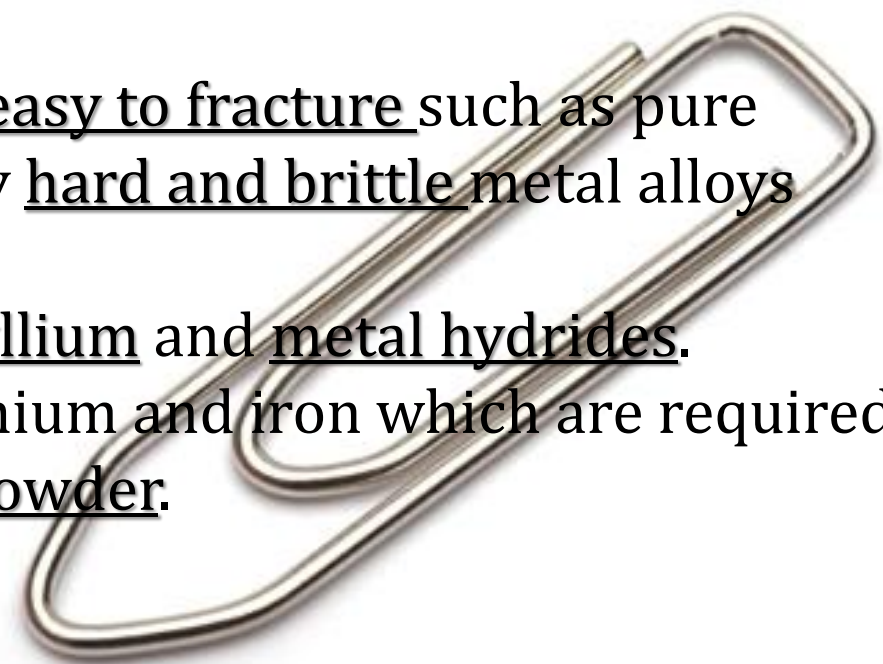# Milling

These processes are <u>not much used as primary methods</u> for the production of <u>metal</u> powders. Mechanical comminution is possible by methods such as <u>impact</u>, <u>attrition</u>, <u>shear</u> and <u>compression</u>. The formation of metal powders by mechanical methods relies on various combinations of these four basic mechanisms. Such methods have been used as the primary process for the following cases:

– materials which are relatively <u>easy to fracture</u> such as pure antimony and bismuth, relatively <u>hard and brittle</u> metal alloys and ceramics.

– reactive materials such as <u>beryllium</u> and <u>metal hydrides</u>.

– common metals such as aluminium and iron which are required sometimes in the form of <u>flake powder</u>.

Milling

- Milling is oldest in powder metallurgy and ceramics
- Effective in brittle materials.
- Less effective in metallic materials (ductile)
- Alloys can be effectively grinded by mechanical means

Additionally, there are important mechanical disintegration process in powder metallurgy , in high-energy milling severe embrittlement of the metal may occur.

Milling

The general phenomena during size reduction in the solid state are based on fracture mechanics:

- the nucleation of cracks,

- crack propagation

- fracture, by which new surfaces are formed.

The kinetic energy within the milling aggregate is partially transformed into mechanical stresses in the material causing disintegration (break up).

Milling

The forces acting in these processes cause;

- compression
- shear stresses

applied by the milling balls during vessel rotation or by the rotating arms in an attritor. (impact)

The limit of the minimum obtainable particle size depends on
- the condition of the mechanical process
- the material

- The smaller the particle size → necessary shear stress increases on each particle in order to achieve further particle fracture.

- Small particles exhibit higher surface activity than larger ones and therefore, have a higher probability of being re-welded.

The efficiency of mechanical size-reduction processes is generally very low.

- Only about 0.1 % of the spent energy in the conventional ball milling process is found in the generated new surfaces of the fine particles.

- The efficiency may be somewhat higher in high energy milling processes but is still less than 1 %.

The sources of lost energy:

- elastic and plastic deformation of the particles
- the kinetic energy of the particles in motion, impact and friction energy in the form of heat outside the powder, etc.

The main cause of lost energy, however, is the generation of heat.

Optimizing Milling Efficiency

conventional steel ball mills, size and number of milling balls→up 40-50% of the vessel volume.

size of the balls → 12 and 16 mm(about 10-20 times larger than the initial size of the particles)

other types of fine-milling equipments; planetary ball milling, centrifugal milling and attritor milling.
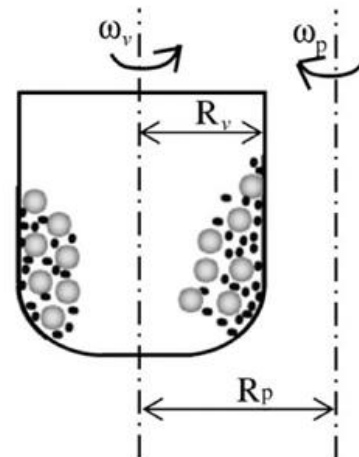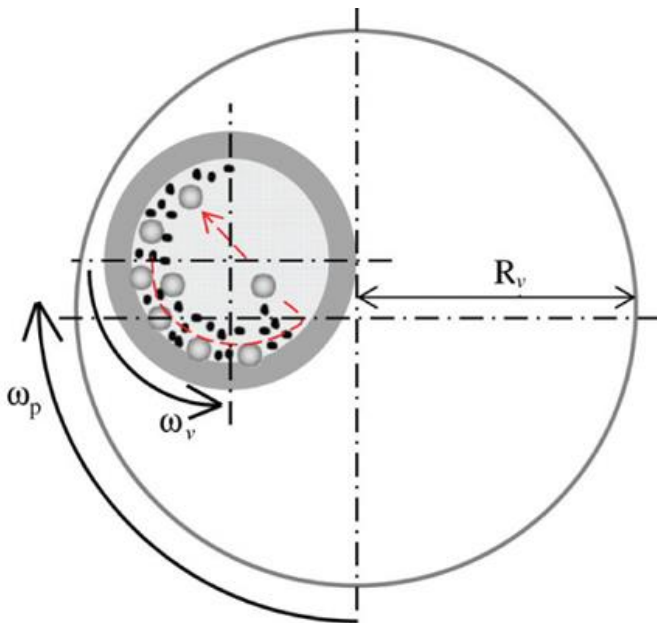
Optimizing Milling Efficiency

<u>Wet Milling</u> instead of dry milling is often advantageous because liquids tend to break up agglomerates as well as reducing re-welding of powder particles.

As milling media, hydrocarbons (hexane, heptane), ethanol and other organic liquids, which help to avoid oxidation of the milled product, are often used.

Impurities

During the milling of hard and abrasive powders the *level of impurities* sometimes rises considerably, because of severe wear loss from walls and milling media.

Rubber liners and ceramic balls which cause less contamination are sometimes advisable.

- Iron contamination can be removed by subsequent acid leaching, if the milled powder itself is acid-resistant.

Impurities

- Rubber liners and ceramic balls (Al_2O_3 or ZrO_2) which cause less contamination are sometimes advisable.

  Cubic Zirconia has a rating of approximately 8 on Mohs hardness scale vs. a rating of 10 for diamond

  Alumina has a rating of approximately 9 on Mohs hardness scale vs. a rating of 10 for diamond

- The best but most expensive solution is to use liners and balls of similar composition to that of the material being milled (e.g., the milling of special ceramic powders, like Si_3N_4)

Attritor Mill
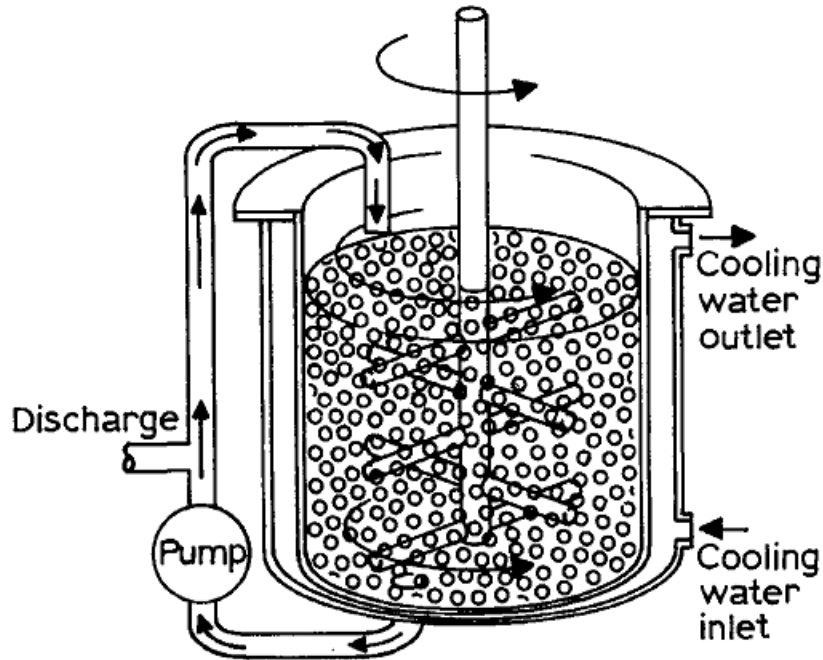
An attritor is a ball mill system in which the balls, together with the material to be milled are set in motion by a shaft with stirring arms, rotating 100-2000rpm.

Cylindrical vessel is usualy water cooled because of the considerable heat generated by the process.

Dry,wet (water, inorganic liquids) milling is possible inert gas supply possible for reactive materials.

More effective than conventional ball mill.

- Dry wet attritors→inorganic pigment and paint production, hard metal industry. In these fields of application of very fine particulates are required.

- Several metals and alloys may become amorphous during extended milling. **Amorphous alloys** (glassy metals developed by this method)

Amorphization of Cobalt-rich Magnetic Alloys by High Energy Ball Milling*

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Abstract

This article reports solid-state amorphization of binary systems of cobalt-rich Co–Zr, Co–Nb and Co–Ti alloys of more than 80 at.% Co by dry mechanical alloying, which provides a route to a development of low magnetostrictive amorphous materials in soft magnetic applications. X-ray diffractometry and differential scanning calorimetry confirm limiting compositions of $Co_{90}Zr_{10}$, $Co_{85}Nb_{15}$ and $Co_{80}Ti_{20}$ for amorphization under these experimental circumstances. The saturation magnetization increases with cobalt concentration, attaining a maximum of 13 400 Gauss for $Co_{90}Zr_{10}$. The dependence on cobalt concentration agrees with that of sputtered amorphous thin films. At the same time, the coercivity decreases from 19 Oe to 11 Oe, mainly because of an increment in the median diameter from 15 µm to 42 µm. Coercive forces for amorphous Co–Zr are smaller than the value of 25 Oe for unreacted crystalline $Co_{95}Zr_5$, 67 µm in size.

1. Introduction

Research on the synthesis of amorphous alloys has focused on solid-state amorphization by mechanical alloying [1]. A high-energy ball mill with a large grinding capability can fabricate uniform amorphous powders, avoiding a mass (size) effect resulting from different quenching rates in rapidly quenched amorphous powders, and realizing mass productivity near ambient temperature. One can then apply previous knowledge of the industrial powder production method of oxide dispersion strengthened alloys and ultrafine ceramics [2].

Solid-state amorphization is favoured in the middle concentration range of a transition metal–transition metal (TM–TM) system, where there is a high negative heat of mixing, which is thought to be one of the important parameters determining glass-forming ability in a solid-state reaction [3]. However, mechanically alloyed amorphous Fe–Zr and Co–Zr near the middle concentration range are not magnetic [1]. So far, there has been no attempt to fabricate cobalt-rich cobalt–transition metal systems by solid-state reactions for soft magnetic applications. It is known that various cobalt-rich Co–TM magnetic amorphous alloys obtained by sputtering provide good soft magnetic characteristics, such as high saturation magnetization, low coercivity and low magnetostriction. However, sputtering produces only thin amorphous films [4], and melt-spinning presents difficulties in preparing continuous amorphous ribbon and powders [5].

Here, we report on the synthesis of mechanically alloyed amorphous powders of binary systems of cobalt-rich Co–(Zr, Nb, Ti) and on their magnetic characteristics, to help develop magnetic amorphous alloys with a low magnetostriction and a relatively high saturation magnetization.

2. Experimental procedure

Powder mixtures of Co–(Zr, Nb, Ti) in the range of 95–75at.%Co were mechanically alloyed by employing a high-energy ball mill (Mitui Miike attritor MAID, Japan) with steel ball media of 18 kg with a revolving velocity of 300 rev min⁻¹ (ref. 6 gives de-

Roller Milling

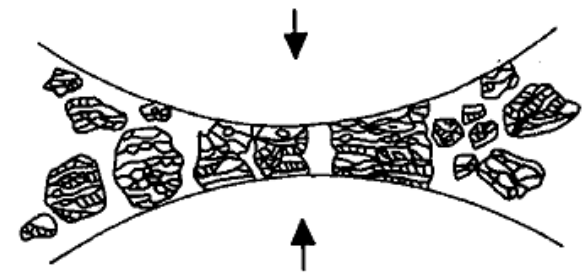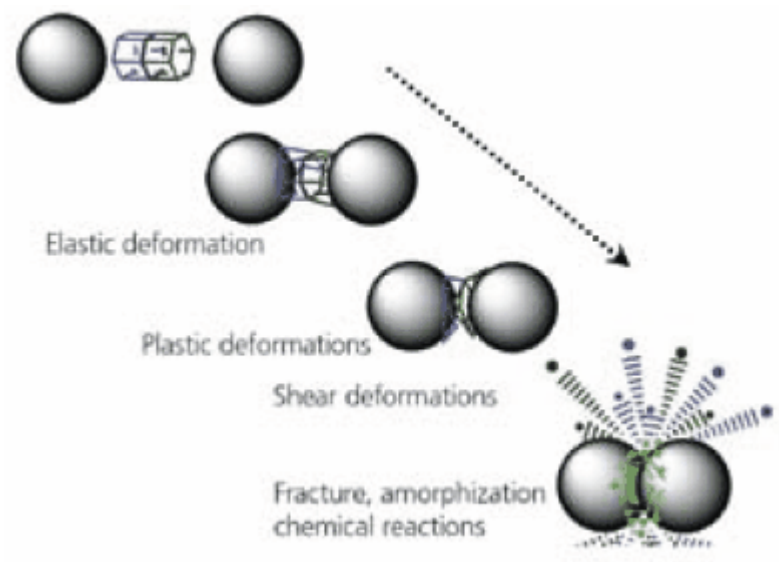For brittle materials a new size reduction technology become important, the high-compression roller mill,which operates with profiled rollers in the pressure range 50-500 MPa.
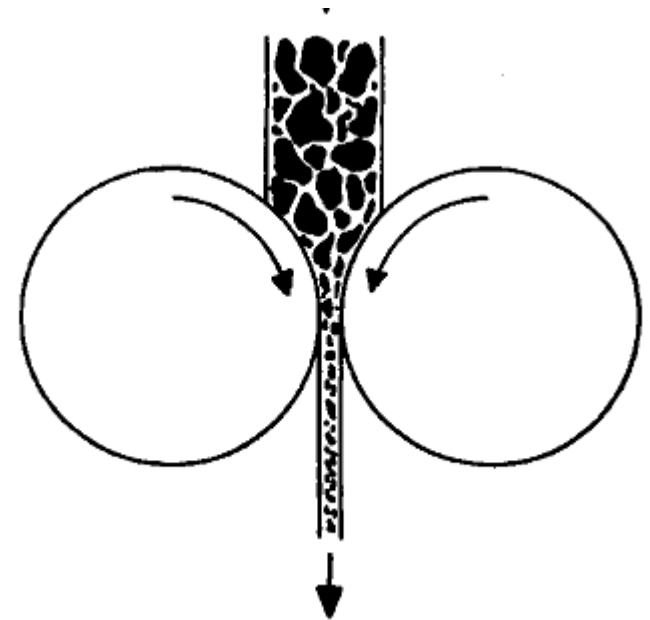
According to the working conditions products with narrow particle size ranges, between 200 and about 5μ are achievable.

Mechanical Alloying

Mechanical alloying is a high-energy ball milling process for producing composites with a controlled, even distribution of a second phase in a metallic matrix.

Elastic deformation

Plastic deformations

Shear deformations

Fracture, amorphization chemical reactions

- developing dispersion-strengthened alloys in which the development of special microstructures essential for achieving good high-temperature mechanical properties in multiphase powder metallurgy materials.

- the distribution of a non-metallic phase in a metallic, ductile matrix can be homogenized to a degree, which can be achieved otherwise only by chemical means.

- chemical reactions and formation of solid solutions can be obtained, in such cases the term *'reaction milling'* is used.
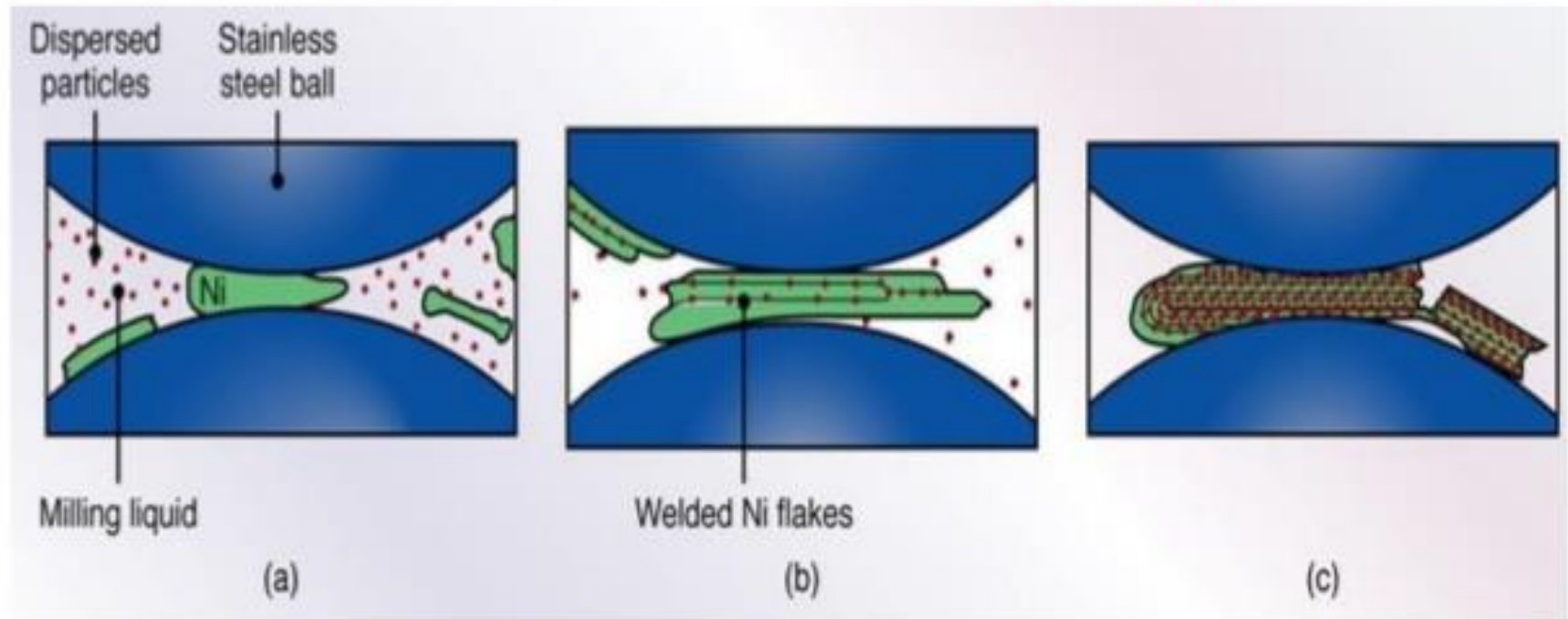
Mechanical Alloying

Figure Mechanical alloying of nickel particles with dispersed smaller particles. As nickel particles are flattened between the two balls, the second smaller phase impresses into the nickel surface and eventually is dispersed throughout the particle due to successive flattening, fracture, and welding events.

72

The process consists of long period milling of mixtures, in which the main component (matrix) is ductile.

- the ductile phase undergoes a continuous cycle of plastic deformation, fracture and re-welding processes, by which the fine dispersoids are implanted step-by-step into the interior of the ductile phase.

- Mechanical alloying is applicable to nearly all combinations of brittle phases (oxides,carbides, nitrides, carbon, intermetallics) and ductile metallic powders, which demonstrates the possibilities for extensive composite materials development.

Chemical Methods

These methods can be further classified as <u>chemical reduction</u> and <u>chemical decomposition</u>
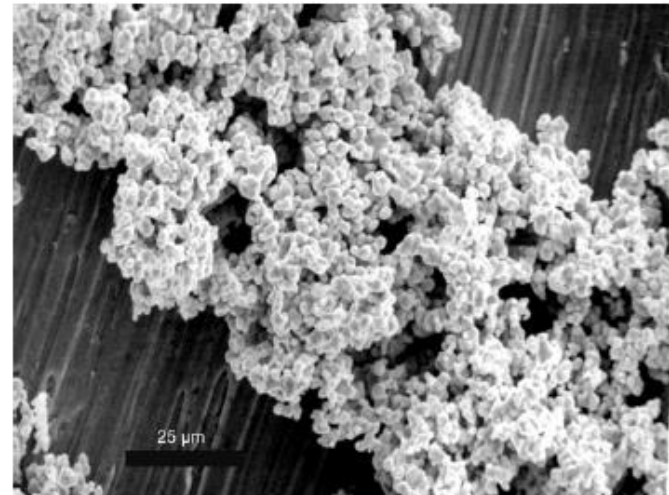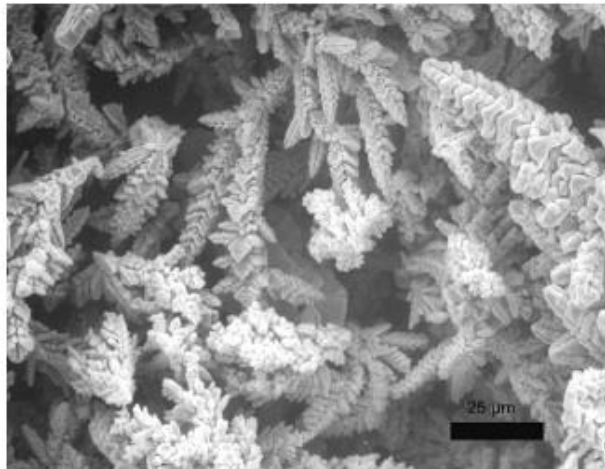
Chemical Reduction

Chemical reduction involves chemical compound most frequently an oxide, but sometimes a halide or other salt of the metal. This may be carried out;

- Chemical reduction from solid state
- Chemical reduction from the gaseous state
- Chemical reduction from aqueous solution

Electrolytic Production of Powders

➢ This powder production route is used to produce high purity metal powders

➢ Applications include

  ➢ Basic metals: Iron, copper, aluminum, chromium, zinc and magnesium
  ➢ Precious metals: Niobium, tantalum and silver
  ➢ Reactive metals: Titanium and palladium

➢ It involves two operations

  ➢ Electrodeposition of the metal in spongy or powdery state
  ➢ Milling of the deposited metal

➢ Electrolytic powders are in tens of microns size range, and typically have irregular, porous and dendritic shapes with poor packing characteristics

Electrodeposition of Metals

➢ **Fundamentals**

   ➢ **Electrochemical reactions**

      Cathode: $A^+ + e = A$

      Anode: $B = B^+ + e$

      Overall: $B + A^+ = A + B^+$
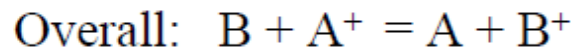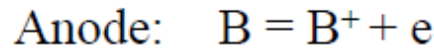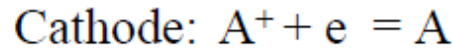
   ➢ **Free Energy of reactions**

      Electrode: $\Delta G^o_{ele} = - n\, F\, E_{ele}$

                $E_{ele} = E^o_{ele} + RT/nF \ln k$

      Overall: $\Delta G^o = - n\, F\, E = (E^o_B - E^o_A) + RT\, a_{B+}/\, a_{A+}$

E = cell potential; E_{ele} = electrode potential; k = Equilibrium constant
n = valance of ion; F = Faraday's number (96495 C/ g-equivalent)

   ➢ **Typical standard potentials E^o_{ele} (v)**

      $Cu^{2+} + 2e = Cu$ $E^o_{Cu} = 0.34$

      $Fe^{2+} + 2e = Fe$ $E^o_{Fe} = - 0.44$
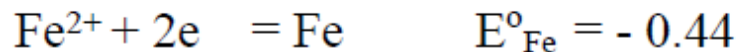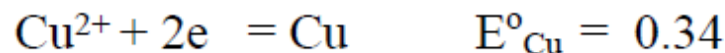
   ➢ **Theoretical deposition rate, current efficiency**

$$R_{A\;theortical} = \frac{I}{F}\left(\frac{MW_A}{n_A}\right) \quad gm/s \qquad Efficiency = \frac{R_A}{R_{A\;theortical}} \quad 100$$

DC power Source

Current (I)

Electrons (e)

Electrolyte

Anode   Cathode
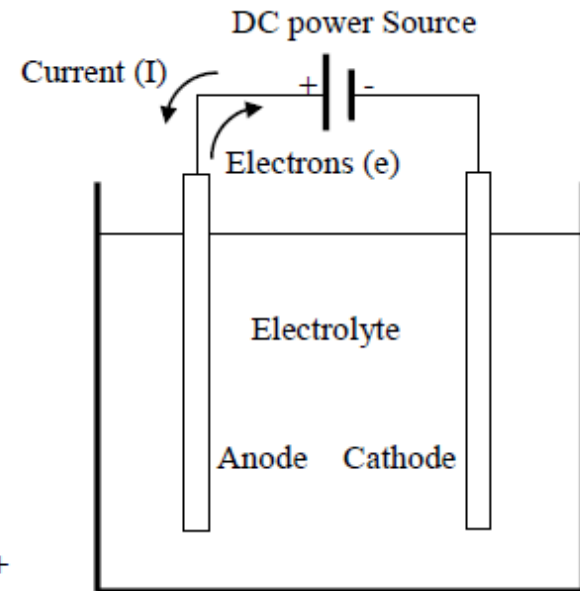
Electrodeposition of Metals (cont.)

➤ Technology

  ➤ Electrodeposition is in essence a refining process of impure metal ingots

  ➤ It involves dissolution of the impure metal from the anode in an electrolyte and depositing the dissolved metal ions on the cathode.

  ➤ Industrial electrorefining cells use a set of 20 to 40 anodes and cathodes connected in parallel to the power supply.
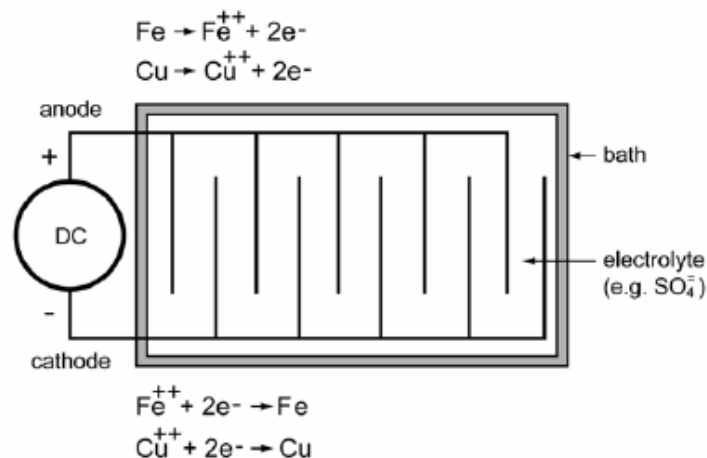
  ➤ Cell tanks are 3-4 m long, 1m wide and 1m deep

  ➤ The cell voltage is low, typically between 1 and 2 volts, while the current density is quite high ranging from 300 to 4000 A/m^2

$$Fe \rightarrow Fe^{++} + 2e^-$$
$$Cu \rightarrow Cu^{++} + 2e^-$$

anode

\+

DC

\-

cathode

← bath

electrolyte
(e.g. $SO_4^=$)

$$Fe^{++} + 2e^- \rightarrow Fe$$
$$Cu^{++} + 2e^- \rightarrow Cu$$

Electrodeposition of Metals (cont.)

➤ Process variables

  ➤ Cell current and voltage

  ➤ Cathode-anode gap thickness

  ➤ Electrolyte concentration and temperature

  ➤ Intensity of bath stirring

➤ Operating conditions favoring spongy and powdery deposits

  ➤ High current density

  ➤ Large cathode-anode gap

  ➤ High bath temperature

  ➤ Low ion concentration of the electrolyte

  ➤ Minimal electrolyte agitation

Ellingham Diagram

Figure 12.13 The Ellingham diagram for selected oxides.

Chemical Methods

Chemical Reduction from the solid state (reduction of iron oxide with carbon or of tungsten oxide with hydrogen)
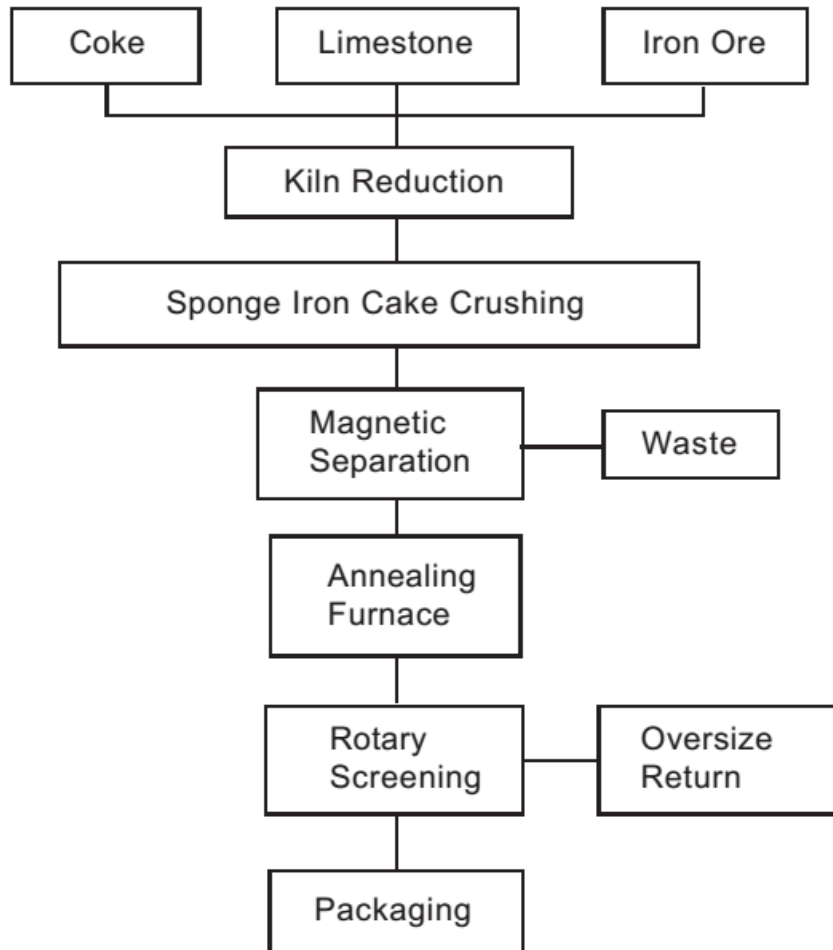
Sponge iron powder produced by the **Höganäs** process is a typical example of this production method.
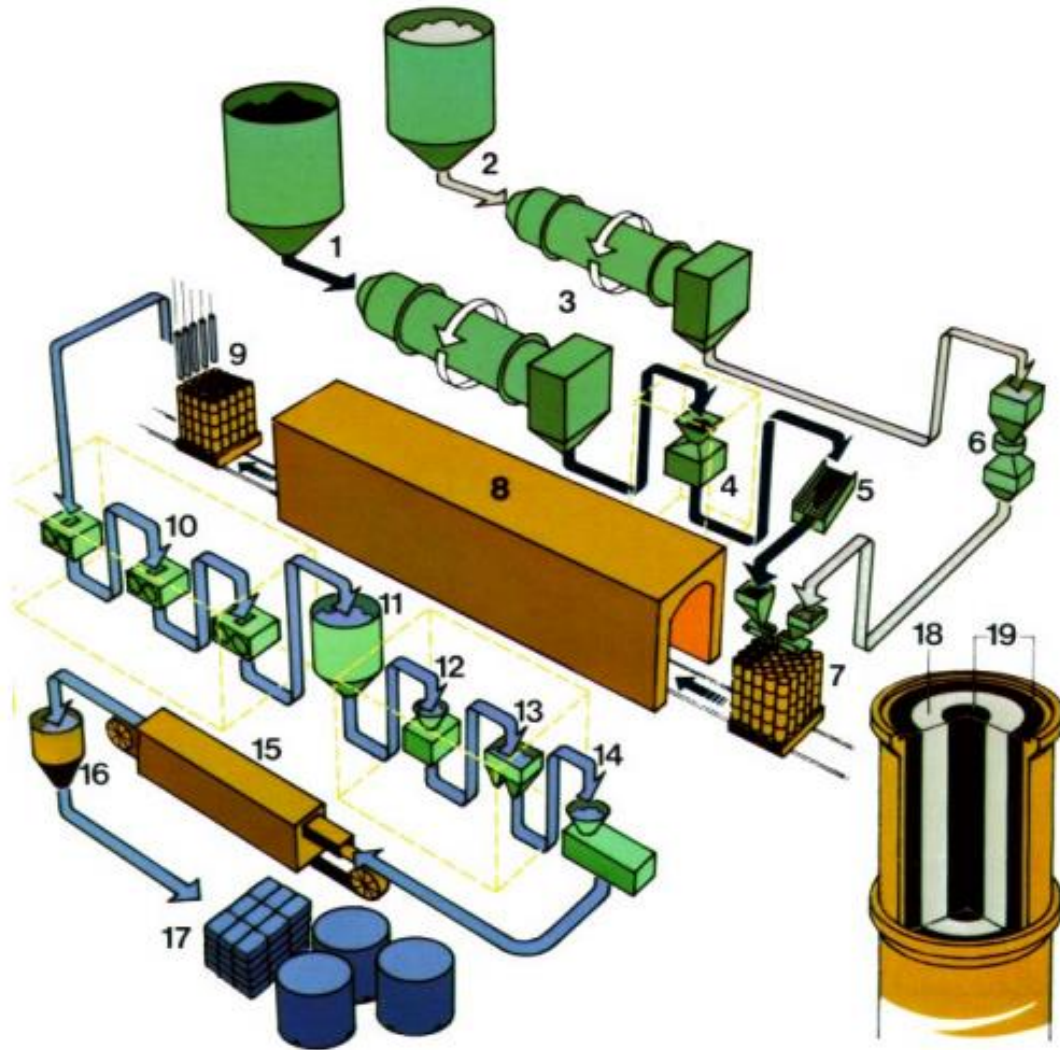
The Höganäs process is based in the use of quite pure magnetite (Fe_3O_4) ores. The iron ore is reduced with a carbonaceous material

Figure shows the steps involved in producing such powder

1. Reduction mix of coke and limestone
 2. Iron ore; 3. Drying;
 4. Crushing; 5. Screening;
6. Magnetic separation
 7. Charging in ceramic tubes;
8. Reduction in tunnelkilns, approximately 1200°C;
 9. Discharging
10. Coarse crushing
 11. Storage in silos
 12. Crushing;
13. Magnetic separation
 14. Grinding and screening; 15. Annealing in belt furnace, approximately 800-900°C
16. Equalizing
 17. Automatic packing of pressing powder, welding powder and cutting powder;
18. Iron ore; 19. Reduction mix

1. The ore is ground to a particle size distribution determined by each of the desired iron powder.

2. The ore powder is placed in the centre of cylindrical ceramic containers ('saggers' made of silicon carbide) surrounded on the outside (and inside) by a concentric layer of a mixture of coke and limestone.

3. The saggers are placed in layers upon cars which are pushed through a fuel fired tunnel kiln.

4. The carbon monoxide produced from the coke reduces the ore to iron. Total reduction time is of the order of 24 hours at a reduction temperature of 1200^0C.

5. The limestone serves to bind any sulphur in the coke and prevents its contaminating the iron.

6. The sponge iron is mechanically removed from the saggers, ground and the resulting powder magnetically separated from impurities. In a final reduction step the powder is carried through a continuous furnace in hydrogen atmosphere on a belt made of stainless steel.

The overall reduction

$$Fe_3O_4 + 4\,CO \leftrightarrows 3Fe + 4\,CO_2$$
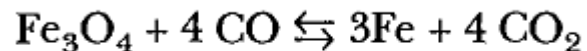
Most of the powder is milled to particle size distributions suitable for powder metallurgy parts production, whilst some (particle size> 150 μm) is sold for the manufacture of welding electrodes.

Example2: 'Pyron iron powder' is produced from mill scale by reduction with hydrogen.

Mill scale, often shortened to just scale, is the flaky surface of hot rolled steel, consisting of the iron oxides iron(II) oxide (FeO), iron(III) oxide (Fe_2O_3), and iron(II,III) oxide (Fe_3O_4, magnetite).

The mill scale is ground, magnetically separated and first roasted in air to convert the Fe_3O_4 to Fe_2O_3 (because the rate of reduction of Fe_2O_3 with hydrogen is faster than that of Fe_3O_4)

The oxide is reduced in a belt furnace at temperature near 980°C. The reduction product is ground.
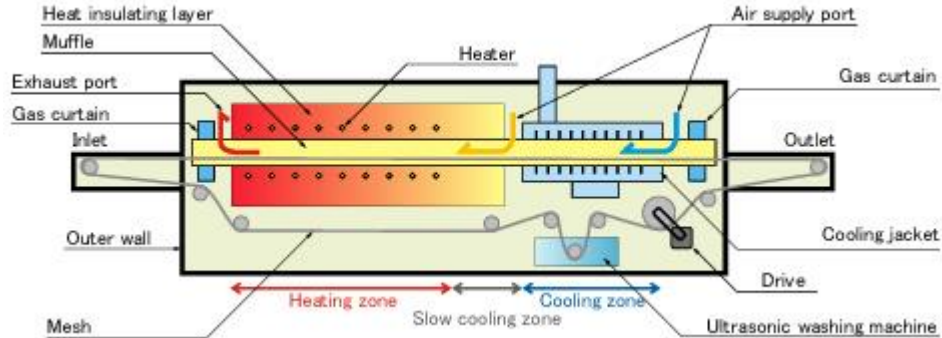
Example3: WO_3 is reduced to tungsten powder with hydrogen.

The important minerals of tungsten are wolframite ($FeWO_4$) and scheelite ($CaWO_4$), often occurring with tin ores.

- Scheelite ores are leached with HCl to form tungstic acid (H_2WO_4 or $WO_3.H_2O$)

- Tungstic acid is dissolved and digested in ammonia solution (NH_3) to give rise to ammonium tungstate solution $(NH_4)_2WO_4$

- APT (Ammonium Paratungstate, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$) is obtained from the crystallization of ammonium tungstate solution.

- APT is then calcined to give blue oxide.

- Tungsten is leached with caustic soda (NaOH) at elevated temperature under pressure to produce sodium tungstate (Na_2WO_4) in solution.

- the solution is purified using solvent extraction

- tungsten finally precipitated as pure WO_3.

$$4WO_3 + H_2 = W_4O_{11} + H_2O$$

$$\frac{1}{3}W_4O_{11} + H_2 = \frac{4}{3}WO_2 + H_2O$$

$$\frac{1}{2}WO_2 + H_2 = \frac{1}{2}W + H_2O$$
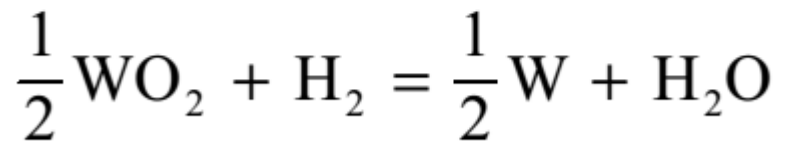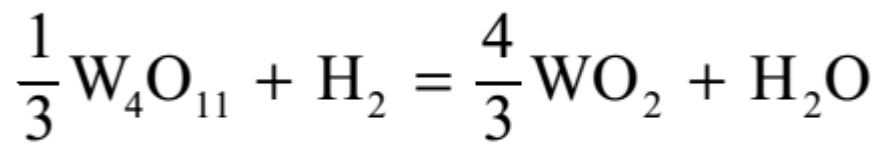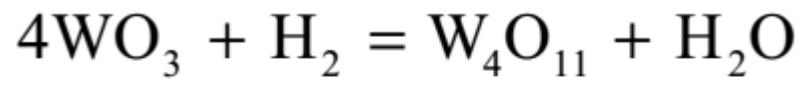
- reduction from WO_2 to tungsten at 850 C,

- The reduction of WO_2 by hydrogen is catalyzed by tungsten metal.

Chemical Reduction from the gaseous state

Gaseous based fabrications fabricate powders from reactive metals and precipitate nanoscale particles. The powders are formed without melting or contact with a crucible, thereby avoiding a major source of contamination.

Obtaining Ti powders from Titanium tetrachloride vapour with molten magnesium – the well-known *Kroll Process*

Chemical Reduction from the gaseous state

Ilmenite ($FeTiO_3$) is the most abundant titanium-bearing mineral and is comprised of about 43% to 65% titanium dioxide (TiO_2). A second major mineral form of titanium is rutile, a crystalline, high-temperature polymorph of TiO_2, containing about 95% TiO_2.

The **chloride process** is used to separate titanium from its ores. In this process, the feedstock is chlorinated at 1000 °C with carbon and chlorine gas, giving titanium tetrachloride. Typical is the conversion starting from the ore ilmenite:

$$2\ FeTiO_3 + 7\ Cl_2 + 6\ C \rightarrow 2\ TiCl_4 + 2\ FeCl_3 + 6\ CO$$
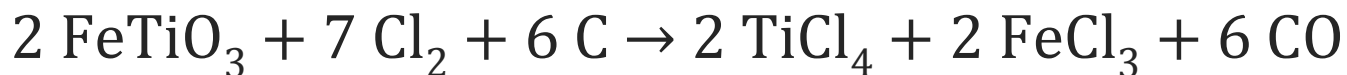
Chemical Reduction from the gaseous state

In a separate reactor, the $TiCl_4$ is reduced by liquid magnesium or sodium (15–20% excess) at 800–850 °C in a stainless steel distiller to ensure complete reduction:

$$2Mg(l) + TiCl_4(g) \rightarrow 2MgCl_2(l) + Ti(s) \ (T = 800\text{–}850 \ °C)$$

<u>*Chemical Reduction*</u> <u>from the aqueous state</u>
(hydrometallurgical method)

Example: Copper
Low cost copper powder is produced from solution obtained by leaching (solve+filtrate) copper ores or copper scrap, where the precipitation of copper powder from an acidified solution of copper sulphate with iron is achieved.

Large quantities of this 'cement copper' are produced from the copper sulphate solutions which are a by-product of the copper refinery industry.

Therefore, copper sulfate is essential to reduce copper.

Chemical Reduction from the aqueous state
(hydrometallurgical method)

Example: Copper

The following competitive reactions occur in the precipitation of copper from dilute acid solutions using metallic iron as the precipitant:

$$Fe\ (metal) + CuSO_4 \longrightarrow Cu\ (metal) + FeSO_4 \tag{1}$$

$$Fe\ (metal) + Fe_2(SO_4)_3 \longrightarrow 3\ FeSO_4 \tag{2}$$

$$Fe\ (metal) + H_2SO_4 \longrightarrow H_2 + FeSO_4 \tag{3}$$

Reactions [1] and [2] proceed almost simultaneously in the cone precipitator followed by reaction [3].

Chemical Reduction from the aqueous state

Example: Copper

Anoher way of copper recovery from copper(II) sulfate solutions by reduction with carbohydrates*

Copper(II) in copper sulfate solutions can be reduced with various carbohydrates to obtain a copper powder.

- Theoretically, the overall reaction for copper reduction with cellulose is:

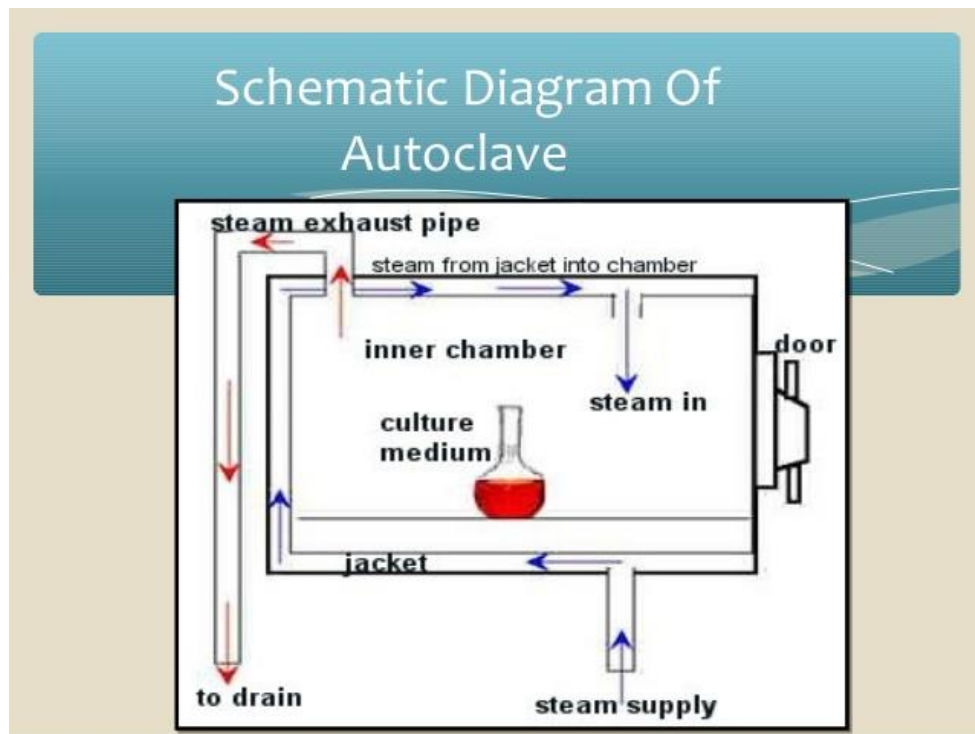$$12n\ Cu^{2+} + [C_6H_{10}O_5]n + 7n\ H_2O \rightarrow 12n\ Cu^\circ + 6n\ CO_2 + 24n\ H^+$$

*R.D. van der Weijden ,J. Mahabir,A. Abbadi,M.A. Reuter,» Copper recovery from copper(II) sulfate solutions by reduction with carbohydrates», Hydrometallurgy Volume 64, Issue 2, May 2002, Pages 131–146

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example: Nickel

The method described for the preparation of extra high purity nickel powder is based on the reduction of nickel sulfate solution by hydrogen under pressure in an autoclave.

An **autoclave** is a pressure chamber used to carry out industrial processes requiring elevated temperature and pressure different to ambient air pressure.
(similar to pressure cooker)

Schematic Diagram Of Autoclave

steam exhaust pipe

steam from jacket into chamber

inner chamber

door

culture medium

steam in

jacket

to drain

steam supply

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example: Nickel

The methods employed for removing the traces of impurities include cementation of the copper, hydrolysis of the iron salts, and chemical precipitation of the cobalt. Unlike commercial practice of the hydrogen reduction process, the reduction of the purified nickel sulfate $NiSO_4$ solution is carried out <u>without</u> a ferrous salt catalyst.

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example: Nickel

To initiate the reduction reaction, a small amount of ammonium carbonate ($(NH_4)_2CO_3$) is introduced into the system. Reduction is carried out at a temperature of 350°F (176^0C) under a hydrogen pressure of 350 psi (2.4 MPa).

The ammonium carbonate presumably promotes the formation of a fine suspension of solid basic nickel carbonate, $NiCO_3$ which then plays the role of a catalyst and provides the nuclei on which the nickel precipitates.

N. Zubryckyj, W. Kunda and D. J. I. Evans, «Extra-High-Purity Nickel Powder from Nickel Sulfate Solution by Hydrogen Reduction», Journal of the Electrochemical Society, 1969

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example 2: Nickel

Nickel powder produced by the Sherrit Gordon process is the typical hydrometallurgy method for production in which reduction of an ammoniacal solution of nickel sulphate $NiSO_4$ with hydrogen under a pressure of 1.38 MPa (200 psi) and a temperature of $190-200^0C$ in an autoclave is carried out.

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example 2: Nickel

A nickel salt solution is obtained by leaching complex Cu–Ni–Co ores. Before the nickel is precipitated as metallic powder the copper is removed from the solution by precipitation as sulphide (CuS). For the precipitation of the first nickel powder nuclei from the solution, catalyst, e.g. ferrous sulphate, is used. The very fine nickel powder nuclei are allowed to settle in the autoclave, the barren solution is decanted and a new batch of solution is introduced into the autoclave.

Chemical Reduction from the aqueous state
(hydrometallurgical method).

Example 2: Nickel

The nickel powder nuclei are suspended in the solution by agitation and the nickel in the solution is reduced with hydrogen at 1.38 MPa (200 psi) and precipitated on the existing nuclei. The process called densification is repeated many times, say 15–30. Finally, the powder is removed from the autoclave, washed and dried. The process permits control of the size and shape of the nickel powder being produced

Chemical Decomposition of Compounds

Under this category of powder production two methods are very common.

These are :

(i) Decomposition of metal hydrides

(ii) Decomposition of metal carbonyls

Decomposition of metal hydrides

This involves first hydriding the refractory metals like Ti, Zr, Hf, V, Th or U by heating the metal in the form of sponge, chip or turnings or even compact metal in hydrogen. TiH_2 is formed from titanium in the temperature range between 300–500^{0}C. These hydrides are quite brittle and can be readily ball-milled into powder of the desired size.

These may be dehydrided by heating them in a good vacuum at the same temperature at which the hydride was formed. Care must be taken to avoid contamination of O_2, N_2 and C during hydriding or dehydriding.

Decomposition of metal carbonyls

Example iron and nickel powder production.
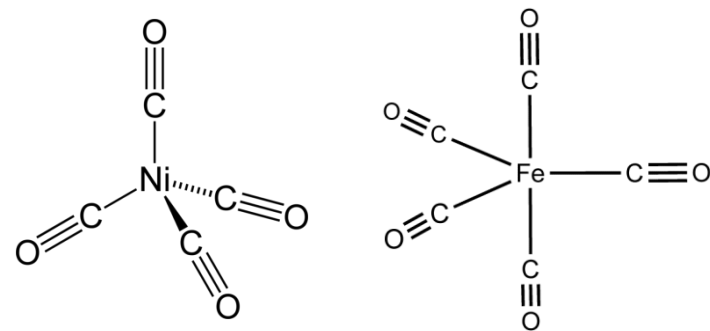
The carbonyls are liquids at normal temperature with a low boiling point. These are formed by reaction of the metal and carbon-monoxide gas under pressure.

For example; iron carbonyl ($Fe(CO)_5$) is formed at 70–200 atmosphere pressure and a temperature of 200–220°C.

The carbonyls can now be decomposed by heating at atmospheric pressure.

Decomposition of metal carbonyls

Example iron and nickel powder production.

Care must be taken to have the decomposition take place in the gas phase and not on the surface of the reaction vessel, in order to obtain metal in the powdery form.

The usual carbonyl iron powder particles are spherical with an onion skin structure, because the iron powder 'nuclei' first formed catalyze the decomposition of CO into C and CO_2.

- This type of iron powder is quite **pure** with respect to metallic impurities, but contains considerable amount of carbon and oxygen (fraction of a percent).

- The amount of such impurities can be reduced by adding ammonia during the decomposition of the carbonyl and by a subsequent annealing treatment.

- But these would naturally enhance the cost. Carbonyl iron powder is usually spherical in shape and very fine (<10 μm), while the nickel powder is usually quite irregular, porous and fine.