Nanotechnology Advancements and Applications

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ABSTRACT

Size reduction into the nanometer size range offers many advantages. These include increased surface area, improved reactivity, efficient absorption and higher efficacy of active ingredients. This presentation will discuss methods for comminution and dispersion of agglomerates and particles into the nanometer range using dry and wet grinding and dispersing techniques. Comminution and dispersion of solids in slurries and suspensions has been more commonly used due to energy efficiency vs. dry grinding. When a dry powder is the final product, a dry method may be preferable and economical. Both are possible with the newest comminution and dispersion technology available.

Keywords: nanonization, micronization, comminution, dispersion

1 INTRODUCTION

As a leading manufacturer of mills used worldwide in the production of dispersions and dry particles, NETZSCH has mastered the science of particle size reduction. NETZSCH grinding mills can achieve particle sizes of 200 nanometers (nm) and finer.

For wet grinding into the nanometer size range, or for the dispersion of nanometer sized particles, the use of very small grinding media is necessary. For certain types of product, in order to prevent changes in crystal structure, mild dispersion is used.

Jet milling of dry particles with superheated steam can also yield particles in the nanometer size range. By using superheated steam as the grinding gas, a fluidized bed jet mill with this innovative technology can produce dry powders with median particle sizes in the range of 130 nm. This technology represents a quantum leap in particle size reduction by a dry grinding process and improves the jet milling process ten-fold.

2 WHY NANOTECHNOLOGY?

The number of products that can benefit from nanometer size particles is large and is growing each day. Two industries that impact our daily life are food and healthcare.

In the food inductry, crop protection companies are now manufacturing herbicides and other products in the particle size range of 10 - 100 nm. A nanoparticle size herbicide contains trillions of particles of active ingredient per liter. The increased surface area as a result of the product fineness greatly improves product potency.

Active pharmaceutical ingredients used in the healthcare industry, also benefit from nanometer size particles. Many potentially effective drug discoveries are abandoned because they are insoluble. By reducing the particles to nanometer size, their surface area and solubility are dramatically increased.

3 AGITATOR BEAD MILL OPERATION

Agitator bead mills evolved from ball mills, which have been used since the nineteenth century. In these horizontally-rotating machines, stones or steel balls cascaded due to the rotation of the ball mill drum and milled solids in a liquid suspension, usually water (or without liquid in the case of dry ball mills) in a batch operation. These mills used grinding media measured in inches.

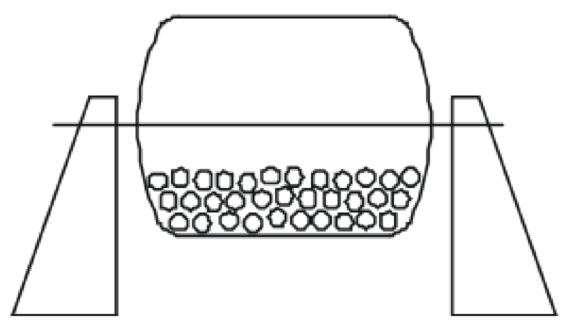

Figure 1: Diagram of horizontal ball mill

Later, in the middle of the twentieth century, attritors, developed by Dr. Andrew Szegvari, began to replace ball mills in many applications. These were vertical stationary drums with a rotating shaft driving the grinding media. Smaller media could be used in attritors, typically 2 mm – 10 mm, enabling attritors to grind finer or reach the desired fineness in a shorter time. Ball mills and attritors are still widely used today, along with the use of newer agitator bead mills.

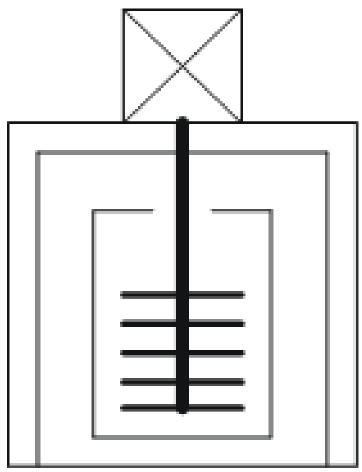

Figure 2: Diagram of vertical attritor

In principle, an agitator bead mill consists of a grinding chamber, an agitator shaft equipped with agitator elements, a pump and a drive motor. The grinding chamber is filled with grinding media up to 95% of the mill volume. Grinding media with diameters between 30 µm and 9 mm are used. The grinding media is made from material such as stainless steel and glass, and also high technology ceramic materials such as yttrium stabilized zirconium oxide and cerium stabilized zirconium oxide.

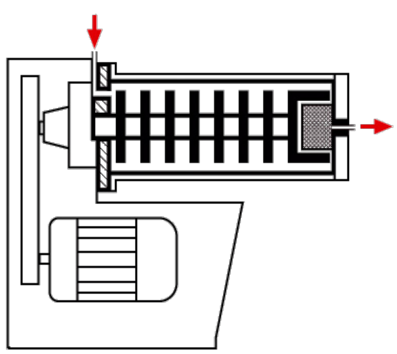

Figure 3: Diagram of an agitator bead mill

Product suspension is pumped through the mill from a feed tank. There are several methods of passage through the mill. The suspension can be passed through the mill once and collected in a product tank (single pass), or passed multiple times through the same mill from tank to tank (pendular), or through a series of mills (cascade). Finally, the suspension can be pumped through the mill multiple times and continuously with short residence time from a single tank until the desired particle size is reached (circulation).

There are advantages and disadvantages to each method. Among the most significant advantages of circulation with a high flow rate are product cooling and residence time distribution. In circulation grinding, the residence time in the mill is quite short during each passage of product. The mill housing and also the rotor are cooled, as is the feed tank. This ensures that the temperature of the product can be accurately controlled and that all particles pass through the high energy area of the mill, statistically leading to a more even residence time. This results in a very steep particle size distribution curve as shown in the graph below.

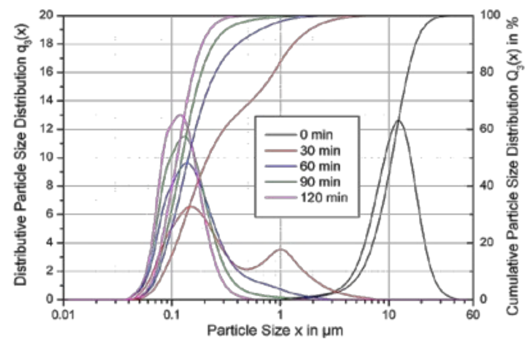

Figure 4: Development of the PSD during circulation grinding

3.1 Mild Dispersion and Real Comminution

In real comminution, the primary particles are ground within a liquid phase by high shearing, pressure, and impact forces. Typically the agitator tip speed is in the range of 13-16 m/sec. Grinding media size and density is selected based on optimal efficiency. The rotor tip speed is maximized in consideration of motor power and product temperature requirements. Particles are de-agglomerated but also crushed and the structure of the particles may be destroyed.

In de-agglomeration or mild dispersion, agglomerates and aggregates are dispersed by shearing, pressure and impact forces. The surface air is also removed and the surface of the particles is wetted. Typical agitator tip speeds are in the range of 4-6 m/sec. The smallest grinding media is selected based on separation techniques, and the lowest tip speed is used that will provide effective bead separation. Naturally in both processes, appropriate additives are used to stabilize the suspension and prevent re-agglomeration.

3.2 Mild Dispersion of Titanium Oxide

A comparison of dispersion techniques was made with titanium dioxide. The objective was to de-agglomerate TiO_2 without degrading the surface as measured by X-ray diffraction. Since the primary particle size of the raw material is already 6 nm, further size reduction was not a consideration. The comparison was made with yttrium stabilized zirconium oxide grinding beads, 0.1 mm diameter

 TechConnect Briefs 2015, TechConnect.org, ISBN 978-1-4987-4730-1

with tip speeds of 4, 6, 10 and 13 m/sec. The measured size of the agglomerated feed material was 0.6 microns.

More important; however, is the advantage the lower tip speed gives in the material properties. From the X-ray diffraction study, TiO_2 after mild dispersion maintained quality much closer to the raw material before the grinding process, while the sample processed at high tip speed was significantly different.

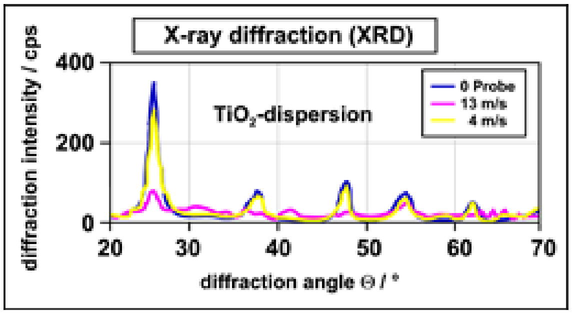

Figure 5: X-ray diffraction results by tip speed

3.3 Real Comminution of Titanium Dioxide

For the production of functional coatings, titanium dioxide with the particle size distribution d_{50} ~ 200 nm and d_{99} ~ 375 nm was to be ground as fine as possible. It was a water based suspension with a solids content of 48.5 wt%, which was stabilized by an appropriate additive.

This product was tested with larger and smaller grinding media to discover which works best. When using the larger grinding media, particle sizes d_{50} ~ 60 nm, d_{90} ~ 92 nm and d_{99} ~ 125 nm were obtained after a grinding time of 6 hours and a specific energy input of 1.83 kWh/kg. When using smaller grinding media significantly better results were obtained, with particle size results of d_{50} ~ 45 nm, d_{90} ~ 76 nm and d_{99} ~ 110 nm after a grinding time of only 2.5 hours and one third of the specific energy input (0.61 kWh/hg).

4 USING A FLUIDIZED BED JET MILL AND SUPERHEATED STEAM

The demand for finer dry powder products in the submicron or nanometer range has led to the development of a new technology that allows real comminution of this scale. Contrary to conventional dry fluidized bed jet mills, this new system uses superheated steam as the grinding gas. Superheated steam as the grinding gas in jet mills has been used for many decades in simple spiral or loop jet mills without an integrated air classifier. Until now it was not possible to produce a material with a well-defined upper particle size limitation. This new technology provides a mill

Figure 6: Cross section of a fluidized bed jet mill

with an integrated air classifier for the separation of the exact particle sizes, and hence the fineness of the product to be milled. "Nanonization" of solids in a dry process with a fluidized bed jet mill, with integral classification, is now possible, with the added benefits of being energy efficientand economical.

4.1 Properties of Steam That Enhance the Jet Milling Process

Three key factors make steam fluidized bed jet milling successful and commercially viable:

1. Steam can be provided to a jet mill at very high pressures compared to air. At higher grinding pressures, higher jet speeds can be attained.
2. As a medium for dynamic classification of particles, steam allows a finer cut-size than air.
3. Higher jet energy, as mentioned above, can also result in significant increases in capacity and improved energy efficiency.

With any grinding process, fine particles have the tendency to re-agglomerate. The finer the particles are, the greater the risk of agglomeration occurring. In a dry grinding process when an air classifier is used to control the final particle size, this tendency has a negative effect on capacity and process efficiency. Large agglomerate (consisting of many fine particles) appears as one large particle to the internal classifier and is therefore rejected as "oversized" to be ground again. A fluidized bed jet mill is essentially a closed system. When the classifier rejects this agglomerate of particles, it remains in the jet mill to be ground finer, resulting in a reduced capacity. This process of grinding and re-agglomeration will continue unless some type of additive is used to modify the surface of the particles so they no longer re-agglomerate.

The positive effects of using a dispersing agent include: an increase in capacity (at the same fineness) of three to four times; higher fineness; improved flowability; higher surface area; and, reduced buildup inside the mill. Dispersing agents are used in small percentages from 0.1-1%.

4.2 Finely-Ground Amorphous Graphite

Grinding graphite with a d_{99} of less than 4 µm by conventional dry milling (and also wet milling) has been problematic. With this technology, it is now possible to obtain particle sizes below D_{99} ~ 1.0 µm.

4.3 Ceramic Materials

A full range of ceramic materials are now being processed. These include aluminum oxide, zirconium oxide, silicon carbide, and calcium carbide, to name a few. As an example, aluminum oxide with conventional dry milling can result in a fineness of about 2.3 µm (d_{99}). It is also now possible to reach d_{50} = 130-140 nm with a d_{99} of .340 to .350 nm.

4.4 A Wide Range of Other Applications

Among the other materials that have been tested and processed are ceramic pigments, iron oxide, silica, various battery materials, titanium dioxide, glass, and activated carbon. Prior to the integration of steam in a fluidized bed jet mill, particle size distributions such as these could only be achieved by wet grinding.

Product examples	**D_{50}**	**D_{99}**
Alumina	0.13	0.35
Amorphous Graphite	0.16	0.58
Barium	0.13	0.34
Iron oxide	0.07	0.37
Glass frit	0.57	1.89
Limestone	0.54	1.87
Silicon carbide	0.24	1.04
Wollastonite	0.30	2.60
Zirconium oxide	0.44	2.59

Table 1: Steam Jet Milling Product Examples

4.5 Steam Jet Milling is Greener

Steam is the oldest utilization of thermal energy known to humankind, and is the driving force of almost all energy production worldwide. In 2012, about 87% of the electrical energy in the U.S. was generated by large power plants (coal, gas and nuclear). Large power plants operate on average with a degree of primary energy efficiency of around 40%. Transformation and line losses cause an additional deficit of about 10%. Therefore, when the electricity arrives at the plant, it has a degree of efficiency (compared to the primary energy) of about 36%. When compressor efficiency is factored in, which is about 45%, the overall energy is only about 16% from primary energy to kinetic (grinding) energy in the mill! By using steam directly, the process becomes two or three times more energy efficient.

5 CONCLUSION AND OUTLOOK

As the trend toward achieving finer products continues, designers of wet milling technology are challenged to use smaller grinding media and processing techniques suited to the application – by means of real comminution or mild dispersion. As the aforementioned examples demonstrate, it is not always a matter of using the highest energy input, largest media, or highest tip speeds. Without a doubt, using more energy than required results in unnecessary wear on the mill and grinding media, increased costs and downtime, and decreased product quality (by the addition of contamination).

The needs of companies developing dry materials in the nanometer size range can be met with the use of steam jet milling technology. Steam jet milling technology can apply to ceramics, alternative energy, optical glass, pigments, and industrial minerals markets. And new markets will be developed based on this new technology.

Further developments in grinding are always possible and are ongoing, but steam jet milling in a mill with an integrated dynamic air classifier is the pinnacle in dry grinding technology. Product engineers should consult with equipment engineers early in the development process. This often involves product trials to learn about the capabilities and limitations of the equipment. NETZSCH conducts hundreds of customer trials each year, and also leases small-scale development equipment to customer laboratories. This relationship allows the mill producer to tailor equipment to the application.

Mill designs will continue to advance to meet the evolving needs of the industry. With over 140 years of experience, combined with engineering and manufacturing know-how, NETZSCH is well able to satisfy those needs, and will continuously raise the bar on what's possible.

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