

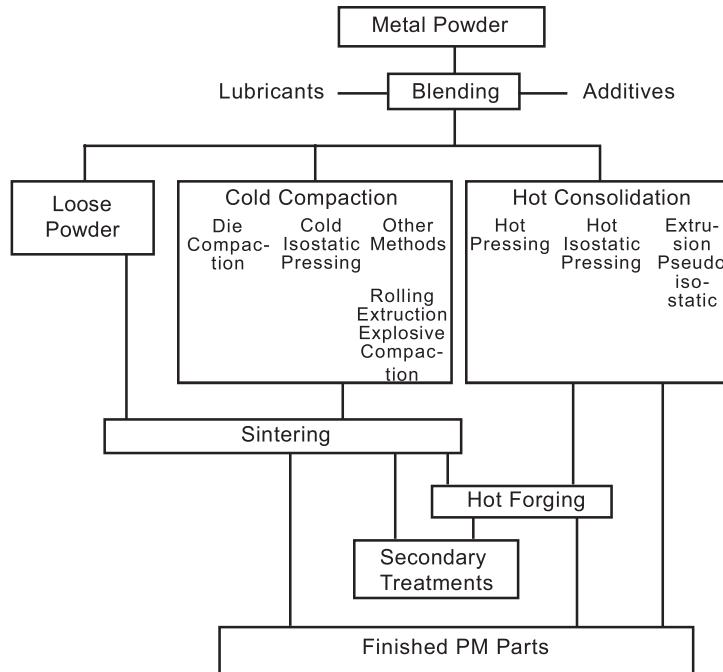
# 1 INTRODUCTION

The technology of pressing metal powders into a specific shape is not new; older civilizations practised the art in prehistoric times, as bear witness the iron pillar in Delhi, certain Egyptian implements and articles of precious metals made by the Incas. Modern powder metallurgy (P/M) technology commenced in the 1920s with the production of tungsten carbides and the mass production of porous bronze bushes for bearings. During the Second World War, further development took place in the manufacture of a great variety of ferrous and nonferrous materials, including many composites and a steady growth period developed during the postwar years until the early 1960s. Since then, growth of P/M has expanded more rapidly, mainly because of three potential reasons – economical processing, unique properties and captive processes. Primarily, the P/M process is a rapid, economical and high volume production method for making precision components from powders. However, there are a number of related consolidation techniques whereby powders can be rolled into sheet, extruded into bars, etc., or compacted isostatically into parts of more involved geometry. Over the last decade, the technology of powder forging has established itself for fabricating powders into precise engineering parts which have properties comparable with those of conventional forgings. Figure 1.1 shows the general flow sheet of powder metallurgy processing.

During the past decade, there have been significant advances in powder manufacturing techniques. New types of powders with superior properties allow the production of larger and higher strength materials. Careful control of the structure of the original powder particles has made it possible to have more intelligent manipulation of the structure of final sintered materials. Difficult to process materials, where fully dense high performance alloys can be processed with uniform microstructure, can now be processed. Multiphase composites with a wide combination of properties can economically be produced by the P/M technique. The nonequilibrium materials such as amorphous, microcrystalline or metastable alloys are also processed by P/M methods. Today, the size has increased many times and large parts including billets are produced in large quantities. Materials with mechanical properties far exceeding those of more conventional materials have been developed by using new alloying elements, by improved heat treatments and by achieving higher densities.

The biggest consumers of P/M parts at present are automotive indus-

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**Fig. 1.1 Basic steps of the Powder Metallurgy Process.**

tries. Hardware, tools, cameras, farm and garden equipment industries, business machines, sporting goods and military products are just a few more areas where usage is on the upswing.

The P/M process is many times more competitive than other fabrication methods like casting, stamping or machining. P/M is the choice when requirements for strength, wear resistance or high operating temperatures exceed the capabilities of die casting alloys. P/M offers greater precision, eliminating most or all of the finish machining operations required for castings. It avoids casting defects such as blow holes, shrinkage and inclusions. Powder injection moulding is coming out as a big challenge for investment casting. P/M is highly competitive with fine blanking, which runs at a slower cycle than conventional stamping and higher equipment cost. Screw machines use bar stock as raw metal and the process is characterized by very poor material utilization, sometimes less than 50 %. However the P/M process is economical only when production rates are higher, since the tooling cost is quite appreciable.

The present book is divided into ten chapters. Chapter 2 describes various metal powder production methods. Emphasis has been placed more on those processes which are of industrial significance. The success of any powder metallurgical process depends to a great extent on the complete characterization and control of the metal powders. Chapter 3 describes these characteris-

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tics and suggests how they are related to powder production methods. The next chapter discusses ‘Metal Powder Treatment’ such as annealing, mixing, milling, granulation and coating. The genesis of such treatment has been also explained. The Chapter 5 ‘Metal Powder Compaction’ deals with the compaction process, tooling design, part classification etc. in addition to details of cold isostatic compaction, roll compaction and dynamic powder compaction. A detailed analysis of compaction defects has been made, which is not generally available in most of the text books. The next chapter on ‘Sintering’ (Chapter 6) discusses solid state and liquid phase sintering, their process and material variables. In addition a full description of sintering atmospheres – their analysis and control and of furnaces has been made. The emphasis is more on the process and equipment selection which is important for technologists. The need to obtain fully dense metal powder compacts with controlled microstructures has never been felt so crucial and with this in view, Chapter 7 (Hot Consolidation) discusses methods like hot pressing, hot isostatic pressing, extrusion and forging, including the much talked spray forming process.

In practice, P/M components may require closer tolerances, increased mechanical properties and features not possible by simply sintering. In Chapter 8 various types of ‘Secondary Post Consolidation Treatments’ have been described.

In potential of ‘Powder Injection Moulding’ for cost effectively forming small, complex precision parts is finding wider applications in the markets. Chapter 9 describes its various steps like selection and production of metal powders, mixing, moulding, debinding, and sintering.

The quality control aspects in P/M industries are very important for the successful exploitation of sintered products. These involve raw material, processing and end products’ quality. The final chapter of this book (Chapter 10) describes in detail various testing methods for a wide range of P/M materials and products.

## **2 METAL POWDER PRODUCTION**

The subject of metal powder production is a very extensive one. In this chapter the description of most important principles and processes is given, which are of technological significance. The significant manufacturing methods may be classed as follows:

1. Chemical methods
2. Physical methods
3. Mechanical methods

Virtually any material can be made into a powder by one or more of these methods. The exact method chosen must be related to the type of application and the desired properties and structure of the final product.

### **2.1. Chemical Methods**

For detailed description of basic thermodynamics and kinetics aspects readers are referred to follow standard text<sup>1</sup> as an introductory guide. These methods can be further classified as chemical reduction and decomposition.

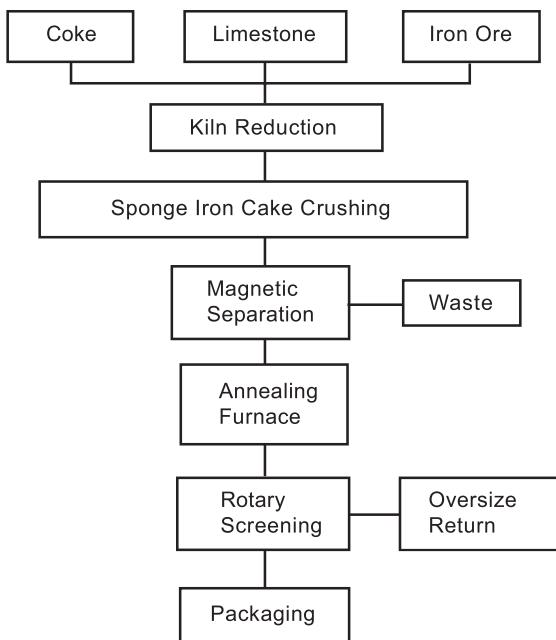
#### **2.1.1 Chemical Reduction**

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

(a) **from the solid state** – as in the 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. This is a batch process in which the ground ore does not move during reduction, but is static in contrast to other direct reduction processes which are continuous. The Höganäs process is based in the use of quite pure magnetite ( $\text{Fe}_3\text{O}_4$ ) ores found in northern Sweden. The iron ore is reduced with a carbonaceous material. Figure 2.1 shows the steps involved in producing such powder. The ore is ground to a particle size distribution determined by each of the desired iron powder. The ore powder is placed in the centre of cylindrical ceramic containers ('saggers' made of silicon carbide) surrounded on the outside by a concentric layer of a mixture of coke and limestone. The saggers are placed in layers upon cars which are pushed through a fuel fired tunnel kiln. 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°C. The limestone serves to bind any sulphur in the coke and prevents its contaminating the iron. The sponge iron is mechanically removed from the saggers, ground

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**Fig. 2.1** Flowsheet for sponge iron powder production from iron ore.

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.

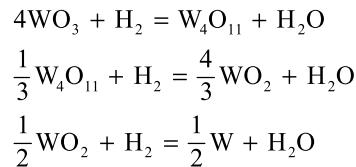
Another iron powder with trade name ‘Pyron iron powder’ is produced from mill scale by reduction with hydrogen. The mill scale is ground, magnetically separated and first roasted in air to convert the  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_2\text{O}_3$  because the rate of reduction of  $\text{Fe}_2\text{O}_3$  with hydrogen is faster than that of  $\text{Fe}_3\text{O}_4$ . The oxide is then reduced in a belt furnace at temperature near  $980^\circ\text{C}$ . The reduction product is ground. It is noticed that the pores in Pyron iron powder particles are considerably finer than those in sponge iron powder particles, because of the coarsening of pores at relatively higher reduction temperature in the latter case.

Another example of metal produced by reduction method is that of tungsten, in which  $\text{WO}_3$  is reduced to tungsten powder with hydrogen. The important minerals of tungsten are wolframite ( $\text{FeWO}_4$ ) and scheelite ( $\text{CaWO}_4$ ), often occurring with tin ores. Scheelite ores are leached with HCl to form tungstic acid. Tungstic acid is dissolved and digested in ammonia solution to give rise to ammonium tungstate solution. APT (Ammonium Paratungstate) is obtained from the crystallization of ammonium tungstate solution. APT is then calcined to give blue oxide.

Tungsten is leached with caustic soda at elevated temperature under pressure to produce sodium tungstate in solution. In either case the solution is purified using solvent extraction and tungsten finally precipitated

as pure  $\text{WO}_3$ .

The reduction of  $\text{WO}_3$  is carried out by hydrogen and the stages can be written as:



For the last stage of reduction from  $\text{WO}_2$  to tungsten at  $850^\circ\text{C}$ , there is still a significant concentration of  $\text{H}_2\text{O}$  vapour in the gas phase. The reduction of  $\text{WO}_2$  by hydrogen is catalyzed by tungsten metal. This is due to the dissociation of hydrogen molecules absorbed at the surface of the metal. This catalytic effect of tungsten is strongly inhibited by the presence of water vapour, with a consequent harmful effect on the reduction kinetics.

In a stationary furnace, the major parameters that affect the reduction rate are the furnace temperature, the amount of oxide loaded in the boat, the speed of boat movement, the rate of hydrogen circulation and the moisture content of the hydrogen. Hydrogen used for reduction is of at least 99.5 % purity and is usually electrolytically produced from distilled water with an addition of NaOH or KOH as the electrolyte. The preferable dew point range is  $-40$  to  $-43^\circ\text{C}$ . Safety devices are employed to avoid air leaks in the system and prevent possible explosion.

In the rotary type furnace, the raw material as described above is fed from a hopper by means of screw feed. The material feeds through the reduction tube by gravity, the tube is inclined towards the discharge end and is slowly rotated. The metal powder produced falls into a sealed container. The drawback of the rotary furnace process is that the powder product is less uniform in particle size than that of a stationary furnace.

As there is large difference between the bulk volume of  $\text{WO}_3$  and  $\text{WO}_2$ , for better utilization of space two stage reduction is preferred. The temperature ranges from  $500$  to  $700^\circ\text{C}$  for the first stage and from  $700$ – $850^\circ\text{C}$  for the second stage.

One of the major problems faced in tungsten powder production is the coarsening effect. At high reduction temperatures sublimation of the oxide is common. This is a function of total pressure, the hydrogen flow rate and the powder particle size. The vapour pressure of small particles is greater than that of large particles, and hence during reduction under such conditions the vapour of fine particles will deposit on the surface of coarse tungsten particles, thus giving rise to coarsening.

(b) from the **gaseous state** as in the reduction of titanium tetrachloride vapour with molten magnesium – the well-known Kroll process.

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(c) from the **aqueous solution** as in the precipitation of cement copper from copper sulphate solution with iron or in the reduction of an ammoniacal nickel salt solution with hydrogen under pressure (hydrometallurgical method). Low cost copper powder is produced from solution obtained by leaching 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. Most of this cement copper is eventually melted and cast rather than used as powder for two reasons: (i) the cement copper produced as a by-product is rather impure unless special precautions are taken and (ii) the powder is quite fluffy, i.e. it has a low apparent density, which is not satisfactory for many copper powder applications. To make the powder suitable, a furnace treatment which would increase the cost would be necessary.

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 with hydrogen under a pressure of 1.38 MPa (200 psi) and a temperature of 190–200°C in an autoclave is carried out. 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. 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. 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.

#### **2.1.2 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°C. These hydrides are quite brittle and can be readily ball-milled into powder of the desired fineness. These may be dehydrated 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 dehydrating.

Uranium hydride may serve as intermediate not only in producing uranium metal powder, but also UC and UN powder.

**Decomposition of metal carbonyls:** The famous example under this category is 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 ( $\text{Fe}(\text{CO})_5$ ) is formed at 70–200 atmosphere pressure and a temperature of 200–220°C. The carbonyls can now be decomposed by heating the vapour at atmospheric pressure. 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  $\text{CO}_2$ . Carbon deposits on the iron powder nucleus; another layer of iron is deposited on top and so on. 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). Powder devoid of such impurities can be produced 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  $\mu\text{m}$ ), while the nickel powder is usually quite irregular, porous and fine. More complex carbonyls, such as carbonyl halides, can also be decomposed. An example is  $\text{Pt}(\text{CO})_2\text{Cl}_2$  for the production of platinum powder.

## **2.2. Physical Methods**

Under such methods the electrolytic method and atomization are prevalent.

### **2.2.1 Electrolytic Method**

It is used extensively in the preparation of copper, beryllium, iron and nickel powders. Adjustment of the chemical and physical conditions during electrodeposition makes it possible to cause the metal to deposit loosely on the cathode of the cell either as a light cake or in flake form. Both are readily crushed to a powder. The method yields a high purity metal with excellent properties for conventional powder metallurgy processing. The process involves the control and manipulation of many variables and in some cases is significantly more costly than other techniques. For example, electrolytic iron powder is more costly than reduced or atomized powder with the same characteristics, while electrolytic copper powder is quite competitive with reduced and precipitated types.

The following are the factors promoting powdery deposits: (a) high current densities; (b) weak metal concentrations; (c) additions of colloids and acids; (d) low temperature; (e) high viscosities; (f) avoidance of agitation; (g) suppression of convection.

It may be very difficult to produce a high purity powdery deposit at relatively