The difference between real comminution and dispersion in stirred media mills

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Abstract

Due to the possibility to achieve higher product homogeneity, strength or solubility and thus higher product qualities by the use of submicron particles the versatility of fields of applications is continuously increasing. Submicron particles are used for instance for the production of pigments, finest coatings, polishing compounds for wafers, pigmented ink jet inks, pigments for plasma and LCD-displays as well as for ITO-dispersions and many other products in the cosmetic industry, biotechnology and life science. One possibility to produce stable suspensions of particles with particle sizes below 100 nm is the wet comminution of coarse particles or the dispersion of nanostructured particles in stirred media mills. The contribution gives an overview about new developments of the NETZSCH-Feinmahltechnik GmbH.

Introduction

The family-owned enterprise NETZSCH is composed of three highly specialized business units, these are Grinding and Dispersing, Pumps as well as Testing and Analyzing, and is a renowned manufacturer of top-quality products on the world market. Originally the company was found in 1873 as sub-supplier to the ceramic industry. The whole group comprises a staff of about 2000 people worldwide, about 1000 of them are based in Germany.
The business unit Grinding and Dispersing comprises of the consolidated companies NETZSCH-Feinmahltechnik GmbH for liquid and pasty products and NETZSCH-CONDUX Mahltechnik GmbH for dry products. The business unit offers a comprehensive product range for all tasks arising in the procedural steps dispersing, de-aerating, wet and dry grinding as well as classifying.
The company NETZSCH-Feinmahltechnik GmbH defines itself as mechanical engineering company aiming at supplying special machines or complete systems to customers from different fields of applications. The machine equipment on offer enables the development of products on a laboratory scale just as well as the scale up to production size machines. The machines excel by their long lifetime and hereby guarantee a high reliability.
With regard to stirred media mills we are particularly proud of our NETZSCH Horizontal ISA Mill, LME 10.000 with a grinding chamber volume of 10 m^3. These mills are used in ore grinding by the most important mine operators worldwide. Their integration into the ore preparation process resulted in a further increase of the total yield of, for example, platinum, gold or copper (see Fig. 1).

Fig. 1: View of the grinding chamber of the LME 10.000 with Udo Enderle, Head of Engineering and Dr. Giacomo Canepa, Managing Director of the NETZSCH business unit Grinding and Dispersing (from left to right)

The smallest mills alike enjoy an always increasing popularity among the customers of NETZSCH-Feinmahltechnik GmbH. Depending on the material design, the machines called *MicroFer*, *MicroPur* or *MicroCer* have a grinding chamber volume of as little as 80 ml (see Fig. 2).
The product spectrum developed with these laboratory mills and later produced on them is very wide. The buzzword "nano" is not really something new for NETZSCH because we have already advised our customers regarding applications in the sub-micron range for many years.

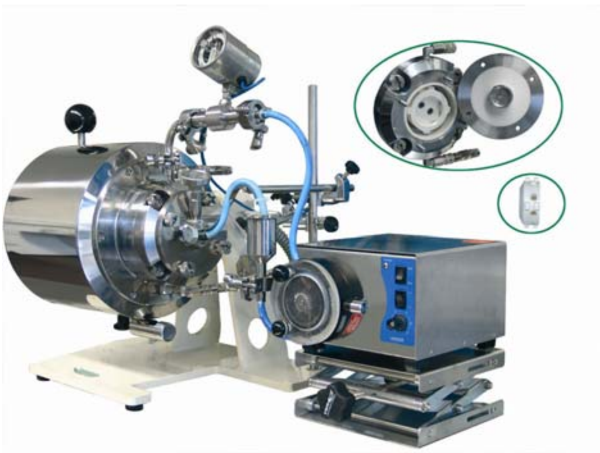

Fig. 2: *MicroCer*

The need of raw materials in the nanometer range steadily increases. The function-oriented advantages of nano technology products speak for a further increase of this trend in the future.
Two different methods are available for nano-sized particle production. The condensation method or bottom-up process where the particles are formed by the aggregation of dissolved molecules in the liquid or gaseous state. The advantages of the bottom-up process are that ultra-pure and almost mono-disperse spherical particle systems are produced. The disadvantage is the normally very low production efficiency, and the fact that these processes offer only a limited scale-up ability.

The second method is the production of ultra-fine particles by the comminution of coarser particles, which is called dispersion method or top-down process. High energy densities are required for comminution processes down to the submicron particle size range which only can be realized by wet comminution in stirred media mills [1, 2]. Stirred media mills are used in many different industries for the comminution of raw materials or the dispersion of products obtained from bottom-up processes. Contrary to bottom-up processes there are non-spherical particles produced by top-down processes. The particles are suspended in a stabilized dispersion, which in many cases can be functional without any further treatment. The main advantage of the top-down process is the nearly unlimited scale-up ability. A disadvantage of this method might be the contamination of the product caused by wear from the mill and grinding media.

Newly Developed Mill *ZETA®* *RS*

In the range of submicron particles it is very important to differentiate between real comminution and desagglomeration or dispersing processes. For real comminution tasks with a breakage or a crack of solid particles and formation of new surface areas, pressure and impact forces are absolutely necessary whereas for desagglomeration and dispersing processes shear forces are sufficient. The main task of desagglomeration processes is to best possible wet the surface of the agglomerated particles. In this case direct pressure and impact forces can lead to mechano-chemical changes and modifications of the morphology of the particles [3].
The reason is the change of the material behavior depending on the particle size. During compression larger particles deform first elastically. When the rupture stress is reached the particles break elastically brittle. Contrary to this behavior smaller particles go to a plastically yielding after a small elastic deformation. These particles do not break. They are only squashed to a flake.
Therefore agglomerates consisting of nanosize particles should be stressed best only by shear forces. In this case to prevent direct stress by pressure and impact forces the use of grinding media smaller than 200 µm with very small stirrer tip speeds is absolutely necessary.
For this task the NETZSCH-Feinmahltechnik GmbH developed a new generation of mills called *ZETA®* *RS*. (see Fig. 3).

Fig. 3: *ZETA®* *RS* – easy handling by swiveling grinding chamber

Thanks to the further developed grinding media separating system with rotating screen, grinding media of a size of 50 µm can be used in the *ZETA®* *RS.* In addition, this new mill is easy to handle because the grinding chamber can be swiveled for filling, operation and emptying similar to a laboratory mill.

Mild Dispersion

If high stirrer tip speeds are implemented this leads to a strong acceleration of the grinding media and consequently to a high approach speed of the grinding media before each collision of two grinding media. Due to the irregular shape and size of the agglomerates they have a high inertia. This leads to a slippage between the displacement speed of the fluid, the approaching grinding media and the subsequent speed of the agglomerates. Therefore the agglomerates cannot escape from direct stress caused by pressure forces and power of impact. As a consequence the primary particles are partly plastically deformed. The direct pressure forces may partly lead to a kind of forging of individual primary particles to a flake-shaped larger particle (see Fig. 4).
If the stirrer tip speed is reduced, the speed of the approaching grinding media and the displacement flow of the fluid between the approaching grinding media is reduced just as well. It is easier for the agglomerates to follow this flow and to escape from the direct stress. If direct stress by pressure forces is still applied the primary particles will not or will be less plastically deformed because of the reduced energy available, the original morphology is maintained and essentially better dispersion results are achieved at a comparable energy input (see Fig. 5).

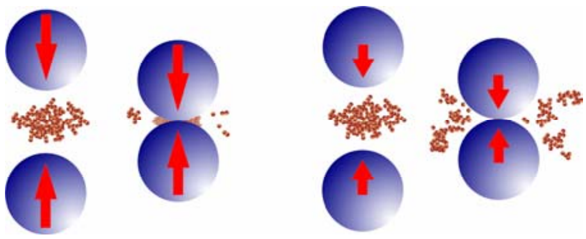

Fig. 4: Illustration of dispersion in stirred media mills high stirrer tip speeds (left), low stirrer tip speeds (right)

For use in photocatalytic coatings nano-structured Titanium dioxide (TiO_2) particles were dispersed in a prototype of the newly developed stirred media mill. We used Yttrium-stabilized Zirconium dioxide grinding media with a diameter of 100 µm at different stirrer tip speeds. First of all, we ran tests at a stirrer tip speed of v_t = 13 m/s. In doing so the requested dispersion result could be obtained (see Fig. 5), however, an essential reduction of the photocatalytic effect was noticed as well as increasingly amorphous properties of the material system. During further fact finding with the x-ray structure analysis it was shown that the crystal structure of the Titanium dioxide was significantly changed by the high energy stress in the mill. Additional peaks in the diffraction pattern are a sign of phase transformations on the surface (see Fig. 6). This result shows that mild dispersing conditions are required for dispersing nano particles without damaging their structure.
During subsequent dispersion tests with a stirrer tip speed of 4 m/s essentially better dispersion results could be obtained without prolonging the necessary dispersion time and at a lower specific energy input. Moreover, by this adaptation of the operation parameters to the task any changes in the chemical structure as well as phase transformations could be avoided. Likewise the photocatalytic properties of the Titanium dioxide particles could be maintained.

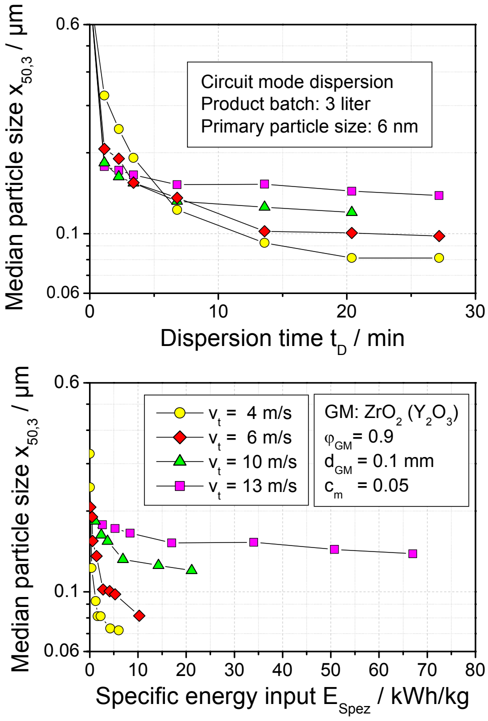

Fig. 5: Dispersion of Titanium dioxide in a high energy mill

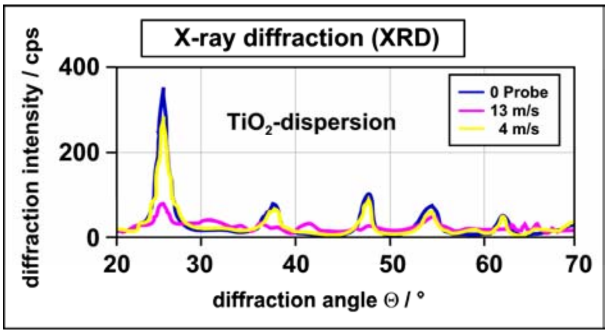

Fig. 6: X-ray structure analysis of dispersed products compared to the raw material

This example clearly shows that a change in the stress mechanism can be obtained by reducing the stirrer tip speed of the agitator. Moreover, it shows the importance of realizing mild dispersion when dispersing nano-structured raw materials. Whereas pressure forces and power of impact are needed for real comminution processes, too high stress energies during dispersion processes lead on the one hand to considerably worse dispersion results against the required dispersing time as well as the required energy input. On the other hand mechano-chemical reactions and changes in the structure are caused, which, in most cases, have a negative effect on the product properties. With regard to dispersion processes it is therefore our target to have as many grinding media / grinding media contacts as possible with a low stress energy.

The following table gives a survey of the different applications for the use of very fine grinding media tested in the newly developed stirred media mill under mild dispersing condition. Excellent dispersion results were obtained without any changes in the product properties.

Product	Application	Grinding media material	Grinding media diameter	Stirrer tip speed	Obtained particle size x_{50}
Pigment	LCD	$ZrO_2(Y_2O_3)$	0.1 mm	6 m/s	40-60 nm
Pigment	InkJet	$ZrO_2(Y_2O_3)$	0.1 mm	6 m/s	13 nm
TiO_2	Photo catalyst	$ZrO_2(Y_2O_3)$	0.1 mm	6 m/s	44 nm
ITO	Electronics	$ZrO_2(Y_2O_3)$	0.1 mm	6 m/s	44 nm
ZrO_2	Electronics	$ZrO_2(Y_2O_3)$	0.05 mm	4 m/s	37 nm
Diamond	Polishing	$ZrO_2(Y_2O_3)$	0.1 mm	10 m/s	19 nm
Nickel	MLCC	Glass	0.1 mm	3 m/s	200 nm
SiO_2	Paper	Glass	0.1 mm	8 m/s	40 nm

Comminution with very small grinding media

Numerous tests showed that the comminution result is strongly influenced by the grinding media size. In order to obtain finer and finer particle sizes the grinding media size used in industrial-scale production is also getting smaller and smaller.
A comparative test for grinding titanium dioxide in oil in an LMZ 10 (grinding chamber volume 10 l) and in a *ZETA®RS* 4 (grinding chamber volume 4 l) showed the result depicted in Fig. 7. The titanium dioxide was partly strongly aggregated as well as in primary particles.
Both mills were run in circulation operation. In the LMZ 10 Yttrium-stabilized zirconium oxide grinding media with a diameter of 0.3 mm were used. In the *ZETA®RS* 4 we used Yttrium-stabilized zirconium oxide grinding media with a diameter of 0.1 mm. Both mills were operated at a stirrer tip speed of 12.5 m/s. The LMZ 10 could be run with a maximum throughput of 520 kg/h. Due to the further developed grinding media separating system a throughput rate of 410 kg/h could be reached on the *ZETA®RS* 4, which is less than half the size of the LMZ 10. Moreover, the results show that a better result could be obtained within less than half the time and an eight times lower energy input.

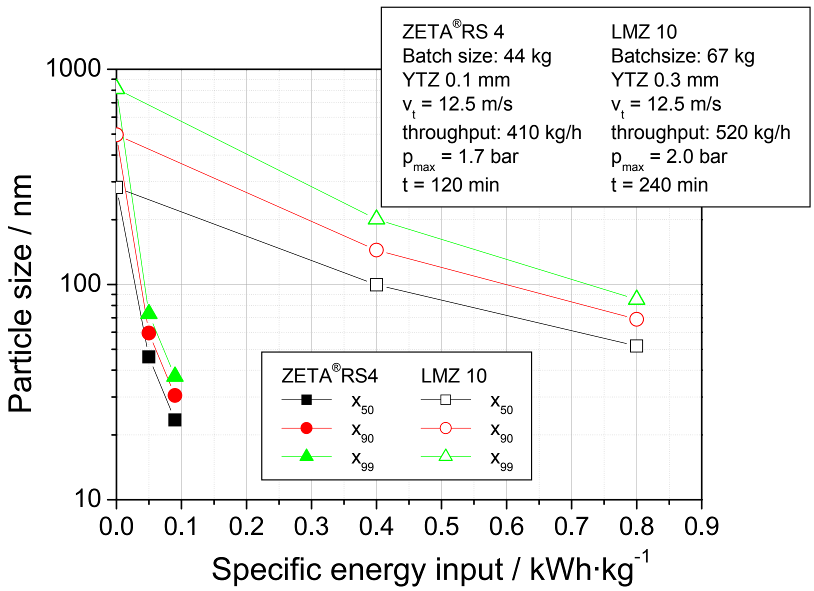

Fig. 7: Comminution of titanium dioxide in oil, comparison between the LMZ 10 and the *ZETA®RS* 4

The clearly better comminution result of the *ZETA®RS* 4 arises from using the Yttrium-stabilized zirconium oxide grinding media with a diameter of 0.1 mm. When using the same grinding media sizes in both mills at comparable stirrer tip speeds they would deliver a comparable result. Therefore the *ZETA®RS* 4 is exclusively designed to be used with grinding media of a size between 0.05 to 0.3 mm.

Conclusion

At their headquarters in Selb the company NETZSCH-Feinmahltechnik GmbH holds a very well equipped laboratory available for comprehensive tests. Basic tests on laboratory mills as well as on smaller production-size mills can be carried out there. A comprehensive range of analysis equipment is available to determine the comminution and dispersion success as well as to measure the change of the product viscosity. Based on more than 50 years of experience NETZSCH-Feinmahltechnik GmbH offers their customers the possibility to optimize the comminution or dispersion process and to subsequently scale-up the results to production-size mills.

The company NETZSCH-Feinmahltechnik GmbH consider themselves as developer and manufacturer of machines and equipment meeting the requirements of the nano age. Extremely small grinding media with a diameter of as little as 50 µm can be used in most modern machines which are easy to handle. Comminution or dispersion problems can be discussed with our specialists for different product groups. Excellent connections to universities and institutes all over the world supported by NETZSCH-Feinmahltechnik GmbH with equipment or services rendered by their laboratory, ensure that NETZSCH-Feinmahltechnik GmbH can rely on the excellent equipment of their partners with regard to the chemical analysis for special tasks. The customers benefit from these contacts and can develop individual solutions in direct cooperation with the universities or institutes without fully disclosing their product idea.

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