Physical Methods

- Atomization
  - Gas Atomization
  - Water Atomization
  - Cyrogenics Liquid Atomization
  - Centrifugal Atomization
Atomization

Atomization is the most important production method for metal powders. The process generally consists of three stages:

- melting
- atomization (dispersion of the melt into droplets)
- solidification and cooling.

Additional processing becomes necessary before the powders attain their desired properties, (reduction of surface oxides, degassing, size classification, etc.)
Classification

For each of the process stages different methods can be used, resulting in a large number of variants.

<table>
<thead>
<tr>
<th>Crucibles/Liners</th>
<th>Heating Source</th>
<th>Melt Volume</th>
<th>Energy Input</th>
<th>Solidification/Cooling</th>
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<td>melt pool</td>
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<td>electron beam</td>
<td>melt droplet</td>
<td>ultrasonic vibrations</td>
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</table>

- commercially used; ○ experimental state
Melting

• In this stage **the most important criterion** is whether melting and melt distribution require a crucible system or not. Crucibles are one of the main sources for contamination of atomized powders.

• The **second criterion** is the heating source. Essentially all melting techniques known in metallurgy can be used, e.g., induction, arc, plasma, and electron-beam melting, but some of these may also contribute to contamination, as for example in arc melting.
Solidification

During the solidification and cooling stage, the cooling rate is the controlling parameter.

Cooling rate depends on:

- the dimensions of the liquid droplets or solid powder particles,
- the type of heat transfer from the particles to the surrounding medium.

The undercooling prior to nucleation and cooling rate are the controlling factors for determining the microstructure of the powder particles, as well as for the dimensions of the atomization unit.

Depending on the parameters in each stage various disintegration methods are possible:
Disintegration/Dispersion

Disintegration step:
The energy for disintegration introduced into the melt; by capillary forces (melt drop process),
mechanical impact (impact disintegration),
electrostatic forces (electrodynamic atomization),
liquid or gas streams or jets (liquid or gas atomization),
centrifugal forces (centrifugal atomization),
gas supersaturation of the melt (vacuum atomization),
or ultrasonics (ultrasonic atomization).
Gas Atomization

Air, nitrogen, argon or helium are used, depending on the requirements determined by the metal to be atomized.

Here, melted initial material is collapse with the gas within the chamber. Heat is transfered from the liquid droplets to the surrounding gas. And liquid solidifies.

Vertical atomisation unit

Atomization can be undertaken either in vertical or horizontal units.
Gas Atomization

Production of Fine Particles:

• a high velocity of the atomizing fluid
• small melt stream (droplet) diameters
• high density, and low viscosity and surface tension of the melt

The nozzle design is an important key to success or failure of a gas atomization system.
Gas Atomization

The mean particle size of gas atomized powders is in the range of 20-300 µm.

The particle shape is spherical or close to spherical. Irregular particle shapes can only be produced in systems where reactions between the gas and the liquid metal cause the formation of solid surface layers. This is the case, for example, in the air atomization of aluminium.
Gas Atomization

- Melt atomization by air is used in the production of the so-called 'Roheisen Zunder' (RZ) iron powder. This process starts from a cast iron melt. The surface oxides formed during atomization are reduced by the inherent carbon of the cast iron particles during a simple subsequent annealing treatment.

\[ 3\text{Fe}_3\text{C} + \text{Fe}_3\text{O}_4 \rightarrow 12\text{Fe} + 2\text{CO} + \text{CO}_2 \]
Inert gas atomisation is applicable for all metallic alloys which can be melted. The main application is for high alloy products such as stainless steel, tool steels, iron, nickel- or cobalt-base superalloy powders, as well as aluminium alloy powders.

Limiting factors are the availability of suitable crucible and auxiliary/helpful melting process materials. Powders from refractory metals with high melting temperature and highly reactive materials, such as titanium alloys, are usually produced by other methods.
Physical methods

Liquid atomization

• Water atomization  Cyrogenics Liquid atomization

Water atomization,
Water atomisation is mainly used for the production of iron base powders. Figure shows a scheme for a water atomisation unit.

The starting material is melted and metallurgically treated in a separate furnace and then fed into a tundish. The tundish provides a uniformly flowing vertical melt stream, which is disintegrated into droplets in the focal area of an arrangement of several water jets.

The impact from the high pressure stream of water leads to disintegration of the flowing metal.

A high energy input to the water stream is needed.

Scheme for a water atomisation unit.
In water atomization, a high pressure water stream is forced through nozzles to form a disperse phase of droplets which then impact the metal stream. In this method, large quantities of energy are required to supply the water at high pressure.

This production method is significant for low and high alloy steels, including stainless steel.

Because of oxide formation, water atomization is not likely to be used in the atomization of highly reactive metals such as titanium and the super alloys. In general, water atomized powders are irregular in shape, with rough oxidized surfaces.
Liquid atomization

- Water atomization
- Cryogenics Liquid atomization

**In cryogenic liquid atomisation,** The Krupp Company (Germany) introduced a novel version of atomization in which the melt is atomised with cryogenic liquid gas (argon or nitrogen) at −200 °C. During the process, the pressure of the liquid gas is increased up to 300 bar, while a recooling unit prevents the temperature from rising in spite of compression and prevents the cryogenic liquid from vaporizing instantaneously at the jet opening.
**Liquid atomization**

- Water atomization: Cyrogenics Liquid atomization

*In cyrogenic liquid atomisation.*

The resulting powder has the following properties:

– It is much purer than the powder atomized with water and can be compared to the quality of the gas atomized powder.

– The cooling rate is ten times higher than in gas atomization and almost reaches the quality of water atomization. Particles of 100 µm in diameter, for example, are quenched for approximately 106 K/s.

– The powders are, as in gas atomization, spherical and have an average size of 6–125 µm. show satisfactory results in cold forming, while having a good flowability. Gas atomized powders have poor green strength
**Centrifugal atomization**

The basis of centrifugal atomization is the ejection of molten metal from a rapidly spinning container, plate or disc.

- The material in the form of a rod electrode is rotated rapidly while being melted at one end by an electric arc. Molten metal spins off the bar and solidifies before hitting the walls of the inert gas filled outer container.
Centrifugual atomization

The process was developed primarily for the atomization by high purity low oxygen content titanium alloys and superalloys.

Powder particles are smooth and spherical with an average diameter of \(~200\, \mu m\); the size range is \(50\text{–}400\, \mu m\). Typically, yields run to \(~75\%\) for \(-35\) mesh powder.
Centrifugal atomization

Particle size distribution

• Accurately controlled rotation of the anode is important so as to obtain in a desired range.

• as the surface tension of the liquid metal, centrifugal forces (related to rotation speed) to some extent by the ‘aerodynamics’ of the droplets trajectory through the inert cover gas.
Centrifugal atomization

• Spherical metal powders made by either REP (rotating electrode process) or gas atomization are not well suited for cold pressing into green compacts to be followed by sintering. They are used in more specialized applications where consolidation is achieved by hot isostatic pressing (HIP) or some other high temperature method in which inter particle voids are more readily closed.
ATOMIZATION

Solidification and Cooling
The cooling rate → the powder particle shape, and microstructure

Cooling occurs by
• heat transfer via radiation
• heat flow through the medium which is in contact with the melt.

The cooling rate during solidification depends on;
• The melt volume
• The heat flow

Small melt volumes favor rapid cooling.
Atomization under vacuum or reduced pressure conditions results in relatively low cooling rates
ATOMIZATION

The microstructure of the powder particles is determined by nucleation and growth factors.

• After nucleation has occurred, the relation of the growth rate of the solid from the liquid and the diffusion rate in the liquid determines the microstructure.

A large undercooling increases the growth/diffusion ratio. Low growth/diffusion ratios result in dendritic microstructures as a consequence of segregation.

With increasing cooling rate, the particles tend to form microcrystalline structures, combined with other non-equilibrium states such as high defect concentrations or metastable phases, which promote sintering effectively. Even non-crystalline (amorphous) structures can be obtained.
Spherical particles result from the solidifying droplets in gas and centrifugal atomization as a result of surface tension. Water atomised powders can be produced with very irregular particle shapes for high green strength requirements, but particles close to spherical can also be produced if good flowability and tap density are required.
**Advantages of atomization.**

1. Freedom to alloy
2. All particles have the same uniform composition
3. Control of particle shape, size and structure
4. High purity
5. Lower capital cost

**Fine particle sizes are favored by:**

(a) Low metal viscosity
(b) Low metal surface tension
(c) Superheated metal
(d) Small nozzle diameter, i.e. low metal feed rate.
(e) High atomizing pressure
Atomization

Sphericity of a metal powder is favoured by:
(a) High metal surface tension
(b) Narrow melting range
(c) High pouring temperature
(d) Gas atomization, especially inert gas
(e) Long flight paths

Trends for Future Development

• ultra-high purity
  ultra-rapid cooling rate
  ultra-fine particle size
Powder characterization and microstructure control in powders

The success of any powder metallurgical process depends to a great extent on the complete characterization and control of the metal powders.

These properties also influence the behavior of the powder during compaction and sintering, and the composition, structure and properties of the sintered material.
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.

- Practically any metal powder adsorbs significant quantities of gases and water vapour from the atmosphere during storage.
  - The amount of such contamination increases with decreasing particle size and with increasing chemical activity of the surface.
Some of Chemical Characterization Techniques:
- XRF
- XRD
- EDX or EDXS

XRF; X-Ray Fluorescence
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</table>

**Key to Energy Values in keV**

- 0.052
- 0.110
- 0.245
- 0.463
- 0.843
- 1.61
- 3.22
- 6.45
- 12.8
- 25.6
- 51.2
- 102.4
- 204.8
- 409.6
- 819.2
- 1638.4
- 3276.8
- 6553.6

**Actinides 90-103**

- Lanthanides 57-71
- Actinium - An 93
- Americium - Am 95
- Thorium - Th 90
- Uranium - U 92
X-ray Diffraction

$n\lambda = 2d\sin \theta$ - Bragg's Law
X-Ray Diffraction

\[ t = \frac{0.9 \lambda}{B_{\text{size}} \cos \theta_B} \]

**Scherrer Equation**

Useful for particles less than 100nm

**a**

- **AgO\textsubscript{x}**
  - (O/Ag = 10 at%)
  - \(\text{Ag}_2\text{O}(111)\)
  - \(\text{AgO}(220)\)
  - \(\text{Ag}_2\text{O}(220)\)

**b**

- **Ag (111)**
  - FWHM: 1.13°

- **AgO\textsubscript{x}**
  - (O/Ag = 10 at%)
  - \(\text{Ag}_2\text{O}(220)\)

- **Ag**
  - FWHM: 0.425°
Optical Microscope

The optical microscope method is applicable to particles in the size range 0.8-150 μm. Below that, Electron Microscopy is needed.
**Optical Microscope**

There are image analyser programs to determine particle sizes and distribution from the optical (and/or electron) microscopy images.
Scanning Electron Microscopy

It is also a direct method to measure particle size of the particles. Optical microscopy or electron microscopy can be used to determine particle size.
Scanning Electron Microscopy

Primary Electron Beam

Secondary Electrons
(nm range)

Auger Electrons
5-75 Å Analysis Depth

Backscattered Electrons
(several 10’s of nm to 100 nm)

Characteristic X-rays
1-3 μm Analysis Depth

Samples Surface

Volume of Primary Excitation

1–3 μm
Energy Dispersive X-ray Spectroscopy
Transmission Electron Microscopy
Transmission Electron Microscopy
Sieving

Sieving is used to separate particles according to their particle sizes.
### Sieving

Table shows sieve numbers and their corresponding openings in mm and inches.

<table>
<thead>
<tr>
<th>U.S. Sieve Number</th>
<th>Particle Size</th>
<th>Tyler Screen Scale Equivalent</th>
<th>Sieve Opening Millimeters</th>
<th>Sieve Opening Inches</th>
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Sedimentation

If a particle with diameter \(d\) is dropped into a liquid, two forces act on it. Gravitational force and and the upward thrust of the liquid. (check the units)

Stokes Law

- Drag force \(F_d = 6\pi\eta ru\)
  \(\eta = \) viscosity

- Force of gravity
  \(F_g = \frac{4}{3}\pi r^3 (\rho_s - \rho_f)g\)

- At terminal velocity \(F_g = F_d\)

- Solve for velocity
  \[ u = \frac{d^2 g (\rho_s - \rho_f)}{18\eta} \]

Gravity sedimentation is useful for particle size range 0.2 – 100 \(\mu\)m.
Sedimentation

After calculations, Reynold’s number must be checked. If $R<2$, the result is real. If $R>2$, result is not real.

\[ R = \frac{\rho \nu d}{\eta} \]

\[ C_d = \frac{24}{N_{Re}} + \frac{3}{\sqrt{R}} + 0.34 \]

\[ \nu^2 = \frac{4g(\rho_p - \rho)d}{3 C_d \rho} \]

where; $C_d$ is drag coefficient, $\rho$ is density of fluid, $\nu$ is settling velocity, $\eta$ is the viscosity, $d$ is diameter of particle