focus on

Laboratory Products

Ultrafine Grinding with Laboratory Ball Mills

Dr Tanja Hanke, Product Manager, Retsch GmbH

Nanotechnology is one of the most innovative developments of our time which revolutionises industries such as materials science, pharmaceutics, food, pigments or semi-conductor technology. Nanotechnology deals with particles in a range from 1 to 100 nm. These particles possess special properties due to their size, as their surface is greatly enlarged in relation to their volume (so-called 'size-induced functionalities'). Ultrafine particles are, for example, harder and more break-resistant than larger particles. Nanotechnology brings effects which occur in nature to a commercial scale, such as, for example, the lotus effect: nanocoated fabrics or paints are water- and dirt-repellent just like the lotus flower.

Application Examples for the use of Nanoparticles

Industry	Application
Alternative Fuels	Improved cleaning of solar cells
Automobile	Densification of tyre material, improved colour properties of paint
Cosmetics	Protection against UV radiation
Textiles	Protection against water or dirt (lotus effect)
Medicine	Controlled release of drugs, for example in tumour cells
Food	Non-stick coating of food packaging
Sports	Reinforcing materials, for example for tennis rackets

How are Nano Particles Produced?

The 'Bottom-Up' method synthesises particles from atoms or molecules. The 'Top-Down' method involves reducing the size of larger particles to nanoscale, for example with laboratory mills. Due to their significantly enlarged surface in relation to the volume, small particles are drawn to each other by their electrostatic charges. Nano particles are produced by colloidal grinding which involves dispersion of the particles in liquid to neutralise the surface charges. Both water and alcohol can be used as dispersion medium, depending on the sample material. In some cases the neutralisation of surface charges is only possible by adding a buffer such as sodium phosphate or molecules with longer uncharged tails such as diaminopimelic acid (electrostatic or steric stabilisation).

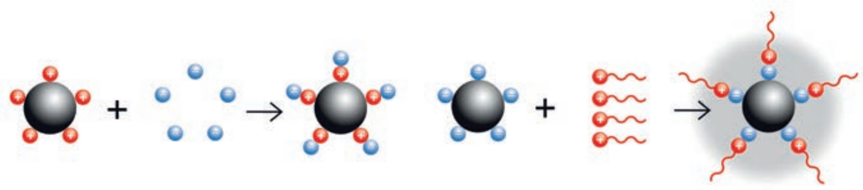

Figure 1. Neutralisation of charged particles by adding a buffer (electrostatic stabilisation, left) or by adding long-chained molecules (steric stabilisation, right)

Factors such as energy input and size reduction principle make ball mills the best choice for the production of nanoparticles. The most important criteria for selecting a mill and appropriate accessories are:

- Material of the grinding tools
- Grinding ball size
- Grinding balls/sample/dispersant ratio
- Grinding time
- Energy input

Top-Down Method: Production of Nanoparticles with Ball Mills

Nanoparticles are created with the Top-Down method by colloidal grinding using a suitable dispersant to keep the particles from agglomerating. To reduce small particles with mechanical force to even smaller sizes, a high energy input is required. The choice of suitable grinding tools and the correct grinding jar filling are further aspects to be considered.

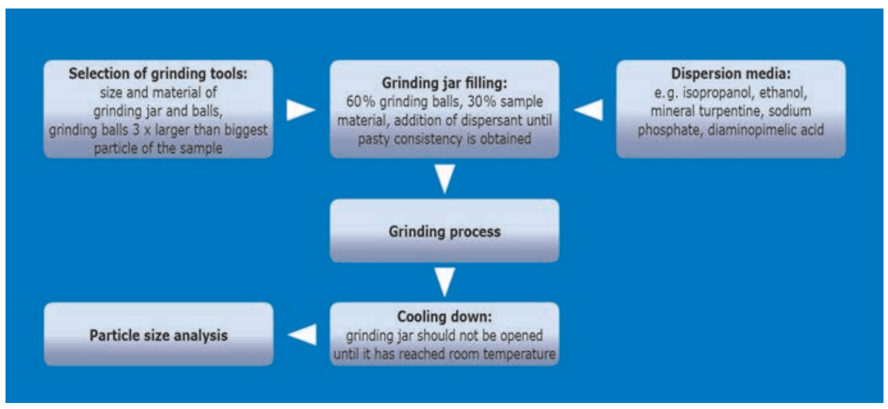

Figure 2. The steps of colloidal grinding

Preliminary Grinding

Depending on the size of the raw material and the desired end fineness it is advisable to prepare the sample first. In dry grinding, grinding balls Ø > 3 mm are usually used. A third of the total volume of the grinding jar is balls, a third the sample and the final third free space to allow movement of the balls. The crushed sample material (approx. < 10 µm) is then used for actual colloid grinding

Colloidal Grinding

With the planetary ball mills and the new high energy ball mill E_{max}, Retsch offers two types of ball mills which provide the required energy input for colloidal grinding down to the nanometre range. Grinding jars and balls made of an abrasion-resistant material such as zirconium oxide are best suited for this type of application. 60% of the grinding jar volume is filled with grinding balls of 0.5 to 3 mm Ø, providing a large number of frictional points. The actual sample fills about one third of the jar volume. By adding a suitable dispersant (e.g. water, isopropanol, buffer), the consistency of the sample should become pasty thus providing ideal preconditions for colloidal grinding. If a very high final fineness is required, it is recommended to proceed with a second colloidal grinding with 0.1 to 0.5 mm Ø grinding balls, particularly if 2 to 3 mm balls were used in the first process (the balls need to be 3 x bigger than the particle size of the initial material). To separate the sample from the grinding balls, both are put on a sieve (with aperture sizes 20 to 50% smaller than the balls) with a collecting pan. For the subsequent colloidal grinding 60% of the jar is filled with small beads. The suspension from the previous grinding is carefully mixed with the grinding beads until a pasty consistency is obtained.

Consistency

Some materials tend to become too pasty during grinding which prevents the grinding balls from moving around in the suspension, thus making further size reduction almost impossible. Therefore it is recommended to check the consistency of unknown sample materials during the grinding process. If needed, the sample/ball mixture can be further diluted by adding more dispersant. If a sample is known to swell easily, the sample/dispersant ratio should be adapted accordingly. Another option is the addition of surfactant to stabilise the consistency.

Removal of the Grinding Jars

Care must be taken when removing the grinding jar from the planetary ball mill as it can have a temperature of up to 150°C due to the heat generated during the grinding process. Moreover, pressure builds up inside the grinding jar. Therefore, it is recommended to use the optional safety closure device for the 'comfort' grinding jars of the PM series which allows for the safe removal of the jar. After the grinding process the jar should cool down for a while. The Emax jar already has an integrated safety closure. Moreover, the effective cooling system of the mill prevents the jars from heating up too much. Both jars can be equipped with optional aeration covers which allow working under inert atmosphere.

Figure 3. Grinding jar

Suitable Ball Mills for the Production of Nanoparticles

With the planetary ball mills and the high energy ball mill Emax, Retsch possesses suitable mill and the required know-how for the production of nonparticles.

Planetary Ball Mills

In the planetary ball mill, every grinding jar represents a 'planet'. This planet is located on a circular platform, the so-called sun wheel. When the sun wheel turns, every grinding jar rotates around its own axis, but in the opposite direction. Thus, centrifugal and Coriolis forces are activated, leading to a rapid acceleration of the grinding balls (see *Figure 4*). The result is very high pulverisation energy allowing for the production of very fine particles. The enormous acceleration of the grinding balls from one wall of the jar to the other produces a strong impact effect on the sample material and leads to additional grinding effects through friction. For colloidal grinding and most other applications, the ratio between the speed of the sun wheel and the speed of the grinding jar is 1: -2. This means that during one rotation of the sun wheel, the grinding jars rotate twice in the opposite direction.

High Energy Ball Mill Emax

The Emax is an entirely new type of ball mill specifically designed for high energy milling. The impressive speed of 2,000 min^{-1}, so far unrivalled in a ball mill, in combination with the special grinding jar design generates a vast amount of size reduction energy. The unique combination of impact, friction and circulating grinding jar movement results in ultrafine particle sizes in the shortest amount of time. Thanks to the new liquid cooling system, excess thermal energy is quickly discharged preventing the sample from overheating, even after long grinding times.

Conclusion

Nanoparticles, ie. particles with a diameter of less than 100 nm, have been the object of scientific research for many years now. There are various techniques to produce nanoparticles. The 'Top-Down' method involves size reduction of larger particles to the nanometre range. This is best achieved with ball mills which provide the required energy input.

With a wide range of ball mills worldwide, Retsch offers various suitable instruments. Apart from the planetary ball mills such as PM 100, PM 200 and PM 400, the new high energy ball mill Emax is especially suitable for colloidal milling down to the nanometre range thanks to the high speed and innovative water cooling system.

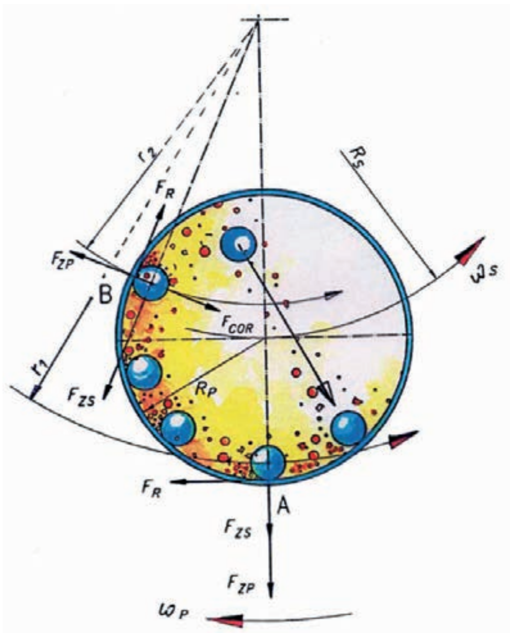

Figure 4. In the planetary ball mill, centrifugal and Coriolis forces permit

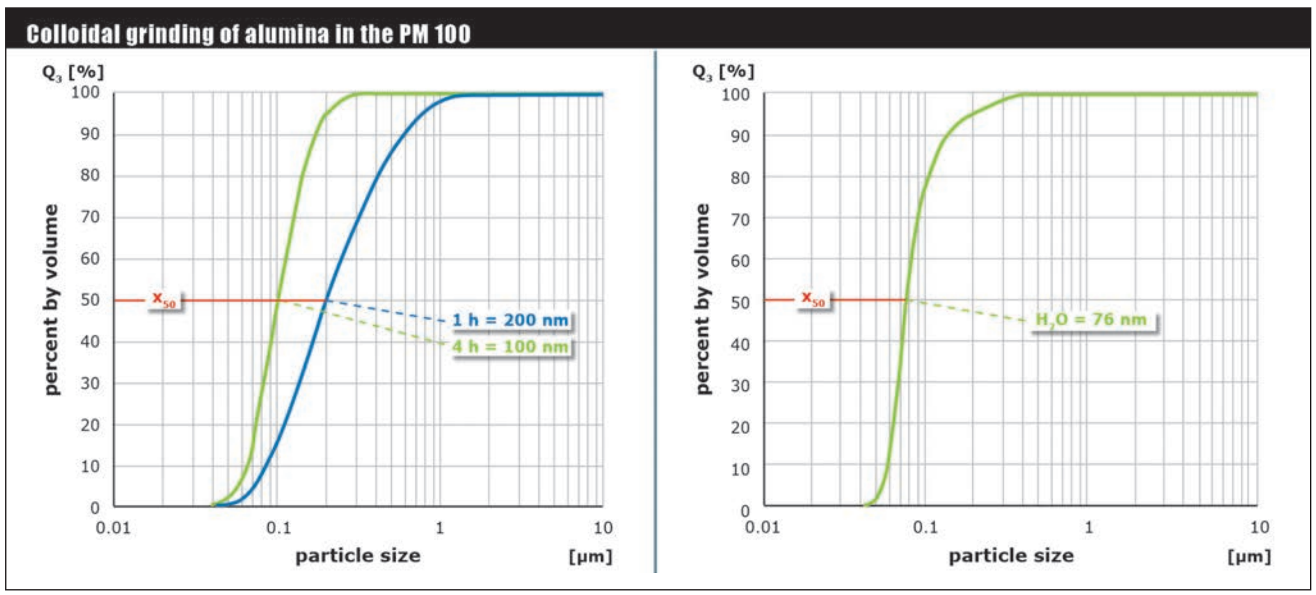

Figure 5. The result of grinding of alumina (Al2O3) at 650 min-1 in the PM 100. After 1 hour of size reduction in water with 1 mm grinding balls, the mean value of the particle size distribution is 200 nm; after 4 hours it is 100 nm. In a further trial, the material was initially milled for 1 hour with 1 mm grinding balls and then for 3 hours with 0.1 mm grinding balls. In this case, an average value of 76 nm was achieved. The milling results show that planetary ball mills can produce particle sizes in the nanometre range.