PARTICLE CHARACTERIZATION OF METAL POWDERS

In this article, we present several examples of how the size and shape of typical metal powders and metal alloys can be characterized by Dynamic Image Analysis (DIA) and Laser Diffraction (LD) technologies, using the Microtrac MRB CAMSIZER X2 and SYNC analyzers. The advantages of these instruments are short analysis times, excellent repeatability, and "infinite" resolution. Many different size and shape parameters are measured and reported, for each individual particle, and all data is available as soon as the measurement ends. Shape parameters are calculated as ratios of various size measurements and are reported on a scale from 0 to 1. The data for each parameter can be reported in both frequency and cumulative distributions, in volume and number format, and the complete parameter data set can be reported for each individual particle.

Image Analysis: What you see is what you get

Image analysis techniques provide a direct approach to particle size analysis. The basic idea is simple: "What you see is what you get". Automatic software algorithms determine size and morphology based on digital photographs of individual particles.

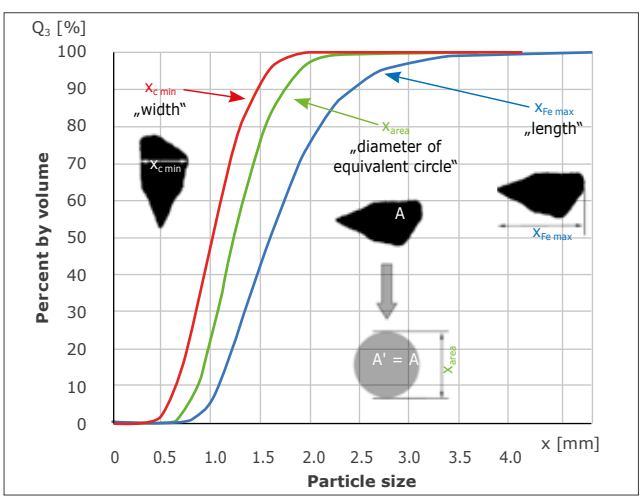


Fig. 1: Selection of CAMSIZER X2 basic size parameters used in image analysis. The size distributions are based on width (red), length (blue) or equal area diameter (green).

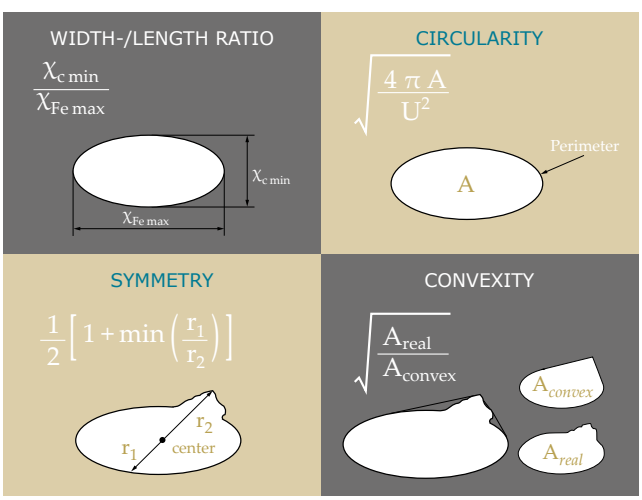


Fig. 2: Selection of basic shape parameters (CAMSIZER X2).

The CAMSIZER X2: DIA Analyzer

The CAMSIZER X2, with the widest dynamic range in the industry, 0.8 µm to 8 mm, can measure both suspensions, or dry samples, using one of three different sample dispersion accessories. Below in Fig 1. particle length, width and equivalent area diameter information from the CAMSIZER X2 are reported. A selection of shape parameters is explained in Fig. 2.

In the measurement set-up of the CAMSIZER X2 (DIA), particles move in front of a camera system, either transported by single pass air flow or recirculating in liquid. Thus, it is possible to obtain data from up to several millions of particles within a few minutes, especially when measuring dry. The results are based on a representative amount of sample material for both methods and are therefore statistically sound.

Fig. 3 displays the principal set-up of the optics for the CAMSIZER X2 Dynamic Image Analyzer. As the particles pass through the field of view a light source illuminates the particles from one direction while a camera system takes pictures from the opposite side. A software evaluates the shadow projections of the particles to determine the size distribution of the sample with a high acquisition rate. A unique feature of the CAMSIZER X2 is the dual camera technology: Two cameras with different magnifications cover a wide measuring range. One camera with high magnification is optimized for the analysis of small particles, a second camera with a lower magnification but wide field of view allows simultaneous analysis of the larger particles with high detection efficiency. The CAMSIZER X2 records more than 300 frames per second with one single frame easily containing several hundreds of particles, depending on the sample size range.

DIA measures the particle size distribution and quantitative particle shape (percentage of round versus irregular shaped particles, agglomerates etc.). Very small amounts of oversized, undersized, or irregular shaped particles can be detected, to a percentage as low as 0.002 %. DIA enables the user to obtain a comprehensive and thorough understanding of size- and morphology-related sample properties. DIA is the ideal method for both R & D applications and quality control because it is accurate, robust, sensitive and easy to use.

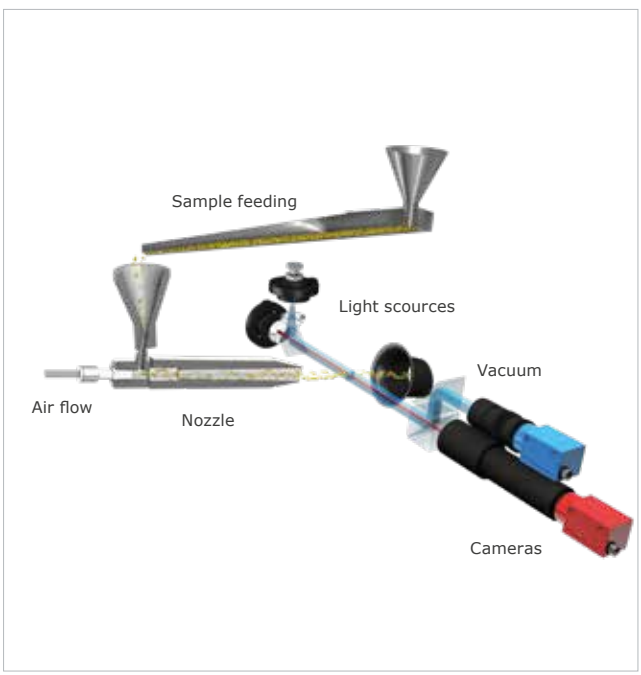


Fig. 3: Unique measurement principle of CAMSIZER X2 for analysis of dry powders.

Wide range of materials, particle sizes and particle shapes

In the following, a selection of application examples demonstrates the suitability of DIA to comprehensively characterize metal powders. Fig. 4 shows the results of the size analysis of ten different metal powders which are typical for powder metallurgical applications. Irrespective of the difference in chemistry, density, size and shape, all samples can be analyzed with the CAMSIZER X2, using one instrument setup. An automatic feeding chute transports the sample to the analyzer where the particles are captured by an air flow. In this case 50 kPa have been found sufficient to achieve thorough dispersion, i. e. separation of individual particles.

The samples show a variety of mean particle sizes between 10 and 50 µm, with different widths of distribution (Fig. 4). In this example, the iron powder (Fe) is the coarsest whereas the steel powder (316) is the finest. The titanium powder is characterized by a very narrow size distribution.

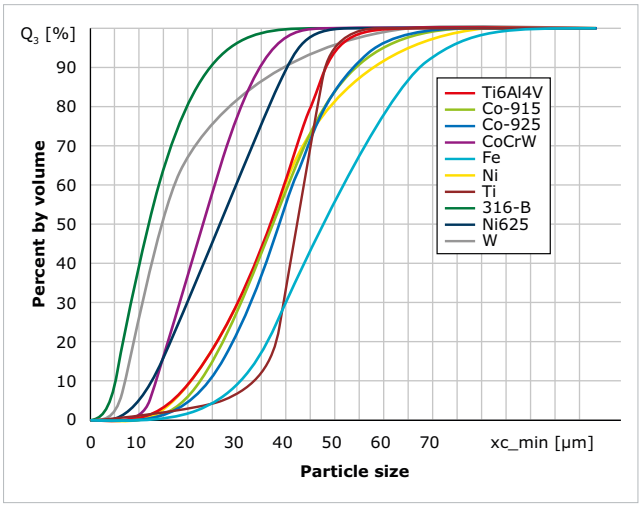
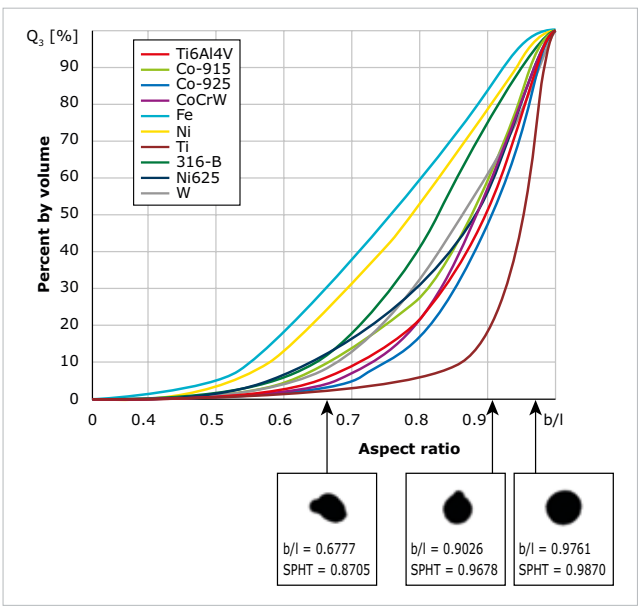


Fig. 4: Particle size analysis of ten different metal powders with the CAMSIZER X2. The direct measurement ensures accurate results.

The shape diagram (Fig. 5) shows that the iron powder has the lowest aspect ratio (breadth/length), whereas the titanium powder has the largest share of spherical particles.



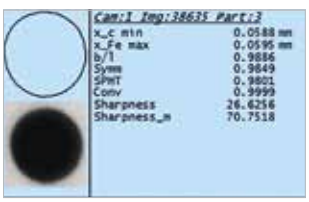
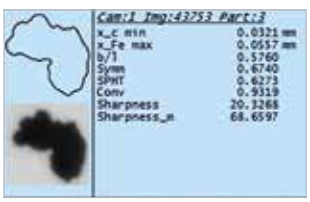


Image of a spherical metal powder particle



Irregular particles are reliably detected

Fig. 5: Analysis of particle shape of 10 different metal powders with Dynamic Image Analysis (CAMSIZER X2). Beside the quantitative results, the recorded images allow an intuitive understanding of morphology and size differences. More spherical particles with higher aspect ratio plot on the right side of the diagram. Detecting the smallest amounts of irregular particles in a large quantity of predominantly spherical particles is a great advantage of DIA.

Powder metallurgical processes usually require a wide size distribution to make packing the powder into the die easier by filling the void spaces between large particles with smaller ones. An irregular shape is often beneficial for the sintering process because it increases the contact between particles. However, the particles must not be too irregular as this will make compaction more difficult. For additive manufacturing, a spherical shape with a broad size distribution provides a smooth layer of powder to ensure proper sintering and good metal parts. The average particle size is usually between 10 – 50 µm, hence the titanium powder in the above example is suitable for additive manufacturing. Oversized particles or very irregular particles need to be detected with great accuracy since these are likely to cause defects in the finished workpiece. DIA reliably detects even small amounts of these undesired particles. Fig. 6 shows clearly how easily DIA can identify defective particles.

The SYNC: Hybrid DIA & Laser Diffraction (LD) Analyzer

The novel SYNC analyzer is a revolutionary hybrid instrument which combines LD and DIA technologies in one unit, measuring the same sample in the same sample cell simultaneously. LD (a type of light scattering) technology has been used by the metal powder industries for decades as the de facto standard for measuring size distributions in outgoing QC certification by metal powder suppliers and incoming QC verification by powder metallurgy parts producers.

The optical bench of the SYNC is shown in Fig. 6. Three lasers, available in blue or red, in combination with two linear diode detector arrays allow the scattered light from the passing particles to be collected over a range of 163 degrees. Smaller particles scatter light at higher angles and lower intensities than do larger particles. The SYNC algorithm for LD back-calculates the particle size distribution that created the light flux distribution measured. Using a modified Mie theory, the algorithm compensates for non-spherical and translucent particles. Simultaneously, a rapid LED strobe lamp illuminates the particles and a set of optics focusses the transmitted light for a digital camera to photograph the complete video file of the particle images, as the CAMSIZER X2 does, except that the SYNC uses one camera.

The display shown in Fig. 7 is the LD size distribution report used by the metal powders industries.

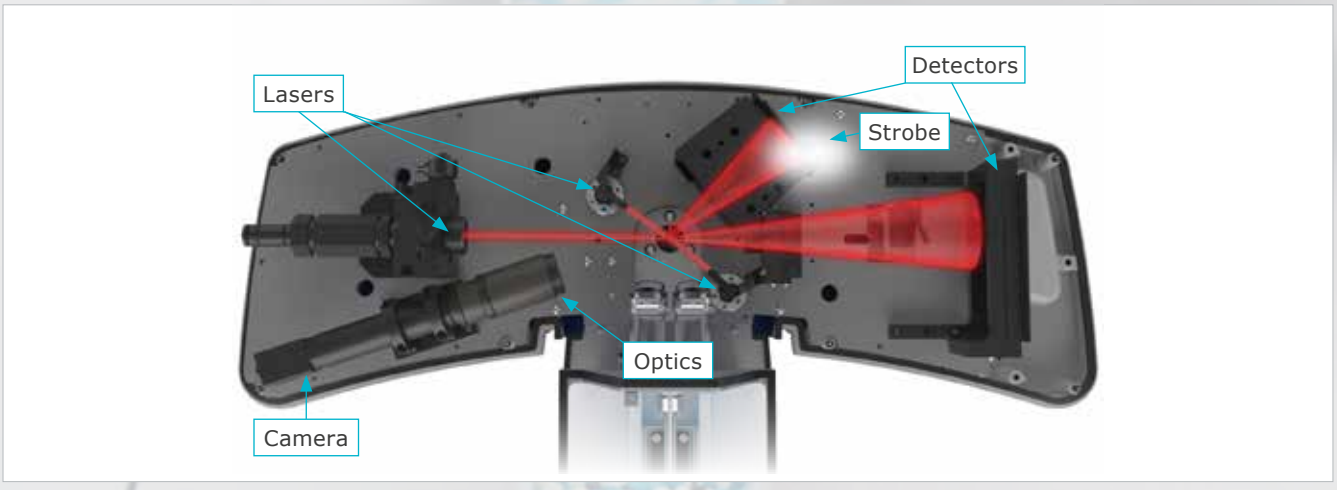


Fig. 6: Layout of the SYNC optical bench, combined LD and DIA components

The DIA post-measurement software features a Particle Viewer display (GUI) and a Scatter Diagram display. These can be used to identify and quantify the percentage of agglomerates in the metal powder batch. This allows metal powder suppliers to recycle a bad batch (too many agglomerates) before shipping to a customer, and it allows parts producers to reject a bad incoming batch and avoid wasting time and money processing it.

Both the CAMSIZER X2 and the SYNC can be relied on to quantify the agglomerates in a metal powder sample using two shape parameters. Size can't be used, because these agglomerates exist throughout the size distribution. The shape parameters consist of a parameter that measures aspect ratio and one that measures how convex the outer boundary of the particle is.

An example using the SYNC will be explained here. The parameters used will be the width to length aspect ratio (W/L Aspect Ratio) and Solidity. A particle with a solidity of 1 is a particle with a completely convex outer boundary with no concave indentations. A particle with a W/L Aspect Ratio of 1 would be a perfect sphere. In the CAMSIZER X2, the parameters are convexity (Conv) and breadth divided by length (b/l) respectively.

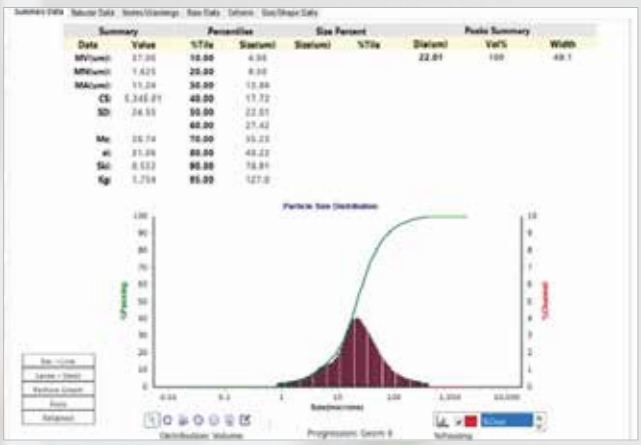


Fig. 7: LD particle size report from SYNC, including percentiles, summary statistics data and frequency / cumulative distribution graphs

The Search feature of the SYNC software was used to isolate and quantify the agglomerates, which include all particles not within the red rectangle in Fig. 9. The agglomerates were found to make up 23 % by volume and 12 % by number of the total sample. This is key QC information for the metal powder and parts industries.

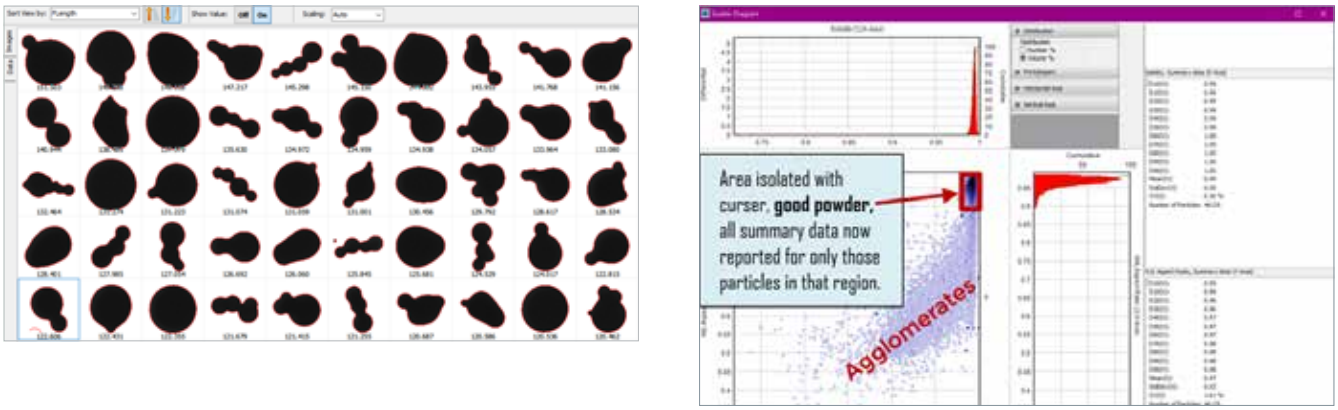


Fig. 8: Analysis of particle shape of 10 different metal powders with Dynamic Image Analysis (CAMSIZER X2). Beside the quantitative results, the recorded images allow an intuitive understanding of morphology and size differences. More spherical particles with higher aspect ratio plot on the right side of the diagram. Detecting the smallest amounts of irregular particles in a large quantity of predominantly spherical particles is a great advantage of DIA.

Advantages of DIA and LD over other particle sizing techniques

For metal powders, mechanical sieve analysis is still used by some companies for particle size analysis. The absolute lower size limit for sieve analysis is defined by the smallest practically usable mesh size of 20 µm (air jet sieving), which is well above the average particle size of many samples for AM or MIM. As a consequence, air jet sieving is not suited for the precise and reliable analysis of the whole size distribution of fine powders. It is often used for detecting the amounts of oversized particles with one sieve only, for example with 45 µm or 63 µm aperture size. Another drawback is that sieve analysis does not deliver any information on particle morphology.

The metal powder industries began replacing sieves with Laser Diffraction in the 1970's. Since then, Laser Diffraction became, and still is, widely used throughout these industries and is expected to remain their standard method for certifying and verifying particle size distributions. Laser diffraction analyzers are easy to operate, and provide fast, robust results, and their technology and characteristics are well understood. Dynamic Image Analysis is finding rapidly growing use by these industries for morphological analysis to set QC specifications on shapes to control properties that can't be identified by size analysis alone.

Comparison & Conclusion

With metal injection molding and additive manufacturing becoming increasingly prevalent techniques, there is an increased demand for specially designed metal powders with specific characteristics. Not only chemical composition, but also particle size & shape are of vital importance for the processability of powders. Depending on the application, the powder must meet a variety of specifications. Laser Diffraction size analysis for metal powders is embedded in these industries and expected to remain that way. Laser Diffraction (LD) plus Dynamic Image Analysis (DIA) with the SYNC, and DIA with the CAMSIZER X2 provide all relevant data on particle size & shape for metal powders. DIA, compared to (electron / optical) microscopy, measures a much larger number of particles and is therefore statistically more relevant and offers better reproducibility. One measurement only takes 1 to 3 minutes which allows for a high sample throughput and continuous quality control. For both powder producers and manufactures of metal parts the SYNC and CAMSIZER X2 are precise, efficient tools which greatly improve the quality control process.

Performance Feature	DIA (CAMSIZER X2 & SYNC)	Laser Diffraction	Sieve Analysis
Wide dynamic range	⊕⊕	⊕⊕⊕	⊕⊕
Reproducibility	⊕⊕⊕	⊕⊕⊕	⊕⊕
High resolution for narrow distributions	⊕⊕⊕	⊕⊕	⊖
Particle shape analysis	⊕⊕⊕	⊖	⊖
Compatibility of results with other techniques	⊕⊕⊕	⊕⊕	⊖
Reliable detection of oversize	⊕⊕⊕	⊕⊕	⊕⊕⊕
Robust, easy operation	⊕⊕⊕	⊕⊕⊕	⊖
Measurement speed, sample throughput	⊕⊕	⊕⊕⊕	⊖
Analysis of individual particles	⊕⊕⊕	⊖	⊕⊕

Characterization of Metal Powder and its AM Products – Density, surface and porosity

Measurement of the density of finely divided metal powder and porous metal bodies with a gas pycnometer (ISO 12154)

Knowledge of the density, in particular the true density, is of fundamental importance for the characterization of all materials. Density as a quotient of mass and volume is usually determined by determining these two quantities separately, and weighing the measuring is relatively simple. In the case of metallic materials, the volume is often measured on a specially manufactured cuboid test specimen or determined according to Archimedes' principle by displacement of a liquid. This is not possible with powdered metals. Therefore, gas pycnometry using an inert measuring gas such as helium is recommended here. In a measuring chamber of known volume, the gas displacement caused by an inserted specimen is determined by measuring the changed pressure. The fully automatic helium multi-volume gas pycnometer BELPYCNO L is the measuring instrument for determining the volume and density of powders, granulates and porous solids, as well as pastes and liquids. Due to an integrated temperature control (Peltier elements) it is possible to measure in the range of 14 °C to 40 °C ± 0.01 °C (at 20 °C) without influence of the room temperature. Thus, for a given temperature and sample vessel size, only a single calibration is sufficient to measure permanently with an accuracy and reproducibility of 0.01%. Due to the enormous savings in calibration time, the effective sample throughput can be significantly increased.

The multi-volume concept allows the best possible characterization of the materials to be investigated through the optimal combination of sample vessel sizes and three corresponding reference chambers. The use of a high-precision absolute pressure sensor (+/- 0.002 kPa) allows permanent correction of atmospheric pressure variations during a measurement.

Depressurizing the test gas from the reference chamber into the sample chamber (DIN 66137) reliably prevents contamination of the reference chamber by fine metal powders.

A bayonet lock ensures reproducible and easy closing of the sample chamber. Convenient operation is ensured by using computer control or as standalone system via an alphanumeric keypad and a display. These features make the BELPYCNO L perfectly suitable for very rough environments.

An integrated microprocessor controls the complete measurement and performs the calculation of the results. Interfaces allow for connection of a PC, a balance, as well as a printer. The BELPYCNO L can be equipped with a vacuum pump and optionally with a humidity sensor. The possible separation of the measuring chamber and control unit enables use of the instrument in a glove box, e.g. for applications in nuclear technology or oxygen-free handling for pure metal applications.

Furthermore, the current pressure is displayed and recorded, an essential point to determine adequate pressure equilibrium times for volume determination of very fine-pored materials [2]. Complete measurement protocols are also stored.

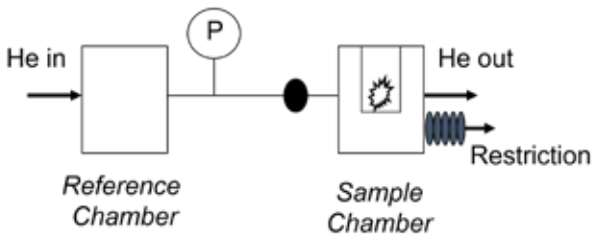


Fig. 1 Principle of the temperature-controlled helium pycnometer BELPYCNO L (DIN 66137), with absolute pressure sensor P.

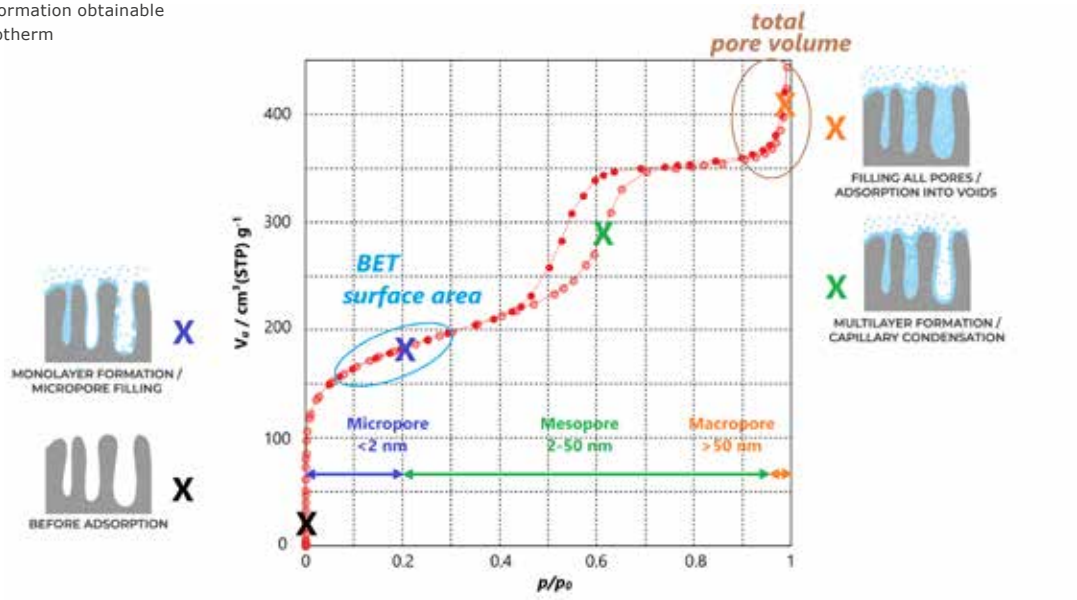
BELSORP Mini X – Determine BET surfaces of metal powders quickly, easily, accurately, and economically (ISO 15901-2, ISO 9277)

The surface area related to the mass as specific surface area (m^2/g) is an important parameter in the characterization and evaluation of metal powders and other materials. For example, the surface area is relevant for the achievable effect in catalysts, carrier materials (pharmaceuticals, electronics) and filters. Another aspect is the optimum application of coatings or, in the case of metallic powders, as a quality characteristic for processability. Sorption techniques are used in which an inert measuring gas adsorbs on the particle surface at a constant temperature near the condensation point. With increasing concentration or relative pressure, the thickness of this adsorbed layer will grow.

There are methods to calculate the number of adsorbed molecules in a monomolecular layer from such an experiment, the best known being the BET method. Knowing the surface area of a single molecule, it is easy to calculate the surface area of the whole sample. Furthermore, in case of porous materials the pore size can be determined from the measurement curve (isotherm) in the area of capillary condensation or pore filling using various models (e.g. BJH, NLDFT). As a rule, nitrogen is used as the sample gas for sorption measurements at a temperature of 77K (liquid nitrogen). Alternatively, measurements with argon gas at 87K are possible.

The BELSORP Mini X is a sorption measuring instrument which works according to the static volumetric principle. For this purpose, the sample vessel is first evacuated by a vacuum pump at liquid gas temperature, and then the sample gas is successively intruded, and the resulting increasing pressure is measured.

Fig. 2 Graphic: Information obtainable from a sorption isotherm



The adsorbed molecules generate a pressure difference from the expected theoretical pressure according to the ideal gas law. From this, the adsorbed amount and thus the adsorption isotherm are determined. After a given final pressure or saturation pressure has been reached, it is then possible to evacuate successively again and thus determine the desorption curve. Precise sorption measurements require a very accurate temperature measurement and control as well as precise pressure measurements, as technically implemented in the BELSORP Mini X.

By means of a control and evaluation software, the BELSORP Mini X can be operated from a PC to store and analyze measurement results.

In addition to pore size determinations, which typically take several hours, the purely rapid determination of BET surfaces is possible with up to 12 BET analyses per hour on the 3-port instrument - perfect for quality control of fine powders with high sample throughput.

The sum of these features results in a sorption device that meets today's quality control requirements with its accuracy and high sample throughput but can also be used in research.

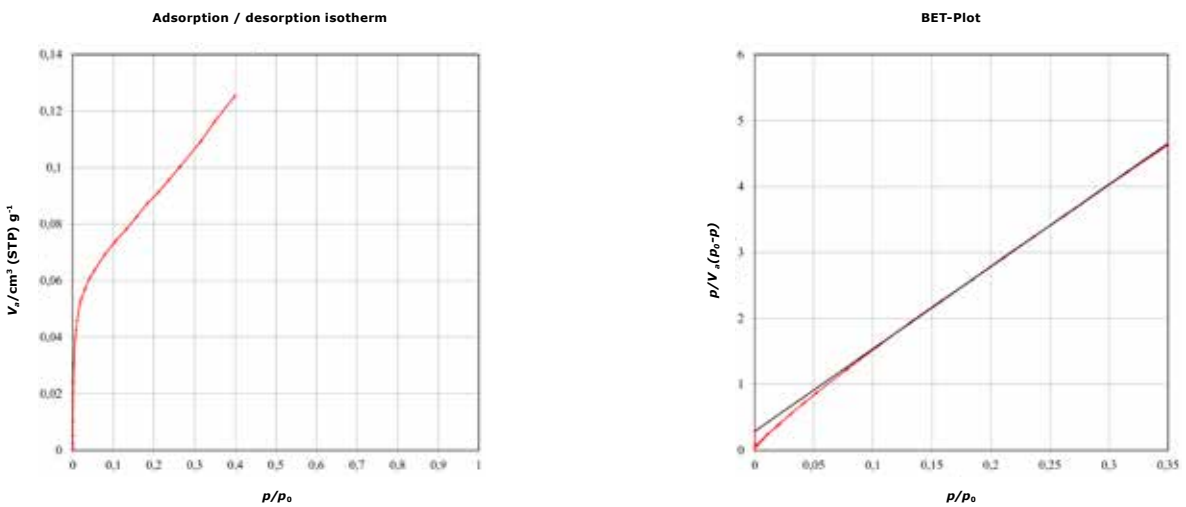


Fig. 3 BET Specific Surface Area (SSA) of Metal-powder - Lithium-Nickel-Mangan-Cobalt-Oxide with 0.34m²/g

Pore size measurement of AM manufactured porous metals with a mercury porosimeter (ISO 15901-1)

Porous materials include e.g. building materials, ceramics but also metal screens and metal foams which are produced from metal powders by additive manufacturing. Porous metals can be used for filtering particles (diesel soot), as catalyst supports or heat exchangers. On the other hand, porous metals can be interesting as components with lower density and due to their potential weight saving.

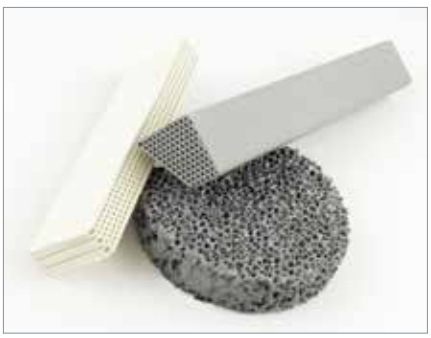
Knowledge of porosity, pore sizes and pore volume is fundamental to characterize porous materials. A widely used technique is mercury porosimetry, in which the non-wetting mercury is forced into the pores at room temperature with pressure up to 414 MPa. Any undesirable reaction of the porous metal with mercury can be prevented by passivation, e.g. by oxidation. The pore volume corresponds to the amount of mercury introduced. According to the Washburn equation, the pore size (radius, diameter) is inversely proportional to the applied pressure.

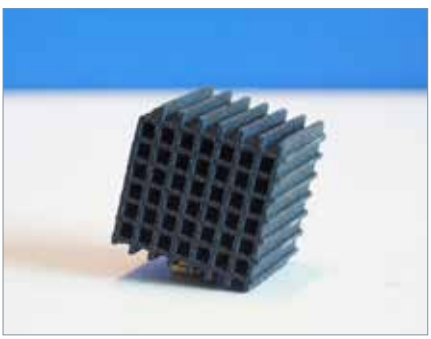
$$r = \frac{2\gamma \cos\theta}{p}$$

With pore radius r [m], surface tension of mercury γ **= 0.48 N/m**, intrusion pressure p [Pa]

With a contact angle θ **= 143.3°** a simple estimation is obtained ***r ≈ 0.7500/p***

The BELPORE mercury porosimeters measure pore diameters from 3.6 nanometers to 1 millimeter. BELPORE mercury porosimeters work according the P.A.S.C.A.L. principle which is not only a pressure unit. In the BELPORE porosimeter it means the equilibrium-controlled and optimized control of the pressure build-up by "Pressurization by Automatic Speed-up and Continuous Adjustment Logic".





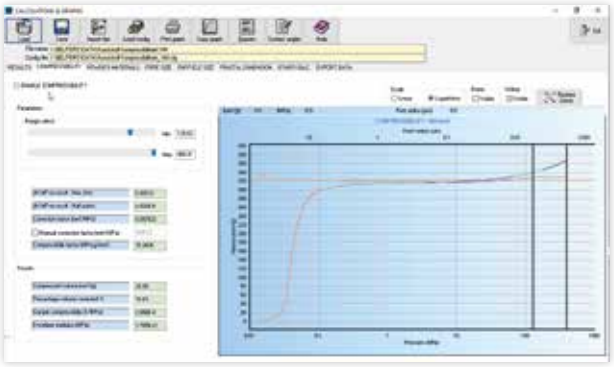


Fig. 4 Pore size distribution results

This automatic control is driven by the real pore system and allows shorter measuring times with guaranteed equilibrium conditions and detection of all pores within the specification, up to 20000 measuring points per analysis. Pressure tables are thus superfluous. Since only two types of dilatometers (sample vessels for powder or solids) are sufficient for all measuring tasks, and furthermore no gases or liquid nitrogen are required, operating costs can be kept significantly low.

Other innovations include simplified operation of the BELPORE LP low-pressure porosimeter, as well as an extended measuring range down to pore sizes of 1 millimeter! Vertical degassing and filling with mercury on the BELPORE LP allows the degassing pressure to be adjusted, and thus makes it possible to measure moist samples without changing the material moisture. The 3D evaluation software PoreXpert is optionally available. With this software, e.g. tortuousness, diffusion, percolation and much more can be derived from the porosimetry data.

BELPORE porosimeters are available in pressure ranges from 0.01 kPa to 450 kPa (and mercury filling), 0.1MPa to 228 MPa or up to 414MPa.