New Dimensions of Nano-Particle Size- and Shape -Characterisation

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ABSTRACT

Nowadays, the characterisation of nano-particle size and distribution is mostly done by indirect, quantitative measurement methods like BET, "Fischer-sizing", or laser scattering. The results of these measurements are often combined with images taken by SEM, or TEM for giving additional qualitative information on the true geometric dimensions and shape of the particles. However, the quantitative shape distribution of particles is of importance for process control and quality assurance. Another point of increased interest is the characterisation of multi-modal particle distributions as it is the case for the determination of the degree of agglomeration and the size of stable agglomerates. Nano-Powdershape, a new, fully automatic image analysis combined with SEM, TEM opens a new possibility for the statistically reliable evaluation of nano-particle size distribution and shape. This paper describes the experimental evaluation of nano-particles using this new measurement method. Aim of the study is to investigate the influence of sample preparation, system adjustment (measurement mode, brightness, contrast a.s.o.) and parameter settings for analysing. The significance of the measurement results and the technical limitations will be presented. It will be shown that even with a conventional scanning electron-microscope (without special features) particles with a size down to a few tens of nanometers can be detected and statistically analysed.

1 INTRODUCTION

The characterisation of size and shape distribution of nanoparticles is of common interest. Nanoparticles are typically characterised by gas adsorption methods (BET), by X-ray diffraction patterns, by sedimentation or by laser scattering methods. Although the first three methods deliver no statistical information on the size distribution or shape. Furthermore sedimentation, BET and laser scattering require spherical shaped particles with smooth surfaces to deliver values that correlate well with the real geometrical dimension of the powder. Laser scattering requires a good dispersion of the powders which often can only be achieved in liquids. Another problem rises when the particle size is in the range of or below the wavelength of the scattering light. In that case the calculation of particle grain size becomes more complex and requires information on the optical properties of the powder, which are usually unknown [1-4]. To obtain information on the true geometrical dimensions of nanoparticles scanning or transmission electron microscopy is applied additionally. Image analyses of such photographs allow the determination of grain size distribution and shape of the particles as well. However, conventional image analysis is also very critical due to limited statistics, strong influence of the operator on the results (semi-quantitative) and the need of isolated particles.

A particle analyser called “Powdershape” offers new opportunities for analysing powders by image analysis. The Powdershape system is originally designed for the analysis of micron sized particles combining a high resolution slide scanner (5400 dpi) with a specialised, fully automatic image analysis software system. Due to the large view field, the auto focus and high depth of focus of optical scanning systems thousands of micron sized particles can be measured within one measurement [5]. For shape analysis this system needs a minimum 4 by 4 pixel matrix for a description of the evaluated particles. However in this configuration the minimal particles size is limited to 5 microns for size analysis and 19 microns for shape analysis. Therefore, for the characterisation of submicron or nanopowders scanning has to be done using a scanning - or transmission electron-microscope. At a magnification of 10.000x and an image size of 2048 by 2048 pixels the minimum particle that can be characterised is 18 nm or at 5000x magnification it is still 36 nm. That means that at relatively low magnification levels nano-powders can be characterised with sufficient statistic. Besides the analysis of digitalised images of powders with a high amount of isolated particles, one also can analyse images of agglomerated powders. This is more often the case for nanopowders. Here a newly developed fractal algorithm is used. However, the question rises, how far the achieved results by “Powdershape” are comparable to other established particle analysis methods.
2 EXPERIMENTS AND DISCUSSIONS

2.1 Isolated mode

For comparison with other methods three commercial micron and submicron narrow fractioned Alumina powders were chosen with particles having a round shape and smooth surface (Sumitomo Chemical Co., LTD; Alumina powder grade AA-05, AA-07, AA-5).

Figure 1: SEM image of as received Al$_2$O$_3$ powder (-0.6 +0.4µm Type AA-05).

Figure 2: The left hand side shows a SEM image of Al$_2$O$_3$ powder (-6 + 4µm Type AA-5) recorded in the secondary electron mode. The right hand side shows the image in the backscattered electron mode of the same powder and position on the sample.

To analyse submicron powders as given in figure 1 with image analysis, the powder has to be dispersed homogeneously on the sample holder with a high amount of single isolated particles. The software includes filters that allow the automatic discrimination of single particles.

In case of application of electron microscopy the adjustment of the image acquisition has to be done by the operator for obtaining a contrast and a large difference in grey scale between background and particles. Back scattered electron images are preferred in relation to achieve maximum contrast. Figure 2 shows typical images that can be used for analysis of a submicron powder with Powdershape. For quantitative image analysis the results should be independent of the operator. Therefore, the measurement of a digitalised image has to be done with a stable set of parameters which each operator can determine easily. The existence of such a stable operating window is demonstrated in figure 3.

Figure 3: Mean grain size of AA-5 powder as determined with Powdershape vs. the minimum grey value of the digital image (maximum value in all cases 255). The upper dotted straight line indicates the mean particle size of the same powder determined with sedimentation and the lower dashed line corresponds to the grain size determined by BET.

Figure 3 shows the average grain size (vol.% and nb%) as function of maximum grey value setting measured with POWDERSHAPE on the secondary emission (SE) and backscattered images (BS) given in figure 2. The upper dotted straight line indicates the mean particle size of the same powder determined with X-ray sedimentation (SediGraph 5000ET by Sumitomo) and the lower dashed line corresponds to the grain size determined by BET (Sumitomo and authors). In case of the BS image the grey level setting can be in the range of 40 to 110 and for the SE image in the range of 160 to 210 without having an effect of more than 5% on the final result (minimum setting = 0; maximum setting = 255).

The histogram shown in figure 4 compares the mean diameter of all three Alumina powders measured by X-ray sedimentation, BET and image analysis (POWDERSHAPE). For image analysis the grey level was chosen in the middle of the stable regime as described above. For the submicron
The three measurement techniques delivered comparable values. For the micron size powder AA-5, the mean value determined with BET differs more strongly from the average particle size measured by X-ray sedimentation or by image analysis.

The advantage of the image analysis compared to the other chosen techniques is that besides the mean value one can also get detailed statistical information, even on powder shape as demonstrated in Figure 5 showing a typical printout given by Powdershape.

For the Alumina powder AA-05 the image analysis determines a value of 1.6 for the formfactor “Ellipticity” (ratio between major axis and minor axis of an ellipse with same geometrical momentum of inertia). This indicates that the projected form of investigated particles corresponds more to an ellipse than to a circle, which is also confirmed by the visual comparison with the electron-microscopic image as shown in Figure 1.

2.2 Fractal mode

Nanoparticles are often agglomerated; therefore it is nearly impossible to prepare a sample with high amounts of isolated particles for adequate image analysis. A typical TEM picture of agglomerated nanoparticles is shown in Figure 6. Fractal analysis of the complex shaped agglomerates can be the solution to determine the particle size distribution. Fractal analysis has also been proposed earlier for the quantitative characterisation of complex shaped single particles, e.g. for carbon black [6].

Figure 4: The average grain size for the several Sumitomo (Al2O3) powders as determined by sedimentation (SediGraph 5000ET), BET analysis (Micromeritics, Gemini and Tristar) and Powdershape.

Figure 5: Results obtained from a Powdershape measurement of Al2O3 Type AA-05 powder. The results contain information concerning ellipticity, number and volume mean diameter, mode and median of the particle size distribution and a histogram showing the size distribution in volume percent.

Figure 6: A TEM picture of flame made TiO2 nanoparticles. The black bar on the bottom left is 200 nm. The BET equivalent diameter amounts 48 nm (SSA: 32 m2/g)

However, using SEM or TEM pictures of non-dispersed nanopowders statistically reliable information concerning the particle size and its distribution can be calculated as well by using fractal algorithms. The basic idea of this new approach is the assumption that the borderline of an object contains the information on the size of the elements the whole object is built of. With increasing optical resolution, the borderline will increase more and more until the minimum structure is reached. This type of problem is well known as the “coastline” problem [7]. Additionally to the length of the borderline one can also measure the shape of the
observed object. With changing optical resolution (pixel size) of a digitised image by a fractal algorithm the information on shape will be a function of particle and pixel size. If the pixel size corresponds to the size of observed objects the formfactor (here ellipticity) goes through a minimum (a square and a circle has an ellipticity of 1, all other shapes have values larger than 1). Plotting dEllipticity/dPixelsize against the absolute pixelsize itself shows values below 0 if structures in the image are equal to the corresponding pixelsize. Each local negative minimum of such plot relates to a mean of corresponding structures, for example particles and agglomerates. The absolute value of the different minima correlates likely to the relative quantity of each identified class. The TEM-image of nanoparticles given in figure 6 is analysed according to the description above. Figure 7 shows the resulting graph. According the local minima in figure 7 the average particle size is between 40 to 60 nm. This value is in good agreement with BET analysis of the same powder, giving a equivalent mean particle diameter of 48 nm.

3 CONCLUSIONS

Quantitative image analysis for determination of particle size and shape distribution can be applied on electron microscopic images of nanopowders. However the application of conventional image analysis algorithms is limited to the analysis of images of well dispersed powders. Fractal analysis seems to be a powerful tool to evaluate digitised images of agglomerates of nanopowders. For final conclusions, much more work needs to be done. However, the promising first results in the prospective of this new approach justify the emphasis of the paper presented.

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