

**TP1: Spray Drying, Milling and Granulometry**

(Responsible: Azade Yazdan, MXD334 – azade.yazdanyar@epfl.ch)

**1 Introduction**

Most modern ceramics are made from powders, consolidated and densified by heat treatment. The granulometric characteristics of the raw materials directly influence the preparation process and properties of the final product. Milling and classification are two methods commonly used in mineral processing of powders to modify the granulometry to meet the requirements of the manufacture of traditional ceramics, such as tableware and china. In the case of ceramic powders synthesis, the particle size distribution (PSD) obtained after the reaction rarely corresponds to requirements and often powders undergo a milling or classification process to modify the PSD. These two methods can thus be used to achieve the required size distribution<sup>1</sup>.

When the powder has the required size distribution, (from 0.2 to 2  $\mu\text{m}$  for example), a shaping method must then be chosen. For simple pieces, the most common method is cold uniaxial pressing. It is well adapted for pieces which have simple shape with sizes ranging from millimeter to centimeter. For dry pressing, the mould must be filled in a reproducible and homogeneous way in order to obtain powder compacts or "green bodies" which are homogeneous before the final firing or sintering. This requires a powder with good flowability. The latter is provided by using spherical granules prepared by spray drying and whose size varies between 25 and 250  $\mu\text{m}$ . Ceramics of larger sizes and more complex shapes, like a porcelain sink, are manufactured using wet shaping methods. These methods require the use of pastes or suspensions which will be studied in TP2. During this practical class, the milling of dry powder will be made and the size distribution of particles before and after milling will be compared. Then, the granules will be prepared by atomizing a suspension. The size distribution and flowability of the granules thus obtained will be characterized for a dry pressing to be carried out in TP2. The spray dried granules will then be sieved to provide narrow granule size distributions and the quality of the sieve characterized.

**2 Milling of ceramic powders**

Before being used, raw materials, natural minerals and synthetic ceramic powders often require milling to obtain a distribution of particle sizes desired<sup>2</sup>. It can be done by dry milling for dry minerals or wet methods if the powder is to be used in the form of a slurry. In the laboratory, the milling is mostly done in small batches in a rotary ball mill. On an industrial scale, automated continuous milling equipment is more often used, which can be coupled with classification equipment enabling the recycling of coarse materials. Figure 1 shows a diagram of a milling cycle with a recycling step, classification and

separation of the carrier fluid. The classification is performed using screens, centrifuges, cyclones or air classifiers<sup>2</sup>.

During this lab, the principles of milling and classification will be defined and discussed. An alumina powder will be ground using a typical example of the many different types of equipment available: a rotary ball mill. This method is very simple but still widespread, especially in the world of traditional ceramics such as porcelain. Currently, the breaking and fragmentation of particles is used in most industrial processes. However, despite its technological importance, the milling is still poorly understood and modeled. Moreover, this type of operation has very low energy efficiency (from 1 to 7%) and requires a consumption of about 6% of global electricity (10% in the U.S.) <sup>2</sup>. Improved prediction, modeling and milling efficiency is therefore of great importance at both energy and economic levels. Substantial progress has been made recently for fine milling (especially through attrition), particularly in process development and milling machines and materials<sup>3</sup>. The use of population balance modeling of particles in milling by Randolph and Larson<sup>3</sup> have shown that this theory is well suited to modeling milling. This model has proven useful for representing data and predictions of operating mechanisms<sup>3</sup>.

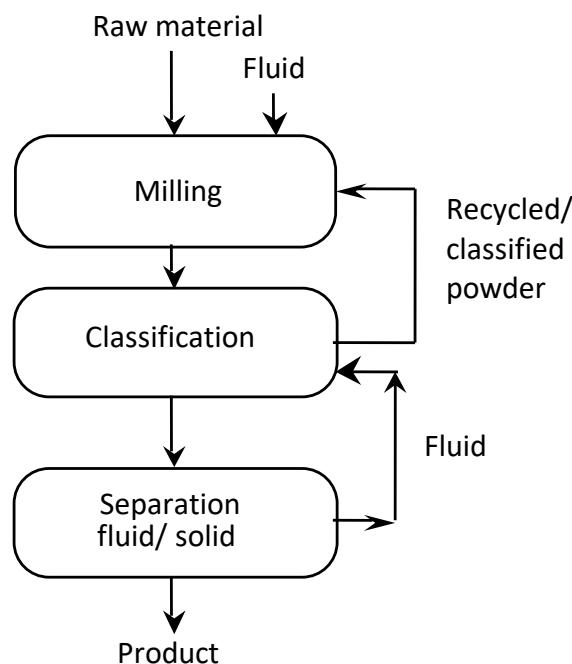


Figure 1. Schematic representation of an industrial milling process.

Reducing the particle size can be done in different ways. In ceramics, various types of equipment are used to reduce the particle size depending on the type of material, the size distribution of the initial particles and final distribution desired<sup>2</sup>. In the field of ceramics, there are three categories of size reduction methods depending on the size interval to which we are interested: crushing, milling and fine milling or de-agglomeration. Crushing is used to break large pieces of minerals (m) into smaller

pieces whose size is adapted to milling (from cm to mm). The milling is applied to input particle size ranges from mm to several hundred microns and reduces the size to values between 1 and 50  $\mu\text{m}$  (ball mill). Finally, fine milling reduces particles to submicron sizes, typically between 0.1 and 1 micron in diameter (vibratory mills, jet mills and attrition mills). A major drawback of ceramic powders milling is the contamination of ground powders due to wear of milling media (beads, pots, stirrers). The material used in the manufacture of milling media is selected according to the powders to be ground, but also of its mechanical properties (hardness and tenacity) and will depend on the effect of contamination on the sample to be ground.

## 2.1 Practical points

Milling of a coarse alumina; the key factors to be examined are: choice of the jar, beads, powder load and rotation speed.

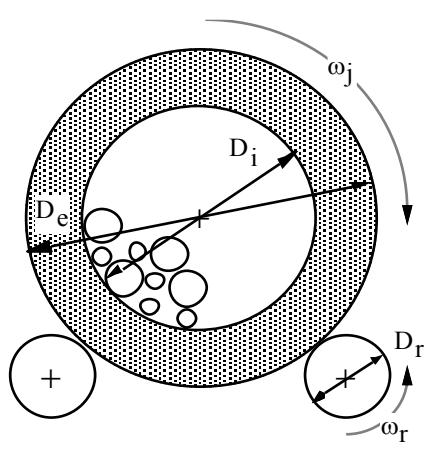
### 2.1.1 Principles of operation

This section will present the rules for good practice in the rotary ball milling of ceramic powders using beads. The proposed rules below are a guide to maximize the efficiency of the ball milling process, that is to say, to obtain the desired particle fineness in a short time (hence minimal energy consumed), with minimum wear of the jar and milling beads (thus minimal contamination of the ground powder) 4. Rotary ball milling loads a jar with the sample to be ground and the beads andis set to rotate around its axis at a certain speed. The rotation of the jar is usually done with a roller machine (Figure 2). The sample may be ground in dry form or dispersed in a suitable solvent (e.g. in water or in alcohol). The dispersion may also contain certain additives (such as a dispersant or anti-foaming agent).

### 2.1.2 Rotation speed

For the inside jar diameter  $D_i$ , there is a critical rotation speed above which the contents of the container remain held on the wall under the effect of the centrifugal acceleration. This critical speed is given by equation [1].

$$\omega_c = \frac{42.3}{\sqrt{D_i}} \quad \begin{aligned} &\text{where } \omega_c \text{ is the critical rotation speed (rpm)} \\ &D_i \text{ is the inner diameter of the milling jar (m)} \end{aligned} \quad [1]$$



## Process parameters

- The volume of the jar
- The inner and outer diameters of the jar
- The total volume of milling beads
- The diameter(s) of the milling beads
- The volume of material to be milled
- The speed of rotation of the jar
- The duration of milling

- $D_r$ : diameter of the roller (m)
- $\omega_r$ : rotational speed of the roller (rpm)
- $D_o$ : outer diameter of the milling jar (m)
- $D_i$ : inner diameter of the jar (m)
- $\omega_j$ : rotational speed of the jar (rpm)

Figure 2. Operating principles of the rotary ball mill.

To optimize the milling, it is recommended to use a rotation speed of about 60-65% of the critical speed. This velocity is called the nominal rotational speed,  $\omega_n$  ( $\omega_n = 0.60\omega_c$ ), given in equation [2].

$$\omega_n = \frac{25.4}{\sqrt{D_i}} \quad [2]$$

If the dimensions of the jar and the rollers are known, the rotational speed of the drive roller,  $\omega_r$ , can be determined using the equation [3].

$$\omega_r = \frac{25.4 D_e}{D_r \cdot \sqrt{D_i}} \quad [3]$$

The diameters are in meters and the speed of rotation in turns per minute. In the case of a jar with a relatively thin wall ( $D_e \approx D_i$ ), equation [3] is reduced to:

$$\omega_r = \frac{25.4 \sqrt{D_e}}{D_r} \quad [4]$$

### 2.1.3 Selection of milling beads

To minimize contamination, we must choose a jar and beads made of a material with high tenacity and if possible harder than the sample to be milled. Alumina and stabilized zirconia (much more expensive) are commonly used in the manufacture of jar and beads. The average diameter of milling beads must be adapted to the size of the particles to be ground. The finer the particles are, the smaller the diameter of the beads needs to be. For a common ceramic powder, ball diameter chosen will be about a centimeter. The milling efficiency is maximized by using a mixture of beads of three different diameters (e.g. 20,10 and 5mm). The ratio of the diameters of the beads is 1:2:4. The total volume of

beads, including pores, will be approximately 50-60% of the volume inside the jar. The beads of different sizes are distributed in the following proportions, expressed in weight percentage: 25% small, 50% medium and 25% large.

#### **2.1.4 Volume of material to be ground**

To reduce wear on the bearings, the load must completely cover the milling ball charge (i.e. the powder to be milled). In general, it will represent a volume corresponding to approximately 25% of the volume of the jar. If the load to be ground is a dry powder, the beads volume can be adjusted after a few minutes of milling or vibration. Milling reduces the particle size and the volume of pores between particles. It is necessary to periodically check if the volume of powder is sufficient to cover all the beads. If this is not the case, it is necessary to remove the excess beads to minimize contamination of the powder. After calculating the parameters of milling, the alumina powder to be ground, the jar and beads will be weighed. Then milling is carried out for 2 hours. At the end of milling, the powder will be recovered and its size characterized using the laser diffraction particle size analyzer. Finally, the jar and beads will be cleaned and weighed to determine the weight loss to monitor the wear rate during milling.

### **2.2 To do list**

- Materials needed
  - Alumina powder
  - Milling jar, milling beads, roller machine
  - Results of size distributions (before and after milling)
  - Mortar mill, balance accurate to 0.01g, spatulas, shovels
  - Surfactant solutions ready (1of demineralized water wash bottle and Isopropyl alcohol)
- Procedure
  - Presentation of milling results
  - Discussion of the effects of milling on the size distribution
  - Is it good for the production of alumina ceramics of high quality with very good mechanical properties?
  - How can we improve the quality of the milling product?
  - Were the wear of the pot and milling beads acceptable?
- Report (Results)
  - Distributions of size before and after milling
- Report (Discussion of results)
  - Choice of mill
  - Choice of parameters and material for ball milling
  - Effect of milling on the size and size distribution - possible improvements

### 3 Classification

The classification is the separation of particles into two or more coarse and fine powder fractions. Classification should not be confused with the process of solid-liquid separation, where sieves or filters are used to recover particles from a suspension. Classification is usually done by size but can also depend on other particle properties such as their density, shape, electrical, magnetic or surface properties. Usually, the classification of particles is done in a carrier fluid: a liquid or a gas. Most classification equipment by size, operate in size ranges from 1000 to 0.1 microns; taking advantage of one or more of the following forces: gravitation, drag forces, centrifugal forces or collisions. The most widely used techniques are sieving and air classification<sup>1, 2</sup>.

The classification technique used in this practical work is sieving<sup>2</sup>. It allows the separation of particles down to around 30 microns for dry powders and down to 5 microns in the wet state (e.g. classification in air vs. classification in suspension). The particle separation is done by size, using grids, perforated plates or metallic wire meshes. Different wire mesh fabrics are available. The plain fabric gives often a better sieving performance and is easier to clean than the crossed wire meshes. In the ceramics industry sieving is generally carried out in water such that the benefits of plain fabrics have little interest and crossed wire meshes are preferred because they last longer and are more economic.

Sieving is a simple technique, but improper user protocols lead to errors that are detrimental to the efficiency and quality of the sieving result. For instance, clogging or blocking of the mesh by the grains reduces the efficiency (e.g. increases required sieving time) and deformation of the wire meshes — distorting the dimensions of openings, especially for fine meshes — reduces the selectivity of a wire mesh. Therefore, the sieve quality (and usage) have to be characterized by parameters such as (1) the selectivity, (2) recovery, (3) the efficiency/yield and (4) the sharpness index<sup>1,3</sup>. These parameters can depend on the powder, the sieve state and the used protocol. For example, clogging of the wire mesh increases the required time of sieving to achieve the theoretical selectivity of the used wire mesh.

In this practical work, sieving will be used to classify an atomized ceramic powder and to calculate the characteristic parameters of the sieve and the sieving protocol.

#### 3.1 Practical points

Sieving will be used to classify an atomized (granulated) ceramic powder. A spray dried powder with a size distribution from about 35 to 100  $\mu\text{m}$  will be classified into two fractions by sieving. The size distribution of the two fractions ( $< 50$  and  $> 50 \mu\text{m}$ ) will be measured using the laser diffraction method and with the obtained information a selectivity curve will be drawn. The sharpness index and the recovery will be calculated.

### 3.1.1 The sieving parameters

The selectivity (by size) is the best parameter to determine the performance of a classifier under defined operating conditions. It can be evaluated at given intervals on a powder sample (mass) or continuously in a production line (flow). The selectivity,  $S_c$  (function of diameter  $d$ ) is defined as the ratio of the amount of particles of size  $d$  that are found in the large particle fraction divided by amount of particles of size  $d$  in the initial particle flow<sup>1,3</sup>.

$$S_c(d) = \frac{W_c M_c^d(d)}{W_f M_f^d(d) + W_c M_c^d(d)} \quad [5]$$

where:

$W_c$  is the total mass (or mass flow) of the large particle fraction;

$W_f$  is the total mass (or mass flow) of the fine particle fraction;

$M_c^d$  is the cumulative mass percentage of particles having a diameter smaller than  $d$  in the large particle fraction (or particle flow);

$M_f^d$  is the cumulative mass percentage of particles having a diameter larger than  $d$  in the small particle fraction (or particle flow).

Although the selectivity gives a complete analysis of the performance of a classifier, it is slow to obtain and other parameters may give a fast and reasonable performance index for a specific type of input material. For a given application, we can obtain a practical measure of classifier performance by computing the recovery (2), the efficiency/yield (3) and the sharpness index (4).

The recovery ( $R$ ) is expressed in the following way when the fine particles are the sieving product:

$$R_{d,f} = \frac{W_f M_f^d}{W_f M_f^d + W_c M_c^d} \quad [6-a]$$

and when the coarse powder fraction is the desired product:

$$R_{d,f} = \frac{W_c M_c^d}{W_f M_f^d + W_c M_c^d} \quad [6-b]$$

The difference between the recovery of fine particles and large particles, may be defined as the efficiency of the classifier,  $E = R_{d,f} - R_{d,c}$ . A perfect classifier would be able to send all particles larger than a size limit in the current of large particles, and any smaller particles in the current of fine particles. This assumes that the size is the only characteristic that influences particle trajectory. Other features,

such as density and shape may also affect the forces acting on the particles, which influence the effectiveness of classification. On the other hand, the yield is a measure of the product obtained, regardless of its quality, and is calculated in terms of a fraction of the input current when the stream of the fine particles is the product:

$$Y_f = \frac{W_f}{W_f + W_c} \quad [7-a]$$

and when the stream of coarse particles is the desired product:

$$Y_c = \frac{W_c}{W_f + W_c} \quad [7-b]$$

A measure of the slope of the probability function to the diameter  $Sd_{50}$  is the sharpness index, that is to say, the ratio of the particle size with a 25% probability to go into the stream of large particles and the particles with a probability of 75% to go into the same outlet.

$$s = \frac{Sd_{25}}{Sd_{75}} \quad [8]$$

### 3.2 To do list

- Materials needed
  - Sprayed dried zirconia powder (Tosoh TZ-3YB)
  - Beakers
  - Sieve of 50 microns
  - Precision balance (0.01g)
- Procedure
  - Classify 10 g of atomized powder with a size distribution of about 35 to 100 microns in two fractions by sieving.
  - The size distributions of two sieve fractions < 50 and > 50 microns will be measured (Malvern Mastersizer, laser diffraction).
- Report (Results)
  - Report results and indicate the precision
  - Sieve recovery
  - Results of size distributions
  - Draw a selectivity curve (for 10 values of  $d$ ) and calculate the sharpness index, recovery and yield to 50 microns (coarse fraction)
- Report (Discussion of results)
  - Choice of method

- Selectivity curve and classification parameters
- Why is the selectivity not perfect? Discuss the advantages and limitations of a sieve as a classifier
- Discuss the limitations and benefits of a screen as a classifier
- The particle size distribution of the zirconia powder before sieving can be found in the appendix. Compare it to the results you have obtained for this powder, after sieving.

## 4 Spray Drying

Spray drying transforms a suspension into powder by evaporation of a dispersive liquid in a warm and dry environment <sup>5</sup>. To do this, the suspension is mixed with a stream of high velocity gas through an orifice, and then the mixture is dispersed into a large number of droplets. These droplets are contacted with a hot gas (air) and quickly take a spherical shape because of surface tension. The droplet size varies between 20 and 500µm depending on the device used. Their large surface area allows rapid evaporation of the liquid phase in contact with hot gas to give granules. The characteristics of these granules may be influenced by spray drying conditions such as temperature, gas flow, or the flow rate of suspension. Knowing these parameters, the droplet size can be calculated <sup>6</sup>.

The spray drying method preserves the homogeneity of a powder mixture in the granule, as in the case of porcelain (mixture of quartz, feldspar and clay). Spray drying is also the primary method for adding processing additives such as a binder (e.g. polyvinyl alcohol, PVA), plasticizers (e.g. polyethylene glycol, PEG) and lubricants (e.g. oleic acid) to the ceramic powders for dry pressing. The addition of binders is very important for increasing the mechanical strength during handling and machining of green bodies. Plasticizers facilitate granule deformation during dry pressing, the granules are somewhat brittle with the binder alone. The lubricant plays a role during deformation and rearrangement in the compaction of granules but also reduces friction with the mould walls.

Moreover, the granules prepared by spray drying present better flowability than untreated powder. This is an important characteristic for the automation of the dry pressing process, as often encountered in industry. However, the flowability of a powder is often difficult to define and measure because of its sensitivity to several factors such as size, the nature of the particles (ceramic or metallic), shape of the apparatus used, and moisture of the powder <sup>7</sup>. Several different methods can be used: angle of repose, slip angle, angle of spatula and free flow time<sup>7</sup>. In this practical session, the flowability of the powders prepared by spray drying will be measured and compared to the commercial powders using a modified Hall flowmeter. This method involves pouring the powder through a cone and then measuring the amount of powder required to fill a container of given volume. It is a method that measures the bulk density. Another density which is often used to characterize a powder is the “tap density”, that is to say, the density obtained after the powder is vibrated or packed in a certain way.

The ratio of tap density to apparent density (free flow) is called the Hausner ratio. This ratio is interesting for the characterization of powders for several reasons: it is sensitive to the flowability, the ease of being compacted, friction of the powders, the particle shapes and sizes. It increases as the particle size decreases. Moreover, it is almost independent of humidity when the two densities may vary themselves with significant amounts of moisture.

#### **4.1 Practical points**

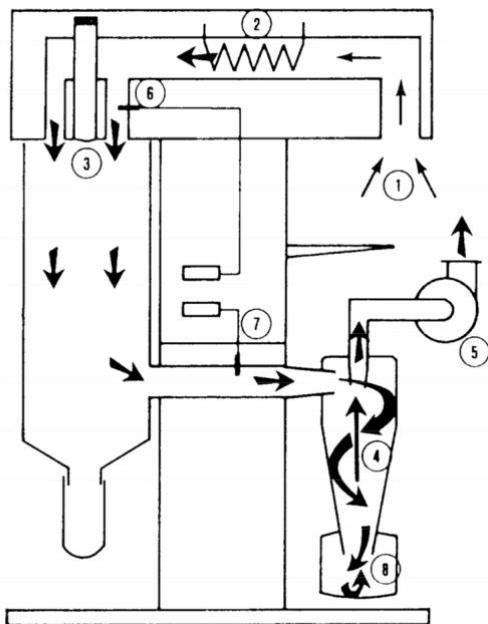
We will spray dry a powder of submicron alumina (AA04) with different types and amounts of additives such as dispersant, binder and plasticizer. First, we will prepare a suspension of our alumina powder designed to be dried by spray drying. After drying, the obtained powder will be compared with a commercial spray dried powder. Measurements made on these two types of powders are size, apparent density and tapped density followed by a calculation of the Hausner ratio related to the flowability of the granules.

##### **4.1.1 Preparation of the suspension for spray drying**

Weight 80 g powder ( $\text{Al}_2\text{O}_3$ ). Add the powder to a solution of  $\text{HNO}_3$  (45 g of 0.005 M) Mix this suspension with a magnetic stirrer for 5 min to wet the powder and then treat it 5 min with the ultrasonic horn (140 W, 20 KHz) to break the agglomerates (always stirring). Then add the polyvinyl alcohol solution (aqueous) (15g of a solution of 1.5% weight) and the solution of polyethylene glycol (PEG, Mw 3350, 10 g of a solution of 2% weight). Then treat the suspension for 5 min with the ultrasonic horn (140 W, 20 KHz). Finally move to ultrasonic bath (protected with parafilm) for degassing (5 minutes).

##### **4.1.2 Getting Started with the Spray dryer (Figure 3)**

The parameters for the flow of cooling water (about 1l/min), the gas flow (500 on the flow meter), the temperature (15 min to give 220 °C at the inlet and 120 °C at the outlet), vacuum (maximum) are explained during the practical course. The heating takes about 15 minutes. During this period, the suspension for spray drying is treated with ultrasonic horn etc. Check that the atomizer is working properly by passing 10 ml of water with the peristaltic pump to the atomizer. The prepared suspension is atomized with a given flow rate and the pump is stopped when the outlet temperature reaches 110 °C (about 5 ml of water is used to purge inlet pipes before the pump is stopped). It takes about 5 minutes for the outlet temperature to warm up to 128-130 °C. When the whole suspension is atomized, the heater and pump are stopped and the spray is allowed to cool to 35 °C (~ 30 min). The sample is collected and weighed. The portion of particles too large which fall directly into a collector without going through the cyclone are also collected.



#### Operating principle

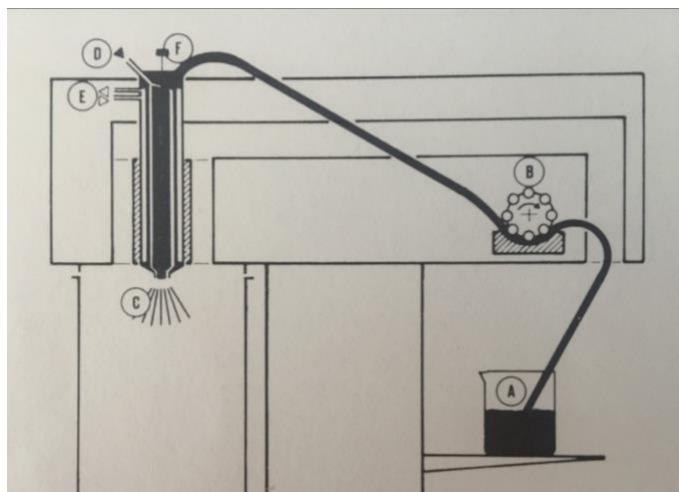
The Mini Spray Dryer BUCHI operates on the principle of nozzle atomization in parallel flow. That is to say that the atomized product and drying air flow in the same direction.<sup>2</sup>

#### Diagram of the flow of air

1. Suction port
2. Heating
3. Entry of stabilized flow into drying chamber
4. Cyclone. The product is here separated from the air flow
5. Aspiration device
6. Temperature measurement of the inlet air. This temperature can be adjusted as needed.
7. Temperature measurement of the air at the outlet. The optimal choice of the temperature difference between the input and the output is one of the important points of the drying operation. The outlet temperature cannot be arbitrarily adjusted, it results from the combination between the inlet temperature, the suction and the pump flow controls.
8. Product collection container.

#### 4.1.3 Tap density and flowability measurements

Tap density measurements are made with the Hall flowmeter with an extension (the same container is used for the flowability with the Hall flowmeter). The flowability is assumed to be inversely proportional to the apparent volume. The powder sample (about 40 g) is poured through the cone to fill the container and “tapped” to pack the powder by dropping the container from a height of 15 mm for 20 times. The extension is removed and excess powder that goes beyond the edges of the container is removed with a straight piece without producing any vibration to the surface. The remaining powder in the container is weighed and the tap density is calculated (the volume of the container is 25 cm<sup>3</sup>). The test is done twice with the commercial powder and twice with a spray dried powder from a previous lab session. The two powders are recovered and stored for later use.



- A: Suspension
- B: Feed pump
- C: product channel
- D: Input for compressed air
- E: Input for cooling water
- F: The nozzle

Figure 3. Schematic diagrams of the spray dryer.

#### 4.2 To do list

- Materials needed
  - Powders for flowability: non-atomized alumina and atomized commercial alumina
  - Plastic containers (250 ml)
  - Acid polyvinyl alcohol (PVA), polyethylene glycol (PEG),  $\text{HNO}_3$  (solutions)
  - Büchi Atomizer "Lab Spray Dryer"
  - 50 ml glass beakers (2x), 100 ml (2x), 250 ml (2x)
  - An ultrasonic probe
  - Magnetic stirrer and bar
  - Modified Hall Flowmeter
  - Powder Scoops, 250 ml graduated cylinder
  - Spatulas, precision balance 0.01 g
- Report (Results)
  - Yield on Spray drying, and vibrated apparent densities, Hausner ratio
  - Calculate the% wt of PEG and PVA in the granules compared to the dry powder
- Report (Discussion of results)
  - Size distribution of primary particles and granules, shape of granules
  - Comparison of the Hausner ratio and flowability for the two types of powders (commercial and TP)

### 5 Granulometry

The particle size analysis method differs depending on the size of particles to be studied. For ceramic powders at LTP, four methods are generally used: a) laser diffraction for powders with a size between 100 nm and 1 mm, b) centrifugal sedimentation for powders with a size between 10 nm and 300

microns, c) photon correlation spectroscopy for powders ranging in size from 2 nm and 500 nm and d) image analysis - for all sizes but of particular interest for non-spherical particles.

The purpose of this practical course is an introduction to the most versatile and widely used method namely the static light scattering method known as laser diffraction. The other methods are described in detail in the Ceramic and colloids Processing course or can be found in the literature <sup>2, 8,9</sup>.

## 5.1 Practical points

### 5.1.1 Distributions and average diameters

The powders are rarely single size or monodisperse particles and are part of a size distribution. Distribution can be represented in different ways, such as a frequency distribution (Fig. 4-a) or combined (Fig. 4-b). Some measurement techniques provide a direct distribution based on the number (microscopy) or mass (sieving).

The mean of a distribution is a measure of central tendency. Among the central tendencies of the most used and found are the mode, median and average, illustrated in Fig. 4-a. The mode is the most common diameter in a distribution that represents the maximum of the frequency curve. The median represents the value where the total frequency of values above and below is identical (i.e., one finds the same number or total volume of particles below the median than above) (Fig. 4-b). The average should be calculated in turn and determines the point where the moments of the distribution are equal. For a normal distribution, the mode, mean and median coincide, while they differ in the case of a non-normal distribution (Fig. 4-a).

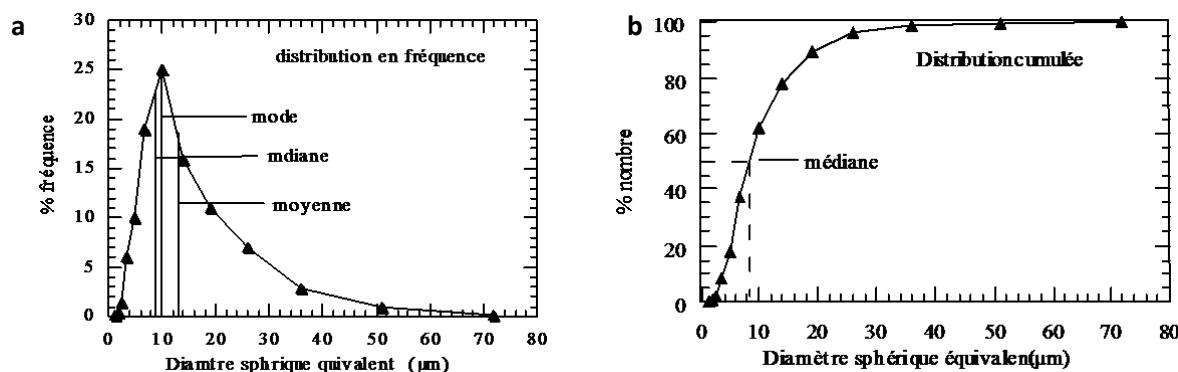


Figure 4. Examples of a) frequency distribution and b) cumulative distribution.

The mean of a distribution indicates the central tendency while the standard deviation ( $\sigma$ ) describes the width of the dispersion or spread of the distribution around its mean. It is the square root of variance. Each standard deviation is calculated with respect to the central tendency used, which in the case of the formula of equation 9, is  $d_v$ , the volume average diameter.

$$\sigma_v = \sqrt{\left( \frac{\sum f_i (d_i - d_v)^2}{V} \right)} \quad [9]$$

where  $f$  is the frequency of particles (by volume) and  $V$  is the total volume for all intervals of the diameter.

Distributions can often be represented by mathematical expressions that describe the entire distribution from two parameters: the central tendency (mean) and standard deviation. Reference 1 presents a thorough measurement of different distributions of particle size (Normal, log-normal, Rosin-Rammler).

*Table 1. Some examples of different mean diameters and their mathematical representation.  $i$  = class of particles,  $N_i$  = number or percentage of particles in class  $i$ ,  $S_{BET}$  = specific surface area [ $m^2/g$ ] and  $\rho$  = density of the powder [ $g/cm^3$ ].*

Diameter	Definition	Diameter	Definition
Number - length	$d_{nl} = \frac{\sum_{i=1}^n d_i N_i}{\sum_{i=1}^n N_i}$	Volume - moment (Weight - moment)	$d_{vm} = \frac{\sum_{i=1}^n d_i^4 N_i}{\sum_{i=1}^n d_i^3 N_i}$
Number - volume	$d_{nv} = \sqrt[3]{\frac{\sum_{i=1}^n d_i^3 N_i}{\sum_{i=1}^n N_i}}$	Specific Surface Area	$d_{BET} = \frac{6}{S_{BET} \cdot \rho} (\mu m)$ $SSA = \frac{6}{\rho} \cdot \left[ \frac{\sum n_i d_i^2}{\sum n_i d_i^3} \right]$

### 5.1.2 Method – laser diffraction

A schematic representation of the laser diffraction method is presented in Figure 5. Laser diffraction can measure powders from 3000  $\mu m$  to about 0.1  $\mu m$ .<sup>2,7,8</sup> The main limitations appear when particles are non-spherical, and when the optical properties of materials are not available.

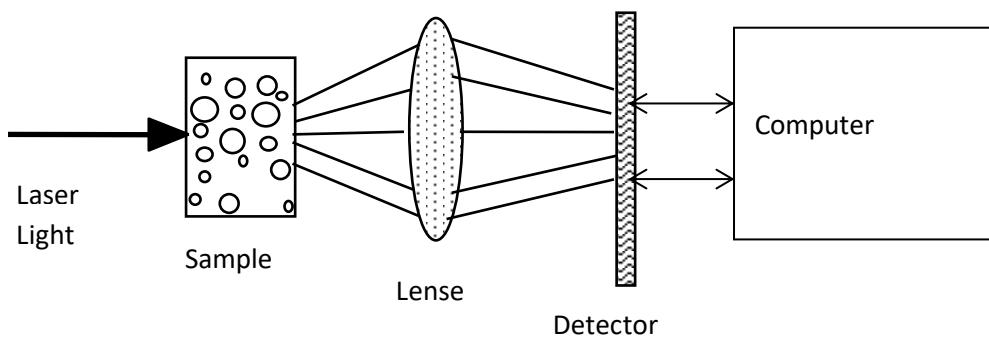


Figure 5. Schematic representation of laser diffraction method for particle size measurement.

Laser diffraction analyzers can be used with suspensions and dry powders. The diffraction pattern is a superposition of the pattern of each particle size in powder analyzed. In the data analysis, an initial size distribution is "estimated" and a theoretical diffraction pattern is calculated and compared with experimental data. The differences between the "estimated" and "experimental" data are then minimized using the method of least squares. The residue resulting from the difference gives a guide to the validity of the model used to represent data. The software then calculates the volume distribution as a fundamental result and other information is deduced from this result by assuming that the particles have a spherical shape.

Several studies using this type of instrument with various particules <sup>7,8</sup> show very good results for particle sizes  $> 1 \mu\text{m}$ . For spherical particles, the results are accurate and reproducible, making this instrument a good tool for granulated powders. The results with quartz powder standard, irregular geometry, in the range of  $0.3 - 200 \mu\text{m}$ , are less accurate but still very reproducible <sup>7,10</sup>. The method is very popular because of its high speed; the analysis only takes a few minutes. Again, the main limitations of this type of instrument appear when 1) the particles analyzed are smaller than  $1 \mu\text{m}$  (Mie theory must be used), 2) in the presence of non-spherical particles or 3) the difference between the refractive index of the solvent and the powder is low (e.g. polymeric materials).

## 5.2 To do list

- Procedure
  - Measurement of particle sizes distributions of alumina powder before and after milling
  - Analysis of granulometry of spray dried powders from both a commercial source and from the laboratory spray dryer.

## 6 Report

### 6.1 Brief Introduction

- Brief description of experimental details

- Do not repeat the script of TP, a brief description of experiments and equipment used and any special comment on certain points if necessary

## 6.2 Results

- Milling
  - Distributions of size before and after milling
- Classification
  - Report results and indicate the precision
  - Draw a selectivity curve (for 10 values of d) and calculate the sharpness index, recovery and yield to 50 microns (coarse fraction)
- Spray drying
  - Yield on Spray drying, and vibrated apparent densities, Hausner ratio
  - Calculate the% wt of PEG and PVA in the granules compared to the dry powder

## 6.3 Discussion of Results

- Milling
  - Choice of mill
  - Choice of parameters and material for ball milling
  - Effect of milling on the size and size distribution - possible improvements
- Classification
  - Choice of method
  - Selectivity curve and classification parameters
  - Why is the selectivity not perfect? Discuss the advantages and limitations of a sieve as a classifier
- Spray drying
  - Size distribution of primary particles and granules, shape of granules
  - Comparison of the Hausner ratio and flowability for the two types of powders (commercial and TP)

## 6.4 Conclusions

Approximate Timing	Section [min]	Total [h]
Milling – Weighing and launch	30	0.5
Preparation of the suspension of alumina and heating	30	1
Atomizer		
Spray drying	30	1h30
Measures of apparent density and tapped density	60	2h30
Sieving (Strain 10 g of atomized powder included)	15	2h45
Recovery milling	15	3
Particle size measurements and cleaning	30	3h30
Discussion of result	30	4

## Annexes

### A. Transformation-Toughened Zirconia (TTZ)

Transformation-toughened zirconium oxide (TTZ) is another important high-strength, high toughness ceramic that has been developed during the past 20–25 years. Transformation toughening was a breakthrough in achieving high-strength, high toughness ceramic materials. For the first time in history a ceramic material was available with an internal mechanism for actually inhibiting crack propagation.

Transformation toughening requires a bit of explanation. It is one of those properties that involves control of composition and manipulation of microstructure. Zirconia is a material that undergoes a change in the way its atoms are stacked at different temperatures (polymorphic transformation). Zirconia has the monoclinic crystal structure between room temperature and about 950 °C. Above 950 °C zirconia converts to the tetragonal crystal structure. This transformation is accompanied by larger than one percent shrinkage during heating and equivalent expansion during cooling. At a much higher temperature, the zirconia changes from tetragonal to a cubic structure.

With proper chemical additions and heat treatments, a microstructure can be achieved during cooling that consists of lens-shaped “precipitates” of tetragonal zirconia in cubic grains of zirconia, as shown in Fig. 2-16. Normally, the tetragonal material would transform to the monoclinic form during cooling, but it must expand to do so. The high strength of the surrounding cubic zirconia prevents this expansion, so the tetragonal form is retained all the way down to room temperature. As a result, each tetragonal zirconia precipitate is under stress and full of energy that wants to be released, sort of like a balloon that has been stuffed into a box that is too small. As soon as the box is opened, the balloon is allowed to expand to its equilibrium condition and protrude from the box. The same thing happens for each tetragonal precipitate if a crack tries to form or if someone tries to break the ceramic. The crack is analogous to opening the box. Tetragonal precipitates next to the crack are now able to expand and transform back to their stable monoclinic form. This expansion adjacent to the crack, presses against the crack and stops it. This is the mechanism of transformation toughening. It is similar to the toughening mechanism in some forms of steel, so the TTZ has sometimes been called “ceramic steel.” TTZ has been developed in a couple of different forms. The one described above is typically called partially stabilized zirconia (PSZ). The second form consists of nearly every crystallite or grain in the material being retained in the tetragonal form to room temperature so that each grain can transform instead of only the precipitates. This material is referred to as tetragonal zirconia polycrystal (TZP). Both types are mentioned because they have different properties, and one may be preferable for a specific application.

A crack, in a normal ceramic, travels all the way through the ceramic with little inhibition, resulting in immediate brittle fracture. TTZ has fracture toughness (resistance to crack propagation) 3–6 times higher than normal zirconia and most other ceramics. It is tougher than cast iron and comparable in

toughness to WC-Co cermet. TTZ is so tough that it can be struck with a hammer or even fabricated into a hammer for driving nails. Figure 2-15 displays examples of TTZ tooling for fabrication of aluminium cans. For a part such as an extrusion die, TTZ typically costs around four times as much as steel and two times as much as WC-Co. The suppliers can provide information on life-cycle cost for existing applications and can probably estimate for similar applications.



Fig. 2.15. Variety of SiC parts for wear-resistance applications, thermal applications and semiconductor industry applications. Source: Saint-Gobain/Carborundum Structural Ceramics, Niagara Falls, N.Y.

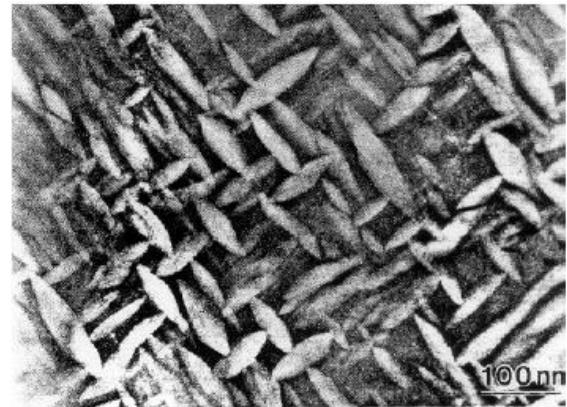
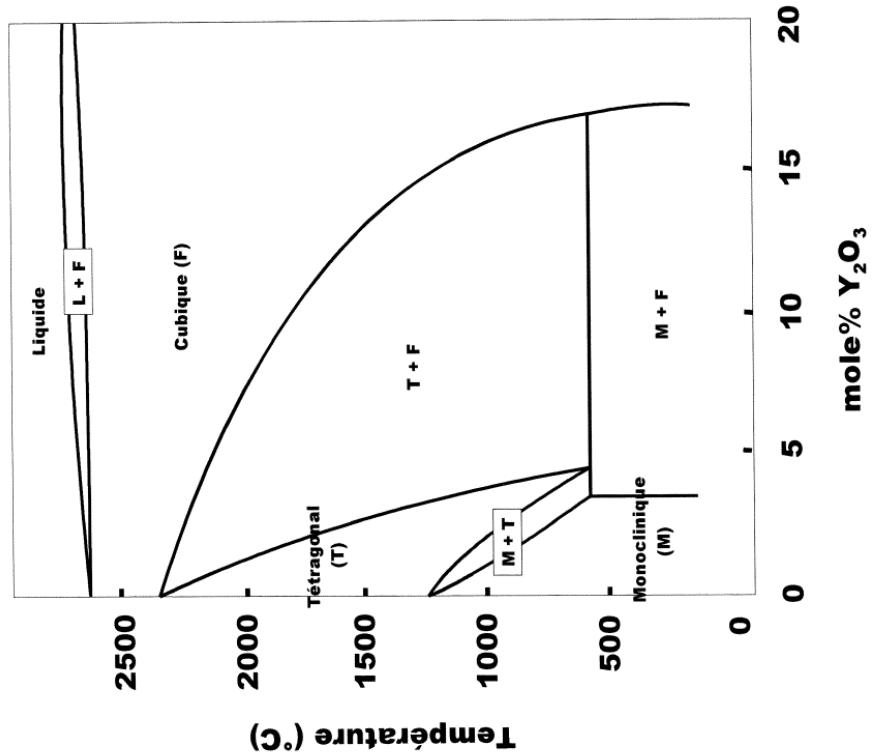


Fig. 2.16. Microstructure of one form of transformation-toughened zirconia. Source: David W. Richerson, *Modern Ceramic Engineering*, Marcel Dekker, New York, 1992.



**B. Particle size distribution of the zirconia powder before sieving****Result: Analysis Report**

Sample Details			
Sample ID: RO 08-05-03	Run Number: 2	Measured: Wed 21 May 2003 11:39	
Sample File: ZRO2	Record Number: 24	Analysed: Wed 21 May 2003 11:39	
Sample Path: D:\MALVERN\OESCH\		Result Source: Analysed	
Sample Notes: ZrO2 TZ_3YB lot 304149 pour TP2 (Y.H) direct ds. récipient de brassage avec iso-propanol			

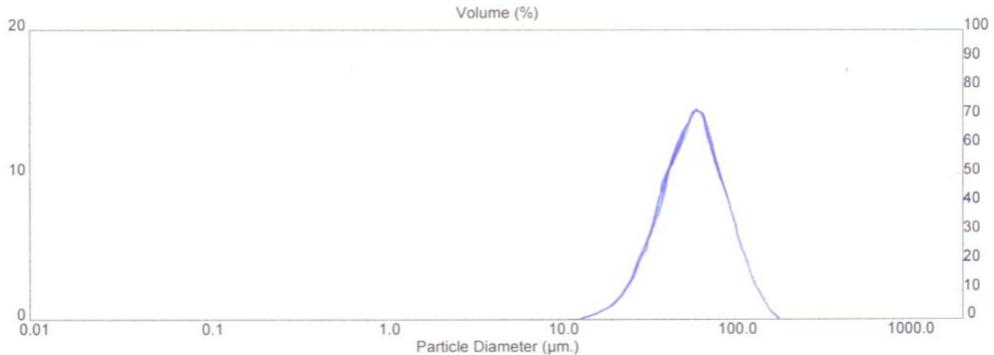
System Details			
Range Lens: 300RF mm	Beam Length: 2.40 mm	Sampler: MS1	Obscuration: 15.6 %
Presentation: 3THD	[Particle R.I. = ( 2.5935, 0.1000); Dispersant R.I. = 1.3300]		
Analysis Model: Polydisperse			Residual: 0.626 %
Modifications: None			

Result Statistics			
Distribution Type: Volume	Concentration = 0.1189 %Vol	Density = 6.050 g / cub. cm	Specific S.A. = 0.0193 sq. m / g
Mean Diameters:	D (v, 0.1) = 31.68 um	D (v, 0.5) = 57.88 um	D (v, 0.9) = 99.12 um
D [4, 3] = 62.21 um	D [3, 2] = 51.31 um	Span = 1.165E+00	Uniformity = 3.599E-01

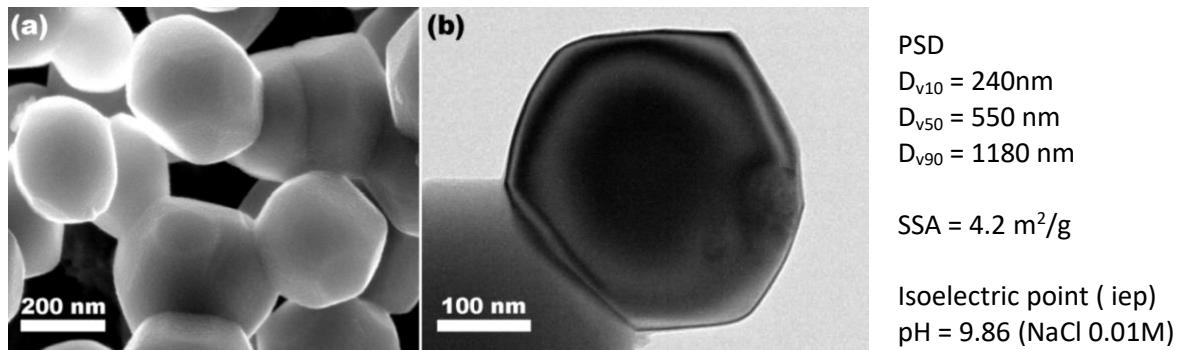
  

Size Low (um)	In %	Size High (um)	Under%	Size Low (um)	In %	Size High (um)	Under%
0.05	0.00	0.06	0.00	6.63	0.00	7.72	0.00
0.06	0.00	0.07	0.00	7.72	0.00	9.00	0.00
0.07	0.00	0.08	0.00	9.00	0.00	10.48	0.00
0.08	0.00	0.09	0.00	10.48	0.03	12.21	0.03
0.09	0.00	0.11	0.00	12.21	0.09	14.22	0.12
0.11	0.00	0.13	0.00	14.22	0.25	16.57	0.38
0.13	0.00	0.15	0.00	16.57	0.62	19.31	1.00
0.15	0.00	0.17	0.00	19.31	1.31	22.49	2.31
0.17	0.00	0.20	0.00	22.49	2.42	26.20	4.73
0.20	0.00	0.23	0.00	26.20	3.99	30.53	8.73
0.23	0.00	0.27	0.00	30.53	6.03	35.56	14.76
0.27	0.00	0.31	0.00	35.56	8.46	41.43	23.21
0.31	0.00	0.36	0.00	41.43	11.03	48.27	34.24
0.36	0.00	0.42	0.00	48.27	13.07	56.23	47.31
0.42	0.00	0.49	0.00	56.23	14.33	65.51	61.63
0.49	0.00	0.58	0.00	65.51	12.77	76.32	74.40
0.58	0.00	0.67	0.00	76.32	10.15	88.91	84.55
0.67	0.00	0.78	0.00	88.91	7.27	103.58	91.82
0.78	0.00	0.91	0.00	103.58	4.64	120.67	96.46
0.91	0.00	1.06	0.00	120.67	2.52	140.58	98.98
1.06	0.00	1.24	0.00	140.58	1.02	163.77	100.00
1.24	0.00	1.44	0.00	163.77	0.00	190.80	100.00
1.44	0.00	1.68	0.00	190.80	0.00	222.28	100.00
1.68	0.00	1.95	0.00	222.28	0.00	258.95	100.00
1.95	0.00	2.28	0.00	258.95	0.00	301.68	100.00
2.28	0.00	2.65	0.00	301.68	0.00	351.46	100.00
2.65	0.00	3.09	0.00	351.46	0.00	409.45	100.00
3.09	0.00	3.60	0.00	409.45	0.00	477.01	100.00
3.60	0.00	4.19	0.00	477.01	0.00	555.71	100.00
4.19	0.00	4.88	0.00	555.71	0.00	647.41	100.00
4.88	0.00	5.69	0.00	647.41	0.00	754.23	100.00
5.69	0.00	6.63	0.00	754.23	0.00	878.67	100.00

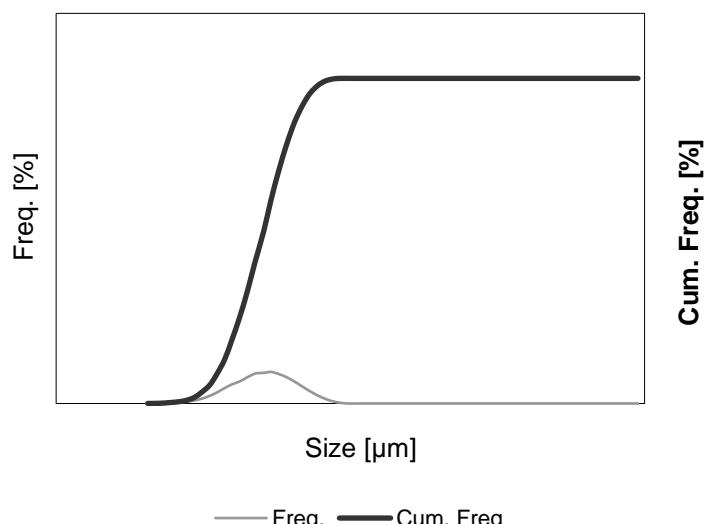


### C. AA04 Powder characteristics

A high purity  $\alpha\text{-Al}_2\text{O}_3$  (Sumitomo AA04, batch YD9812, Solvadis Chemag GmbH, Germany); the total impurity concentration is less than 0.01 mass% ( $\leq 5$  ppm for Si, Na, Mg, Cu and Fe)

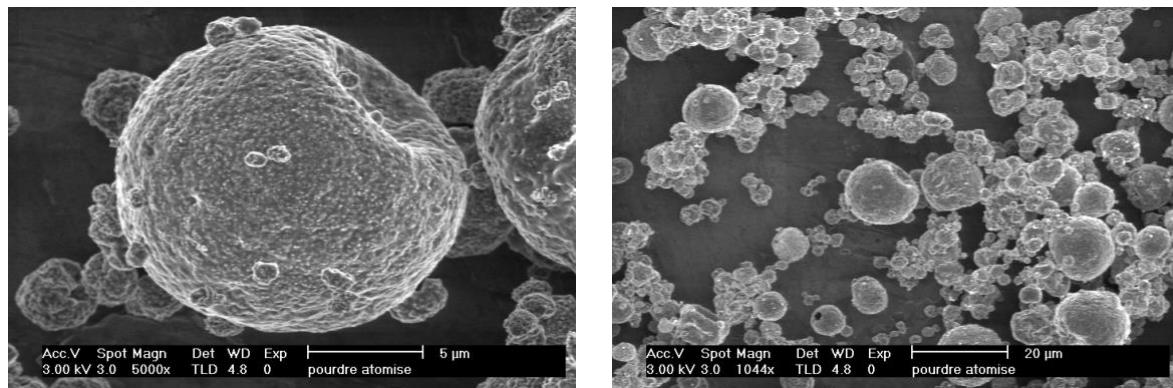


(a) SEM image and (b) TEM image of the AA04  $\alpha\text{-Al}_2\text{O}_3$  powder.



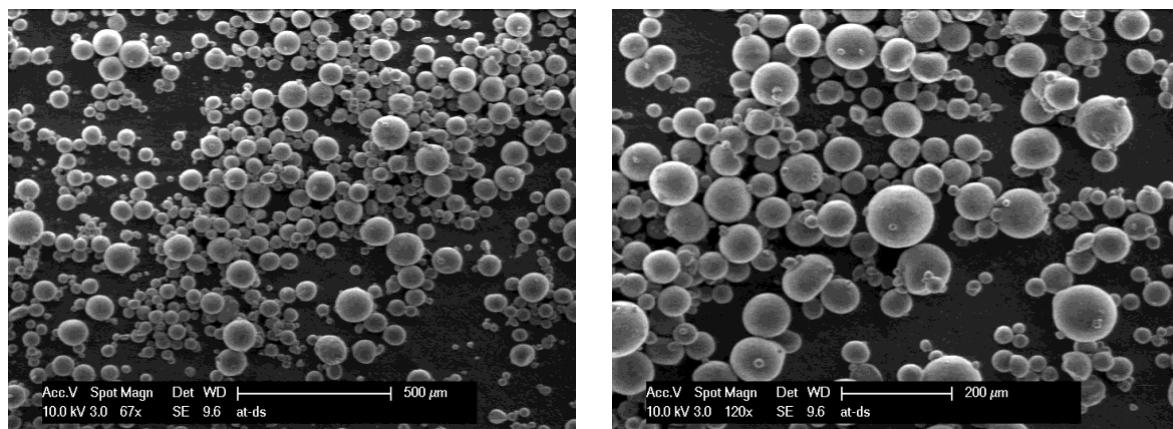
**D. Atomization - SEM micrographs of spray dried powders used in TP1**

Powders spray dried at LTP – laboratory style powders

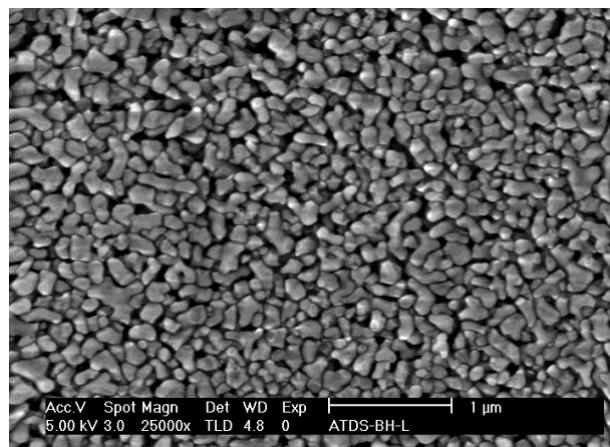


Atomization of the commercial powder

AT-DS – Commercial powders – used for TP1 &amp; TP2



Name	Powder type	Supplier (type, lot No.)	Purity [%]	SSA (m²/g)	D <sub>BET</sub> [nm]	D <sub>v5</sub> [nm]	D <sub>v10</sub> [nm]	D <sub>v50</sub> [nm]	D <sub>v90</sub> [nm]	D <sub>v95</sub> [nm]
AT-DS	$\alpha$	Taimicron TAM-DAR	99.99	14.1	107	108	118	165	268	1282



## Bibliography

---

- [1] J.S. Reed, "Introduction to the Principles of Ceramic Processing" 2nd Edition, J. Wiley, NY, 1995.
- [2] J. Barton, P. Bowen, C. Carry and J.M. Haussonne. Traité des Matériaux, Volume 16, Céramiques et Verres : Principes et techniques d'élaboration, ISBN 2-88074-605-1, Presses Polytechniques et Universitaires Romandes, 2005.
- [3] (a) A.D. Randolph and M.A. Larson, "Theory of Particulate Processes", 2nd Edition, Academic Press, NY, 1988.  
(b) J. A. Dodds, C. Frances, P. Guigon, A. Thomas "Méthodologies pour la Modélisation du Broyage Fin", Colloque sur Science et Technologie des Poudres, Lyon, France, Novembre 1994.
- [4] T. Docktor ,P. Weymouth & T. Barson , "Proper Techniques for the Ball-Milling of Ceramic Glazes." Amer. Ceram. Soc. Bull. 73(1) 54-58 (1994).
- [5] S.J. Lukasiewicz, "Spray-Drying Ceramic Powders" J. Am. Ceram. Soc., 72(4) 617-24 (1989).
- [6] D. Kumar, R. Ladisch, E. Lutz et N. Claussen, "Powder Preparation via Spray Dryer", Ceram. Forum Int., 5 (1988) 141-44.
- [7] L. Svarovsky, "Powder Testing Guide: Methods of Measuring the Physical Properties of Bulk Powders", Elsevier Applied Science, London, 1987.
- [8] Bowen, P. "Particle Size Distribution Measurement From Millimeters to Nanometers and From Rods to Platelets", J. Dispersion Science and Technology, 23(5) 631-662 (2002).
- [9] Aimable, P. Bowen, "Ceramic Nanopowder Metrology and Nanoparticle size measurement - towards the development and testing of protocols" J. Processing and Application of Ceramics, 4[3] 147-156 (2010)
- [10] R. Xu et al– Paper 41- «Particle size and shape analysis using light scattering, coulter principle, and image analysis»World Congress Particle Technology, Sydney, 2002.