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Sample Preparation and Particle Measurements in Ceramics Laboratories

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The wide range of analysis and measurement tasks in research and development laboratories or quality assurance in a ceramics company place very different demands on the equipment available. Equipment specialisation for the solution of specific tasks or for particular applications means that the „typical" ceramics laboratory with virtually standard equipment no longer exists today.

Particularly in the research field, new and significant developments have taken place in recent years. Whereas, in the past, the comminution and preparation of initial or raw materials for the ceramics industry concentrated on the range to approx. 20 microns, interest has now turned to appropriate equipment for a much lower size range. Furthermore, this is accompanied by the requirement for the ground sample to be completely free of contamination from the milling equipment, or for the definition of a maximum permissible level of contamination.

Today's units and the grinding or measurement processes they permit are much more closely adapted to specific tasks. When selecting equipment, it is extremely important to understand the relevant relationships and effects on the product, as each process affects the resulting fragments or crushed products in its own specific way. Knowledge of these relationships allows preference to be given to particular methods.

The text below will employ examples in an attempt to provide assistance in selecting equipment for „retrofitting" a laboratory in which mineral raw materials or additive materials are to be ground for new research applications, or where the particle size of the resulting product has to be accurately and quickly determined. Possible applications are found not only in the development of new semiconductors or their substrates, but also, e.g., in research in the field of „superconductivity", in the development of implants or in engine-making where ceramic materials could replace conventional, metal alloys. We shall first consider equipment which can be used to grind brittle materials down to the micron range without the risk of metallic contamination. The section entitled „Measurement of Samples" will then describe methods for measuring the particle size distributions of ceramic samples, as well as the results obtained with these methods.

Preparation of Samples

„Comminution" or „preparation" is taken to mean a reduction in the size of individual particles or the pretreatment of a sample, this being performed until the resulting particles have suitable characteristics for subsequent analysis. The use of suitable equipment in a laboratory dedicated specifically to the preparation and analysis of ceramic materials, ensures that the correct methods and grinding principles are readily adopted.

Precrushing with Jaw Crusher

In laboratory applications, the jaw crusher is the most commonly used crusher. Depending on the type, feed material of up to 100 mm edge length can be crushed to a settable average particle size of 1 mm. Crushing is performed in a crushing chamber formed by two side walls, an adjustable fixed crushing plate and a vibrating, movable crushing plate. The vibrating crushing plate is driven by a disc flywheel and a powerful eccentric cam. The specific movement achieved causes the material to be crushed to be drawn into the crushing chamber while preventing the crushed material from becoming jammed. It can leave the crushing chamber without difficulty, passing through an adjustable discharge slot.

The jaw crusher is especially suitable for this particular task because a variety of materials can be used for the crushing plates which come into direct contact with the sample. When, for example, crushing particularly abrasive samples, a set of tungsten carbide crushing plates and side walls can be used to prevent undesirable metallic contamination from the crushing process. If there is to be absolutely no contamination by metal from the crusher, the ceramic material zircon oxide can be used for the crushing plates.

Crushing in the jaw crusher involves the application of impact and shearing forces on the samples as either the crushing plates press the samples or the particles press against each other.

In the jaw crusher, the elastic component is generally more important than the plastic component in the deformation of the particles. Curved fracture lines occur between the contact area of one crushing plate and the opposing support point of the other. The deformation or fracture behaviour of a sample is not merely a material property, it is also dependent on temperature and particle size. The stress speed, which also has an effect, is relatively low in the jaw crusher and usually cannot be varied. The particles leaving the crushing chamber are sharp-edged and do not have rounded points or edges, and, because of the low stress speed, are relatively free of fines which tend to occur with faster crushing techniques.

Fine-Grinding with the Planetary Ball Mill

Samples which leave the jaw crusher after precrushing have an average particle size of approx. 1 mm or larger. In most cases, they must therefore be ground to the necessary fineness in a further grinding process. Ball mills have proven to be most useful for this task. Ball mill is the general term used to describe units for grinding precrushed material in which many balls in a milling chamber impact and friction-grind the relevant material. This results in a higher number of individual grinding processes and comminution proceeds more quickly.

The planetary ball mill is a particularly sucessful type of ball mill. It owes its name to the planet-like movement of its grinding bowls. These are arranged on a rotating support disc and a special drive mechanism causes them to rotate around their own axes. The centrifugal force produced by the grinding bowls rotating around their own axes and that produced by the rotating support disc both act on the grinding bowl contents, consisting of material to be ground and the grinding balls. (Fig. 1)

Since the grinding bowls and the support disc rotate in opposite directions, the centrifugal forces alternately act in like and opposed directions. This causes the grinding balls to run down the inside wall of the bowl - the friction effect - followed by the material being ground and the grinding balls lifting off and travelling freely through the inner chamber of the bowl and colliding against the opposing inside wall - the impact effect. This impact effect is intensified considerably by the grinding balls impacting with each other.

The grinding balls in pure planetary ball mills attain considerably higher impact energy than is possible with pure gravity or centrifugal mills. Depending on the speed set for the ball mill, this energy can amount to twenty times the earth's acceleration. The high acceleration energy or the resulting high speed of the grinding balls when they hit the material to be ground is responsible for the reduction in the plastic component in crushing the samples. When the balls impact, the fracture lines take the form of clusters going out from the point of impact in streams. Beneath

Fig. 1 Planetary Ball Mill „pulverisette 5"

Fig. 2 Laser Particle Sizer „analysette 22"

Fig. 3 Planetary Micro Mill „pulverisette 7"

the contact surfaces between the grinding ball and sample material, a conical area is driven into the grain interior and the material is pushed out at the side. The material acts as if it were brittler with the result that fines are created at the impact points (where the greatest energy is released).

It is largely fine grinding that occurs when the grinding balls roll down the inside wall of the bowl - the grinding force is more the result of shearing than impact. This also inhibits the formation of agglomerate.

The high acceleration of the grinding balls also permits the use of balls with smaller diameters as their force is still sufficient. The use of a large number of small balls instead of a few large balls considerably accelerates milling due to greater frequency of impact.

The impact energy of the balls is dependent on the speed of the planetary mill. As the speed is reduced the grinding balls lose impact energy, a process which can be continued until grinding ceases and the sample material is only mixed. The grain shape can be specifically influenced at a particular intermediate stage. This is the case when the impact energy has been reduced to such an extent that it can only cause the disintegration of particles when impact involves extremely high specific stress. High stresses of this type occur at corners or edges with the result that small pieces of material can splinter off at these points. This results in the particles being rounded off. Conversely, it can be assumed that if grinding is performed with the mill rotating at maximum speed, virtually no rounding will occur and grinding will proceed through impact and shearing.

The shape of the individual particles of the milled sample can be influenced with the aid of experimentally determined milling parameters, e.g., the speed as in this case. Other parameters such as the size, quantity and specific weight of the grinding balls or volume of the grinding bowl are also variable and affect the final shape of the particles.

Depending on the relevant material, an average final fineness of under 1 micron can be achieved with the „pulverisette 5" planetary ball mill (fig.1) or the version for smaller quantities „pulverisette 7" (fig. 3) (up to 20 ml material to be ground in each of the two bowls instead of up to 280 ml in each of the 4 grinding bowls) after a grinding time of approx. 2 hours. Unless special grinding additives (tensides) are used, lengthening the grinding time any further will not produce any reduction in the proportion of larger particles below a range of approx. 1 micron as agglomerates form again immediately. Only with the aid of additives can the size distribution, i.e., the proportion of coarse grains, be further reduced.

Measurement of Particle Size Distribution

In the field of special ceramics, in particular, the properties of specific products depend on the use of an initial or raw material with a defined particle size or defined surface area of the individual particles. In order to influence product quality in a specific manner, quantitative determination of particle size distribution is essential.

Especially in the development of new types of materials, conventional equipment for size determination, such as sieving machines with woven sieves, is no longer adequate and the units for determining particle sizes or size distribution must satisfy more demanding requirements. The application limits of existing units are being extended or, where this is not possible, new equipment must be provided.

Using modern sieving units with galvanic sieving foils it is, for example, already possible to perform particle size analyses down to 5 microns. Thanks to the use of scanning/sampling devices, sedimentation analysis is also coming back into favour because of the resulting short measurement time and the use of centrifuges, ensuring an extensive measurement range down to 0.05 microns. Specially programmed computers simplify the evaluation of the test results.

A relatively recent development takes the form of laser particle sizers with which particle size distributions can be measured very quickly so that, for example, decision criteria for process control are available immediately, i.e., virtually „on-line".

Sedimentation Analysis with the Scanning Photo-Sedimentograph „analysette 20"

The analysis of the granular size of materials by observing particles sinking in a liquid is a very old method which has been used since the mathematical relationship between the particle size, specific density of the liquid and particle(s), viscosity of the liquid and the sinking speed was established (Stokes' law). The simplest and probably oldest unit for this is the sedimentation balance which, however, requires a much too long measurement time, particularly in the fine particle range. Although visual scanning of the change in concentration due to sedimentation at a fixed point in the sedimentation cylinder - a refinement intended to simplify the process - did bring improvements, the time requirement is still considerable when small particles are to be analyzed with this method.

The scanning photo-sedimentograph „analysette 20" is a major advance in terms of reducing the measurement times. While retaining the advantages of the absorption method (photometer method), the measurement time is shortened by raising the photometer device up the side of the cuvette at a speed calculated by the computer. This permits early detection of slow-sedimenting, small particles in the top section of the measurement cuvette. The facility for entering a lower measurement limit permits interruption of measurement and output of the results as soon as a measurement limit is reached, thereby further shortening the measurement time. This allows a series of measurements to be performed in quick succession. The sedimentograph can thus be extremely useful, e.g., for monitoring of sintering or grinding of ceramic materials.

The application limits of photometric measurement with this unit are physically determined by the extinction coefficient which cannot be regarded as constant with particle sizes < 2 microns. Although the optical system of the „analysette 20" is designed to

produce a correcting effect, which permits comparative measurement of samples with a high proportion of fine material (< 2 microns), absolute measurements become less accurate.

Centrifugal Sedimentation Analysis with the „analysette 21"

In particle size analysis in the range < 5 microns, the effect of gravity in normal sedimentation is very slight. For example, under the effect of gravity, a crystal particle (density 2.64 g cm^{-3}) of 1 micron in size only sinks 1 cm in water over a period of approx. 30 hours. Analysis employing this method are thus time-consuming and are not practical in the size range under 1 micron.

In a centrifugal field, the forces exerted on particles in suspension are considerably greater. Since the same physical laws can be applied here - only centrifugal acceleration in used in Stokes' law - the only real difference is that the glass cylinder (cuvette) is replaced by a rotating measurement drum (centrifuge). In this centrifuge, time-dependent mass determination is performed at a specific radius. The Andreasen pipette method, which has been successfully proven in gravitational applications, is particularly suitable for this purpose.

In the measurement plane, an integrated pipette is used at specific times to withdraw samples through 6 hollow needles which also rotate in the centrifuge. After mathematical evaluation, the solid content of these individual samples can be used to derive particle size distribution of the entire sample.

Since the amount of sample material remaining in the centrifuge is reduced each time individual samples are withdrawn, the distance between the surface of the sample liquid and that of the measurement plane is also reduced. In this way, the sedimentation period of the smallest particles is shortened without causing any reduction in accuracy. The lower measurement limit of the „analysette 21" pipette centrifuge is around 0.05 micron.

Particle Measurement in the Laser Diffraction Spectrometer

The latest development for the quick determination of particle size distribution is the laser diffraction spectrometer. With this universal unit, any type of solid can be analysed dry or in suspension - irrespective of its respective density.

It frequently seems to be the case that the technology of new equipment is based on already well-known physical principles that can, however, only now be applied with the aid of modern electronics. It has, for example, been know for decades that the wavelength of light deflected at a slit or screen with a defined aperture can be determined by measuring the distances between the maxima of intensity of the diffracted light. The converse thesis that the dimensions of a particle standing in the beam of light can be determined if the wavelength is known seemed obvious, and was also applied. In the past, however, difficulties arose with this method if measurement was to be extended to several particles of different sizes. This is precisely the task which is set nowadays and which is solved with modern equipment such as laser emitters, semiconductor sensors, amplifiers and computers (fig. 2).

Operating Principle of the Laser Particle Sizer „analysette 22"

With this new unit, during irradiation of the sample, a laser beam generates a diffraction pattern in which the laser light is deflected at various scatter angles depending on the particle size of the individual particles.

Points of maximum and minimum intensity occur at specific distances from the central beam. Fraunhofer's law describes the physical relationships and can be used to determine the particle size from the distance between the intensity maxima when the wavelength of the light is known. In the ideal case of a monodispersion sample, i.e., a sample comprising particles of one size, the distance between the intensity maxima can be directly converted to the particle cross-section.

In practice, however, a sample comprises particles of varying diameters. This means that each size category generates overlapping maxima and it is only possible to draw conclusions on the particle dimensions if individual maxima are successfully assigned to a particular particle size.

For this purpose, the angle and related intensity distribution of the deflected light is recorded by a special, high-definition multielement detector. The many diffraction patterns generated during a measurement are used in conjunction with an interfaced computer to calculate the particle distribution according to grain size and mass components. The results are displayed in graphic or tabular form on a monitor, or are output at a printer

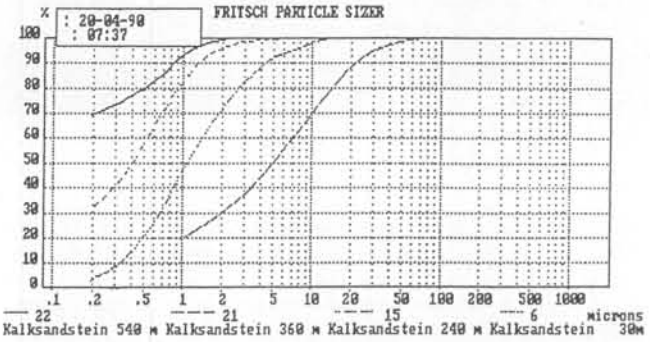

Fig. 4 Chalky sandstone ground in the „pulverisette 7" planetary ball mill in a zircon oxide grinding bowl. Grinding in water with 0.5% sodium pyrophosphate. Measurement of the particle size distribution with laser particle sizer „analysette 22" after grinding times of 30, 240, 360 and 540 minutes.

Fig. 4 illustrates the results of a measurement using the laser particle sizer „analysette 22". In this example, a ceramic coating used in the field of special materials for implants was ground for different periods of time in a „pulverisette 7" (fig. 3) planetary micro mill. In this case, 40-ml agate grinding bowls and 12-mm agate grinding balls were used. The first measurement of size distribution was performed after 15 minutes; measurement then being repeated after successive doubling of the grinding time. The illustrated final fineness of the sample was achieved after 2 hours in this example.

Areas of Application of the „analysette 22"

The „analysette 22" laser particle sizer can be used wherever particle size distributions have to be measured accurately and under reproducible conditions in a very short time, i.e., it is also used for continuous monitoring of product quality or process control.

Since no material-specific data are used when measuring solid samples (dry or in suspension), mixtures of differing composition and density, e.g., sinter materials from initial component materials of differing densities, can be examined to determine their particle size distribution.

As long as the particles do not change their size by swelling or dissolving in the suspension during measuring, there are virtually no restrictions on the use of the „analysette 22". The amount of sample needed is only about 0.1 - 1 g, suspended in approx. 300 ml of liquid. For dry measurement, a sample amount of about 10 ml is needed, with the largest measurable particles not exceeding approx. 1000 microns. Particle sizes below 0.8 micron are only detected as total amounts.

The advantages of the „analysette 22" lie above all in its large measuring range and its fast measurement of particle size distributions. The special design of the optical system means that only one image lense is needed for the entire measuring range, thereby greatly simplifying changing of the range. Since no refitting or alignment work is involved, the „set-up" time required to alter the measuring range is negligible. The construction of the unit is very robust, which means that it will also withstand somewhat rough treatment in long-term use without suffering damage and without falsification of the measurement results.