nitric acid. The intercalation compounds enlarge the distances between the graphene layers so that the attractive van der Waals forces are drastically reduced and an exfoliation is facilitated. In a subsequent thermal treatment, the dried GO is heated rapidly (> 2000 °C/min) to 1050 °C. Exfoliation takes place when the decomposition rate of the oxygen groups exceeds the diffusion rate of the evolved gases and the resulting pressure overcomes the van der Waals forces [McAl 07]. Solution-based methods mainly describe the subsequent exfoliation of the intercalated graphite by mechanical forces applied by ultrasound or even simple stirring [Stan 06b]. However, the removal of the intercalation compounds is necessary to regain the excellent properties of the pure carbon material. In particular, the electrical conductivity of GO is strongly reduced compared to the pristine graphite. The reduction of the GO can be realized either thermally or chemically, but it was shown that a complete removal of oxygen is difficult [Schn 06], [Stan 07].

Growth methods

Another approach, which is favored if large graphene areas are requested, is their growth either by chemical vapor deposition (CVD) or epitaxial on SiC surfaces. The latter is based on the higher vapor pressures of Si compared to C, so that silicon sublimates at heating temperatures of about 1300 °C

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in ultrahigh vacuum causing a thin carbon layer to remain on the surface [Berg 04]. In CVD processes, an active catalytic polycrystalline metal (Ni, Pt, Co, Ir, Ru) substrate is heated (to 900 - 1000 °C in the case of Ni) and exposed to a diluted hydrocarbon flow under ambient pressure resulting in a growth of a single- or multilayer graphene film on the metal surface [Rein 09], [Kim 09].

Mechanical exfoliation

The strong anisotropy of the bond forces in the graphite crystal enables the mechanical exfoliation of graphene sheets as shown with the scotch tape method by Novoselov and Geim. As the interlayer distances in pristine graphite are very small, higher net forces are required to overcome the attractive forces compared to the intercalated material. The group of Coleman focuses on the exfoliation of graphite particles by means of ultrasound in an aqueous surfactant solution or certain organic solvents such as n-methyl-pyrrolidone [Hern 08], [Loty 09]. A yield of monolayer graphene of about 1 %, which corresponds to a concentration of 0.01 g/l, could be achieved with their method so far. Englert et al. presented the exfoliation of mono- and multilayer graphene sheets by means of sonication in aqueous solution and their stabilization with a perylene-based detergent [Engl 09].
Thin graphite nano-sheets were obtained by mechanical shearing of graphite suspensions in a mortar grinder [Anti 06] and a planetary ball mill [Jano 02] [Mile 08]. In both described methods, a selective size reduction was observed leading to a flaky shape of the graphite sheets down to a thickness of about 6 nm. Besides a pure delamination, also a significant in-plane-fracture of the sheets was observed.

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