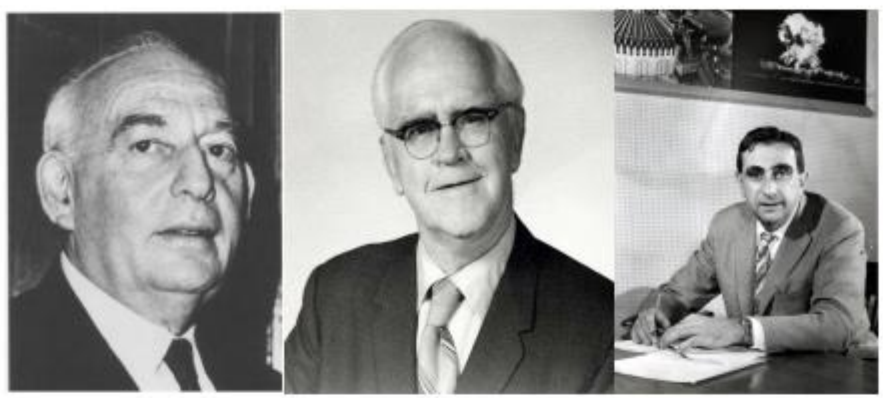
Surface Area Method

Partice size can be calculated by measuring surface area of the particles. The surface area can be measured by adsorbing of surface a monomolecular layer of a gas. The pressure of gas before and after adsorbtion is measured. From the difference in pressure, mass of the gas adsorbed by the powder surface can be calculated. From this mass, total surface area can be calculated.

This method is called BET method. In this method, surface area is used to find the particle size.

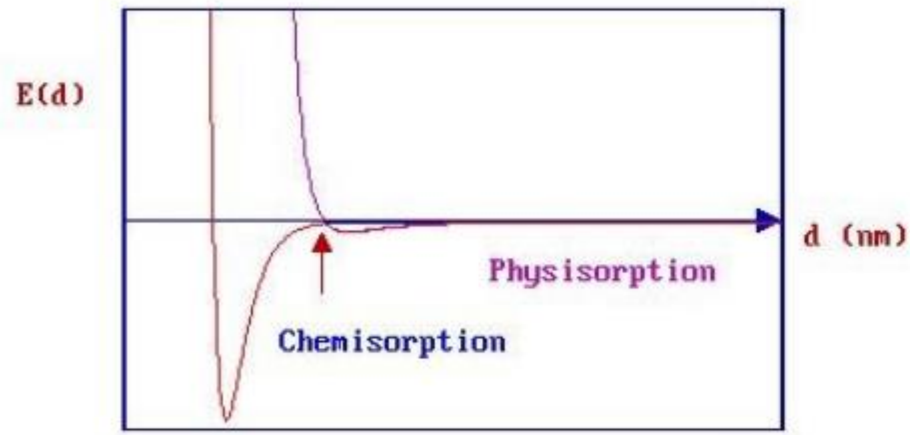


Named after Stephen Brunauer, P.H. Emmet and Edward Teller

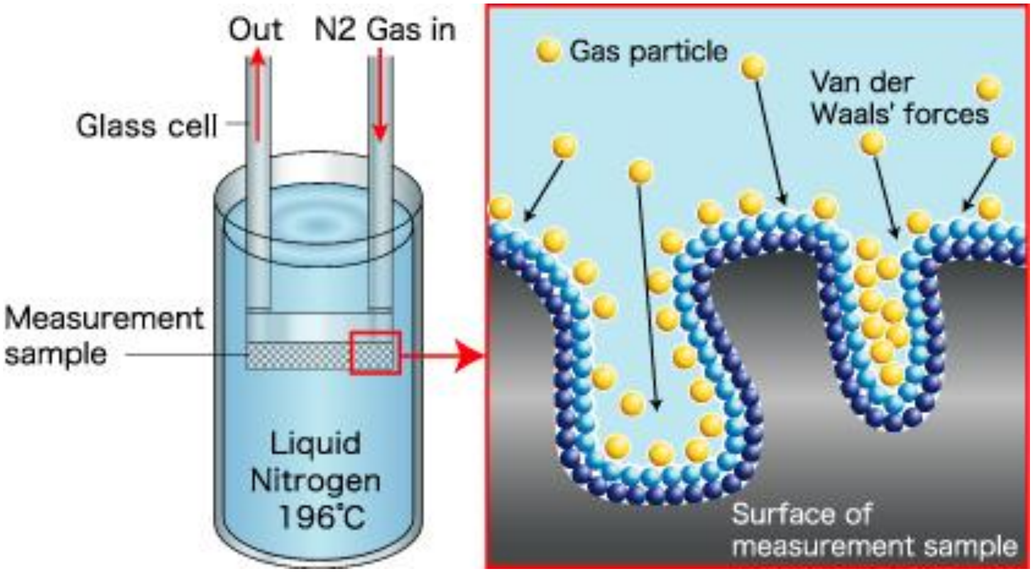
Developed in 1938

Adsorption

Adsorption versus Absorption



Consequence of surface energy. The energy is minimized in the bulk when every atom/molecule is surrounded by neighbors.



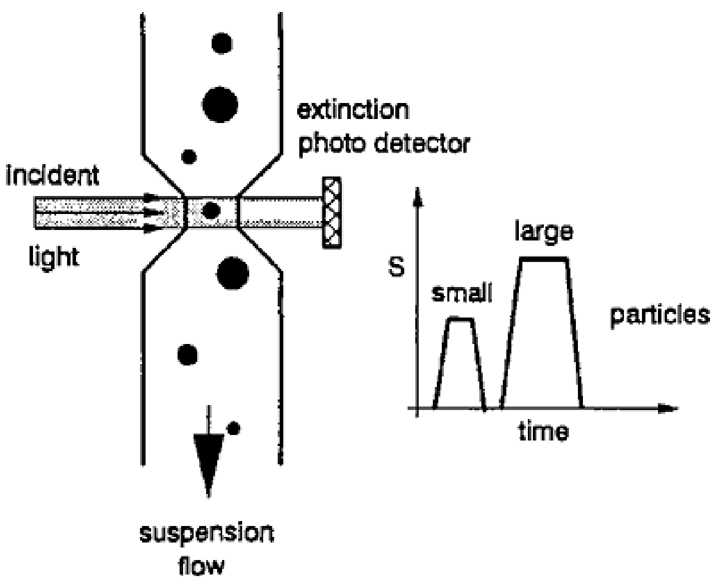
$$Surface\ Area\ of\ a\ Sphere:\ A = 4\pi r^2$$

$$r = 3/\rho S$$; S is total surface area, ρ is density

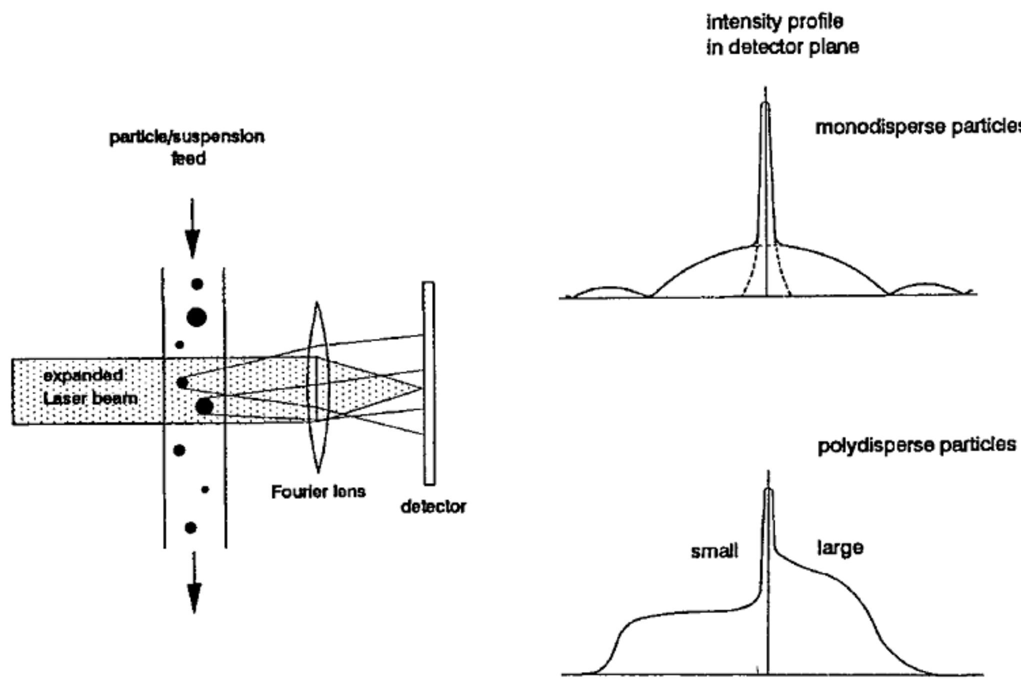
- The BET method is based on adsorption of gas on a surface
- The amount of gas adsorbed at a given pressure allows to determine the surface area
- It is a cheap, fast and reliable method
- It is very well understood and applicable in many fields

Light Scattering and Diffraction Methods

The principles of these methods are based on the interaction of an incident optical beam with a single particle. This beam can either be *absorbed, scattered,* or *transmitted.* Scattering includes *reflection, refraction* and *diffraction.*



Particle size analysis by optical counting



Particle size analysis by laser diffraction

Metal Powder Characteristics

There are a number of powder characteristics which have great effect on the particle properties. These are;

- Chemical Composition and Structure
- Particle Size and Shape
- Particle Surface Topography
- Surface Area
- Apparent and Tap Density
- Flow Rate
- Compressibility
- Green Strength
- Pyrophorocity and Toxicity

Metal Powder Characteristics

- Chemical Composition and Structure

The levels of impurity elements in metal powders can be very significant to both the processing and properties of the final product. It is necessary to know whether such elements are present in their elemental form or whether they are present in the form of a chemical compound. For example, in reduced iron powder silicon is present as impurity in the form of silica, which is insoluble in most acids. The effect of impurity elements on the hardness of the particles and the degree of chemical reactivity during sintering will differ widely, depending on the actual form they are in. The annealing of the powder in a reducing atmosphere is an effective way of reducing oxygen contents.

The **microstructure** of the crystalline powder has a significant influence on the behavior of powder during compaction and sintering and on the properties of the final product.

Fine **grain size** is always desirable, as it improves the mechanical properties apart from the sinterability and the uniformity of dimensional changes.

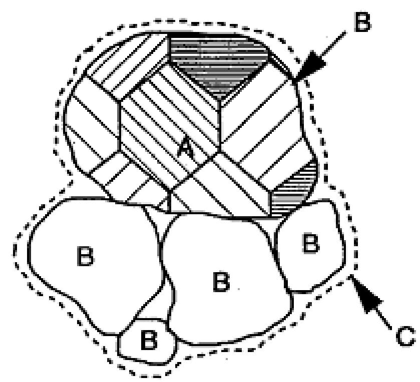
The grain size can be dependent on the powder particle size. The particular powder production method, e.g. rapidly cooled powder, would naturally give rise to small particles and also small grain sizes.

Microporosity associated with entrapped gases is also common. A cold worked powder e.g. ball milled, exhibits a high dislocation density which could be lowered by annealing.

Metal Powder Characteristics

- Partice Size and Shape

The shape of the powder is characterised by the dimensionality of the particle and its contour surface. Most powder particles are three-dimensional in nature and they may be considered as being somewhat equiaxed. Spherical particles represent the simplest and ideal example of particle shape. Porous particles differ from irregular ones because of the presence of the porosity, which itself may be very irregular in both size and shape. A large amount of porosity makes any shape characterisation very difficult.

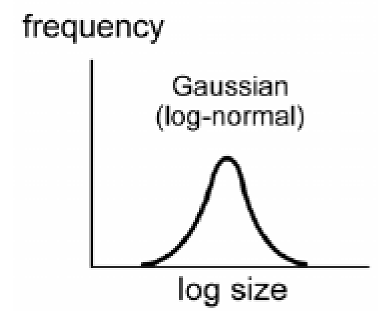


A= Grain
B= Powder Particle
C= Agglomerate

Metal Powder Characteristics

- Partice Size and Shape

In a real mass of powder, all prepared in the same manner, all the particles will not have the same exact size, even though the shape may be essentially the same. Consequently, we must deal with size distribution when accurately describing powders.

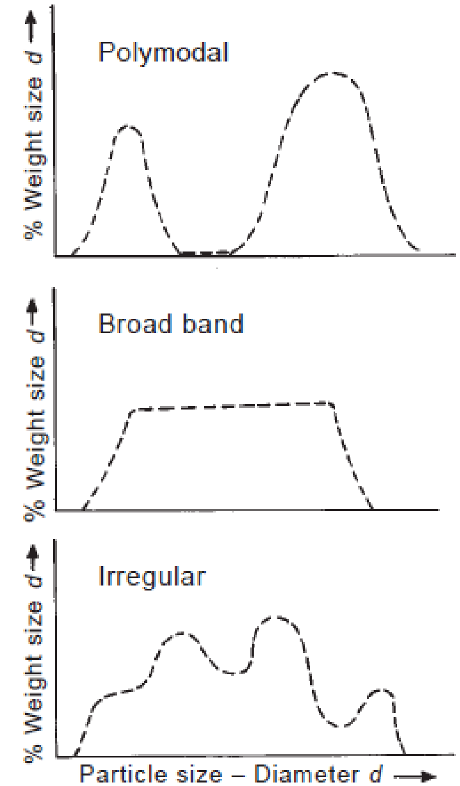


In unimodal distribution, there is one high point or maximum amount of a certain critical size.

The polymodal distribution consists of two or more narrow bands of particle sizes, each with a maximum, with virtually no particles between such band.

The broad band distribution simply corresponds to a uniform concentration of particle sizes over a rather broad size interval with virtually no particles having sizes outside this range.

The irregular distribution represents a continuous and finite variation of particle sizes within a relatively broad range.



Metal Powder Characteristics

- Partice Surface Topography

A spherical particle may appear smooth, but on a closer examination at high magnifications the surface may actually consist of many protuberances. Reduced metal powder has a highly roughened surface.

Atomized metal powders, on the other hand, have finer degree of surface roughness, which are of rounded type rather than sharp and irregular.

Scanning electron microscope is a powerful tool for examining surface topography. Surface contamination of particles and agglomeration of fine particles can also be studied by this technique.

The exact nature of surface topography will influence the frictional forces between particles. These are important in the case of bulk movement of the particles, when the powder is flowing, settling or during compaction.

Metal Powder Characteristics

- Surface Area

The actual amount of surface area per unit mass of powder is of great significance. Any reaction between the particles or between the powder and its environment starts at these surfaces. This affects sinterability. For a very irregular shaped particle with a high degree of surface roughness, the specific surface area can be very high.

The BET method of determining the specific surface is widely used for catalysts. Its use for metal powder is primarily for very fine powders, particularly those of the refractory metals and for characterizing the total surface area of porous powders.

Metal Powder Characteristics

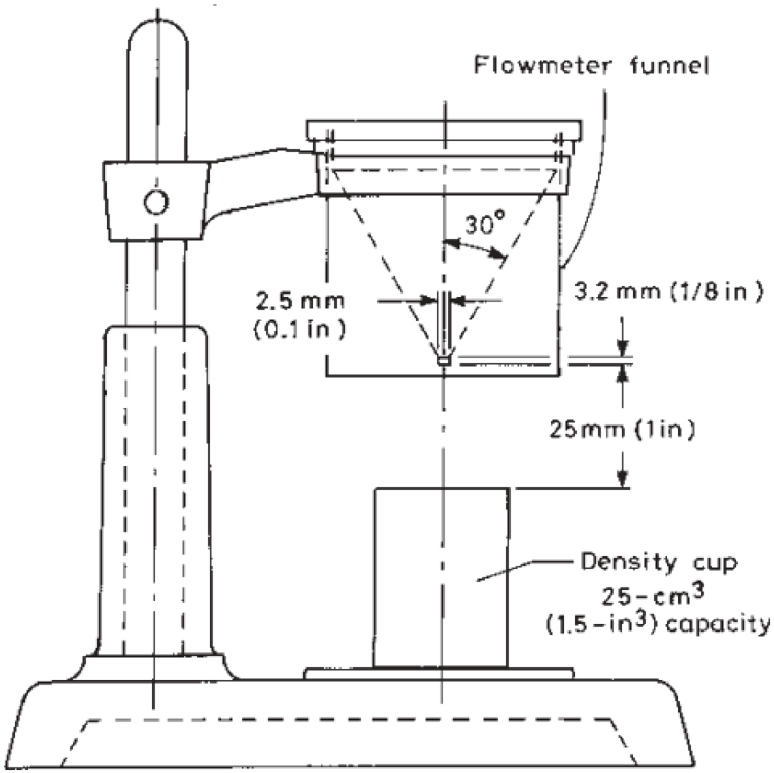
- Apparent and Tap Density

The apparent density of a powder refers to the mass of unit volume of loose powder usually expressed in g/cm^3. It is one of the most critical characteristics of a powder, because of following reasons:

(*a*) It determines the size of the compaction tooling and the magnitude of press motions necessary to compact and densify the loose powder;
(*b*) It determines the selection of equipment used to transport and treat the initial powder;
(*c*) It influences the behaviour of the powder during sintering

Other characteristics which have direct effect on apparent density are the **density of the solid material**, particle size and shape, surface area, topography and its distribution.

Apparent density is determined by the Hall flowmeter, where a container of known volume (25 ml) is completely filled by flowing metal powder through a Hall funnel



Material	Apparent density (g/cc)	Tap density (g/cc)	Percent increase
Copper (a)			
spherical	4.5	5.3	18
irregular	2.3	3.14	35
flake	0.4	0.7	75
Iron (–100+200 mesh)			
electrolytic	3.31	3.75	13
atomized	2.66	3.26	23
sponge	2.29	2.73	19
Aluminium (–200 mesh)			
atomized	0.98	1.46	49

(a) all copper powders with same size distribution; from H.H. Hausner, in: Handbook of Metal Powders, A.R.Poster, editor, Reinhold, N.Y., 1966.

Metal Powder Characteristics

- Flow Rate

The standard method for its determination is by the Hall flowmeter, where the time necessary for 50 g of powder to flow through a prescribed small orifice is measured.

Very fine powders do not flow through a small orifice. This is a result of the drastic increase in the specific surface area as the size becomes very small.

For a given metal powder, the higher the apparent density, the lower the flow time.

Metal Powder Characteristics

- Compressibility

Compressibility is a measure to which a powder will compress or densify upon application of external pressure. Compressibility is reported as the density in g/cm^3, rounded to the nearest 0.01 g/cm3, at a specified compaction pressure, or as the pressure needed to reach a specified density. Typically, a cylinder or rectangular test piece is made by pressing powder in a die, with pressure applied simultaneously from top and bottom.

Compressibility of the powder is influenced by factors like:

- inherent hardness of the concerned metal or alloy,
- particle shape,
- internal porosity,
- Particle size distribution,
- presence of nonmetallics,
- addition of alloying elements or solid lubricants.

Compressibility, alternatively, is defined in terms of the densification parameter, which is equal to:

$$\text{Densification parameter} = \frac{\text{Green density} - \text{Apparent density}}{\text{Theoretical density} - \text{Apparent density}}$$

Compressibility, in general, increases with increasing apparent density. A rather large amount of densification occurs at relatively low compaction pressure.

Another term, which is very important for tooling design, is the compression ratio.

It is the ratio of the volume of loose powder to the volume of the compact made from it. A low compression ratio is desirable because of following reasons:

- Size of the die cavity and tooling can be reduced
- Breakage and wear of tooling is reduced
- Press motion can be reduced
- A faster die fill and therefore a higher production rate can be achieved.

Metal Powder Characteristics

- Green Strength

Green strength is the mechanical strength of a green – i.e. unsintered powder compact. This characteristic is very important, as it determines the ability of a green compact to maintain its size and shape during handling prior to sintering.

Green strength is promoted by:
– increasing particle surface roughness, since more sites are available for mechanical interlocking;
– increasing the powder surface area. This is achieved by increasing the irregularity and reducing the particle size;
– decreasing the powder apparent density. This is a consequence of first two factors;
– decreasing particle surface oxidation and contamination;
– increasing compaction pressure
– decreasing (optimizing) the amount of interfering additives.

Metal Powder Characteristics

- Pyrophorocity and Toxicity

Pyrophorocity is a potential danger for many metals, including the more common types, when they are in a finely divided form with large surface area-to-volume ratios.

The toxicity of powder is normally related to inhalation or ingestion of the material and the resulting toxic effect.

The chemical reactivity of a material increases as the ratio of surface area-to-volume increases. For this reason, fine particles of many materials combine with oxygen, ignite and result in explosive conditions.

Metal Powder Treatment

Only in exceptional cases metal or ceramic powders can be introduced directly into a powder metallurgy shaping operation.

Usually, additional treatments are required to make a powder suitable for further processing. These operations are often summarized by the term 'powder conditioning'. They depend on the nature of the powder, the size and shape of the final part, and the subsequent operations to be carried out.

HEAT TREATMENT

Raw powders resulting from various production processes often exhibit a reduced compressibility, due to rapid cooling during atomization, work hardening from mechanical comminution, residual interstitial impurities such as oxygen, carbon or nitrogen, and to oxide layers formed during production or storage.

Annealing is therefore common for many metal powders, when a good subsequent compressibility is required.

Annealing

The aims of annealing are:
1) to soften the powder
2) to reduce the residual amount of oxygen, carbon and/or nitrogen from the powder.

The annealing operation may be done in an atmosphere furnace or a vacuum furnace.

Annealing temperatures are kept as low as possible to minimize sintering.

Powder Mixing

The term ‘blending’ is strictly applied to a one component operation, whereas mixing involves more than one type of powder, e.g. mixing of solid lubricant with a metal powder or powders of several other metals. Sometimes the additive acts as lubricant as well as alloying addition, e.g. graphite in iron powder

Mixing efficiency is best when the powder volume is about 50% to 60% of the mixer volume. Optimum mixing time may be from between 5 to 30 minutes but this can be determined only by experience with a given mixture in a particular mixer. The aim is to mix the powders only as long as necessary to achieve a thorough mix and to fix a uniform apparent density of the mix from batch to batch.

Particle Size Reduction

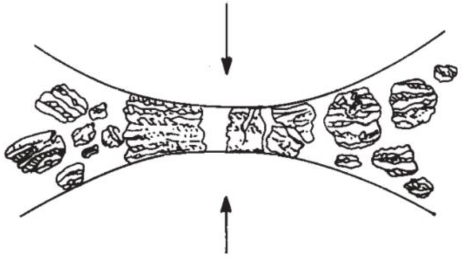
Suitable size reduction processes normally produce an increase in the surface area (as a result of decreasing the average particle size) with narrow particle size distribution

This results in increased homogeneity of nonuniform mixtures, increased chemical reaction rate.

The actual requirements of a suitable size reduction process are extremely varied and depend on several parameters.

(*i*) **Crushing**: The major equipments are mortar and pestle, heavy drop hammer, and jaw crushers.

(*ii*) **Ball Milling**:



Effect of single collision between two balls on trapped powder

The ductile elemental metal powders are flattened, and where they overlap, the atomically clean surfaces just created weld together, building up layers of composite powder.

At the same time, work hardened elemental or composite powders fracture. These competing processes of cold welding and fracture occur repeatedly throughout the milling, gradually kneading the composites so that their structure is continually refined and homogenized.

Granulation

Fine hard particles such as tungsten, molybdenum and WC–Co are non-freeflowing and are difficult to press. Moreover the handling of such fine particles is also difficult. Consequently, large agglomerates are formed by granulation method. In this case, the continuous stirring of powder-organic slurry is used, while the volatile agent is removed by heating.

Granulation

One of the better form of processing the slurry is known as **spray drying**. The slurry is sprayed into a heated free-fall chamber where surface tension forms spherical agglomerates. Heating of the agglomerate during free fall causes vaporization of the volatile agent, giving a hard dense packed agglomerate.

Three standard techniques are used to atomize slurry for spray drying:

1. single-fluid nozzle atomization;
2. centrifugal (rotating disc) atomization,
3. two-fluid nozzle atomization.

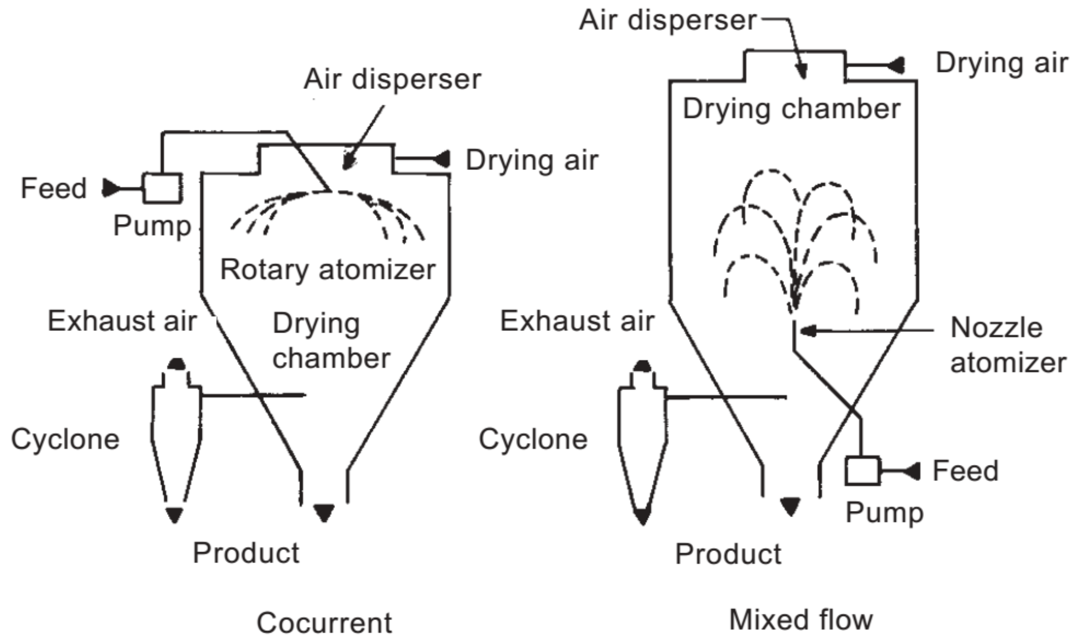
The largest agglomerate sizes(600 μm) are achieved by the single-fluid nozzle. The centrifugal atomizer yields agglomerate sizes up to 300 μm, and the two-fluid nozzle produces agglomerates only up to about 200 μm in size.

Suitable binder materials must be homogeneously dispersable (preferably soluble) in the liquid used to form the slurry. Plasticizers, e.g. ethylene glycol, may be used with binding materials that are hard or brittle and that tend to crack during drying.

Suspending agents, e.g. sodium carboxymethyl cellulose, may be needed to prevent solids from settling within the slurry.

Deflocculating agents, e.g. sodium hexametaphosphate, aids in the formation of slurry by preventing the agglomeration of fine particles.

Wetting agents, e.g. synthetic detergents, also may be used to maintain solids in suspension



The atomized slurry is of maximum liquid content when it encounters the laminar flow of hot incoming air. The maximum product temperature is relatively low and the evaporation time is relatively short. The atomizer and the inlet for the drying air are positioned at the top of the dryer.

Fine products in the exhaust air are separated using a cyclone or bag filters. They may be used in some pressing operations, but are often recycled into the feed slurry.

A **major precaution** in spray drying is the fact that the granules should not be so strong that it does not loose its identity during compaction.

A **disadvantage** is that the organic binder must be removed in the sintering cycle.

It is used generally for most ceramic powders and for hard metal powder mixtures

Coating on Metal Powders

In number of cases, the base metal powders may be coated by another chemical species. The purpose may be to produce a homogeneous mixing, e.g. W–Cu, a hard surface or deposition of soft low melting point metals on ceramics to give better compressibility during compaction. One of the simplest method may be the mechanical method, say **ball milling** of WC– Co.

However, the uniformity of coating in such case is questionable. Some of the more common methods

Electroplating, Electroless Deposition and

Coating by Hydrometallurgical Process

Applications of Powder Fabrication Techniques

Materials	Common Methods
Alloy steels (e.g. tool steel)	water atomization, gas atomization, centrifugal atomization
Alumina	milling
Aluminum	air atomization, gas atomization, milling
Beryllium	milling, gas atomization
Cemented carbide (WC-Co)	milling, attritor milling
Cobalt	oxide reduction, chemical precipitation
Composites (e.g. Al-SiC)	mechanical alloying, plasma atomization
Copper	electrolytic, water atomization, gas atomization, chemical precipitation, oxide reduction, salt decomposition
Copper alloys (e.g. brass)	water atomization, air atomization
Gold	electrolytic, air atomization, chemical precipitation
Intermetallics (e.g. NiAl)	gas atomization, reactive synthesis, centrifugal atomization

Characteristics of Fabricated Metal Powders

Powder	Process	Shape	D_{50}, µm	O_2, ppm	Apparent density, g/cm^3	Tap density, g/cm^3	Flow time, s
Al	gas atomized	spherical	30	6000	1.3	1.4	nf
Al alloy	air atomized	rounded	65	11000	0.9	1.4	—
Ag	milled	flake	10	100	1.5	—	nf
Au	air atomized	spherical	130	50	7.8	11.9	—
brass	water atomized	irregular	38	800	2.7	3.3	35
bronze	air atomized	spherical	125	700	5.0	5.4	—
Co alloy	gas atomized	spherical	90	400	4.3	5.2	—
Cu	water atomized	nodular	62	3300	2.3	3.4	48
Cu	electrolytic	dendritic	40	1700	2.8	3.6	29
Fe	water atomized	irregular	75	1100	2.9	3.4	26
Fe	gas atomized	spherical	66	1500	4.5	5.0	9
Fe	carbonyl	spherical	5	3800	2.7	4.3	nf
Fe	oxide reduced	porous	50	10000	1.9	3.0	35
Fe	centrifugal	spherical	75	1000	4.7	5.0	14
Hf	milled	angular	9	1200	4.2	6.5	nf

Characteristics of Fabricated Metal Powders

Powder	Process	Shape	D_{50}, µm	O_2, ppm	Apparent density, g/cm^3	Tap density, g/cm^3	Flow time, s
Mo	oxide reduced	angular	6	1200	2.0	3.1	nf
Nb	hydride milled	angular	10	3800	0.9	1.0	nf
Ni	hydromet	spherical	1	4000	1.3	2.6	nf
Ni	carbonyl	spiky	5	1500	2.5	3.3	nf
Ni_3Al	reactive	rounded	14	2000	3.1	3.8	nf
Pb	water atomized	ligamental	42	3000	5.2	—	24
Sn	air atomized	ligamental	18	7000	3.3	—	nf
stainless	gas atomized	spherical	12	1000	3.8	4.7	38
stainless	water atomized	irregular	60	2000	2.6	3.7	30
Ta	hydride milled	angular	9	1700	3.7	5.8	50
Ti	chloride	sponge	75	1500	2.0	2.5	nf
TiAl	gas atomized	spherical	180	800	2.2	2.4	30
Ti alloy	centrifugal	spherical	175	1300	2.6	2.9	28
tool steel	water atomized	nodular	70	1000	1.8	2.4	50
WC-Co	attritor milled	angular	0.7	800	2.5	4.3	nf
W	oxide reduced	polygonal	3	640	3.4	6.7	nf

Production Cost

Fabrication Route	**Cost range, $/kg**
carbonyl decomposition	7 – 10
centrifugal atomization	4 – 20
electrolytic deposition	6 – 10
gas atomization	3 -18
hydrothermal	6 – 25
mechanical alloying	10 – 40
milling	2 – 12
oxide reduction	1 – 2
plasma atomization	6 – 40
reaction synthesis	2 – 12
sol-gel precipitation	10 – 80
vapor condensation	100 – 1000
water atomization	1 - 2