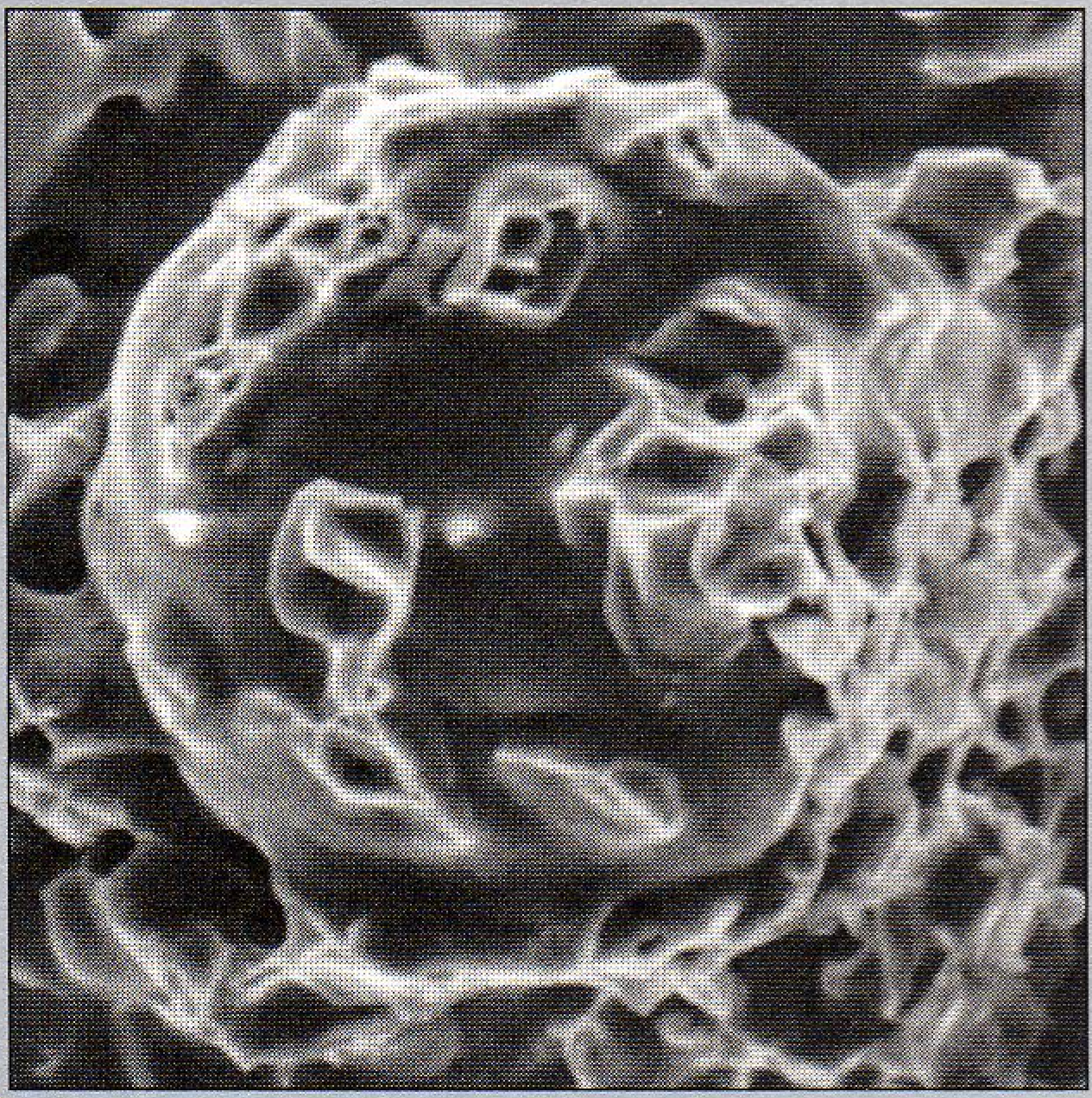
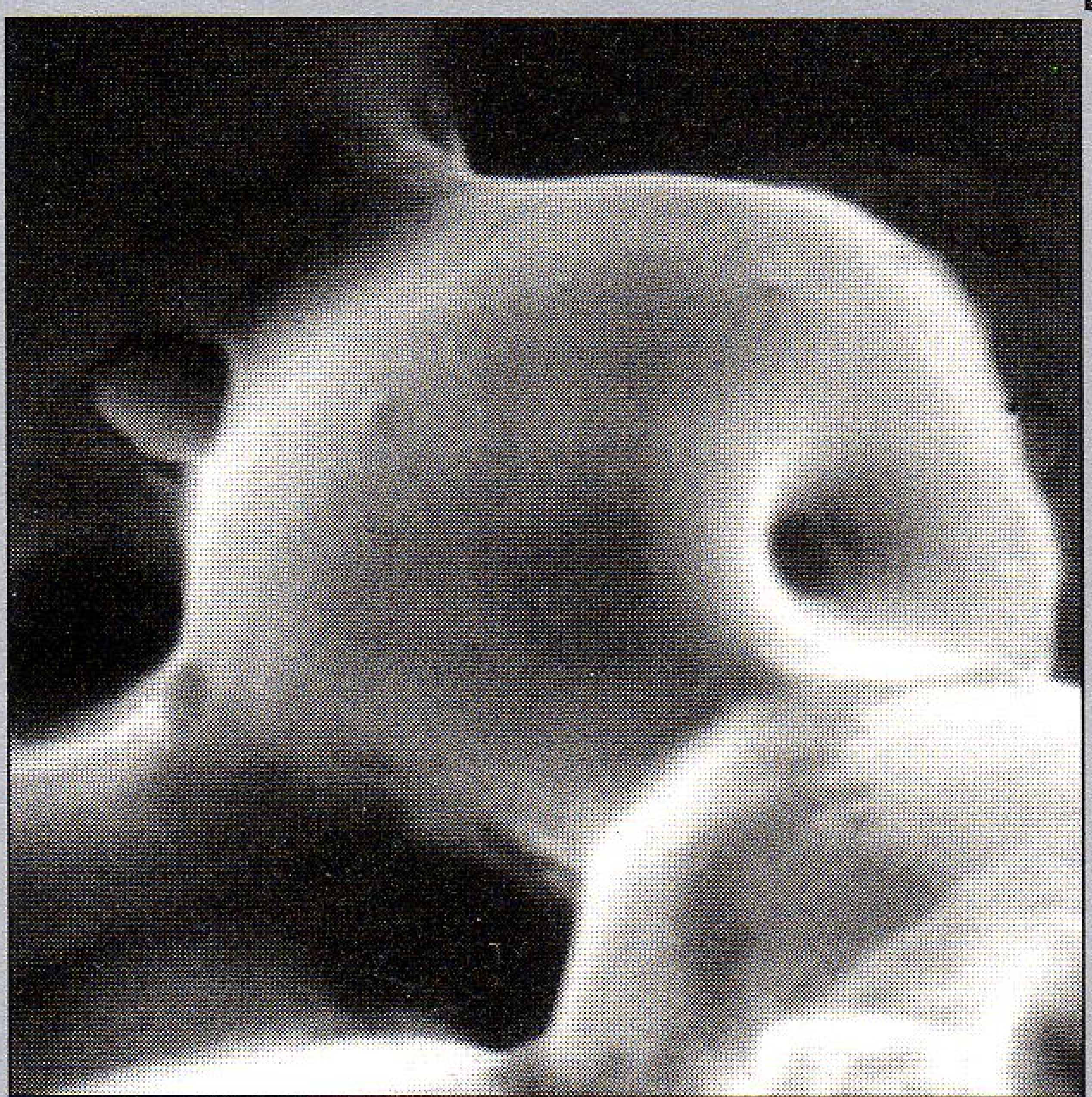
# POWDER METALLURGY TECHNOLOGY





**G S UPADHYAYA**

CAMBRIDGE INTERNATIONAL SCIENCE PUBLISHING

# POWDER METALLURGY TECHNOLOGY

# POWDER METALLURGY TECHNOLOGY

G. S. Upadhyaya

*Department of Materials and Metallurgical Engineering*
*Indian Institute of Technology, Kanpur, India*

CAMBRIDGE INTERNATIONAL SCIENCE PUBLISHING

**Published by Cambridge International Science Publishing**
7 Meadow Walk, Great Abington, Cambridge CB1 6AZ, England
http://www.cisp-publishing.com

*First published August 2002*

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

**ISBN 1 898326 40 1**

*Dedicated to*

Late Professor **Dr. Henry H. Hausner,**

who inspired me to write this book

Author

## About the Author

Dr. **G.S. Upadhyaya** was educated at Banaras Hindu University (B.Sc. Met. Engg.) and earned M.Sc. (Phys. Met.) and PhD from the University of Birmingham (UK) and the Kiev Institute of Technology (Ukraine), respectively. At Kiev, he worked under the world famous scientist Academician G.V. Samsonov. He began his career as a PM educator at the University of Roorkee (1964). In 1976, he joined the Indian Institute of Technology, Kanpur, as a Professor in powder metallurgy in the Department of Materials and Metallurgical Engineering, where he proceeded to build a reputation for himself as well as for the IIT as an authority on powder metallurgy. Here, through his numerous publications (over 250 papers and eight books) and his students, who are spread throughout the country, he advanced the cause of powder metallurgy not only in India but also abroad as well. Dr. Upadhyaya has received various honours, like Hon. Diploma of IISS (1979), Full member of IISS (1983), Niobium Medal of the Max Planck Institute (1989), MRSI Medal (1993), the Samsonov Prize of IISS (1993) and G.D. Birla Gold Medal of the Indian Institute of Metals (1994). He has been the President of the Powder Metallurgy Association of India for two consecutive terms (1987-88 and 1988-89), a Visiting Associate Professor at the Rennselaer Polytechnic Institute, USA (1970) and a Guest Scientist at the Powder Metallurgy Laboratory of the Max Planck Institute for Metals Research, Stuttgart. He is on the Editorial Board of several international and national journals related to powder metallurgy.

# Preface

Having taught a course on Powder Metallurgy for 30 years, a need has been felt for quite some time for a textbook exclusively on Powder Metallurgy Technology for students as well as practising engineers. There are books on scientific aspects of powder metallurgy, but details of technological aspects are not available. The emphasis has been not to treat the present book as a handbook, but as a handy textbook. The existing books either deal the subject too elaborately or leave out some of the recent but important technological developments.

Although this is essentially a textbook, I have planned it in such a way that I hope will also make it of use to designers and engineers in a variety of fields. I have not included details of sintered alloys and products in order to contain the book within reasonable proportions. These topics shall be discussed by me in another future publication.

The boundary between powder metallurgy and ceramic technology is gradually getting difficult to be drawn. With this in view, the book can be of use to ceramic engineering students as well.

The detailed outline of various chapters in the book is given in Chapter 1 (Introduction). The overview of the subject has sufficient breadth for an introductory course while providing enough depth to prepare a student for further study.

I am grateful to various authors and publishers who permitted to reproduce their illustrations.

Lastly, the author would request for the indulgence of the readers for any inaccuracies, which might have crept in, even after all the possible care.

G.S. UPADHYAYA

# Contents

Chapter 1 INTRODUCTION

Chapter 2 METAL POWDER PRODUCTION

Chapter 3 METAL POWDER CHARACTERISTICS

Chapter 4 METAL POWDER TREATMENT

Chapter 5 METAL POWDER COMPACTION

## Chapter 6 SINTERING

## Chapter 7 HOT CONSOLIDATION

## Chapter 8 SECONDARY TREATMENT

## Chapter 9 POWDER INJECTION MOULDING

## Chapter 10 QUALITY CONTROL OF POWDER METALLURGY MATERIALS

# 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-

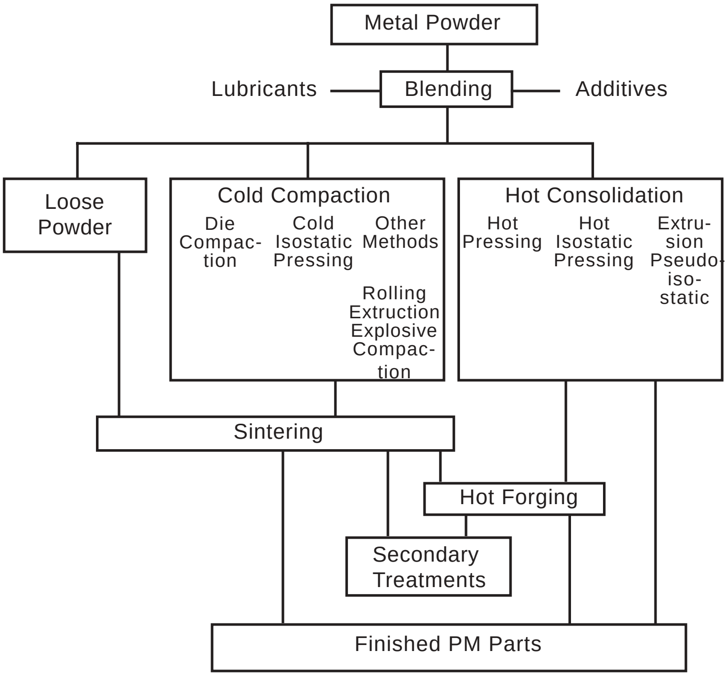


**Fig. 1.1** Basic steps of the Powder Metallurgy Process.

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 characteristics 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[1] 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 ($Fe_3O_4$) 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

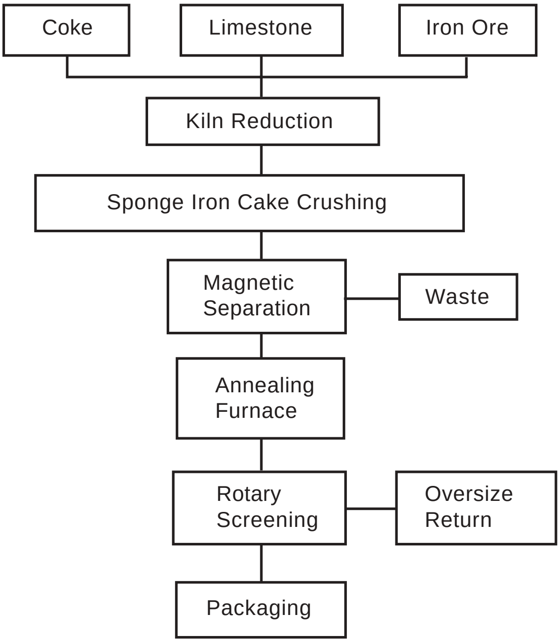


**Fig. 2.1** Flowsheet for sponge iron powder production from iron ore.

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 $Fe_3O_4$ 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 then reduced in a belt furnace at temperature near 980°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 $WO_3$ 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. 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 $WO_3$.

The reduction of $WO_3$ is carried out by hydrogen and the stages can be written as:

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

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

$$\frac{1}{2}WO_2 + H_2 = \frac{1}{2}W + H_2O$$

For the last stage of reduction from $WO_2$ to tungsten at 850°C, there is still a significant concentration of $H_2O$ vapour in the gas phase. The reduction of $WO_2$ 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°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 $WO_3$ and $WO_2$, for better utilization of space two stage reduction is preferred. The temperature ranges from 500 to 700°C for the first stage and from 700–850°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.

(*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 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.

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 ($Fe(CO)_5$) is formed at 70–200 atmosphere pressure and a temperature of 200–220°C. The carbonyls can now be decomposed by heating 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 $CO_2$. 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 μm), 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 $Pt\,(CO)_2Cl_2$ 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 fast rates economically. Consequently, in many cases the deposit is a solid and must be pulverized, for example iron. Electrolytic deposits, powders or solids are usually very reactive and brittle. For both these reasons the material may be given a special annealing treatment. Powders formed during electrolysis have a characteristic dendritic shape; however, this could be changed substantially due to subsequent processing.

The electrolytic process for copper powder is similar to that in copper refinery. However, instead of using impure cast copper anodes, electrolytically refined copper anodes are used. The cathode is generally cast antimonial lead. The electrolyte concentration is 50 g/l of $CuSO_4 \cdot 5\, H_2O$ (in contrast to 150 g/l for refining) while the current density is 535 $A/m^2$ (in contrast to 107–215 $A/m^2$ for refining). The copper powder is washed and filtered and finally given an annealing and reducing treatment at temperatures between 500–800°C in a belt furnace with an atmosphere of partially combusted hydrocarbon gas. Powder properties, particularly its apparent density, are primarily controlled by the reducing treatment after electrolytic deposition. The reduced powder forms a cake which must be broken up into powder by a hammer mill.

In contrast to copper powder, electrolytic iron is not deposited as powder but as a brittle lightly adhering sheet like deposit on stainless steel cathodes. The anodes are usually Armco iron or low carbon steel. The electrolyte is a chloride or sulphate solution. The brittle nature of the deposit is because of hydrogen and or oxygen as impurities and can be readily milled into powder in ball mills. Powder must be annealed so as to make it soft and pure and the resulting cake is again ground into powder in a hammer mill. Electrolytic iron powder is a premium product because of its purity and its better compressibility (higher green density) compared with reduced or atomized powder and demands a price much higher than that of reduced powder. Figure 2.2 shows the schematic of the electrolytic process for making metal powders.

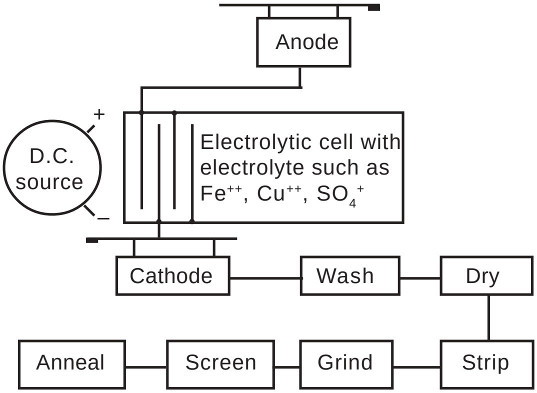


**Fig. 2.2** Schematic of the electrolytic process for making metal powders.

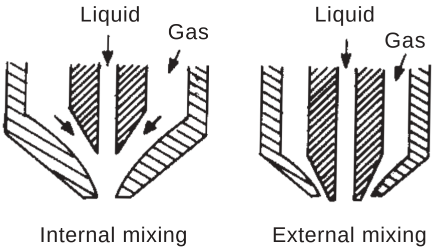


**Fig. 2.3** Two fluid atomization design.

### 2.2.2 Atomization

Atomization has been classified into categories, namely gas, water and centrifugal.[1] Virtually, any material that can be melted can be made into powder by disintegration of the liquid. Aside from chemical reactivity, which may necessitate specific atmosphere or materials, the process is independent of the normal physical and mechanical properties associated with the solid material. The method is being widely adopted, especially because of the relative case of making high purity metals and prealloyed powders directly from the melt. The basic procedure employed is to force a liquid through an orifice, possibly at a bottom of a crucible and impinge a gas or liquid stream on the emerging melt. A great deal depends on the exact design of the orifice. It may induce turbulence in the melt which atomizes the material directly and allows the impinging gas or liquid to reduce the size of the particle still faster.

**Gas atomization:** The general atomizing media are nitrogen, argon or air. Various atomization geometries are used in commercial practice. In what is known as 'external mixing' (Fig.2.3), contact between the atomizing medium and melt takes place outside the respective nozzles. This type of mixing is used exclusively for the atomization of metals. 'Internal mixing' (Fig.2.3) is quite common for the atomization of materials which are liquid at room temperature. The axes of the gas jets are equally inclined to the melt stream axis and intersect this axis at the geometrical impingement point. The process is governed by a number of interrelated operating parameters. Controllable variables include jet distance, jet pressure, nozzle geometry, velocity of gas and metal, and melt superheat.

Gas atomized powders are typically spherical, with relatively smooth surfaces. Higher pressure and/or a smaller jet distance produce finer powder. Gas atomization pressures are typically in the range $14\times10^5$ Pa to $42\times10^5$ Pa at gas velocities from 50 $m\cdot s^{-1}$ to 150 $m\cdot s^{-1}$; under these conditions, the particle quench rate is ~$10^2$ $K\cdot s^{-1}$. Such production method is used for preparing powders of the superalloys, titanium, high speed steel and other reactive metals. The method suffers from a very low overall energy efficiency (~3 %) and is expensive if inert gases other than nitrogen have to be used.

**Water atomization:** 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. It is estimated that the overall energy process efficiency is ≤4 %. 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.

The advantages of atomized powders and more specifically, of high pressure water atomized powders are summarized by Gummeson.[2] These are:

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

Fine particle sizes are favoured 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
(f) High atomizing agent volume
(g) High atomizing agent velocity
(h) High atomizing agent viscosity
(i) Short metal stream ($F$)
(j) Short jet length ($E$)
(k) Optimum apex angle ($\alpha^o$).

Figure 2.4 illustrates some major variables in the atomizing process.

Particle shapes of atomized powders can be modified from almost perfectly spherical to highly irregular, by controlling the processes which take place in the interval between disintegration of the liquid metal stream and the solidification of the drop. 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) Low jet velocity
(f) Long apex angles in water atomization
(g) Long flight paths.

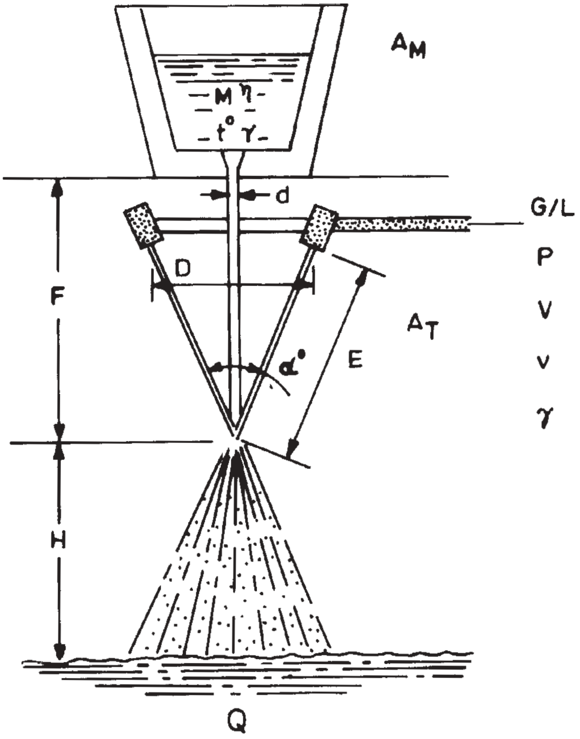


**Fig. 2.4** Major variables in the atomizing process.[2]

In water atomization, water pressures are commonly in the range of $35\times10^5$ Pa to $210\times10^5$ Pa with associated water velocities from 40 $m\cdot s^{-1}$ to 15 $m\cdot s^{-1}$ . The particle cooling rate is ~ $10^3$ $K\cdot s^{-1}$ to $10^4$ $K\cdot s^{-1}$.

The surface tension of liquid metals is high and a droplet once formed tends to assume the spherical shape. The higher the viscosity of the atomizing medium, the greater is the deformation of the droplet. The higher the cooling rate, the shorter is the time during which the surface tensional forces can operate to spheroidize the droplet and, therefore, the more irregular the particle shape. Impurities and alloying elements in the metal or reactions on the surface of the droplets that decrease the surface energy, will promote irregular particle shapes. Small quantities of phosphorus in copper lead to formation of a $P_2O_5$ film at the particle surfaces which increase the surface energy and results in the formation of spherical droplets. The existence of a solid oxide film such as ZnO acts in the opposite fashion, tending to give less rounded particles. The addition of silicon is a well-known method of influencing the particle shape of atomized stainless steel powder.

While the particle shape is not appreciably influenced by metal pouring temperatures in gas atomization, it is in water atomized powders. At higher pouring temperatures, there remains enough superheat after atomization to allow surface tension forces to create spheroids. Higher water pressure results in more irregular particle shapes due to greater impact forces and to larger volumes of water with resultant more rapid quench.

Another aim during atomization of particularly multiphase alloy systems is the elimination of gross metal segregations. The particle structure is therefore, a function of the solidification rate. A fine microstructure particle is promoted with water atomization as opposed to gas atomization, by lower metal pouring temperatures, higher atomizing agent pressure, flow rate and viscosity and by shorter particle flight paths.

**Liquid gas atomization**: 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. An even stream is generated, which atomizes the melt comparably to water atomization and which cools rapidly. Since the atomization liquid vaporises completely, gas and powder can be easily separated in the cyclone. 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 $10^6$ K/s.

– The powders are, as in gas atomization, spherical and have an average size of 6–125 µm. Due to the distinctive presence of satellites mainly low alloy powders show satisfactory results in cold forming, while having a good flowability. Gas atomized powders, on the other hand, 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 rotating electrode process (REP) is a further example of centrifugal atomization.[3] 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 (Fig.2.5). 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 µm; the size range is 50–400 µm. Typically, yields run to ~75% for –35 mesh powder.

Tungsten contamination from the stationary electrode is a limitation of REP powders. To eliminate this, the PREP (Plasma Rotating Electrode Process) method has been commercialised (Fig.2.6). It is important that the electrodes are precisely dimensioned and straight. This can be achieved by

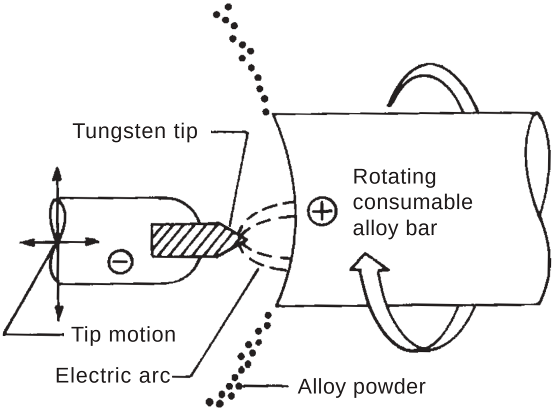


**Fig. 2.5** Rotating electrode process – schematics[3].

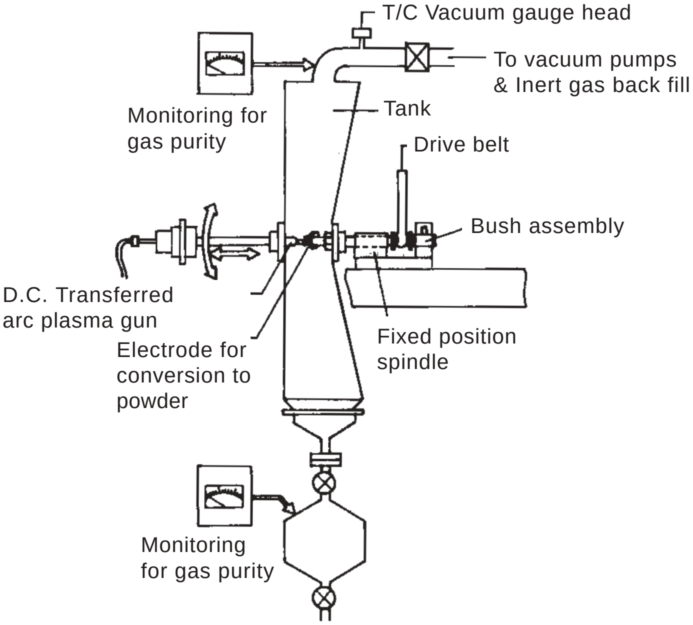


**Fig. 2.6** Short bar PREP machine.

subjecting cold drawn rod to cross roll straightening.

Resonance effects are experienced in the REP. The natural frequency experienced is a function of the modulus of elasticity (*E*), the sectional moment of inertia (*I*), the beam length (*l*) and the beam weight (*w*) or weight per unit length (*m*) and is given by the relationship:[3]

$$f = C_n\sqrt{\frac{EI_g}{Wl^3}} \quad \text{or} \quad C_n\sqrt{\frac{EI_g}{ml^4}}$$

where $C_n$ is a constant depending upon beam support conditions and mode number of vibration and $g$ is the gravitational constant (9.81 $m/s^2$).

Accurately controlled rotation of the anode is important so as to obtain a desired range of particle size distribution. The molten droplet diameter in a given material is determined by such parameters as the surface tension of the liquid metal, centrifugal forces (related to rotation speed) and to some extent by the 'aerodynamics' of the droplets trajectory through the inert cover gas.

The design of REP or PREP equipment includes sufficient damping to suppress or withstand resonant vibrations of moderate amplitude. However, when the electrodes are marked by out of tolerance for straightness, severe loading is imposed on the spindle and seal mechanism.

Spherical metal powders made by either REP 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.

There are various mechanical atomization methods like Roller atomization, vibratory electrode atomization and ultrasonic atomization. An excellent review has been made by Lawley.[1] The details of such methods are out of scope of the present book.

**Vacuum atomization**: Vacuum or soluble gas atomization is a commercial batch process based on the principle that when a molten metal supersaturated with gas under pressure is suddenly exposed to vacuum, the gas expands, comes out of solution, and causes the liquid metal to be atomized. Alloy powders based on nickel, copper, cobalt, iron and aluminium can be vacuum atomized with hydrogen. Powders are spherical, clean and of a high purity compared to powders produced by other processing methods. The process was developed and patented by Homogeneous Metal, Inc. Figure 2.7 illustrates a schematic of the equipment used for the atomization process. The principal use of powder made by vacuum atomization has been for the production of gas turbine disks and intricate parts by injection moulding.

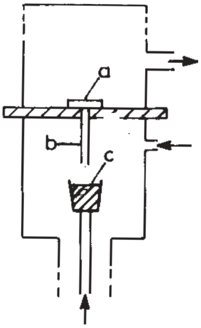


**Fig. 2.7** Schematic representation of vacuum atomization. (a) trap door, (b) transfer tube, (c) molten metal.

**Table 2.1** P/M grade copper powder: Specific equipment requirements

| Process | Cementation | Electrolysis | Oxide reduction | Water atomization |
|---|---|---|---|---|
| Equipment | Reaction cells | Melting furnace (for melting anodes) | (Drying) | Melting and atomization device and pump |
| | Purification device | Electrolysis cells and current rectifier | Magnetic separator | |
| | Cementation cells | Washing and neutralizing device | Mill air separator | |
| | Washing device | | Atmosphere generator | |
| Number of handling | 4 | 3 | 2 | 1 |

## 2.3 Mechanical Methods

These processes are not much used as primary methods for the production of metal powders. Mechanical comminution is possible by methods such as impact, attrition, shear and compression. 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 easy to fracture such as pure antimony and bismuth, relatively hard and brittle metal alloys and ceramics.

– reactive materials such as beryllium and metal hydrides.

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

A common method is the use of a ball mill consisting of a rotating drum with hard wear resistant balls. The critical factor is the speed of the drum's rotation. A very high speed will cause the material and the ball to be pressed against the walls of the drum, because of the centrifugal forces and prevent relative motion between the material and the balls. Too low a speed will result in an insignificant amount of movement in the lower part of the drum. The optimum speed corresponds to a situation in which some amount of ball and material is lifted up to the top of the drum and falls down on the remaining material.

Another type of mill is a vortex mill in which particles of materials to be ground are fractured by mutual contact or collision. Such mills consist of two or more very rapidly rotating propellers within the mill casing and gas flow systems which remove a desired size fraction of particles. Other types of mills have been described in Chapter 4, where they are used as secondary processes. A disadvantage of mechanical method for powder production is the potential contamination from the balls and mill walls.

Flake metal powders are produced by flattening equiaxed particles produced by another method. These may employ ball, hammer or roll mills. When milling the original particles lubricants are added to prevent them from welding or sticking to each other. Aluminium, copper, bronze, silver, gold, iron and stainless steel flake powders are produced commercially by the milling method.

## 2.4 Selection of Metal Powder Production Method

Selection of the production method for a particular metal powder would depend on:

(a) Raw Material Available
(b) Type of End Application

Table 2.1 gives the list of specific equipment required for various methods of copper powder production. It confirms the simplicity in the case of atomization which has one handling in contrast to the cementation process, which has four. The process selection according to end applications depends on the powder characteristics. A detailed description of metal powder characterization shall be given in the next chapter.

## References

1. A. Lawley (1978), Preparation of Metal Powders, In ‘Annual Review of Materials Science’, **8**, 49–71.
2. P.U. Gummeson (1972), High Pressure Water Atomization, in ‘Powder Metallurgy for High Performance Application’/ Ed. J.J.Burke and V. Weiss, Syracuse University Press, Syracuse, 27.
3. P.R. Roberts (1984), Commercial Atomization by the Rotating Electrode Process, in ‘Atomization Processes’, Current and Future’, P/M 84 Seminar Preprints, MPIF, Princeton, 51.

# 3 METAL POWDER CHARACTERISTICS

## 3.1. Introduction

The success of any powder metallurgical process depends to a great extent on the complete characterization and control of the metal powders. The method of powder production influences particle chemistry and structure, apart from the precise nature of particle size distribution. These properties also influence the behaviour of the powder during compaction and sintering, and the composition, structure and properties of the sintered material. In the present chapter, various characteristics of the powder, some interrelated, are considered. Table 3.1 gives a brief summary of principles involved in the characterization of various powder properties which shall be described in subsequent sections.

## 3.2 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

**Table 3.1** Powder properties and methods of mesuring them

| | |
|---|---|
| Particle size and size distribution | Sieve analysis: Permeability: Sedimentation electrical resistance; Light obscuration; Light scattering; Microscopy; Surface area. |
| Particle shape [external] | SEM; Shape parameters; Morphological analysis; Fractals. |
| Particle shape [external and internal] | Stereology; Mercury Porosimetry; Gas absorption. |
| Particle density | Pycnometry; Mercury porosimetry. |
| Specific surface area | Gas absorption; Permeametry. |
| Surface chemistry | X-ray photoelectron spectroscopy (ESCA); Auger electron spectroscopy; Secondary ion mass spectroscopy; Ion scattering spectroscopy. |
| Alloy phases and phase distribution | Optical metallography; Stereology; Electron microscopy; EDAX; X-ray diffraction. |
| Quality of mixing [segregation] | Macroregion:Variability coefficient (by chem.anal.);<br>Microregion: Variability coefficient ($2^{nd}$ comp. >5%);<br>Homogeneity coefficient ($2^{nd}$ comp. <5%); by metallography |

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. Other ceramic and rather inert compounds may exist; these may be reported in terms of an acid insoluble figure. 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 hydrogen loss is a common parameter to know the level of oxygen impurities in those metal powders whose oxides are easily reducible by hydrogen, e.g. iron, tungsten, copper, nickel, etc. However, this value can be in error due to incomplete reduction of oxides, and some oxides may not be reduced at all. The annealing of the powder in a reducing atmosphere is an effective way of reducing oxygen contents. Details of procedures for determining these parameters can be had from the standards of Metal Powder Industries Federation (MPIF) and the American Society for Testing and Materials (ASTM).

Practically any metal powder adsorbs significant quantities of gases and water vapour from the atmosphere during storage. Such adsorption can lead to the formation of surface oxides on metals which may interfere with compaction and sintering and possibly remain in the sintered material. The amount of such contamination increases with decreasing particle size and with increasing chemical activity of the surface.

The microstructure of the crystalline powder has a significant influence on the behaviour 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.

Prealloyed powders may contain various phases depending on their exact composition, the appropriate phase diagram, their thermal history and the method of powder production used. Multiphase microstructures may result from alloying such as those in steels, cast irons and superalloys. In the case of water atomized solid-solution type alloys, the microstructure, like that of the chilled structure, consists of a cored structure. 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. Such imperfections influence the compaction and sintering response of the concerned powders.

## 3.3 Particle Size and Shape

The shape of the powder is characterised by the dimensionality of the particle and its contour surface. An ideal system of shape characterisation is given in Fig.3.1, together with the major manufacturing techniques which produce such shapes. 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 this 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.

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. There are various methods one may use to calculate average diameters. Particle size, therefore, is not a concise quantity but for any given nonspherical particle may have several values with different meanings, depending on the sizing method used.

Particle size distribution curves relate the particle size to the corresponding fraction of the powder with that size. Figure 3.2 illustrates various size distributions. 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. It can be thus concluded that the particle size distribution is necessary for a complete char-

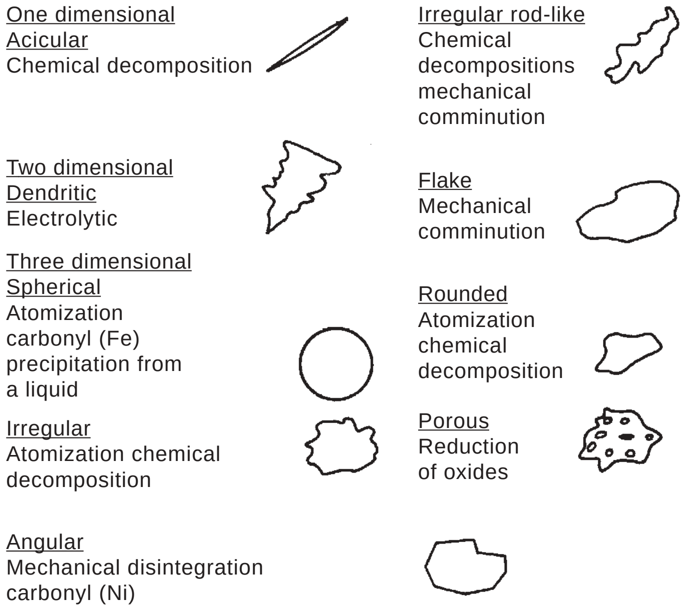


**Fig.3.1** System of particles shape characterization.

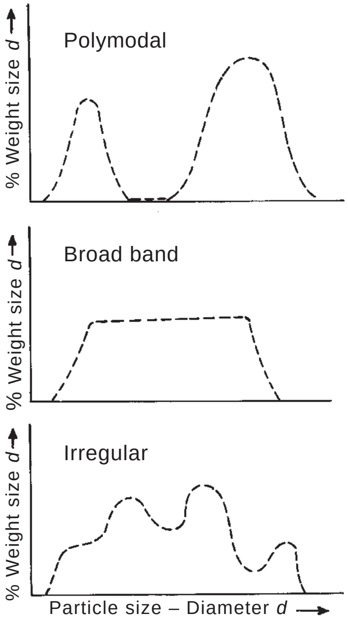


**Fig. 3.2** Schematic illustrations of some realistic particle size distributions.

acterization instead of an average value or even maximum or minimum values of size.

There are a number of particle size measurement techniques available in powder metallurgy, each having their own limitations. Table 3.2 classifies some of the common methods of particle size determination and their limits of applicability.

Out of all the methods, sieving is technologically most satisfactory for reporting and plotting particle size distribution, in which the successive sizes form a geometrical series. The reference point for their scale has become 75 micrometer which is the opening of the 200-mesh woven wire screen standardized by the National Bureau of Standards. Because of the widespread use of this method, one distinguishes between particles which are larger than 44 micrometers and fines or subsieve powder that is smaller than 44 micrometers. Table 3.3 gives some of the most pertinent data for both the Tyler standard and United States sieve series. Micromesh sieves are also available with openings down to at least five micrometers, but are rather difficult to use and maintain, are very fragile and have low load capacities. These sieves are produced by electrodepositon of nickel or copper on to photosensitized machine ruled lines.

Another advantage of screening is that one may synthesize a desired distribution, according to the type of blend required by the manufacturer. Conventional sieving requires a sample of 50 g for accurate analysis and this becomes difficult in analysis of expensive metal powders.

**Table 3.2** Common particle size determination methods and their limits of applicability[2]

| Class | Method | Approximate useful size range (microns) |
|---|---|---|
| Sieving | Sieving using mechanical agitation or ultrasonic induced agitation and screens | 44–800 |
| Microscopy | Micromesh screens | 5–50 |
| | Visible light | 0.2–100 |
| | Electron microscopy | 0.001–5 |
| Sedimentation | Gravitational | 1–250 |
| | Centrifugal | 0.05–60 |
| Turbidimetry | Turbidimetry (light intensity attenuation measurements) | 0.05–500 |
| Elutriation | Elutriation | 5–50 |
| Electrolytic resistivity | Coulter counter | 0.5–800 |
| Permeability | Fisher sub-sieve sizer | 0.2–50 |
| Surface area | Adsorption from gas phase | 0.01–20 |
| | Adsorption from liquid phase | 0.01–50 |

**Table 3.3** Information on sieves used in powder metallurgy

| Mesh designation number | Sieve opening (μm) | | |
|---|---|---|---|
| | New US series | Old US series | Tyler series |
| 20 | 850 | 841 | 833 |
| 35 | – | – | 417 |
| 40 | 425 | 420 | – |
| 60 | 250 | 250 | 295 |
| 80 | 180 | 177 | 175 |
| 100 | 150 | 149 | 147 |
| 140 | 106 | 105 | – |
| 150 | – | – | 104 |
| 200 | 75 | 72 | 74 |
| 230 | 63 | 63 | – |
| 250 | – | – | 63 |
| 325 | 45 | 44 | 44 |

This is now overcome with the development of small sieves. A Ro-tap type machine is a common sieve shaker used in size analysis. Sieve shakers with different shaking mechanisms are used which depend on the shape of powder. A swirling motion is effective for round particles but is extremely slow for elongated particles. A jumping motion is very effective for elongated particles because it throws them into the air and allows them to rotate and perhaps land point first in a hole and pass through it. This means that a very consistent shaking motion is needed.

Another important industrial method for measuring the subsieve particle size is by what is known as the Fisher Subsieve Sizer. This is very much common in refractory metal powder and cemented carbide industries. In this case, the measured surface area is converted into an equivalent spherical surface diameter, which is only an approximate measurement tool. The technique does not measure the surface-connected porosity. A preweighed amount of powder is exposed to a known flow rate and the pressure drop is measured to determine permeability. From the knowledge of powder porosity and theoretical density, the surface area is calculated. The advantage of this method is that it is a direct reading one, which is very convenient for quick industrial quality control of fine powders. It must be clearly recognised that the value of specific surface obtained from a permeability experiment is representative of the ‘friction’ surface presented by powder mass to the flowing fluid.

For the details of other methods of particle size determination, one can refer to the book by German.[1]

## 3.4 Particle Surface Topography

The nature of the surface of the individual particles is also an important powder characteristic. 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. The extent of actual particle-to-particle contact during sintering will also be affected by the nature of the surface roughness. Chemical reactivity of the powder will also tend to increase with increasing surface roughness, especially the irregular type.

## 3.5 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 surface area of a given powder is measured by the BET method, in which an adsorption of a species in solution may be used to obtain a value of specific surface ($S_w$) if the surface is completely covered by a monomolecular layer of the solute. From a knowledge of the area occupied by one molecule, the total area of the powder sample and, finally, $S_w$ can be obtained. The amount of gas adsorbed in a monomolecular layer in $m^2$ is calculated from an adsorption isotherm, i.e. a series of measurements of the volume $V$ of gas adsorbed as a function of pressure $p$.

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.

## 3.6 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 bearing 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 (Fig.3.3).

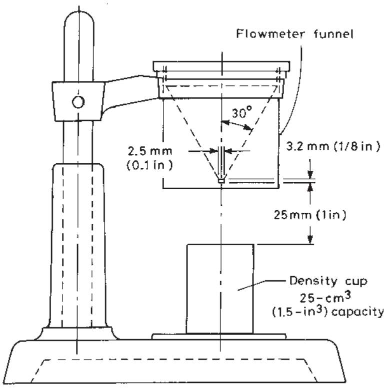


**Fig.3.3** Hall flowmeter.

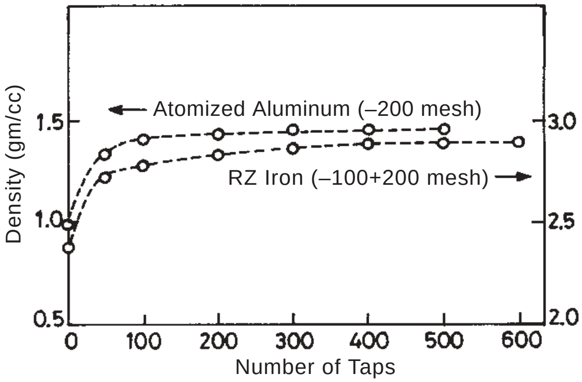


**Fig.3.4** The density of loose powder as a function of the number of taps, for atomized aluminium and atomized/reduced iron powders[2].

Very often a mass of loose powder is mechanically vibrated or tapped. The density of the loose powder increases due to this treatment and is always higher than the apparent density. The greatest increase in density occurs during the initial tapping period and eventually the density becomes constant. The final stable density is the value reported as the tap density (Fig.3.4). The amount of increase in density due to tapping depends on the extent of original friction forces between the particles. The greater the frictional conditions in the original powder (small sizes, irregular shapes and roughened surface), the greater the increase in density due to tapping.

Table 3.4 gives some typical data of apparent and tap densities of iron powder produced by different methods.

## 3.7 Flow Rate

Rapid rates of P/M parts production require a relatively rapid flow of pow-

**Table 3.4** Apparent and tap densities of various powders[2]

| 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.

der from storage containers to dies. 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. The test offers only a means of comparison and evaluation because in the majority of operating conditions the powder does not have to flow through a small orifice. Flow times are, therefore, proportional to the reciprocal of the flow rates. 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. When a fine size powder is mixed in a coarse powder, because of the increase in the apparent density, the flow time is decreased irrespective of whether the particles was irregular or spherical. However, in case of irregular powder additions an amount is reached for which no flow behaviour is observed. This corresponds to the presence of an excessive amount of frictional surface area.

## 3.8 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/cm$^3$, 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 thus a higher production rate can be achieved.

**Table 3.5** Green density and green strength for various types of iron powders

| Powder | Apparent density (g/cm$^3$) | Compaction pressure | | Green density (g/cm$^3$) | Green strength | |
|---|---|---|---|---|---|---|
| | | (N/mm$^2$) | (tsi) | | (psi) | (N/mm$^2$) |
| Sponge [(a)] | 2.4 | 415 | 30 | 6.2 | 14.41 | 2100 |
| | | 550 | 40 | 6.6 | 22.05 | 3200 |
| | | 690 | 50 | 6.8 | 28.25 | 4100 |
| Atomized sponge [(b)] | 2.5 | 414 | 30 | 6.55 | 13.09 | 1900 |
| | | 550 | 40 | 6.8 | 18.80 | 2700 |
| | | 690 | 50 | 7.0 | | |
| Reduced [(a)] | 2.5 | 415 | 30 | 6.5 | 15.85 | 2300 |
| | | 550 | 40 | 6.7 | 20.67 | 3000 |
| | | 690 | 50 | 6.9 | 24.11 | 3500 |
| Sponge [(a)] | 2.6 | 415 | 30 | 6.6 | 18.60 | 2700 |
| | | 550 | 40 | 6.8 | 24.80 | 3600 |
| | | 690 | 50 | 7.0 | 26.87 | 3900 |
| Electro [(c)] | 2.6 | 415 | 30 | 6.3 | 31.69 | 4600 |
| | | 550 | 40 | 6.7 | 42.72 | 6200 |
| | | 690 | 50 | 6.95 | 53.74 | 7800 |

[(a)] powders contained 1% zinc sterate blended in
[(b)] powders contained 0.75% zinc stearate blended in
[(c)] unlike the other powders, this one was isostatically pressed (from C.E.Buren and H.H.Hirsch, in: Powder Metallurgy, Interscience, New York, 403–440)

## 3.9. 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 green density (or compaction pressure);

– decreasing the amount of certain interfering additives. For example, the addition of small alloying elements, such as soft graphite to iron and lubricant, prevents mechanical interlocking.

The standard green strength test is a transverse bend test of a 12.7 by 31.7 mm (0.50 by 1.25 inch) rectangular specimen 6.35 mm (0.25 inch)

**Table 3.6** Typical maximum levels for occupational exposure (8 hour day)

| Material | Concentration (μg/m$^3$) |
|---|---|
| Plutonium | 0.0001 |
| Beryllium | 2.0 |
| Nickel-carbonyl | 7.0 |
| Uranium | 80.0 |
| Cadmium | 100.0 |
| Chromium oxide | 100.0 |
| Mercury | 100.0 |
| Tellurium | 100.0 |
| Thorium | 110.0 |
| Lead | 150.0 |
| Arsenic | 500.0 |
| Zirconium oxide | 5000.0 |
| Iron oxide | 15000.0 |
| Titanium oxide | 15000.0 |
| Zinc oxide | 15000.0 |

from F.Clark, Advanced Techniques in Powder Metallurgy, p.161, Rowman and Littlefield, N.Y., 1963.

thick. It is the stress calculated from the flexure formula, required to break the specimen, which as follows:

$$\text{Green strength} = \frac{3PL}{2wt^2}, \text{N/mm}^2$$

where $P$ is the breaking load, N; $L$ is the distance between the supporting rods, mm; $t$ is the specimen thickness, mm; $w$ is the width of the specimen, mm

Table 3.5 shows the relationship among green strength, apparent density, compacting pressure and green density for several types of iron powders.

## 3.10 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. Table 3.6 shows the data for typical maximum permissible levels of toxic powders, while Table 3.7 contains data describing the explosibility and ignition conditions for some materials. The chemical reactivity of a material increases as the ratio of surface area-to-volume increases. For this reason, fine par-

**Table 3.7** Ignition and explosibility of powders[2]

| Material | Size, microns | Ignition temperature °C [a] | | Minimum explosive concentration oz/ft$^3$ | Index of explosibility [c] |
|---|---|---|---|---|---|
| | | Cloud | Layer | | |
| | | | | | Severe |
| Aluminium atomized | –44 | 650 | 760 | 0.045 | >10 |
| Al–Mg Alloy | –44 | 430 | 480 | 0.020 | >10 |
| Magnesium | –74 | 620 | 490 | 0.040 | >10 |
| Thorium Hydride | 3 | 260 | 20 | 0.080 | >10 |
| Zirconium | 3 | 20 | 190 | 0.045 | >10 |
| Uranium Hydride | 3 | 20 | 20 | 0.060 | >10 |
| Titanium | 10 | 330 | 510 | 0.045 | >10 |
| Uranium | 10 | 20 | 100[b] | 0.060 | >10 |
| Thorium | 7 | 270 | 280 | 0.075 | >10 |
| | | | | | Strong |
| Zirconium Hydride | –44 (98%) | 350 | 270 | 0.085 | 3.7 |
| Iron Carbonyl | –74 | 320 | 310 | 0.105 | 1.6 |
| | | | | | Moderate |
| Boron | –44 | 470 | 400 | -0.100 | 0.8 |
| Chromium | –44 (98%) | 580 | 400 | 0.230 | 0.1 |
| Manganese | –44 | 460 | 240 | 0.125 | 0.1 |
| Tantalum | –44 | 630 | 300 | -0.200 | 0.1 |
| Tin | –53(96%) | 630 | 430 | 0.190 | 0.1 |
| | | | | | Weak |
| Lead | –53 | 710 | 270 | - | <<0.1 |
| Molybdenum | –74 | 720 | 360 | - | <<0.1 |
| Cobalt | –44 | 760 | 370 | - | <<0.1 |
| Tungsten | –74 (99%) | 730 | 470 | - | <<0.1 |
| Beryllium | 1 | 910 | 540 | - | <<0.1 |
| Copper | –44 (98%) | 700 | - | - | <<0.1 |

[a] These data apply to relatively coarse dust (–200 mesh) but not to submicron powder

[b] In this test less than one gram of powder used; larger quantities ignited spontaneously

[c] IE = ignition sensitivity X = explosion severity

(from M.Jacobson, A.R.Cooper and J.Nagy, Explosibility of Metal Powders, Bureau of Mines, Report 6516, 1964)

**Table 3.8** Some characteristics of metal powders made by various commercial methods

| Method of production | Typical purity (est.) | Particle characteristics | | Compressibility | Apparent density | Green strength |
|---|---|---|---|---|---|---|
| | | Shape | Meshes available | | | |
| Atomization | High 99.5+ | Irregular to smooth, rounded dense particles | Coarse shot to 325 mesh | Low to high | Generally | Generally low |
| Gaseous reduction of oxides | Medium 98.5 to 99.0+ | Irregular, spongy | Usually 100 mesh and finer | Medium | Low to medium | High to medium |
| Gaseous reduction of solutions | High 99.2 to 99.8 | Irregular, spongy | Usually 100 mesh and finer | Medium | Low to medium | High |
| Reduction with carbon | Medium 98.5 to 99.0+ | Irregular, spongy | Most meshes from 8 down | Medium | Medium | Medium to high |
| Electrolytic | High +99.5+ | Irregular, flaky to dense | All mesh sizes | High | Medium to high | Medium |
| Carbonyl decomposition | High 99.5+ | Spherical | Usually in low micron ranges | Medium | Medium to high | Low |
| Grinding | Medium 99.+ | Flaky and dense | All mesh sizes | Medium | Medium to high | Low |

ticles of many materials combine with oxygen, ignite and result in explosive conditions.

## 3.11 Conclusion

Chapters 2 and 3 suffice to convey the message of the interrelation of the powder production methods and powder characteristics. Such a close relationship is not so prevalent in metal production methods other than for powder production. Table 3.8 summarises different types of metal powder characteristics along with their routes for production.

## Reference

1. R.M. German, Powder Metallurgy Science, 2nd edition, MPIF, Princeton, 1994.
2. J.S. Hirschhorn, Introduction to Powder Metallurgy, American Powder Metallurgy Institute, New York, 1969.

# 4 METAL POWDER TREATMENT

## 4.1 Annealing

It is customary that the powder producer delivers the powder to the fabricator ready for mixing. 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. The former may be of batch or continuous type. The furnace construction is similar to that given in Chapter 6, which deals with sintering technology. Annealing temperatures are kept as low as possible to minimize sintering.

## 4.2 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.

Various variables in the powder mixing process have been highlighted by Hausner.[1] They are:

1. Type of mixer
2. Volume of the mixer
3. Geometry of the mixer
4. Inner surface area of the mixer
5. Constructional material and surface finish of the mixer
6. Volume of the powder in the mixer before mixing
7. Volume of the powder in the mixer after mixing
8. Volume ratio of component powders
9. Volume ratio of mixer to powder
10. Characteristics of component powders
11. Type, location and number of loading and emptying devices
12. Rotational speed of mixer
13. Mixing time
14. Mixing temperature
15. Mixing medium (gaseous or liquid)
16. Humidity, when mixing in air.

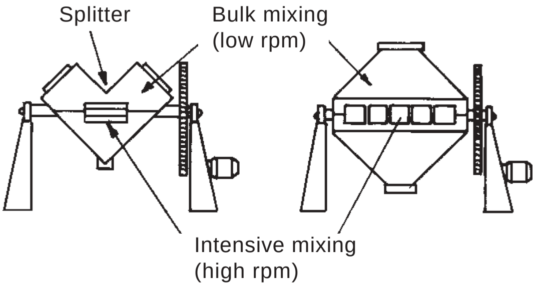


**Fig. 4.1** V-type and double cone mixers.

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. The apparent density of the mix tends to increase with mixing time.

### Types of Mixers

Among various types of mixers available, the following are most common for metal powders (Fig.4.1):

**Double Cone Mixer**: This consists of vertical cylinders with conical ends, which rotate about a horizontal axis. This rotation imparts a continuous rolling motion which spreads and folds the powders as they move in and out of the conical area. This action thoroughly mixes the powders with little or no change in the size and shape of the individual particles. Figure 4.2 shows the double cone mixer flow pattern.

**V-Mixer**: This is constructed by joining two cylinders of equal length into a ‘V’. As the ‘V’ rotates about its horizontal axis, the powder charge splits and refolds. Figure 4.2 illustrates the V-mixer flow pattern.

## 4.3 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 (i.e. small deviation of particle sizes from a mean value). This results in increased homogeneity of nonuniform mixtures, increased chemical reaction rates, to mention but a few examples of applications. The actual requirements of a suitable size reduction process are extremely varied and depend on several parameters.

Before selecting an equipment for size reduction, the following aspects may be looked into:

**(a) Type of Material**: What are the physical and chemical properties of the material? Is the size reduction process affected by, for example, hardness or toughness or by chemical reactions?

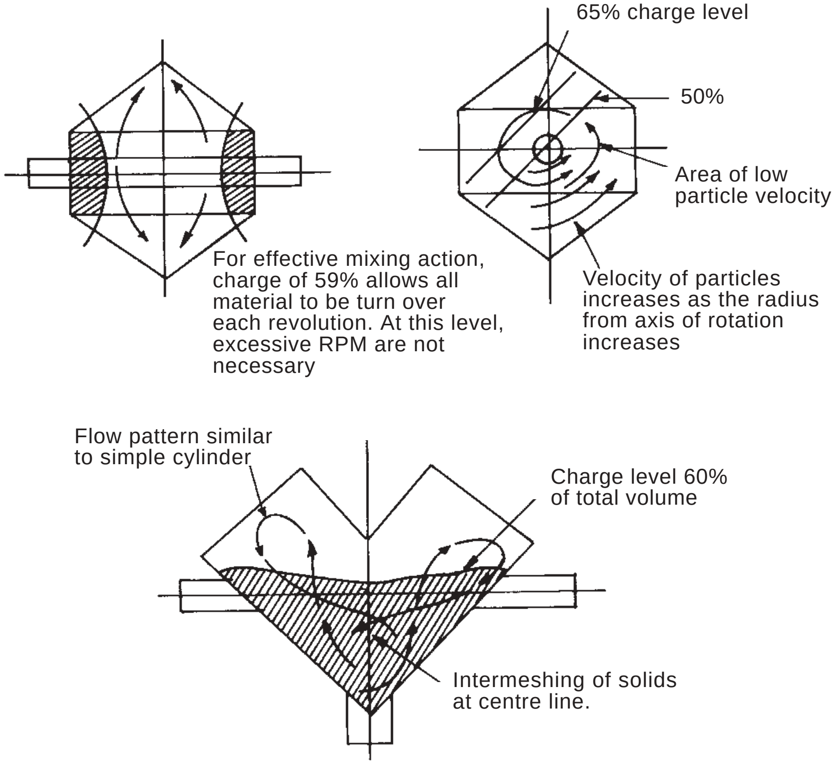


**Fig. 4.2** Flow pattern in (a) double cone and (b) V-type mixers.

(**b) Final Size**: To what particle size the metal be reduced? Should as narrow particle size distribution as possible be achieved?

(**c) Abrasion**: Which impurities caused by abrasion of the grinding elements must be avoided? What quantity of impurities is still permissible in other cases?

**(d) Versatility**: If necessary, should wet size reduction be possible? Should the size reduction be carried out in an inert atmosphere or in a vacuum?

Various methods for size reduction can be classified as:

(*i*) **Crushing**: The major equipments are mortar and pestle, heavy drop hammer, and jaw crushers. In jaw crushing the crushing chamber is formed by one fixed jaw and one movable jaw between stationary side support walls. The movable jaw is mounted eccentrically at the top and is driven by a motor via a flywheel. During the crushing process, the material is drawn down into the tapered crushing chamber as a result of the eccentric jaw motion and is reduced in size by compression and frictional forces. In addition, the angle between the jaws can be altered to give optimum adjustment to the crushing of the material. The final crushed product particle size can be adjusted to values between 15 and 1 mm by adjusting the gap at the base of the jaws. The standards jaws and side walls are manufactured from hardened steel. If the feed material is very abrasive or particular impurities are to be avoided, these components are also available in stainless steel or hard tungsten carbide. If the fixed jaw is removed, access is given to the crushing chamber and the equipment can be cleared easily. In addition, the connection of an exhaust device allows work to be carried out in dust free conditions.

(*ii*) **Ball Milling**: The ball mills can be divided into two types: centrifugal and planetary mills. In a centrifugal ball mill, a single bowl fastener is merely horizontally and eccentrically driven while not rotating itself. In spite of this, the velocity of the grinding balls in this case is still six times that of the grinding balls in the gravity ball mills.

In planetary ball mills two or four bowl fasteners, each of which accommodates one grinding bowl, are attached to a supporting disc. During grinding, the grinding bowls and supporting disc rotate in opposite directions, so that two different centrifugal forces act on the bowl contents. The grinding material is reduced in size as a result of both attrition and impact. The grinding balls have a velocity which is twelve times that of the grinding balls in a grinding ball mill. Each grinding medium influences the grinding process via the specific weight of balls. For example, if a grinding medium of agate (specific weight 2.6 g/cm$^3$) is used, the corresponding balls have a smaller impact energy than those of tungsten carbide (specific weight 14.75 g/cm$^3$). The more mixing grinding process is intended, the smaller is the ball size selected. The grinding time in case of centrifugal ball mill is increased because of smaller ball acceleration.

(*iii*) **Disc Grinder**: The disc grinders are suited for processing hard brittle materials. A wet grinding in a closed grinding vessel which is driven horizontally and eccentrically and which contains grinding elements (disc or ring) is used to reduce the material to give a final particle size of a few micrometers. Impact and friction between the grinding elements and the grinding vessel cause such grinding energy that the process is generally concluded within a few minutes.

Table 4.1 gives the details of various grinding elements. The chemical composition qualitatively determines the type of contamination which can occur, whilst the abrasion behaviour determines the quantity thereof. Other details like specific weight (ball weight in ball mills), Mohs hardness, compression and breaking strength (in the crushers) and chemical resistance should also be considered.

(*iv*) **Attritor Milling**: Attritor milling or mechanical alloying is achieved by high energy ball milling under conditions such that powders are not only fragmented but also rewelded together. In this case, the ball charge is stirred vigorously with rotating paddles. The first commercial production used attritors able to process up to 34 kg of powder per charge but nowadays, up to 1 t of powder is milled in a 2 m diameter mill containing more than a million balls which weigh a total of 10 t. The charge is a blend of elemental and prealloyed powders at least one of which is

**Table 4.1** Some grinding element materials

| Material | Abrasion behaviour | Specific weight g/cm$^3$ | Mohs hardness | No chemical resistance in |
|---|---|---|---|---|
| Agate ($SiO_2$) | Very abrasion-proof approx. 200 times more resistant than hard porcelain | 2.65 | 7 | Hydrofluoric acid (HF) |
| Zirconium oxide ($ZrO_2$) | Very abrasion-proof approx. 10 times more resistant than sintered corundum | 5.7 | 8.5 | Sulphuric acid ($H_2SO_4$)<br>Hydrofluoric acid (HF) |
| Alumina ($Al_2O_3$) | Good abrasion resistance | 4.0 | 9 | conc. Acids |
| Hard porcelain | Sufficiently abrasion proof | 3.1 | 8 | conc. Acids |
| Hardened chromium steel 2080 | Good abrasion resistance better than CrNi–steel | 7.9 | | Acids |
| Hardened steel CK45 | Good abrasion resistance | 7.9 | | Acid |
| Stainless steel 4301 | Average abrasion resistance | 7.9 | | Acids |
| Hard metal tungsten carbide | Extremely abrasion proof approx.200 times more resistant than agate | 14.75 | 8.5 | Nitric acid ($HNO_3$)<br>Hydrochloric acid (HCl) |

a ductile material. To provide a dispersed phase in superalloys, fine inert oxides can be included in the charge, usually $Y_2O_3$. Mechanical alloying process was first invented by J.S. Benjamin at INCO, N.Y., in early seventies.

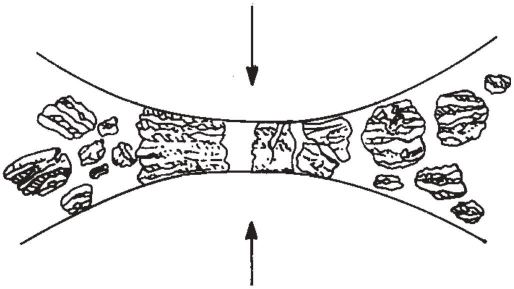


**Fig. 4.3** Effect of single collision between two balls on trapped powder.

Figure 4.3 illustrates the effect of a single high energy collision between two balls or powder trapped between them. 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, between which are trapped fragments of the brittle powder and the dispersoid. 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.

Mechanical alloying is not simply mixing on a fine scale: true alloying occurs. The progress of alloying can be monitored by x-ray diffraction studies.

## 4.4 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. The process is better suited for small batch sizes.

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, and 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. Defloculating 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.

Figure 4.4 illustrates schematics of centrifugal and single-fluid nozzle atomizers. In the former, the atomizer and the inlet for the drying air are positioned at the top of the dryer. 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. However, the product exists with moist air, and the exit

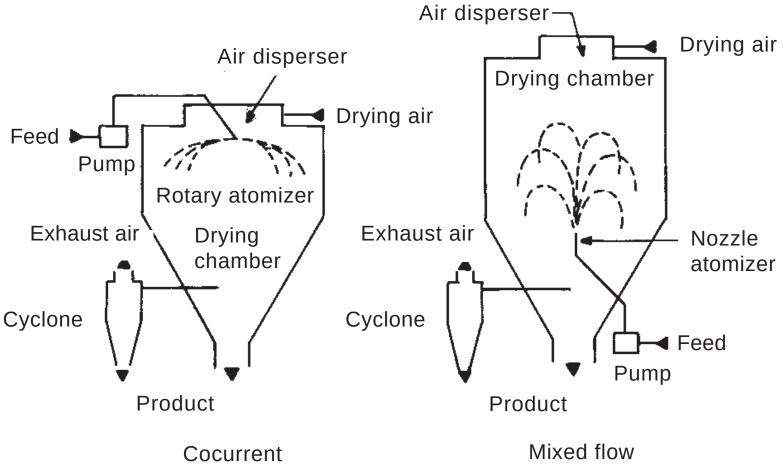


**Fig. 4.4** Spray dryers: (left) cocurrent spray–dryer with centrifugal atomizer and (right) mixer flow spray–dryer with a nozzle atomizer.

temperature must be relatively high to obtain a dry product. In the nozzle atomizer, the slurry and drying air inlet are at opposite ends of the drying chamber. Partially dried droplets encounter the incoming hot air, and the product heating is greater. In the two-fluid nozzle atomization, the residence time of the spray is increased and it provides a means for reducing the size of the chamber needed for drying.

The majority of the spray dried product is discharged through a rotary valve into interchangeable containers attached at the base. Product fines entrained in the exhaust air are separated using a cyclone or bag filters. Product fines may be used in some pressing operations, but are often recycled into the feed slurry. Periodic cleaning of the dryer using a liquid spray is required to remove the granulate crust. Abnormal large granules and flakes of granulate crust from the wall of the dryer are undesirable and are commonly removed by screening.

Air bubbles present in the feed slurry or occluded during atomization using a two-fluid nozzle may persist as relatively large pores in the granule. Granules with a large crater are often noticed in industrial spray dried material. The tendency for these shapes is higher when the inlet temperature is relatively high, the binder content or molecular weight is relatively high and the solids loading in the slurry is relatively low. Rapid surface drying and the formation of the surface of low permeability cause bursting of the granule due to gas pressure.

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. The popularity of spray drying as a means of using fine powder sizes in high productivity forming equipment is increasing. A disadvantage is that the organic binder must be removed in the sintering cycle.

## 4.5 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 impart 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 are described below:

(*i*) **Electroplating**: In this method, a second dispersed phase of controlled particle size may be introduced into a plating solution. This is referred to as dispersion, inclusion, occlusion, composite or electrophoretic plating, deposition or coating. The requisites are:

– The particles must be insoluble (or only slightly soluble) in the solution;

– The particles must be compatible with the solution, i.e. not produce any detrimental effect;

– The particle must be dispersed either naturally (as colloid size particles) or mechanically (stirring, agitation) in order to contact physically the surface being coated.

Electrophoretic coating produces a coating on a conducting substrate from a dispersion of colloidal particles. The powder to be coated is immersed in an aqueous dispersion which dissociates into negatively charged colloidal particles and positive cations. An electric field is applied with the powder mass as anode; the colloidal particles are transported to the anode, where they are discharged and form a film. The coating is air dried and baked to remove the solvent medium. The coating is nonadherent and must be processed faster by compaction and sintering. The coating thicknesses can be varied by controlling voltage, electrode spacing, suspension concentration and time.

(*ii*) **Electroless Deposition**: Electroless plating processes differ from electroplating processes in that no external current source is required. Metal coatings are produced by chemical reduction with the necessary electrons supplied by a reducing agent present in the solution (RA):

$$\mathrm{Mn}^{n+} + \mathrm{n}e^{-}(\text{supplied by RA}) \xrightarrow{\text{Catalytic Surface}} \mathrm{M}^{0}(\text{+reaction products})$$

The significance of the process is that the reaction is catalysed by certain metals immersed in the solution and proceeds in a controlled manner on the substrates surface.

The deposit itself continues to catalyze the reduction reaction so that the deposition process becomes self-sustaining or autocatalytic. These features permit the deposition process of relatively thick deposits. This process is different from other types of chemical reduction by (a) simple immersion or displacement reactions in which deposition ceases when equilibrium between the coating and the solution is established (e.g. copper immersion on steel from copper sulphate solution) and (b) homogeneous reduction where deposition occurs over all surfaces in contact with the solution. The reducing agents most widely used are sodium hypophosphate (for Ni, Co), sodium borohydride (for Ni, Au), dimethyl amine boron (for Ni, Co, Au, Cu, Ag), hydrazine (for Ni, Au, Pd) and formaldehyde (for Cu). To ensure spontaneous reduction other chemicals are added. These are generally organic complexing agents and buffering agents. Other additives provide special functions as in electroplating solutions: additional stabilizers, brighteners, stress relievers.

The following are the advantages of electroless plating over electroplating:

1. Internal surfaces are evenly coated. The uniformity is limited only by the ability of the solution to contact the surface and be replenished at the surface.
2. Deposits are less porous.
3. Almost any metallic, nonmetallic, non-conducting surfaces, including polymers, ceramics, glasses can be plated. Those materials which are not catalytic can be made catalytic by suitable sensitizing and nucleation treatments.
4. Electrical contacts are not required.
5. The deposits may have unique chemical, mechanical, physical and magnetic properties.

However, there are some disadvantages too as compared to electroplating:

– Solution instability
– More expensive
– Slower deposition rates
– Frequent replacement of tanks or liners
– Greater and more frequent control for reproducible deposits.

(*iii*) **Coating by Hydrometallurgical Process**: The details of the hydrometallurgical process for production of metal powders have been described earlier in Chapter 2. A great number of metals, metalloids, non metals, metal alloys, oxide natural minerals, hard metal compounds and plastic powders can be coated with one or more metals selected from Ni, Co, Mo. Cu or Ag to form new materials, called composite powders.

In developing composite powders, the cores must conform to certain requirements: (a) they must be nonreactive in the system selected for metal deposition; (b) they must be catalytically active with respect to the deposited metal, and (c) they should be in such a physical form as to be able to remain suspended in solution in the agitated autoclave. Many metals, metal alloys carbides, nitrides and some nonmetals such as graphite and phosphorus are catalytically active and are readily coated without special treatment of the core but some cores have to be activated. The most effective way of activating is to wash with a stannous chloride solution followed by treatment with palladium chloride. During this treatment, palladium chloride is adsorbed on the surface and is reduced in the autoclave by hydrogen to the metallic form, thus forming catalytically active sites on which the metal precipi-

**Table 4.2** Molybdenum coated composite powders prepared by precipitation of molybdenum from the aqueous ammonical–ammonium sulphate solution by hydrogen and subsequent heat treatment under $H_2$ atmosphere at 950°C[2]

| Composition | Conditions | | | | Core | $PdCl_2$ treatment | Product | | Mo left in reduced solution, g/l |
|---|---|---|---|---|---|---|---|---|---|
| | Temperature, °C | $P_{H2}$, $kg/cm^2$ | Time, min | | | | Mo | Core | |
| Mo/Ni | 160 | 36 | 30 | 22 g/l | Ni powder, 10 µm | no | 69.4 | 29.1 | 0.4 |
| Mo/Fe | 190 | 36 | 30 | 12 g/l | Fe, RZ365 | no | n/a | n/a | 30.0 |
| Mo/Fe | 160 | 25 | 120 | 21 g/l | Fe, RZ365 | yes | 70.0 | 28.8 | 0.1 |
| Mo/Al | 190 | 25 | 120 | 12 g/l | Al, type 40 | no | n/a | n/a | 39.7 |
| Mo/Al | 160 | 34 | 60 | 21 g/l | Al, spherical | yes | 59.4 | 39.7 | 2.2 |
| Mo/W | 160 | 36 | 45 | 21 g/l | W, 7–9 µm | yes | 58.0 | 41.4 | 0.7 |
| Mo/Si | 180 | 35 | 15 | 11 g/l | Si, –325 mesh | yes | 64.0 | 32.5 | <0.1 |
| Mo/C | 190 | 25 | 60 | 22 g/l | Graphite, 38 | no | 69.9 | 27.5 | <0.1 |
| $Mo/Al_2O_3$ | 160 | 38 | 30 | 21 g/l | $Al_2O_3$ | yes | 68.8 | 30.9 | 0.2 |
| $Mo/ZrO_2$ | 190 | 26 | 35 | 21 g/l | $ZrO_2$ | yes | 51.3 | 43.7 | 7.6 |
| $Mo/TiO_2$ | 160 | 36 | 35 | 21 g/l | $TiO_2$, Micria | yes | 60.0 | 39.6 | 18.9 |
| Mo/TiC | 160 | 40 | 20 | 21 g/l | TiC, 3 µm | yes | 60.6 | 38.2 | <0.1 |
| $Mo/Cr_3C_2$ | 160 | 39 | 45 | 21 g/l | $Cr_2C_3$, –325 mesh | yes | 70.4 | 26.0 | 0.8 |
| Mo/SiC | 160 | 35 | 40 | 21 g/l | SiC, 11 µm | yes | 63.5 | 35.5 | <0.1 |
| Mo/WC | 160 | 40 | 90 | 21 g/l | WC,200/325 mesh | yes | 51.4 | 48.5 | 12.8 |
| Mo/Glass | 160 | 39 | 70 | 21 g/l | Glass, –400 mesh | yes | 63.5 | 35.8 | <0.1 |
| $Mo/Si_3N_4$ | 160 | 35 | 15 | 21 g/l | $Si_3N_4$, Un. Carb. | yes | 63.5 | 35.7 | 0.1 |
| Mo/Asbestos | 160 | 38 | 20 | 6 g/l | Asbestos, Merck | yes | 66.6 | 32.7 | <0.1 |

tates preferentially. The metal most easy to coat with is nickel. Coating with cobalt is much more difficult and only the very active cores, such as carbides can be coated completely. The deposition of Cu or Ag can be achieved, but without catalyst forms spotty coating.

There are no restriction on the composition of composite powders and powders containing 1 to 99 % of the coating metal have been prepared. However, in order to ensure complete coating of the core a 2–3 μm layer of the coating metal is considered to be a minimum requirement.

When complete coating is desirable, the specific gravity of the components, and the particle size and shape should be taken into consideration for the calculation of the percent coating.

Table 4.2 illustrates a list of molybdenum coated powders, which is precipitated from aqueous ammonium sulphate–ammonia system as a lower molybdenum oxide containing 4–5% $NH_3$. The reduction takes place in the presence of a catalyst and it was established that palladium chloride and molybdenum powder itself can catalyze the reaction. The molybdenum oxide precipitated on the cores in converted to the metallic form by treatment with hydrogen at 950°C.[2]

Composite powders produced by such method have found commercial applications in flame and plasma spraying. Such powders are useful in preparation of alloys, dispersion-strengthened materials, porous materials, low friction materials and hardfacing coatings.

## References

1. H.H. Hausner and M.K. Mal, Handbook of Powder Metallurgy, 2nd edition, Chemical Pub. Co. Inc., New York, 1982.
2. W. Kunda, New Developments in the Preparation of Composite Powders, in: Proceedings of 7th Plansee Seminar, 21–25 June, 1971, Vol.IV, Metallwerk Plansee, Reutte.

# 5 METAL POWDER COMPACTION

## 5.1 Introduction

The compaction of metal powders has the following major functions:

(a) to consolidate the powder into desired shape

(b) to impart, to as high a degree as possible, the desired final dimensions with due consideration to any dimensional changes resulting from sintering.

(c) to impart the desired level and type of porosity.

(d) to impart adequate strength for subsequent handling.

Several approaches exist for achieving these goals. In general the techniques can be categorised as (a) continuous vs discontinuous process, (b) pressures – high vs low, (c) compaction velocity – high vs low (d) temperature – room to elevated temperature; (e) uniaxial vs hydrostatic pressures.

In the present chapter only cold compaction methods shall be described.

## 5.2 Die Compaction

Die compaction represents the most widely used method and is considered as the conventional technique. This involves rigid dies and special mechanical or hydraulic presses. Densities of up to 90 % of full density can be achieved following the compaction cycle, the duration of which may be of the order of just a few seconds for very small parts.

Powders do not respond to pressing in the same way as fluids and do not assume the same density throughout the compact. The friction between the powder and die wall and between individual powder particles hinders the transmission of pressure. A high uniformity in green parts can be achieved depending on:

– the kind of compacting technique

– the type of tools

– the materials to be pressed and the lubricant.

The compacting techniques used may be characterised by references to the movement of the individual tool elements – upper punch, lower punch and die relative to one another.

Pressing within fixed dies can be divided into:

– Single action pressing

– Double action pressing

In the former the lower punch and the die are both stationary. The pressing operation is carried out solely by the upper punch as it moves into the fixed die. The die wall friction prevents uniform pressure distribution. The compact

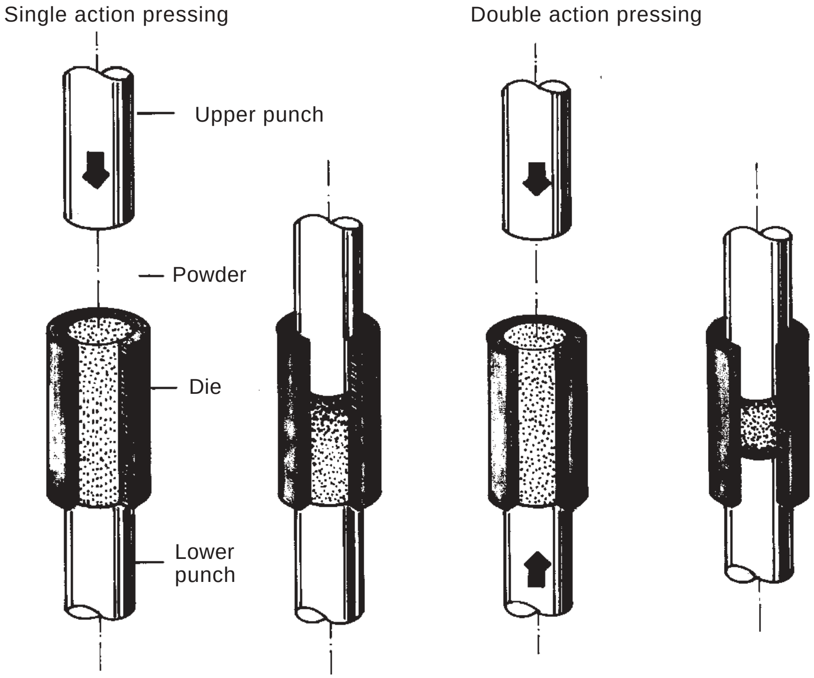


**Fig. 5.1** Single and double acting powder compaction.

has a higher density on top than on the bottom. In the latter type of pressing only the die is stationary in the press. Upper and lower punches advance simultaneously from above and below into the die (Fig.5.1). The consequence is high density at the top and undersides of the compact. In the centre there remains a ‘neutral zone’ which is relatively weak.

### *5.2.1 Pressing Operation*

The pressing operations can be sequenced as follows:

1. **Filling** of the die cavities with the required quantity of powder.
2. **Pressing** in order to achieve required green density and part thickness.
3. **Withdrawal of the upper punch from the compact**: Here the risk of cracking of green parts is felt. As the upper punch withdraws the balance of forces in the interior of the die ends. In the case of parts with two different thicknesses, e.g. flange with a hub, the elastic spring back of the lower punch is the greatest danger. Other problems are protrusions required on the upper face of the part. In the case of thin parts with large projected area, cracking is common due to elastic spring back of the lower punch and the part itself. The former pushes the part still lying in the die cavity upwards, while the latter tends to expand the part.
4. **Ejection**: The tooling must be done in such a manner so that the

ejection of part is feasible. Ejection of a part of complex forms is rather problematic, as it involves friction between the green part and tool walls. The green strength must be high to resist the bending stresses introduced by the ejection force.

There is another type of compaction involving upper punch pressing with floating die. This is characterized by a stationary lower punch the upper punch moves into a die supported by spring. As soon as the friction between the powder and the die wall exceeds the spring power, the die wall is carried down. The friction will vary slightly from stroke to stroke. It also depends on the degree of wear in the tools so that a constant density distribution is difficult to maintain over a period.

During second world war another tooling method was developed in Germany, known as **'withdrawal tooling'**. In this case, the lower punch does not move during compacting cycle. After the upper punch has entered the die cavity, both upper punch and die plate move downwards. After the compact has been pressed, the upper punch moves up, but the die plate and lower coupler move further down until the top of the die plate is flush with the lower punch (Fig.5.2). The compact is ejected and can be moved out of the way by the loading shoe. Die plate and lower coupler then move back into the filling position and the cycle repeats.

The major advantage of withdrawal system of tooling is that the lower punches are relatively short and are well supported during compaction and ejection. When there are multiple lower punches, as many of them as possible rest directly on the base plate. Withdrawal tooling can be built for very complex parts. On the other hand, in the tooling system with ejection by the lower punches the motions of the punches are built into the multiple action presses. In many cases no tool holders are required.

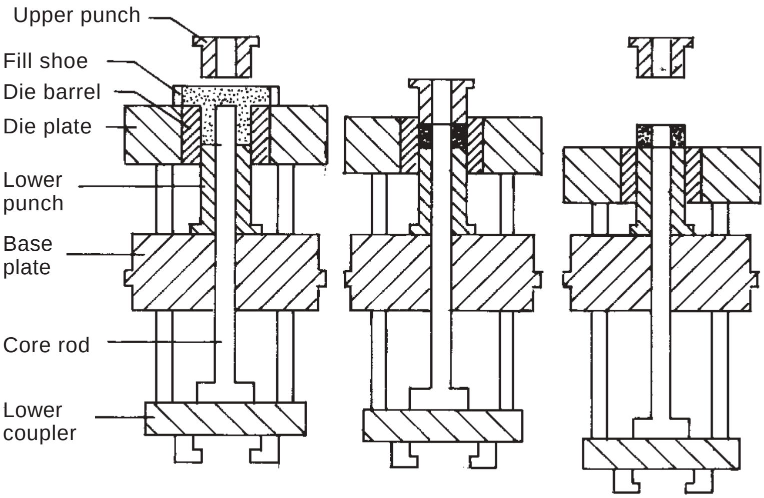


**Fig. 5.2** Sequence of operations for pressing with the withdrawal system.

### Split Die Systems

Another rigid tooling system is known as split die system. It enables the compaction of parts with completely asymmetric upper and lower sections in the pressing directions. This system requires two die holding plates to carry the upper die and lower die. Each plate is controlled and moved independently[6].

### *5.2.2 Compaction Presses*

Compaction presses for powders are of two types – mechanical or hydraulic. There are others partly hydraulic and partly mechanical. Presses from 3 to 1000 tons capacity are available. The optimum operating speed is dictated by the size and complexity of the P/M parts to be made.

**Hydraulic presses** produce working force through the application of fluid pressure on a piston by means of pumps, valves, intensifiers and accumulators. Inherent in the hydraulic method of drive transmission is the capability to provide infinite adjustment of stroke speed, length and pressure within the limits of press capacity. Also, full tonnage can be extended throughout the complete length of the stroke.

In **mechanical presses**, a flywheel stores energy, which is then released and transferred by one of a variety of mechanisms (eccentric, crank, knuckle joint, toggle etc.) to the main slide. In most mechanical presses, the movement or stroke of the slide is adjustable within the limit of daylight of the press. Mechanical presses are classified by one or a combination of characteristics viz. sources of power, method of actuating the ram, type of frame and type of clutch, brake and control system.

The energy stored in the flywheel must be sufficient to ensure that the work per stroke required of the press will not reduce the flywheel's speed by more than 10 to 15 percent. The most common type of mechanical press is the eccentric or crank type which converts rotary motion to linear motion. In the toggle type the eccentric or crank straightens a jointed arm or lever, the upper end of which is fixed at the top, while the lower end is guided for controlled accurate punch guidance into the die. In the cam type of mechanical press, pressing speed, timing, and motion are controlled by changing the contours of the cams or cam inserts. A detailed description of such presses are given elsewhere.[1] Figure 5.3 illustrates a general view of the automatic mechanical press.

### Rotary Presses

A rotary press is a mechanically operated machine, which uses a number of identical sets of tools to produce parts at high production rates. In this machine, the tool sets normally called tool stations, are held in a head or a turret which rotates continuously. The rotation of the head pulls the upper and lower punches past fixed surfaces called cams, and a set of pressure rolls that impart compression force from above and below. All rotary presses are double action. The design of the cam surface moves the punches up or

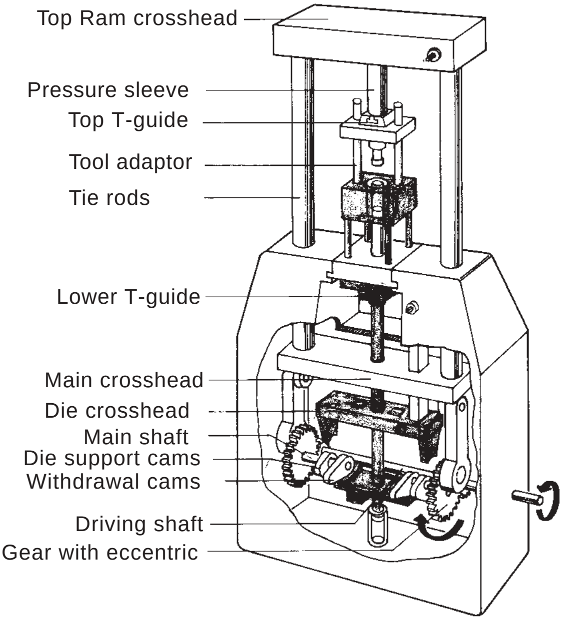


**Fig. 5.3** A general view of automatic mechanical press. (Courtesy: Dorst Machinen und Anlagenbau).

down to provide the cycle of die filling, weight adjustment, compression and ejection. Another feature of rotary presses is that all adjustment can be made while the press is in operation. These presses can be furnished in tonnage ranges up to 100 tonnes.

### *5.2.3 Press Selection*

Hydraulic presses differ from mechanical presses in that fluid pressure rather than a rotated crankshaft is used to actuate the slide. They are slower in operation than mechanical presses. These are generally less economical to operate than mechanical presses that can efficiently perform a specific identical job. One reason for this is that hydraulic presses have no mechanism comparable to the mechanical press's flywheel for storing energy. In a hydraulic system, oil pressure in the cylinder drops after each stroke and has to be build up in a comparatively short time. This requires the use of pumps served by motors, and these pumps draw a large amount of electric power. The motor of a hydraulic press, therefore, has several times the capacity as the motor of a mechanical press of comparable tonnage. Another disadvantage of a hydraulic drive is that the sudden release of pressure with each completed stroke is accompanied by a contraction of the cylinder and its hydraulic conduits, which in turn places great stress on pipe joints, valves, seals etc. Hydraulic presses, however, offer following advantages:

– adjustable tonnage

– Constant pressure can be maintained throughout the entire stroke and applied at any predetermined position. Drawing speeds are adjustable.

In case of mechanical press, the rated tonnage of a press is the maximum force that should be exerted by the ram against a tooling at a given distance above the bottom of the stroke. The higher a press is rated to its stroke, the greater the torque capacity of its drive members and the more flywheel energy it is capable of delivery. Because of the mechanical advantage of the linkage, the force actually transmitted through the clutches to rotating members (cranks or toggles) and reciprocating slides varies from minimum at the beginning of the downward stroke to maximum at the bottom of the stroke. A chart will show the change in tonnage that the drive is capable of delivery at various distances above stroke bottom. Provided its speed is not too high, almost any mechanical press with sufficiently long stroke and large tool mounting space, can be suitably altered for compacting powder, either in spring floated dies or in dies of the withdrawal type.

### *5.2.4. Factors affecting tooling design*

The powder's response to compaction and sintering has a decisive effect on tooling design. Fill, flow, apparent density, fill ratio, compacting pressure and dimensional changes are all contributory in this aspect.

**Fill** – The terms 'fill' signifies the amount of powder taken into the tool cavity prior to compaction. Proper fill is affected by many variables such as flow, apparent density, part configuration and tool design. The ideal fill should be uniform in density, free of bridging and should be fast enough to allow a reasonable speed in the press cycle. Part configuration has a direct influence on the powder filling into the tool cavity. Thin walled parts have narrow cavity sections, which results in poor powder filling. Powder filling in large areas having thin walls may trap air developing air pockets. Filling can be improved by using the three position air core.[3] Raising and lowering the core during the filling cycle helps in releasing entrapped air. As a minimum period of time is required to obtain adequate powder filling, the speed of the press can appreciably affect the fill.

The amount of powder fill to produce a part is determined by multiplying the finished part thickness by compression ratio of the powder to be compacted to the required green density.

In general term:

$$\frac{\text{Height of filling cacity}}{\text{Compact height}} = \frac{\text{Green density}}{\text{Apparent density}}$$

Components with shoulders or projections will therefore need to have these taken into account in the provision of different filling heights for various sections of the part. If these different filling heights are not taken into consideration, then as shown in an example (Fig.5.4) the flange would be very

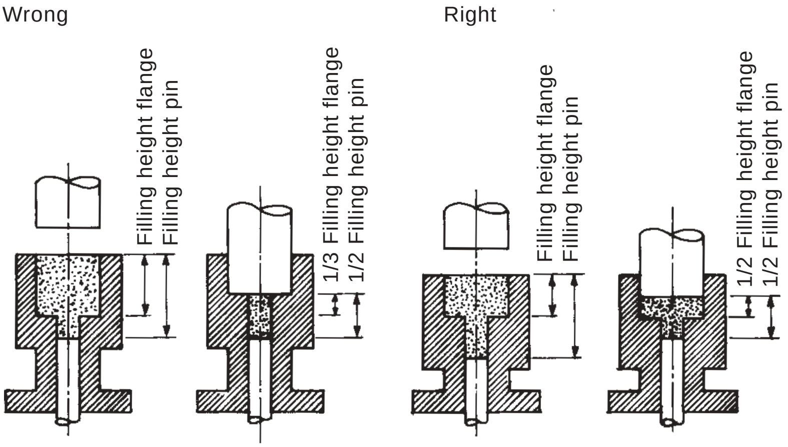


**Fig. 5.4** Correct and incorrect die fills for uniform part density.

highly pressed while the remainder of the part was pressed very little.

**Flow** – Adequate flow of powder is essential for an ideal fill. Many time, the metal powder contains a lubricant, to reduce frictional drag. This prevents galling and cold welding of powder particles to the die and core walls.

**Apparent Density and Fill Ratio**: The density of the finished part is usually specified. Tooling must be designed to provide enough fill to produce a part to the required compacted density. The ratio of apparent density of powder to green density is used to find the fill depth. The fill ratio accuracy can be improved further if compacts are made at the desired rate of speed for producing green parts on the press. The apparent density is affected by the time allowed for the tool cavity to fill. The true fill ratio should be based after including all the variables. If a fill depth is incorrect because of incorrect tool design, it may be compensated for by a change in powder apparent density. Since apparent density adjustment in powders is limited, it should not be relied upon as a tool design solution. Normal apparent density tolerance limits for powders are 0.1 g/cm$^3$. In special cases, it can be reduced to ±0.05 g/cm$^3$.

**Compaction Pressure**: Although very high forces can be developed in press, there are limits to the load a tool bears, which partially determines the density that can be obtained. Other limits to tool load are (*i*) part configuration which may introduce thin wall sections (*ii*) punch face protrusions which form areas of stress concentration. The tensile strength of the tool steels is the limiting factor to the load a punch will stand. 480 MPa (35 t/sq.inch) is the normal tool pressure allowed for powder compaction or coining. It is advisable to add coining operation, rather than to overload the tool to obtain higher green densities and risk tool breakage. Powder manufacturers have developed improved compressibility powder in order to achieve high green densities. Table 5.1 illustrates compaction pressure requirements for various powders.

**Table 5.1** Compaction pressure requirements and compression ratios for various materials[1]

| Type of material | Compaction pressure |  | Compression ratio |
|---|---|---|---|
|  | tsi | N/mm$^2$ |  |
| Aluminium | 5–20 | 70–280 | 1.5 to 1.9:1 |
| Brass | 30–50 | 415–690 | 2.4 to 2.6:1 |
| Bronze | 15–20 | 205–230 | 2.5 to 2.7:1 |
| Copper–graphite brushes | 25–30 | 345–415 | 2.0 to 3.0:1 |
| Carbides | 10–30 | 140–415 | 2.0 to 3.0:1 |
| Ferrites | 8–12 | 110–165 | 3.0:1 |
| Iron bearings | 15–25 | 205–345 | 2.2:1 |
| Iron parts: |  |  |  |
| low density | 25–30 | 345–415 | 2.0 to 2.4:1 |
| medium density | 30–40 | 415–550 | 2.1 to 2.5:1 |
| high density | 35–60 | 430–825 | 2.4 to 2.8:1 |
| Iron powder cores | 10–50 | 140–690 | 1.5 to 3.5:1 |
| Tungsten | 5–10 | 70–140 | 2.5:1 |
| Tantalum | 5–10 | 70–140 | 2.5:1 |

The above pressing force requirements and compression ratios are approximations and will vary with changes in chemical, metallurgical, and sieve characteristics of the powder, with the amount of the binder or die lubricants used and with mixing procedures.

### Dimensional Changes

As green parts after sintering usually undergo dimensional changes, this factor must also be included in tool design. Green density variation, material variation, temperature variation, furnace load conditions, furnace atmospheres all combine to affect dimensional change. Alloying many times affects dimensional change. For example nickel blended in iron imparts shrinkage after sintering, while copper does the reverse. In cases where a tool has been incorrectly factored for dimensional change, the powder blend can be changed to obtain a suitable growth or shrinkage. However, it must be borne in mind that the ultimate physical properties of the part are not adversely affected. Sintering temperature can also be adjusted to control growth, the details of which shall be described in the next chapter.

### 5.2.5 Tooling Materials

Tooling materials can be classed into three categories: steels, carbides and coated steels. Powdered metals are generally abrasive, which cause tool wear. Apart from abrasion resistance, tools must have the properties of high compression strength and toughness. The steels generally used for

**Table 5.2** Cemented carbide for powder metallurgy tooling: properties and typical applications.

| No. | % of binder | Hardness, RA | Transverse rupture strength, MPa | Compressive strength, MPa | | Tool applications | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Cores | Punches | Dies |
| C-4 | 3% | 92.3 | 1220 | 5510 | WEAR RESISTANT | | | |
| C-9 | 6% | 91.5 | 1580 | 4890 | | | | Bearing Dies |
| C-10 | 6-9% | 90.6 | 1930 | 4480 | | Simple shapes<br>Short lengths | | Straight thru dies - simple cavity contour |
| C-11 | 12-13% | 89.7 | 2140 | 4130 | SHOCK RESISTANT | | Ceramics-Ferrites<br>High polish & No Face projections | |
| C-12 | 14-15% | 88.5 | 2340 | 4000 | | Step cores & complex contours | | Complex shapes<br>Gear forms<br>Sectioned dies |
| C-13 | 15-20% | 87.4 | 2580 | 3790 | | All cores within physical limits of carbides | All within physical limits of carbide | Multi-level dies vulnerable projections |
| C-14 | 20-30% | 82-86 | 2510 | 3240 | | | | |

All property data represent average for grade

tool making are A2, D2, M2 and SAE 6150 type, the details of which can be seen in any Metal Hand Books. 12% cobalt-containing tungsten carbide is used by many for solid dies and die sections. Modern techniques such as spark erosion machining make this material relatively inexpensive to work. Due to the low pressing forces required for compacting ceramic and carbide powders, punches may be tipped with carbide.

Another application for carbide material is core rods where maximum wear resistance is required. Table 5.2 illustrates various grades of cemented carbides and their typical P/M tooling applications. Among the third category of tools carburized and nitrided coatings are very common. The principle limitations to the use of coated steel tooling is the method of applying the coating to the tool member. Most coatings are difficult to apply uniformly on irregular surfaces. Usually only round core rods are subjected to these coatings, although at present the technology has developed too fast.

Heat treatment of tools is to be controlled to minimize distortion. Heat treatment stresses must be relieved by proper tempering, since untempered tools will warp as they are machined. All tools should be normalized prior to machining operations to relieve heat treatment stresses.

Punches must be tough, and able to take repeated deflections. Although punch wear is important it is sometimes sacrificed to obtain other properties in the tool. Large chamfers on punch faces for examples are subjected to higher loads than the main tool body. Sharp corners at the chamfer root cause stress risers. Punches with these design features should be made of ductile tool steel. On the other hand when punches have fixed steps or depressions for protrusions or pockets in the sintered parts a wear resistant steel is used. A need for auxiliary mechanisms, e.g. floating core arrangement, improves the performance of tool materials. In brief, the tool designer must consider a variety of physical properties of tool materials, selecting the ones which best suit the requirements of the particular design.

The die barrel components of compacting tools usually consist of wear resistant insert or inserts which are held in a retaining ring made of tough steel. Most commonly the insert or inserts are shrunk into the retaining ring which has the advantage that the compression stresses induced in the die-barrel during shrinkage counteract the radial stress during compaction. Although quite complex internal contours can be produced in single piece inserts by electric discharge machining, it is more common to fix several carbide inserts together (Fig.5.5). The entry edges to the die cavity in the die barrel are levelled or radiused. In order to minimize spring back strain during ejection, the die barrels are sometimes made taper, but the taper should be less than the spring back of the part during ejection.

Punch and core rod dimensions are generally relieved behind the forming face making the close fitting portion as short as possible to permit the escape of powder.

### *5.2.6 Part Classification*

P/M parts usually are classified by evaluating the complexity of part design on a range of I though IV. They are signified by:

**Class I parts**: Single level components with the compacting force applied from one direction only. In this case the part thickness is generally limited to a maximum of 6–7 mm.

**Class II parts**: Single level components with the force applied from two directions.

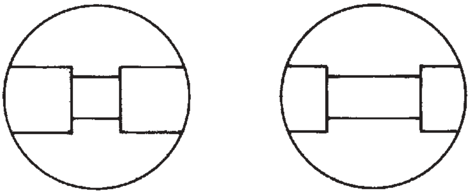
**Class III parts**: Two level components pressed with forces from two directions.

**Class IV parts**: Multilevel parts pressed with forces from two directions.

A detailed discussion on tooling details of parts of varying complexities has been made elsewhere.[2,5] Figures 5.6–5.9 illustrate such classes of P/M parts.

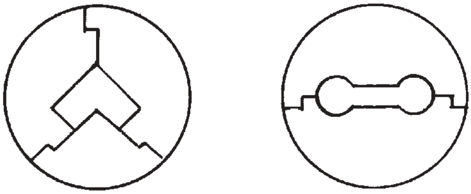
### *5.2.7. Guidelines of Part Geometry:*

The following guidelines related to conventional die compaction would be highlighted.



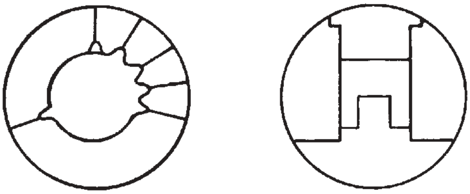
Joints for a Square die cavity

Joints for a Rectangular cavity



Joints off the centerline

Joints for a Symmetrical cavity



Joints for a gear profile

Non radial joints

**Fig. 5.5** Design of carbide inserts for fitting into retaining ring of die barrel

1. **Wall thickness** – Minimum wall thickness is governed by overall component size and shape. Where the ratio of length to wall thickness is 8:1 or more, special precautions must be taken to achieve uniform fill. The tooling required for long, thin walls is quite fragile and has low life.

2. **Holes** – Holes in the direction of pressing, produced with core rods extending up through the tools can be readily incorporated in the tooling. While round holes are least expensive, other shaped holes, including splines, keys, keyways, D-shapes, squares and hexagonals, can also be produced. Blind holes on blind steps in holes, and tapered holes which could be difficult to machine, are also readily produced. Side holes or holes not parallel to the direction of pressing cannot be made in the pressing operation and are produced by secondary machining. In big heavy parts many times holes are intentionally incorporated in order to make them light.

3. **Tapers and drafts (Fig.5.10)** – Draft is generally not required on straight-through P/M parts. Tapered sections usually require a short, straight level to prevent the upper punch from running into the taper in the die wall

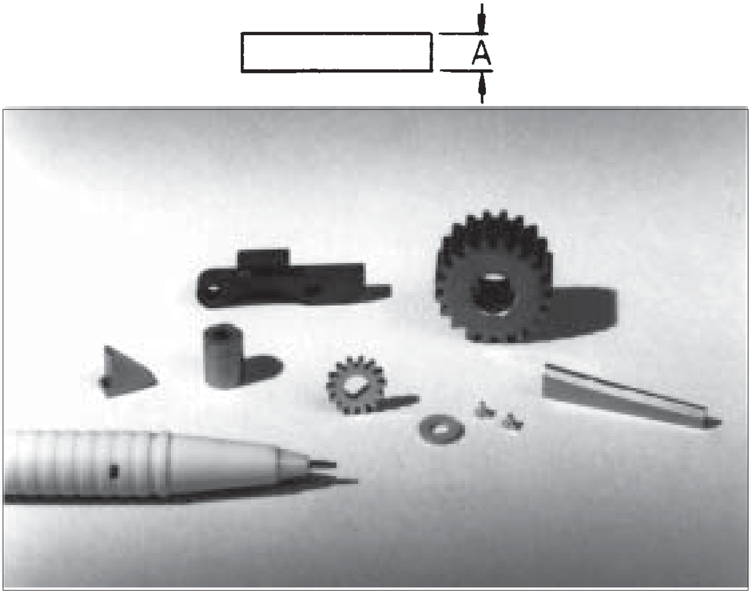


**Fig. 5.6** Class 1 components (reprinted with permission from The Powder Metallurgy Design Manual, 1995 edition Metal Powder Industries Federation, Princeton, New Jersey, USA, 1995).

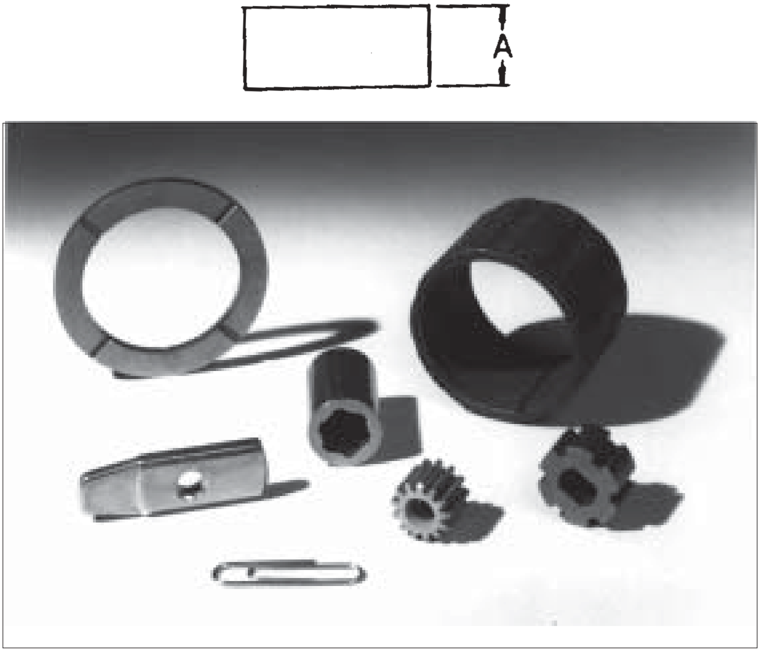


**Fig. 5.7** Class 2 components (reprinted with permission from The Powder Metallurgy Design Manual, 1995 edition Metal Powder Industries Federation, Princeton, New Jersey, USA, 1995).

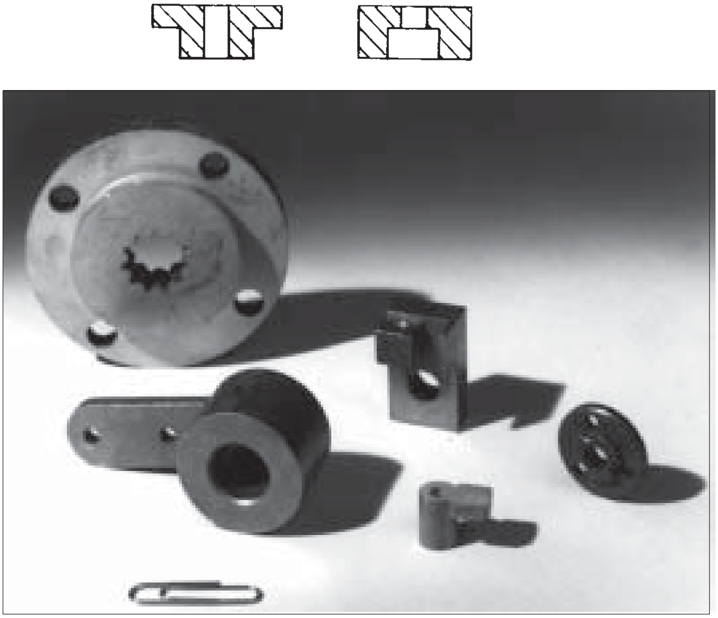


**Fig. 5.8** Class 3 components (reprinted with permission from The Powder Metallurgy Design Manual, 1995 edition Metal Powder Industries Federation, Princeton, New Jersey, USA, 1995).

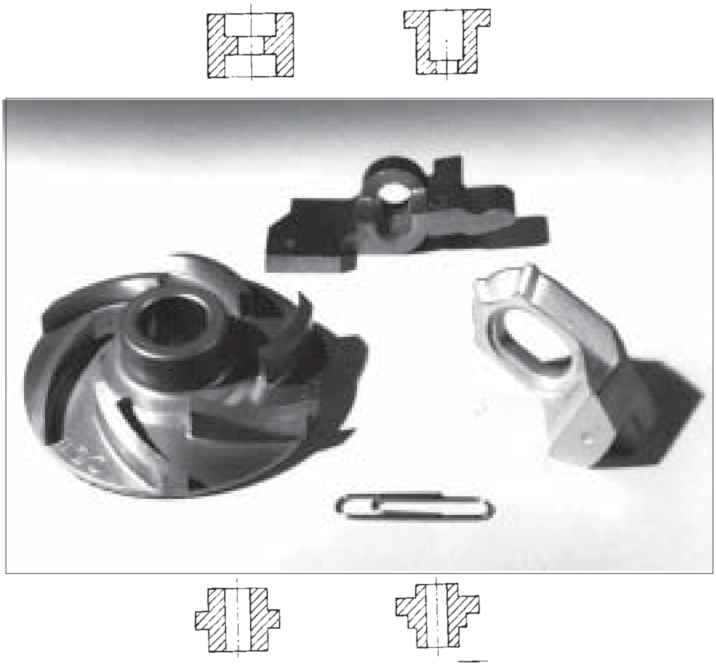
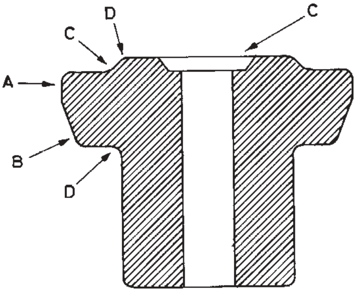


**Fig. 5.9** (right) Class 4 components (reprinted with permission from The Powder Metallurgy Design Manual, 1995 edition Metal Powder Industries Federation, Princeton, New Jersey, USA, 1995).



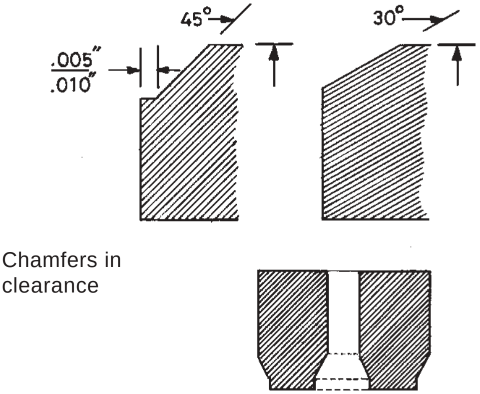


**Fig. 5.10** Tapers and drafts.
**Fig. 5.11** (right) Chamfers in P/M parts.

or on the core rod. When a flange type section is made on a step in the die, a draft is desirable to assure proper part ejection. Similarly drafts on the sides of bosses or counterbores made by the punch face aid tool withdrawal and minimize possible chipping of part.

4. **Fillets and Radii**: Generous radii fillets are desirable for most economical design of tools and production (D, Fig.5.10). A true radius is not possible at the junction of a punch face and a die wall. A full radius is, therefore, approximated by hand finishing or some other processes such as tumbling.

5. **Chamfers and Bevels**: Chamfers, rather than radii are preferred on part edges to prevent burring. A 45° angle and 0.125 mm minimum flat is common practice to eliminate feather edges (Fig.5.11). The preferred chamfer and most economical to produce is 30° maximum from radial, so as to minimize the chance of breaking the punch protrusion. When chamfers with a large angle from horizontal are required for punching of a part or when a step would create a problem (Fig.5.11), the chamfer may be produced by a bevel in the core rod or die. Chamfers on irregular shapes are more costly than on a plain round part or on two sides of a square part.

6. **Countersinks**: A countersink is a chamfer around a hole for a screw or bolt head. A flat of about 0.25 mm is essential to avoid fragile, sharp edges on the punch (Fig.5.12).

7. **Bosses**: A boss can be located on top or bottom of a part. To produce bosses with perpendicular sides, special punches are required to give positive part ejection.

8. **Hubs**: Hubs, which provide for drive or alignment rigidity in gears, sprockets and cams, can be readily produced by the P/M process. A generous radius between the hub and flange is preferred, as well as maximum permissible material between the outside diameter of the hub and the root diameter of components (Fig.5.13).

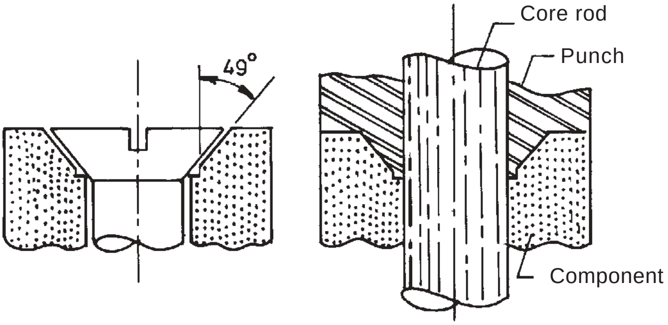


**Fig. 5.12** A standard countersink.

9. **Studs**: Shallow studs with drafted sides are made in the regular tools.

10. **Knurls**: Vertical, but no diamond or angled, knurls can be made on inside and outside diameters because they interfere with ejection.

11. **Under Cuts**: Undercuts on the horizontal plane, cannot be produced, as they prevent the part from ejecting from the die.

A part with a reverse taper (large on bottom than on top) cannot be ejected from the die.

12. **Slots and Grooves**: Grooves can be pressed from projections on the punch into either end of a component, within the following limits. (a) curved or semicircular grooves to a maximum depth of 30 % of overall component length, (b) rectangular groovers to a maximum depth of 20 % of the overall component length.

13. **Threads**: These cannot be incorporated in holes or outside diam-

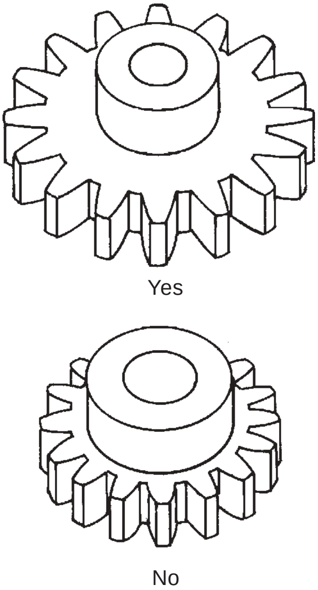


**Fig. 5.13** Hubs' location for gear's root.

eters, as they prevent the part being ejected from the die. They are produced by secondary machining operations.

## 5.3 Cold Isostatic Compaction

In cold isostatic compaction a flexible mould is filled with the powder and pressurised isostatically using a fluid such as oil or water. Compaction pressures up to 1400 MPa have been achieved in this manner, however, cold isostatic compaction is usually performed at pressures below 350 MPa. The use of rubber mould provides a means of creating complex shapes. Cold isostatic compaction has following advantages:

1. Uniform density of compacted bodies.
2. High green density, about 5–15 per cent higher than that achieved with die compaction at the same pressure.
3. High green strength and good handling properties of the powder body.
4. Reduction in internal stresses.
5. Possibility to compact powder without binding or lubricant additives.
6. Possibility to compact bodies having complex shapes or with a large length to cross-section ratio and achieve a high, uniform density.
7. Composite structures can easily be obtained.
8. Low tool costs through the use of rubber or plastic moulds.
9. Low material and finish machining costs.

On the other hand, isostatic compaction has some disadvantages too. They are:[2]

1. Dimensional control of the green compacts is less precise than in rigid die pressing.
2. The surfaces of isostatically pressed compacts are less smooth.
3. In general the rate of production in isostatic pressing is considerably lower.
4. The flexible moulds used in isostatic pressing have shorter lives than rigid steel or carbide dies.

### *5.3.1. Isostatic Press Equipment*

The main sub groups of isostatic presses are described below (Fig.5.14):

**Pressure Vessel or Cavity**: The pressure vessel is the most important element of an isostatic press. Of all the various high pressure structures known, the monolith forged type is preferred. While forging, care is taken that the grain structure is similar in all directions so that with a closely controlled heat treatment the high mechanical properties obtained in tangential, radial and longitudinal directions of the forging will be as desired and with in close tolerance of each other. The pressure vessel must be designed to withstand the severe cyclic loading imposed by rapid production rates and must take into account fatigue failure. Pressure vessels designed and constructed per section VIII, Division 2, of the ASME Code are available for pressures up to approximately 276 N/mm$^2$ (40,000 psi). Devices, including an absolute closure control, absolute pressure restrictor and an energy

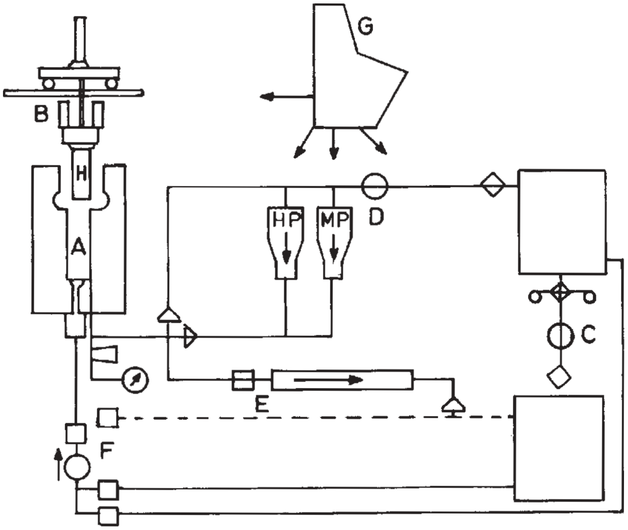


**Fig. 5.14** Principal schematic of the composition of an isostatic press. A – pressure vessel, B – closure with mechanism; C – reservoir(s) with filtering system; D – high pressure generator group; E – depressurisation system; F – fluid transfer system; G – controls; H – tooling.

absorption protection shield, should be installed in direct combination with the pressure vessel.

**Closure System**: This seals the pressure vessel cavity. Threaded covers are extensively used. However proper design must be made, otherwise any stress concentration at the root of the first thread could restrict the life of the vessel assembly. Quicker and more economical automated closing mechanisms can be effected by closure with interrupted threads.

**Reservoir with filtering system**: In case of dry bag the contamination of the fluid is avoided by the use of normal hydraulic systems reservoirs and good conventional filters. For wet bags, where mostly water is used, the contamination is very acute, which adversely affects the pumps and seal life.

**High Pressure Generator**: From small high pressure hand pumps, pressure generators have developed by the use of small air hydraulic intensifiers. In these, large air driven piston moves a small high pressure hydraulic piston which pumps the liquid to the desired pressure. The surface ratio of the low pressure air piston versus the hydraulic piston can reach 600:1 and more.

**Depressurisation System**: There are various depressurisation systems capable of almost any decompression profile to help eliminate compact breakage that may occur by too rapid depressurisation.

**Fluid Transfer System**: After the compaction step, the superfluous quantity of liquid in the pressure vessel must be evacuated as rapidly as possible at the end of depressurization stage. All such transfer can be accomplished by an appropriate standard transfer pump and the correct valving between the reservoirs and the pressure vessel.

**Controls**: Most simple units have manual control of the pumps, valves and cover mechanisms. However, automatic controls by servo-operated valves with identical closing and opening forces are used. This enhances the service life of high pressure valves.

**Tooling**: There are various factors[4] to be considered when designing a proper tooling, for example:

1. Type of press
   (a) wet or dry bag
   (b) automatic, semiautomatic or manual
   (c) top or bottom ejection
2. Properties and type of powder:
   (a) metal, ceramic etc.
   (b) flowability
   (c) compression ratio
   (d) green strength
   (e) adhesion to bag or punches
   (f) density
3. Bag Material
   (a) dipped latex, natural rubber, Neoprene
   (b) PVC
   (c) moulded natural rubber, Neoprene, nitrile
   (d) polyurethane Table 5.3 summarises main properties of flexible die materials [7].
4. Production Rate
5. Life of Tooling
6. Accuracy of compact
7. Shape of compact
8. Operator's skills

In the **wet bag** tooling, the filled and sealed mould is immersed into a fluid chamber which is pressurized by an external hydraulic system (Fig.5.15). After pressing, the wet mould is removed from the chamber and the compact removed from the mould. In case of **dry bag** tooling, both powder filling and ejection are performed without removing the bag assembly. Sealing is achieved by an upper punch which enters the bag before pressurization. The compaction stresses are generated by isostatic compression of the bag through a fluid without loading the punch. The dry bag method is much more rapid because the bag is built directly into the pressure cavity. In general, the more versatile wet bag process is used for the batch production of small number of shapes whereas the dry bag process is used for the semiautomatic or automatic production of large number of shapes often of smaller dimensions.

### *5.3.2 Isostatic Pressing Cycle*

A typical isostatic pressing cycle comprises of the following:

(i) Insertion of compact – The material filled with the material to be

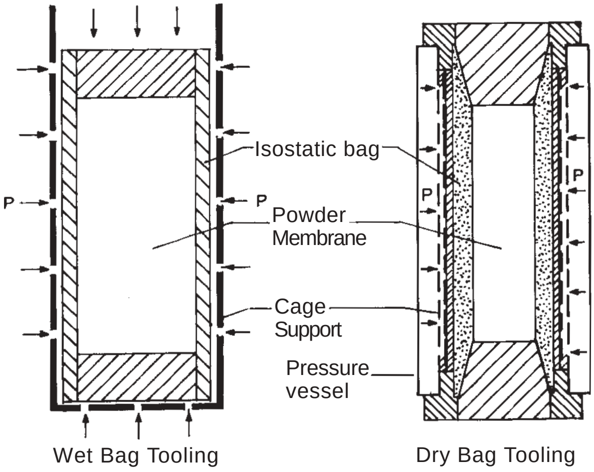


**Fig. 5.15** Wet bag and dry bag tooling in cold isostatic pressing.

**Table 5.3** Type of mould materials and their properties[7]

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Water resistance | G | G | G | G | G | F | P → Ex |
| Oil resistance | P | P | G | Ex | G | F | G → Ex |
| Aging resistance | P | F | G | G | G | P | P → Ex |
| Toughness | VG | VG | VG | VG | P | P | G → Ex |
| Tear resistance | VG | VG | VG | VG | VP | P | G → Ex |
| Cut resistance | VG | VG | VG | VG | VP | P | G → Ex |
| Resilience | Ex | Ex | G | G | VG | P | P → Ex |
| Set resistance | Ex | Ex | VG | VG | G | P | VP → Ex |
| Availability | R | S | R | S | S | R | S |
| Cost | L | M | L | M | H | L | L → M → H |

R = Readily available; S = Subject to mould;
L = Low; M = Medium; H = High;
VP = Very poor; P = Poor; F = Fair; G = Good;
VG = Very good; Ex= Excellent.

pressed is sealed and placed in the partially filled vessel. This causes the liquid level in the vessel to rise.

(ii) Filling and Venting – The upper closure is installed and locked. Any air remaining above the fluid level is removed. Otherwise greater amount of energy would be used before the vessel reaches operating pressure, because of the fact that air is highly compressible. The displaced air is vented through the valve in the top closure.

(iii) Pressurizing – The high pressure pumping system pressurises the water to the operating pressure. Water is added during pressurization in order to compensate for the volume reduction of the powder being pressed and the compressibility of water at these pressures. Table 5.4 gives some typical values for pressures required for isostatic pressing.

(iv) Depressurizing – During this stage, the extra amount of water is expelled from the vessel.

(v) Compact removal and draining system – The green part and mould are now removed from the pressure chamber. The water level drops, but subsequently gets overflown if another uncompacted mould is inserted.

### *5.3.3. Defects due to Tooling Limitations*

The major defects associated with the improper tooling are :

1. **Elephant's Footing**: If the modulus of the bag is less than that of the closure then the bag will distort or compress more than the closure. The result is the elephant footing. Figure 5.16 shows the problem and a suggestion for it's remedy.
2. **Poor consolidation**: If the modulus of the bag is too high or the wall thickness is too great then insufficient pressure will be exerted on to the powder. Altering the hardness of the bag and or its gauge normally eliminates the problem.
3. **Radial Cracking**: When a very thick wall bag is used the pressing pressure causes the material to 'ruckle'. This gives differing radial pressures along the length of the form and the resultant differing densities can cause cracking on decompression. Thinner gauge sections are usually required to reduce or eliminate this problem.
4. **Preform Cracking**: If the bag properties are poor, then powder sticking can be a major problem. On decompression a surface layer can be turn out of the preform resulting in cracking which is noticed on sintering. A change in the grade of bag material is called for.

**Table 5.4** Typical pressures required for isostatic pressing powders

| | Ksi | N/mm$^2$ |
|---|---|---|
| Aluminium | 8-20 | 55-138 |
| Iron | 45-60 | 311-414 |
| Stainless steel | 45-60 | 311-414 |
| Copper | 20-40 | 138-276 |
| Lead | 20-30 | 138-207 |
| Tungsten carbide | 20-30 | 138-207 |

These pressures are approximate since every application presents its own requirements of density, configuration and size.

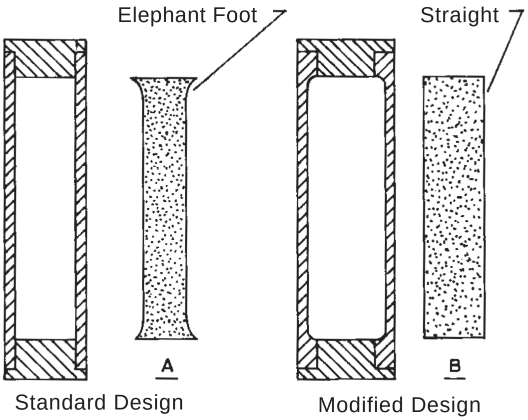


**Fig. 5.16** Modified tooling design for cold isostatic pressing.[7]

### 5.3.4 Cold Isostatic Applications

Some examples of applications taken from industrial processes in use today can be listed below:

**Graphite**: Cold isostatic pressing of electrographite, refractory graphite and graphite used in nuclear reactors.

**Ceramics**: Cold isostatic pressing of tubes, tiles, nozzles and linings made out of special ceramics.

**Ferrites**: Parts used for permanent magnets, computer memories, electronics etc.

**Cemented Carbides**: Cold isostatic pressing to preform powder products.

**Metal Powder**: High speed tool steels, superalloys, stainless steel, titanium alloys, beryllium etc.

## 5.4 Dynamic Powder Compaction

Dynamic powder compaction is a single compaction/ sintering operation brought about by the impact of a high speed punch on powder. This produces a discrete shock wave in the powder, which under optimized conditions, results in metallurgical bonding and sometimes fusion of the particles surface. The work of compaction produced by inter particle shear is transferred on the surface of the powders in such a short time (microseconds or less) that there is no possibility for heat to be conducted away from the surface and thus localized melting or welding occurs. The welding is similar to that which occurs during the seizure of a bearing or during friction or explosive welding. The production of greater than 99% theoretical density compacts is facilitated by the inter particle lubrication that the melted surface of the particle provides. The temperature rise of the interior of each particle is small. Dynamic powder compaction differs from such high speed techniques as Petro forge or Dynapak, in that the latter processes are closely related to crank presses and drop forges. They involve large mass travelling at a low velocity, whilst dynamic powder compaction involves a very light punch travelling at a very high velocity. The actual compaction press consists of a high pressure reservoir, fast action valve, guide tube, compaction chamber and ejector unit. Compressed air is usually used as the drive system. At very high velocities helium may be used. It has been noticed that in dynamic powder compaction, the liquid zone between the particles resolidifies in the same time scale as its formation. This is in the range $10^6 – 10^8$°C/sec. These cooling rates result in a rapidly solidified material with an extremely fine structure or even an amorphous glassy structure. Such a rapidly solidified material imparts unique properties to the compacts. Depending upon the material, the weld zone may have a hardness above or below that of the work hardened particles. Heat treatments may be given to bring out a specific property in either the weld zone or the particles. For instance, the rapidly quenched weld zone may be given an ageing treatment or the heavily work hardened particles may be made to recrystallize.

Among possible applications, the process allows nonequilibrium powder or powder mixtures to be consolidated with neither chemical reactions nor a degeneration of metallurgical structures. For example, aluminium compacts with very good wear and seizure resistance have been made from Al-steel mixed powders. Conventional sintering of these would result in the formation of a brittle intermetallic. It is also possible to compact add-mixed carbides in steels.

In an extreme case, it has been possible to consolidate amorphous materials without crystallization occurring. The finer grain size, higher solute contents, uniform alloy distribution and cleanness of the powder make rapidly solidified powders of great interest for many demanding applications, especially with regard to superalloys and aluminium alloys for aircraft. Dynamic powder compaction can also consolidate nonmetals and again several interesting possibilities exist in this area.[9]

## 5.5 Powder Roll Compaction

Powder rolling, also called roll compacting, is the important process to produce metal strips. In powder rolling metal powder is fed from a hopper into gap of a rolling mill and emerges from the gap as a continuous compacted green strip. The rolls of the mill may be arranged vertically or horizontally. The latter type of arrangement is more common, with either saturated feed or starved feed.[2]

The powder characteristics have the following effect on powder rolling:

**Particle Shape**: The generation of maximum ‘green’ strip strength to withstand the rigours of handling through the process line require the particle shape to be very irregular.

**Compressibility**: Good compressibility is required to ensure that sufficient particle interlocking takes place to give adequate ‘green’ strip strength. Good green strip has a density of at least 80/85 % theoretical. Compressibility is also of importance in determining the limiting dimensions of the roll compaction mill.

**Particle Size**: The thickness of the finished strip and particle segregation severely restricts the maximum particle size which can be tolerated in the powder feed to the compaction mill.

**Flowability**: The powder must flow smoothly and quickly through hopper systems with minimum tendency to stick slip or bridging.

**Surface Oxidation**: This plays a significant part in determining subsequent powder behaviour.

The roll compaction operation can be divided into three distinct zones (Fig.5.17):

1. The free zone where blended powder in the hopper is transported freely downward under gravity. Here all the usual criteria of hopper flow apply.

2. The feed zone where the powder is being dragged by the roll surface into the mill bite, but has not yet attained coherence.

3. The compaction zone close to the roll nip, where the powder becomes coherent, the density changes rapidly and air has to be expelled.

In contrast to conventional rolling, the thickness of the strip can be rolled in powder rolling is closely limited by the diameter of the rolling mill rolls. The change in density is accomplished as the powder is transported through the feed zone and the compacting zone. The length of these zones is determined by the diameter of the rolls (*D*), the internal friction between the powder particles and the friction between powder and rolls. With the geometry shown in Figure 5.17, the nip angle α may be defined as

$$\cos \alpha = \frac{x}{D/2}$$

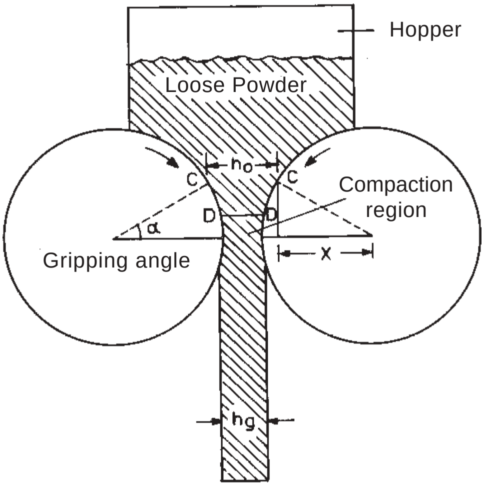


**Fig. 5.17** Schematic of powder rolling with saturated feed, rolling mill rolls arranged horizontally.[6]

The dimension $h_0$ would be equal to $D(1–\cos\alpha) + H_g$. The strip thickness $h_g$ is equal to $h_0/C$, where $C$ is the compression ratio. The strip thickness would then be

$$H_g = \frac{D(1 - \cos\alpha)}{C - 1}$$

Evans and Smith[8] showed that, due to slipping between powder particles, the actual angle at which the powder is gripped is much lower than the calculated friction angle, *f*. As a result it is found that in order to roll compact a certain thickness of strip it is necessary to use very much larger diameter rolls than are required for producing similar strip from solid material. Roll diameters of between 50 and 150 times the strip thickness are often required. The maximum strip thickness can be increased by increasing the ‘μ‘ i.e. by roughening the roll surface, although during rolling the conditions change as the surface ultimately gets polished. Figure 5.18 shows the strip thickness that can be obtained with different roll diameters with two types of nickel powders.

The green powder strip should have uniform thickness and density across the width of the strip, and its edges should be well formed and as dense as the centre of the strip. Edge controlling is, therefore, essential to process control. Figure 5.19 illustrates typical methods for such a control.[6] In Fig.5.19a floating flanges that are attached to one roll and that overlap the other roll are used. Pressure is applied to the flange as they approach the roll gap, thus preventing powder loss from the gap. A continuous belt that covers the gap at edge of the rolls also is effective in preventing powder loss (Fig.5.19b).

If the air entrapped in the powder is not properly released, the distur-

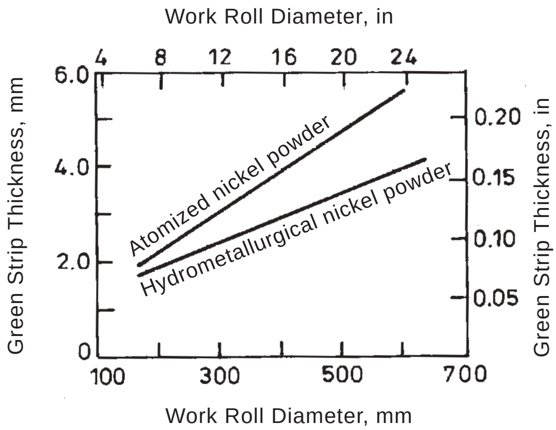


**Fig. 5.18** Effect of work roll diameter on green strip thickness for two types of nickel powder.[6]

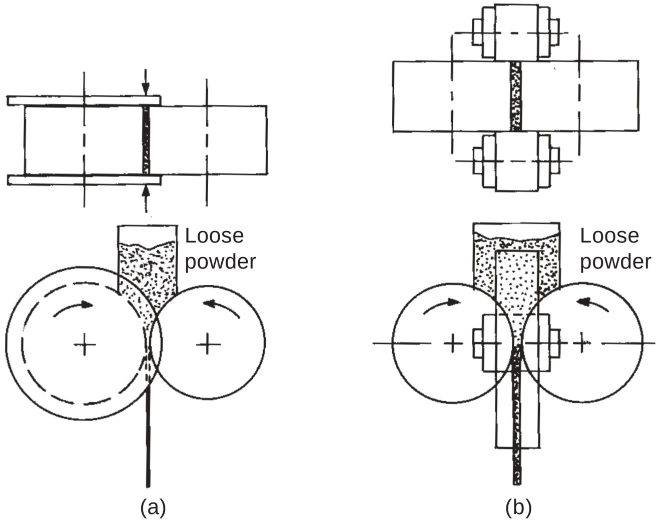


**Fig. 5.19** Methods of controlling powder feed to compacting rolls (a) flange edge control; (b) belt edge control.[6]

bance of the powder in the hopper can be sufficient to interface with the smooth flow of powder to the roll nip and the strip produced will not be of uniform density. Up to a given speed, called the ‘flow transition speed’, the flow rate of powder increases linearly with roll speed. Above this critical speed, relatively less and less powder flows into the roll gap, until at speeds considerably above the transition speed, continuous strip can no larger be rolled.

Subsequent to green strip formation, the next operation is sintering, in which the strip shrinks in all three dimensions depending as process parameters and material composition. For all applications except porous strip, the sintered strip is rerolled. In one of the scheme; in order to obtain completely dense strip, addition cold rolling and annealing steps are incorporated in the total cycle. The main problem with this type of mill is to synchronize the rate of rolling with that of sintering and annealing. In another scheme, the rolled strip is fed into a continuous sintering furnace, from where it goes to cooling zone and then on a coiler. This coiled strip is rerolled and annealed in separate operation. In another modification, the coiled green strip is sintered as such. In such types of schemes, the difficulties with synchronization are either partially or completely removed.

In addition to using powder rolling for the large scale production of strip and sheet of base metal and alloys, the technique has also been employed for a number of speciality type strip materials, e.g. nickel and cobalt alloys for electronic and magnetic applications, porous powder rolled strip, in particular stainless steel strip for filters and nickel strip for electrodes and also an aluminium alloy strip for bearing applications.

Another speciality application of roll compaction is the production of bimetallic strip consisting of layer of Al–8.5 Pb–4.0 Si–1.5 Sn–1.0 Cu prealloyed powder sandwiched to a pure aluminium layer. For such a production, three powder hoppers are required as well as a powder flow blade that controls the flow of the powders into the roll gap. The coil of the composite strip is then sintered, and eventually the pure aluminium layer is roll bonded to a steel backing material.

## References

1. S. Bradbury (Ed.), Powder Metallurgy Equipment Manual, 3rd Edition, MPIF, Princeton, 1986, p. 42.
2. F.V. Lenel, Powder Metallurgy Principles and Applications, MPIF, Princeton, 1980, p. 128.
3. R.N. Kunkel, Tooling Design for powder metallurgy parts, American Society of Tool and Manufacturing Engineers, Dearborn, 1968, p. 26.
4. K.J. Morris, In ‘Isostatic Pressing Technology”, Ed. P.J. James, Applied Science Publishers, Barking, 1983, p. 102.
5. Powder Metallurgy Design Manual, 2nd edition, MPIF, Princeton, 1995.
6. Metals Hand Book, Vol.7, Powder Metallurgy, ASM International, Material Park, Ohio, 1984, p. 327.
7. R.M. Broughton, Flexible Tooling for Cold Isostatic Pressing, Brochure by Watts Urethane Products Ltd., U.K.
8. P.E.Evans and G.C.Smith, *Powder Metallurgy*, No.3,1959, 1.
9. D. Raybould, *Metal Powder Report*, Vol.35, No.10, 1980, 467–469.

# 6 SINTERING

## 6.1. Introduction

Sintering may be considered the process by which an assembly of particles, compacted under pressure or simply confined in a container, chemically bond themselves into a coherent body under the influence of an elevated temperature. The temperature is usually below the melting point of the major constituent. Much of the difficulty in defining and analyzing sintering is based on the many changes within the material that may take place simultaneously or consecutively. Densification or shrinkage of the sintered part is very often associated with all types of sintering. However, sintering can take place without any shrinkage; expansion or no net dimensional change is quite possible. From the tooling point of view it is preferred to avoid very large amount of dimensional changes. The driving force for solid state sintering is the excess surface free energy. Sintering is a complex process and for any given metal and set of sintering conditions there are likely to be different stages, driving forces and material transport mechanisms associated with the process.

Various stages of sintering can be grouped in the following sequence:

(1) Initial bonding among particles
(2) Neck growth
(3) Pore channel closure
(4) Pore rounding
(5) Densification or pore shrinkage
(6) Pore coarsening

A detailed description of these stages is given by Hirschhorn[1] and German.[2] Sometimes some stage overlaps over the later stages.

Among various mechanisms evaporation and condensation, surface, grain boundary and volume diffusion and plastic deformation mechanisms are prevalent. The description of such topic is beyond the scope of this book. However, a detailed account is given in the book by Lenel.[3]

## 6.2. Liquid Phase and Activated Sintering

Liquid phase sintering method is getting more and more common, in which the presence of liquid phase during all or part of the sintering cycle of material is used for enhanced densification. There are two variations of the process:

(a) normal liquid phase sintering for which the formation of the liquid phase is associated with one or more components contained in the original green compact.

(b) infiltration of the original green compact with a liquid formed outside the compact during the very early period of sintering. Although simultaneous infiltration and sintering appears to be dominant, infiltration of a previously sintered part is also practised.

During liquid phase sintering three stages 'rearrangement' or 'liquid flow', 'accommodation' or 'dissolution and reprecipitation and 'coalescence' or 'solid phase sintering' take place. These stages follow in the approximate order of their occurrence, but there may be significant overlapping for any specific system. Figure 6.1 shows the densification stages during liquid phase sintering. With progress in liquid phase sintering the densification kinetics is lowered. Increasing the liquid content up to approximately 35 volume percent aids initial densification. A coarse particle size and a high green density act to offset the favourable effects of the melt. In case the second stage is not effective, the melt will penetrate along the interparticle interfaces and cause particle separation. This will contribute in swelling. A small dihedral angle inhibits coalescence of neighbouring particles. A detailed account on the theory of liquid phase sintering in given in the book by German.[4] Application of liquid phase sintering technology is widely made in the field of sintered steels, cemented carbides, heavy alloys, bronzes and silicon nitride systems.

**Activated sintering**, in general, refers to process in which the activation energy for sintering is lowered. This is mostly achieved by chemical addition to the powder. For certain metals, particularly refractory metals, the addition of dopant causes the densification kinetics to increase as much as 100 times compared with undoped compacts. The best activators are palladium and nickel. Nickel is often added as a solution of its salt which

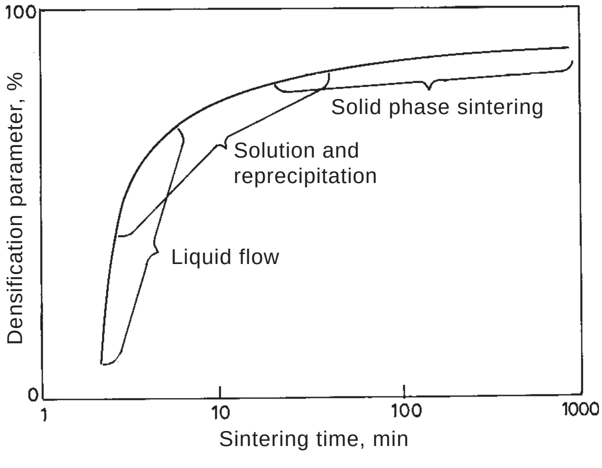


**Fig. 6.1** A schematic plot of the densification of a powder compact during liquid phase sintering, showing the three stages.

is reduced to the metal and forms a layer several monatomic layers thick on the surface of the tungsten powder particles.

## 6.3. Loose Sintering

This method is quite widely used for manufacture of highly porous parts like filters. Basically, metal powder is poured or vibrated into a mould which is then heated to the sintering temperature in an appropriate atmosphere. The form and complexity of shape which can be made by this method depend to a large extent on the flow characteristics of the powder. Since shrinkage usually takes place during sintering, only shapes where this can occur without mould constraint causing cracking can be used. The characteristics required of the mould material for loose sintering are:

(*i*) It should be easily machined or formed into the required shape, (*ii*) it should withstand the sintering temperature without appreciable deformation and (*iii*) it should not weld to the powder during sintering. For most applications machined or welded metal moulds are used, although graphite may also be employed where no reaction with the powder is likely, and even here a refractory mould wash may suffice to prevent reaction. Since no pressure is applied to the powder any unreducible oxide skin on the particle will prevent metal-to-metal contact and inhibit sintering. For this reason it is virtually impossible to loose sinter aluminium powder.

## 6.4. Process Variables

The most important factors involved during sintering process are temperature, time and furnace atmosphere. The influence of these factors on the sintering process is described below:[5]

**Sintering Temperature**: Increasing the sintering temperature greatly increases the rate and magnitude of any changes occurring during sintering. Figure 6.2 illustrates the effect of increasing temperature for a constant green density.

**Sintering Time**: Although the degree of sintering increases with increasing time the effect is small in comparison to the temperature dependence. The loss of driving force with increasing time at any temperature is one of the reasons why it is so very difficult to remove all porosity by sintering. An attempt should be made to achieve the desired properties of the sintered parts by shorter sintering times and correspondingly higher temperatures. However, the maintenance costs and energy consumption of a furnace increase when its operating temperature is raised.

**Sintering Atmosphere**: The proper production, use and control of sintering atmospheres which are essential for the optimum use of the powder metallurgy process are described in a later section.

## 6.5 Material Variables

**Particle Size**: In terms of the basic stages of sintering, decreasing particle size leads to increased sintering. The smaller particle size has a greater

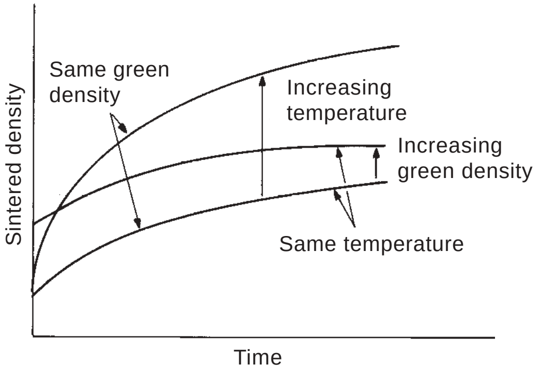


**Fig. 6.2** Sintered density time curves illustrating effects of increasing green density and sintering temperature on densification.

pore/solid interfacial area producing a greater driving force for sintering. It promotes all types of diffusion transport, e.g. greater surface area leads to more surface diffusion, small grain size promotes grain boundary diffusion and a larger interparticle contact area to volume diffusion.

**Particle Shape**: The factors that lead to greater intimate contact between particles and increased internal surface area promote sintering. These factors include decreasing sphericity and increasing macro- or microsurface roughness.

**Particle Structure**: A fine grain structure within the original particles can promote sintering because of its favourable effect on several material transport mechanisms.

**Particle Composition**: Alloying additions or impurities within a metal can affect the sintering kinetics. The effect can either be deleterious or beneficial depending upon the distribution and reaction of the impurity. Surface contamination, such as oxidation is usually undesirable. Dispersed phases within the matrix may promote sintering by inhibiting grain boundary motion. Reaction between impurities and either the base metal or alloying additions at the relatively high sintering temperature may be undesirable.

**Green Density**: A decreasing green density signifies an increasing amount of internal surface area and consequently, a greater driving force for sintering. Although the percentage change in density, increases with decreasing green density, the absolute value of the sintered density remains highest for the higher green density material.

## 6.6 Dimensional Changes

Changes in dimensions resulting from sintering represent an important field in powder metallurgy, especially with respect to large scale production of parts with small dimensional tolerance. The fundamental process of sintering leads to a reduction in volume because of pore shrinkage and elimination. Following factors in this regard may be considered:

**Entrapped Gases**: The expansion of gas in closed porosity has been postulated as producing compact expansion.

**Chemical Reactions**: Hydrogen is a common component of sintering atmospheres and can often diffuse through the metal to isolated portions of the compact where it reacts with oxygen to form water vapour. The pressure of the water vapour can lead to expansion of the entire mass. It is also possible to have reactions that lead to the loss of some element from the sinter mass to the atmosphere, such as volatilizing, and result in a shrinkage of the material.

**Alloying**: Alloying that may take place between two or more elemental powders very often leads to compact expansion. This effect which is due to the formation of a solid solution is often offset by shrinkage of the original porosity. Dimensional changes may also occur in a binary system where the rate of diffusion of each metal into the other is different.

**Shape Changes**: Green parts invariably contain variations in green density. Such variations can lead to substantial changes in shape because of the strong dependence of sintering, especially shrinkage, on green density. Low green density regions will exhibit a greater amount of shrinkage during sintering. For example, a cylinder with a relatively high *L/D* ratio compacted by a single action method would have a gradually decreasing green density from one end to the other. Such as cylinder would change during sintering into a truncated cone, as shown in Fig.6.3. A cylinder prepared by a double action method, on the other hand, would likely achieve an ‘hourglass’ shape (Fig.6.3). Many times, the shrinkage (or expansion) is different in two directions – axial and radial, and must be taken into account during design of the compacting tools. Parts with complex and asymmetrical shapes, exhibit uneven shrinkage during sintering and loss of the desired tolerances. To restore lost tolerance sizing operation is generally carried out. This will be described later in Chapter 8. For the users point of view it is easier to maintain narrow tolerances on the contours than on the axial dimensions.

## 6.7 Microstructural Changes

When a green compact is sintered, the original particle boundaries can no longer be observed. Instead, the structure becomes similar to that of the

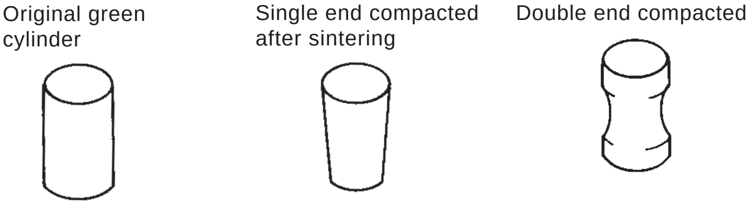


**Fig. 6.3** Illustration of changes in shape of cylindrical compact due to sintering for single and double end compaction.

metal in wrought and annealed conditions, except that it contains pores. Pores are of two types open or closed. With progression of sintering, pores continue to shrink. At about 5% total porosity, the formation of closed pores commences. Many of the microstructures seen in P/M parts are caused by porosity and by the blends of elemental powders that constitute many alloys. These blends do not always result in homogeneous, well diffused structures. Such heterogeneity is not necessarily detrimental and in certain nickel steels and diffusion alloy steels, may be advantageous.

The heating or annealing of cold worked metals leads to three distinct microstructural changes: recovery, recrystallization and grain growth. Grain growth is the most important one for sintering. There is normally a large driving force for grain growth. Grain growth in a sinter mass can be somewhat different than the conventional metal, since the former can be treated as a two phase material, the second phase being pore. Porosity in green compacts and in the developing sinter mass represents a very effective hindrance to grain growth. The addition of other component in the powder blend may drastically hinder bonding between adjacent particles and the formation of grain boundaries. Grain boundary grooves, may also tend to inhibit grain growth, since the movement of grain boundary away from its groove leads to an increase in grain-boundary area and energy.

The control of grain growth so that grain boundaries do not pull away from pores is an essential part of sintering to zero porosity. The more nonuniform the grain structure, particularly if it develops discontinuous grain growth, the earlier in the sintering process is the separation of pores from grain boundaries likely to occur. It is therefore important to have as uniformly sized a starting powder as possible, so as to reduce this tendency. Many times a proper additive also plays a vital role. An ideal example for this is the sintering of MgO (0.05 %) doped alumina where the additive is preferentially concentrated at the grain boundaries. Such a control has been able to impart full densification to alumina.

Many types of phase transformations may occur in the solid state during sintering at a constant temperature or during the cooling of the metal from the sintering temperature. Porosity and fine grain structure influence on the transformation. The best example of a phase transformation associated with sintering is the production of sintered steels. Since the porosity reduces the thermal conductivity of the mass, for a given set of cooling conditions the actual cooling rate throughout a sintered metal is considerably less than for a conventional solid one. Such an effect would have bearing on martensitic transformation, which is dependent on cooling rate. Precipitation from solid solution is also a very common type of transformation associated with sintering.

During liquid phase sintering porosity level falls down, while grain size increases. The shape of the pores varies rapidly during liquid phase sintering. In the first stage, the pores are irregular. Later they form a cylindrical network and finally attain a spherical shape. The interfacial energies can change during liquid phase sintering, since they depend on solubility, surface contamination and temperature.[4] Hence the microstructural parameters shall be shifting with time during liquid phase sintering. A proper development of microstructure during liquid phase sintering is very important for attaining mechanical properties, particularly ductility. A typical example of Fe–P alloy can be cited for this.

## 6.8 Sintering Atmosphere

Nearly all metals of technical importance react with the gas of their surrounding atmosphere even at room temperature, but more so when treated at higher temperatures. The most important reason for using special sintering atmospheres is to provide protection against oxidation and re-oxidation of the sintered metal powders. There are many other ways in which a sintering atmosphere can influence the basic sintering process. By reducing the oxides the atmosphere may create highly mobile metal atoms. Gas atoms of the sintering atmosphere can enter the sintering compact via interconnected pores. They may later get trapped in closed pores, thus hindering their shrinkage. Gas atoms of the sintering atmosphere may also diffuse into the metal. At times these atoms might also alloy with the metal. In the following sections the details of different sintering atmospheres are given.

### *6.8.1 Hydrogen*

Reducing atmospheres are, by far, most commonly used for sintering metal parts. Pure hydrogen is an excellent reducing gas, but it is not economical except in case of high valued products. Hydrogen is very flammable, having an extremely high rate of flame propagation. Because of its high flame propagation, hydrogen burns with a short, hot flame immediately upon contact with air. The flame is an almost colourless blue. Hydrogen is the lightest element; its specific gravity being only 0.069 as compared to 1.0 for air. It is easily displaced by air, and rushes out the top of the furnace door openings rapidly when free to do so. The gas has thermal conductivity seven times greater than air. Because of this, it accelerates both the heating and cooling rates of the work in furnaces. The thermal losses in furnaces are higher with hydrogen than when using heavier, less conductive gases. Typical applications of hydrogen are in the reduction of oxides of iron, molybdenum, tungsten, cobalt, nickel and 18–8 stainless steel, annealing of electrolytic and carbonyl iron powders and carburizing of tungsten powders in lamp black to form tungsten carbide.

### *6.8.2. Reformed Hydrocarbon Gases*

These are low cost gaseous mixtures made by reforming hydrocarbon gases. Widely these can be classified into categories – exothermic and endothermic.

**Exothermic Gas**: Exothermic gas is produced in specially designed generators, where fuel gas and air are mixed in such a ratio that incomplete combus-

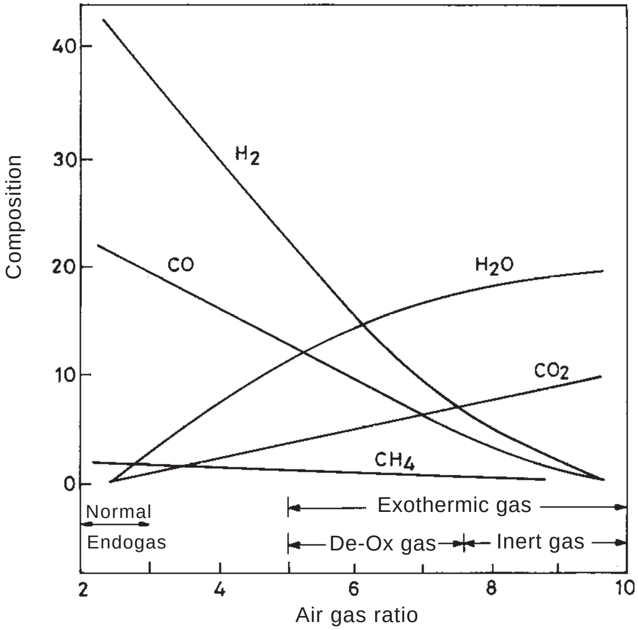


**Fig. 6.4** Influence of air gas ratio on exo- and endogas assuming the fuel is pure methane.

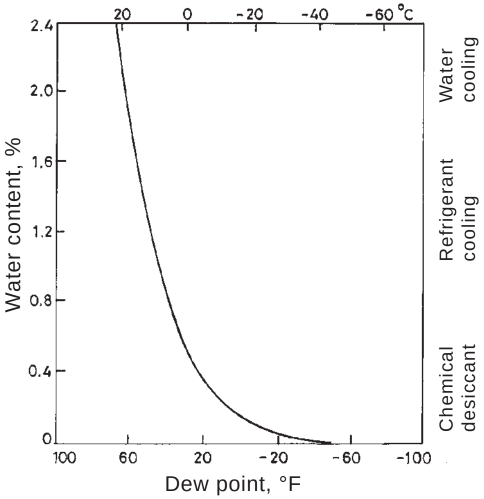
tion takes place. The heat generated in the combustion chamber, however, is sufficient to support the reaction. Figure 6.4 shows the common range of analysis for an exothermic gas. This graph is based on the assumption that the fuel gas is pure methane, which corresponds reasonably well to a natural gas. In all cases, nitrogen is actually the largest single constituent. At an air to fuel ratio of 10.25:1, there is practically complete combustion. This gaseous mixture is relatively inert to metals such as hot copper, tin or silver. It will however oxidize hot iron and the reactive metals because of the high proportion of $CO_2$ and water vapour as opposed to extremely low percentages of reducing components hydrogen and carbon monoxide. This gas is known as ‘lean exothermic gas’ and has very little application in powder metallurgy.

The exothermic gas generator is a refractory lined, water jacketed combustion chamber that operates at 1100–1425°C. The internal temperature of the chamber depends on (1) the ratio of air to fuel gas, (2) the volume of gas being burned and (3) the effectiveness of the heat transfer from the inside of the chamber to the water jacketed exterior.

The water content in the gas mixture is very important for sintering. Upon leaving the combustion chamber, the gas has a water vapour content of approximately 5 to 15%. This makes the atmosphere oxidizing on most types of sintered products. The gas has, therefore, to be dried to at least below 1% $H_2O$. This may be accomplished, for example, in a refrigerant cooler by lowering the gas temperature to approximately 10°C. In many cases

**Table 6.1** Composition of common sintering atmospheres

| Factor | Endothermic | Exothermic | Dissociated ammonia | Nitrogen based |
|---|---|---|---|---|
| % nitrogen | 39 | 70–98 | 25 | 75 to 97 |
| % hydrogen | 39 | 2–20 | 75 | 20–2 |
| % carbon monoxide | 21 | 2–10 | - | - |
| % carbon dioxide | 0.2 | 1–6 | - | - |
| ppm oxygen | 10–150 | 10–150 | 10–35 | 5 |
| dew point, °C | –16 to 10 | –25 to –45 | –30 to –50 | –50 to –75 |



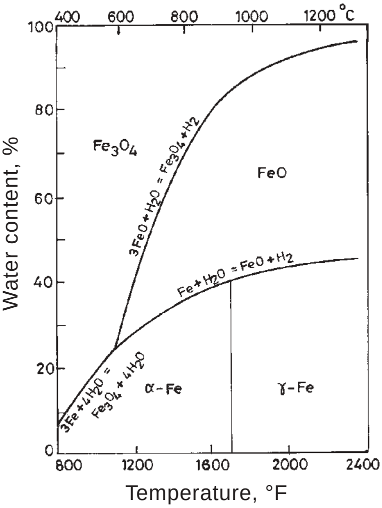


**Fig. 6.5** Water content % by volume/versus dew point.

**Fig. 6.6** (right) Equilibrium diagram for the system Fe–O–H. %$H_2O$ in $H_2/H_2O$ mixture (100 %) versus temperature.

when a stronger reducing atmosphere is needed a chemical desiccant agent is used, by which the dew point of the gas is lowered to –40°C, or approximately 0.1% $H_2O$. This dry gas is especially useful in a continuous belt furnace where air may enter from both ends of the furnace. Table 6.1 shows the compositions of some of the principal furnace atmospheres according to the classification of the American Gas Association (ACA).

The correlation between the dew point of the gas and water vapour content is shown in Fig.6.5. Figure 6.6 illustrates the amount of water vapour which can be present in a pure mixture of water vapour and hydrogen, without oxidizing iron. The slope of the curve in this figure shows that water vapour is more oxidizing at low temperature than at high temperature. This means that even a fairly low water vapour content – which may not be

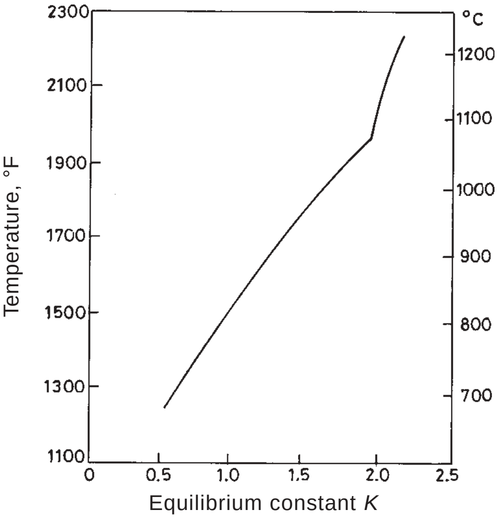
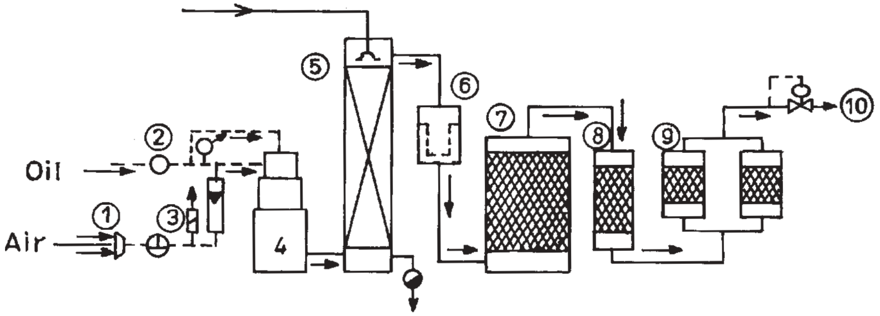


**Fig. 6.7** Equilibrium constant *K* of water-gas reaction $H_2 + CO_2 \rightarrow CO + H_2O$ versus temperature.

dangerous at the actual maximum temperature in the furnace – might very well oxidize the compact in the cooling or in the preheating zone. Figure 6.7 shows the equilibrium constant (*K*) for the water gas reaction as a function of temperature. High temperatures favour the creation of CO and water vapour whereas low temperatures stabilize $CO_2$ and $H_2$.

Production of exogases from hydrocarbon (petrol, crude oil, LPG) has become widely used. From crude oil, an exogas containing 20–30 % CO and $H_2$ can be obtained. Figure 6.8 shows a schematic diagram of an exothermic gas generator operating with crude oil. The air and crude oil enter the system at points 1 and 2, respectively, and then pass to the retort 4 through flow meters. A pressure gauge 3 is provided to check the air pressure. The oil is burned in the retort and the generated gas passes to the cooler 5 and filter 6. The crude oil contains about 1% sulphur in form of $H_2S$ or



1. Air inlet, 2. Inlet for crude oil, 3. Pressure gauge, 4. Retort, 5. Gas cooler, 6. Filter, 7. Sulphur removal unit, 8. Oxygen removal unit, 9. Absorption dryer, 10. Gas outlet.

**Fig. 6.8** Schematic flow diagram of an exothermic gas generator operating with crude oil.

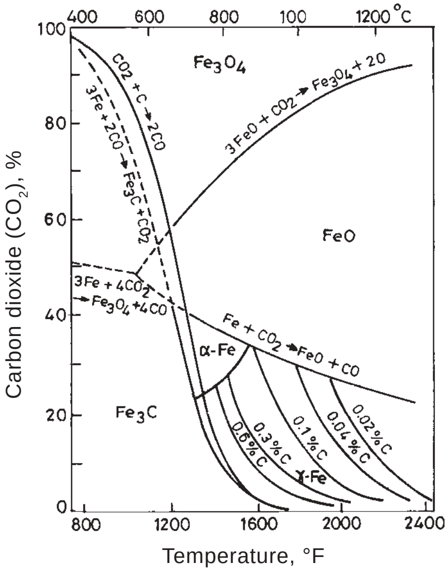


**Fig. 6.9** Equilibrium diagram for the system Fe–O–C.%$CO_2$in CO/$CO_2$ mixture (100%) versus temperature.

$SO_2$ and is removed to a level of 1 ppm. The gas then passes to the $O_2$ removal unit 8 and hence to the dryer 9. The gas finally leaves the system at point 10 ready to use.

**Endothermic Gas**: Endothermic gas is produced at a lower air:gas ratio, and heat must be supplied to support the reaction. It is richer than exogas in CO, $H_2$ and $CH_4$. This gas is not only strongly reducing, but is also carburizing. Endothermic gas is most suitable for sintering compacts of mixtures of iron–carbon and other alloy steels. The composition of the endogas is controlled, so that it is in equilibrium with the carbon potential of the steel to be sintered. The gas formation is facilitated over a clean catalyst such as nickel oxide in an externally heated chamber. Typically the generator operates at temperatures at about 1060–1100°C. The factors that influence the composition of the produced endogas are:

1. Temperature in the cracking zone
2. The air-to-gas ratio
3. The efficiency of the catalyst
4. The time in the cracking unit.

The temperature of the cracker should be kept close to the maximum temperature in the sintering furnace. Otherwise, the gas may not be stable in the sintering furnace. This could cause sooting or uneven properties of the sintered steel.

Figure 6.9 illustrates how at lower temperatures the CO is strongly carburizing and reducing. At higher temperatures, however, the action of gas is weaker. The two almost parallel inverted S-shaped curves show the producer gas reaction;

$CO_2 + C \rightarrow 2CO$

and the carburizing effect of CO on iron:

$3Fe + 2CO \rightarrow Fe_3C + CO_2$

At lower temperatures, the producer gas reaction is generally the most prevalent and results in the soot deposition on the sintered parts. However, at higher temperatures, say at 800°C, the carburizing action is dominant. Soot deposition can be suppressed by fast heating and cooling in the furnace. The effect of methane is different from that of CO. Methane, with increasing temperature, increases the reducing action and the rate of carbon deposition. Figure 6.10 presents the equilibrium between a methane–hydrogen atmosphere and iron with different carbon contents, at various temperatures.

The extent of decarburization and recarburization determines the finished carbon content at or near the surface of the sintered steel. Carbon content can be controlled by the dew point or the carbon dioxide content in the endogas. Most sintering under endothermic atmosphere is done at dew point ranging from –5 to 15°C. Endogas is reducing to iron above 260°C, because its typical 40% $H_2$ and 0.8% $H_2O$ (dew point 5°C) contents

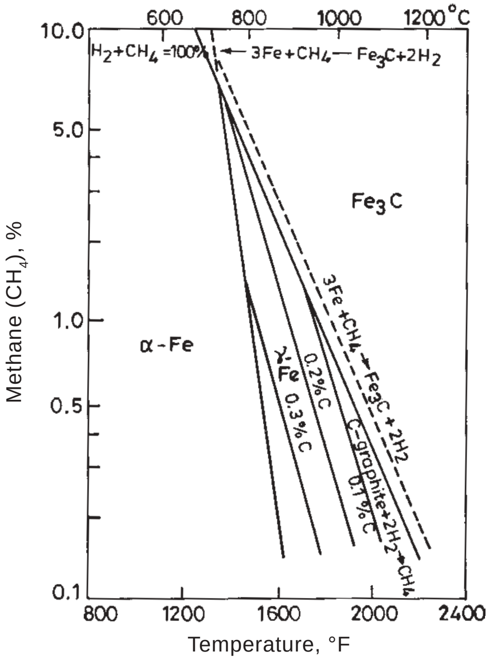


**Fig. 6.10** Equilibrium diagram for the system Fe–C–H. $CH_4$ content in $CH_4/H_2$ mixture versus temperature.

provide a hydrogen to water ratio of 50 to 1. Although this ratio achieves acceptable oxide reduction, other atmospheres notably those based on hydrogen or dissociated ammonia or synthetic nitrogen based atmospheres – can provide higher ratios.

Figure 6.11 illustrates a schematic diagram of an endothermic generator. The air and gas enter the flow meters (2 and 4) and then the mixing unit 5 through filter 1 and valve 3 respectively. The mixture is then passed in the catalyst filled reaction chamber of the generator by means of the compressor 6. The retort 7 is heated to the desired temperature by heating equipment 9. The gas leaving the retort is cooled to about 200 to 300 °C in the cooler 8 and leaves the system at point 10.

Table 6.2 gives the main characteristics of exo and endo gas generators showing different output capacities.

### *6.8.3. Nitrogen and Nitrogen-Based Atmospheres*

Nitrogen is inert to most of common metals and alloys. Because it is nonflammable, it is also used as a safety purge for flammable atmospheres.

The main constituent of the nitrogen-based system is molecular nitrogen. Molecular nitrogen is obtained from air, which consists of approximately 78% $N_2$, 21% $O_2$, 0.93 % argon, 0.03 % carbon dioxide and a small amount of such rare gases as neon and helium. Nitrogen is most commonly produced through air separation, i.e. liquefaction and fractional distillation. Air is filtered, purified, compressed to drive it through the rest of the sys-

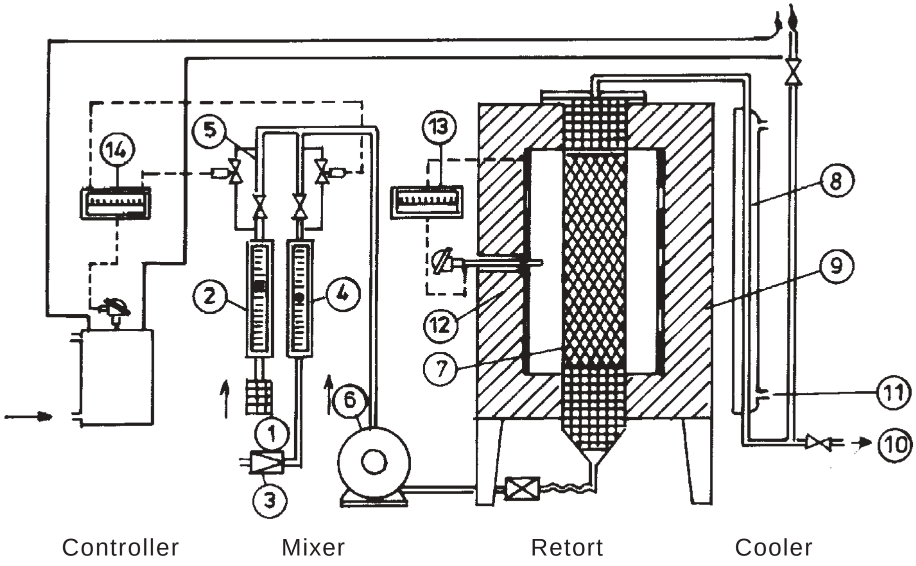


**Fig. 6.11** Schematic flow diagram of an endothermic generator: 1 – Air filter; 3 – valve; 2 and 4 – flow meters; 5 – mixer; 6 – compressor; 7 – retort; 8 – gas cooler; 9 – heating equipment; 10 – endogas outlet; 11 – cooling water; 12 – thermocouples; 13 – dew point analyser.

**Table 6.2** Main characteristics of exothermic gas generators

| ($m^3$/h at NTP) | Overall dimensions (m) | | | Base gas demand ($m^3$/h at NTP) | | |
|---|---|---|---|---|---|---|
| | length | width | height | propane | natural gas | town gas |
| 20 | 1.5 | 1.4 | 2.2 | 1.1–1.6 | 3–4 | 6.5–10 |
| 80 | 1.8 | 1.7 | 2.4 | 3.5–5 | 10–13 | 22–30 |
| 300 | 2.6 | 2.9 | 3.8 | 14–19 | 37–48 | 85–115 |
| 500 | 3 | 3 | 3.8 | 23–31 | 60–80 | 140–180 |

tem, and cooled to remove $H_2O$ and $CO_2$. After being liquefied it is distilled into major constituents, the most abundant being nitrogen. In addition to being plentiful and independent of natural gas, the nitrogen thus produced has the following characteristics:

– It is very dry, having a dew point of less than –65°C.

– It is very pure, having less than 10 ppm of oxygen.

– It is essentially inert to materials most commonly sintered and to furnace components such as muffles, conveyer belt, heating element, radiant tube, fixtures, etc.

In actual practice, furnaces are not very tight and some air does get in. Nitrogen by itself does not control the resulting surface oxidizing and decarburizing. Chemically 'active' gases are, therefore, added to the nitrogen, when the atmosphere has to perform functions requiring transfer of some element such as carbon from the atmosphere to the component being treated or such as oxygen from the oxide to the atmosphere. These active ingredients can be divided into the following categories:[7]

(1) Oxide reducing agents – The most desirable ingredient for reducing surface oxides is hydrogen. It can be derived from liquid hydrogen storage tanks or dissociated ammonia. It can also be derived from endogas or dissociated alcohols. Methanol dissociates or cracks at temperatures above 815°C to produce $H_2$ and CO in the same ratio (2:1) as normally found in the endogas generated from natural gas:

$$CH_3OH \rightarrow CO + 2H_2 + \text{small amount of } CO_2, H_2O \text{ and } CH_4.$$

Dissociated or cracked methanol when mixed with appropriate amounts of nitrogen can produce an atmosphere almost identical to endogas.

(2) Carburizing Agents – The most desirable ingredient to carburize is CO. It can be derived from endogas or dissociated alcohols such as methanol, or by reacting a hydrocarbon such as natural gas or propane and an oxidant such as water in the carburizing zone. It is generally found that in order to maintain effective carburizing rates, the CO level in the carburizing zone should not be less than 10 percent.

(3) Oxidant – Small but controlled amounts of oxidants such as $CO_2$, $H_2O$, $O_2$ or some combination of them can be added to nitrogen at selected sections of the furnace to provide decarburizing, oxidizing or burning of lubricants just before sintering P/M parts.

Manufacturing the nitrogen consumes less energy than producing an equivalent volume of endogas: 44% less energy in the liquid storage process and 80% less energy in the 'on site' separator process. Nitrogen allows smaller volumes of atmosphere to be used because it permits reduced flow rates, increase in production rates, lower part rejection and increased furnace utilization.

With the proper choice of enrichment gas, nitrogen based atmospheres can be used to sinter and infiltrate iron, carbon steel and other ferrous and nonferrous alloys. Stainless steel and refractory metals can be sintered in nitrogen based atmospheres when nitriding is not critical.

### 6.8.4 Dissociated Ammonia

Dissociated ammonia consists of 75 % hydrogen–25 % nitrogen by volume. Liquid ammonia from the tank enters a vaporizer at high pressure where heat converts the liquid in vapour. The pressure of the vapour is then reduced in an expansion valve and the low pressure vapour passes through a dissociator element filled with catalyst. Heated at a temperature in the range 900–1010°C, ammonia is dissociated into hydrogen and nitrogen. Figure 6.12 illustrates the flow diagram of an ammonia dissociator. Normally the gas contains only a trace (0.05% or less) of uncracked ammonia, which can be eliminated by passing it through either water or activated alumina. The dissociated gas at elevated temperature is highly flammable. Its specific gravity is 0.295 and thermal conductivity 5.507 compared to air, which is unity. Typical applications of dissociated ammonia include sintering of brass, copper, iron–copper, tungsten and tungsten alloys, aluminium and its alloys, and stainless steels.

### 6.8.5 Argon and Helium

Argon and helium are nonflammable and are inert to all application. They are used for sintering refractory and reactive metals and also as a back fill in vacuum furnaces. Argon is cryogenically produced from air. Its purity is

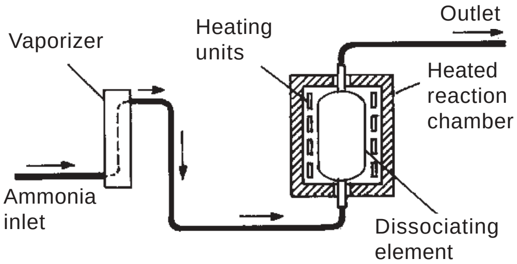


**Fig. 6.12** Flow diagram of an ammonia dissociator.

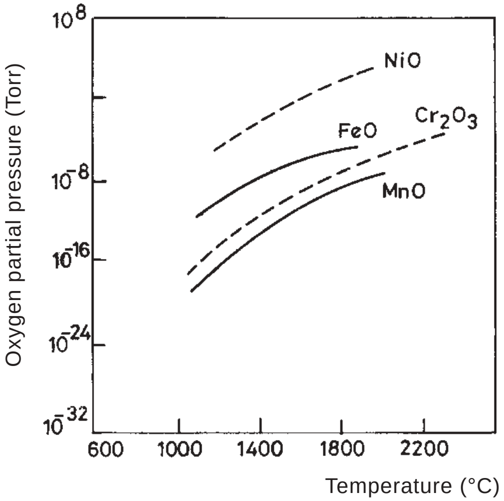


**Fig.6.13** Variation of equilibrium $O_2$ partial pressure with temperature for selected metal oxides.

very high, less than 0.0005 % oxygen and a dew point lower than –68°C. Its specific gravity is 1.379 g/cm$^3$, while thermal conductivity is 0.745.

### 6.8.6 Vacuum

Vacuum retains the proper chemistry of the parts during sintering. It is often more economical than atmosphere gases, particularly bottled gas. The only operating costs involved in producing the vacuum are for electrical energy and oil for the pumps. Vacuum pumps commonly used are mechanical pumps and oil vapour pumps. Vacua are generally classified with four ranges: rough (>1 to 1 torr), medium (1–$10^{-3}$ torr), high ($10^{-3}$ to $10^{-7}$ torr) and ultimate vacuum (< $10^{-7}$ torr). Most sintering furnaces are medium or high vacuum furnaces and such vacua are readily created by oil vapour pumps backed by a mechanical rotary pump.

All metallic oxides have a so-called dissociation pressure which is equal to the partial pressure of the oxygen present in the gas atmosphere at equilibrium with the oxide. If the partial pressure of the oxygen is lower than this, the compound will be transferred into a lower value oxide or metal and oxygen. If the partial pressure of the oxygen is higher than the dissociation pressure, the metal or the metallic oxide will oxidize. Figure 6.13 shows the dissociation pressure of some of the metal oxides as a function of temperature. During sintering an alloy, the selective evaporation of some alloying elements, due to the different vapour pressures of the individual metals, must also be taken into account. This naturally depends on the duration and temperature of vacuum sintering. Table 6.3 gives data of vapour pressures of some common metals.

Table 6.4 illustrates the dew point existing at different degrees of vacuum

**Table 6.3** Vapour pressures of some common metals

| Vapour pressure, torr | Temperature, °C | | | | | | Melting point, °C |
|---|---|---|---|---|---|---|---|
| | $10^{-5}$ | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ | 1 | |
| Aluminium | | | | 1210 | | | 660 |
| Carbon | | 2100 | 2250 | 2430 | | | 3730 |
| Chromium | 1060 | 1160 | 1270 | | | | 1875 |
| Cobalt | 1160 | 1260 | | | | | 1495 |
| Copper | | 1030 | 1140 | 1270 | 1430 | 1620 | 1083 |
| Iron | 1110 | 1210 | 1320 | | | | 1537 |
| Lead | 490 | 550 | 630 | 720 | 830 | 980 | 327 |
| Manganese | 700 | 770 | 850 | 950 | 1070 | 1230 | 1245 |
| Molybdenum | 1990 | 2170 | | | | | 2610 |
| Nickel | 1140 | 1250 | 1360 | | | | 1455 |
| Niobium | 2190 | 2360 | 2500 | | | | 2470 |
| Silicon | 1180 | 1280 | 1360 | 1550 | 1720 | 1930 | 1410 |
| Silver | 760 | 830 | 920 | 1030 | | | 960 |
| Tantalum | 2400 | 2590 | 2810 | | | | 3000 |
| Tin | | | 1090 | 1230 | 1400 | | 231 |
| Tungsten | 2550 | 2760 | 3010 | 3330 | 3650 | | 3410 |
| Vanadium | 1430 | 1551 | | | | | 1900 |
| Zinc | | 250 | 290 | 340 | | | 420 |

**Table 6.4** Dew point as a function of water vapour content for different vacua

| Vacuum (torr) | Dew point (°C) for different volumes percent of water vapour in the gas | | |
|---|---|---|---|
| | 20 % | 70 % | 100 % |
| 1 | –35 | –21 | –17 |
| $10^{-1}$ | –55 | –43 | –40 |
| $10^{-2}$ | –70 | –61 | –58 |
| $10^{-3}$ | –86 | –77 | –74 |
| $10^{-4}$ | –92 | –90 | –89 |

for different levels of water vapour in the gas. From the Table it can be seen that for a vacuum of $10^{-1}$ torr the dew point is between –40 and –55°C, depending upon the water vapour content.

Most of the vacuum sintering is on the reactive metals which are highly susceptible to the formation of hydrides, nitrides or oxides in gaseous atmospheres. Refractory metal carbides, stainless steels, beryllium, titanium, zirconium, tantalum, niobium, vanadium, thorium, uranium and cermets are best examples for vacuum sintering.

## 6.9 Sintering Atmosphere Analysis and Control

### *6.9.1 Gas Analysis*

Gas analysis is done either by an Orsat type analyzer or infrared analyzer. In the Orsat type the complete analysis of a gaseous mixture is divided into the absorption phase and the explosion or burning phase. The amount of carbon dioxide, oxygen and carbon monoxide are determined by chemical absorption. These units are portable and permit relatively rapid analyses.

The infrared analyzer depends on the principles that different gases absorb infrared energy at characteristic wave lengths. Because of this property, changes in the concentration of a single component in a mixture, produce corresponding changes in the total energy remaining in an infrared beam passed through the mixture. Proper selection of apparatus permits accurate, rapid analyses for such constituents as carbon monoxide, carbon dioxide and methane. Such analyzers are not suitable for measuring oxygen, hydrogen and nitrogen which have no infrared absorption band. Such analysers are highly sensitive and are successfully applied for analyzing gases with high carbon potential, such as purified exothermic gas or dry endothermic gas, and those with high purity such as dry hydrogen or argon.

### *6.9.2 Specific Gravity Analysis*

The specific gravity of gases can be measured and compared against that of air. Since carbon dioxide is much heavier than the other sintering atmosphere constituents, this analysis is especially sensitive to changes in carbon dioxide. In case carbon dioxide appears in the influent or effluent furnace atmosphere, the specific gravity analyser could be used for corrective measures. This analysis is useful for example, in checking sintering furnace atmospheres of purified rich exothermic or rich endothermic gas which are supposed to be free from carbon dioxide. By continuously measuring the specific gravity of the effluent gas from the furnace, the completeness of purge can be established.

### *6.9.3 Moisture Determination*

The moisture content of the sintering atmosphere has significant effect on sintering. One of the simplest method for determining moisture content is by checking the dew point. The device used to determine this is called ‘dew cup', which contains a glass thermometer. The cup is placed directly in the gas stream so that the entering gas impinges on its polished surface. To begin the test, the atmosphere gas is flown through the container, and acetone is poured into the cup. After about 5 minutes, small amounts of crushed dry ice are added to the acetone while stirring constantly with the thermometer. At the first sign of dew or moisture on the polished surface of the cup, the temperature is read from the thermometer, which happens to be the dew point of the gas.

In a more instrumented type of indicator, the sample of the gas is compressed, and then quickly expanded. In case the gas got cooled down below its dew point due to its rapid expansion, a fog is noticed in the expansion chamber. The pressure ratio of the gas is converted to dew point.

The dew point measurements of a gas either entering or leaving a furnace give an excellent indication of the carbon potential. For example, an excess moisture in a supposedly non-decarburizing atmosphere can cause decarburization. The measurement is also an indicator whether water gas reaction is occurring within the atmosphere by reaction of carbon dioxide with hydrogen at elevated temperatures. In nutshell, the dew point determination is a convenient quick check to see whether conditions are right throughout a furnace system.

### *6.9.4 Carbon Potential Control*

Carbon potential control of sintering atmosphere is important during sintering of steels, since it should be in equilibrium with the carbon potential of the steel concerned. Such a control would prevent the steel from either carburizing or decarburizing. Either dew point or carbon dioxide analysis of the atmosphere can be used as a measure of its carbon potential. The gas sample taken for measurement of the carbon potential should be from the high heat zone of the sintering furnace. As the furnace is usually not under positive pressure, a pump is required to pump a gas sample from the furnace through the instrument. Dew point analysers are not as sensitive, and are slower in response than carbon dioxide infrared analyzers. Because of the fast response, infrared analyzers are used for multipoint control systems. Dew point on the other hand is not satisfactory to use for multipoint control because water molecules are difficult to purge from an instrument in a short time.

The first thing, before controlling the process, is to refer the equilibrium data of dew point vs carbon content, or carbon dioxide vs carbon content, at the operating temperature of sintering. Such data (Fig.6.14) have been determined by actual measurement and are fairly accurate. However, they should be used only as a guide and the final adjustment should be made after the carbon analysis of the steel concerned.

The sintering furnace has different zones, each requiring a unique combination of temperature, time and atmosphere composition. To achieve this many times the atmosphere is either diluted or enriched by hydrocarbon.

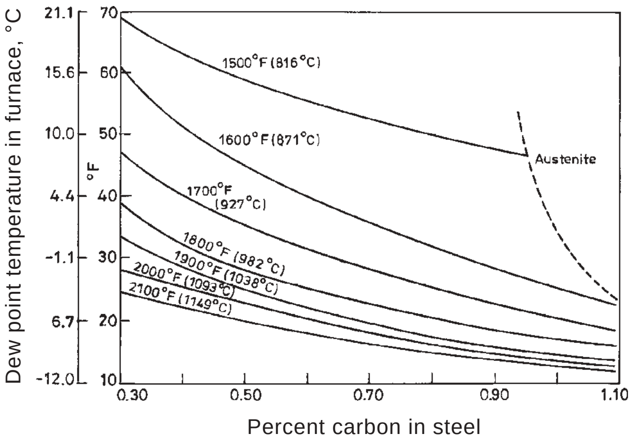


**Fig. 6.14** Dew point and carbon equilibrium diagram.

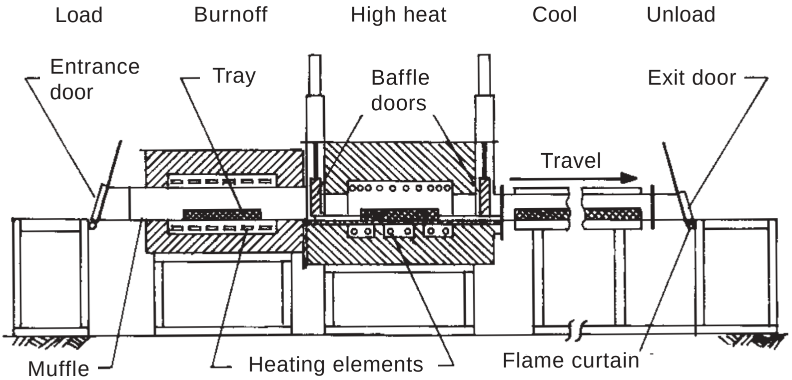


**Fig. 6.15** Box-type, manually operated sintering furnace.[3]

To achieve a specific carbon content in the sintered steel, it is, therefore, important to understand the effect of temperature of each zone on the final carbon equilibrium of the concerned steel.

## 6.10 Sintering Furnaces

Sintering furnaces may be classified as batch-type or continuous furnaces. They have invariably gastight furnace shell or gastight muffle to maintain a reducing atmosphere.

### *6.10.1 Batch-Type Furnaces*

Batch-type furnaces are used for sintering in protective atmospheres when the quantities produced do not warrant installing continuous furnaces. A typical box-type sintering furnace is shown in Fig.6.15, which is similar to pusher-type continuous furnaces except that the boats are stoked through the furnace by hand rather than with a mechanical stoker.

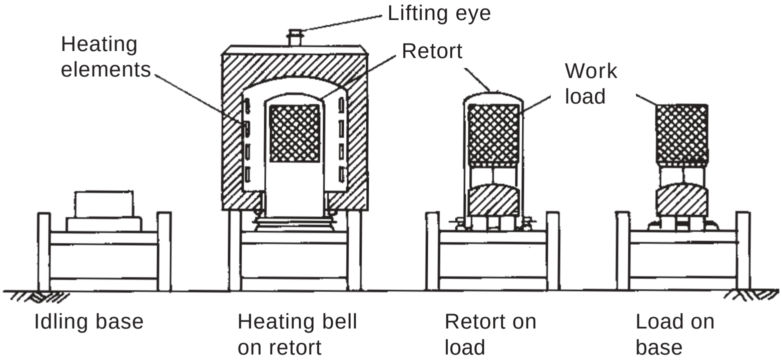


**Fig. 6.16** Bell-type sintering furnace showing stationary bases, retorts and heating bell.[3]

Small pilot plant or laboratory muffle furnaces are similar to box furnaces. Heating through a muffle is less efficient than having the electric heating element exposed to the furnace atmosphere and furnace chamber. Full muffle furnace reduces the need for the flow of atmosphere purging gas, particularly while using expensive gases like hydrogen or dissociated ammonia.

In addition to box-type furnaces, bell-type furnaces are also used for batch-type sintering of metal powder compacts, particularly in cases when very good atmosphere control is required. Figure 6.16 shows a typical bell-type furnace. The compacts are arranged on a load supporting base with a removable sealed retort over the load to contain the protective atmosphere. A portable heating bell is lowered over load and retort for the heating cycle.

### 6.10.2 Continuous Sintering Furnace

Most sintering furnaces are used for large volume production work and are of the continuous type, that is there is a continuous movement of compacts through the three zones of the furnace. There are three major methods used to convey the compacts. They are:

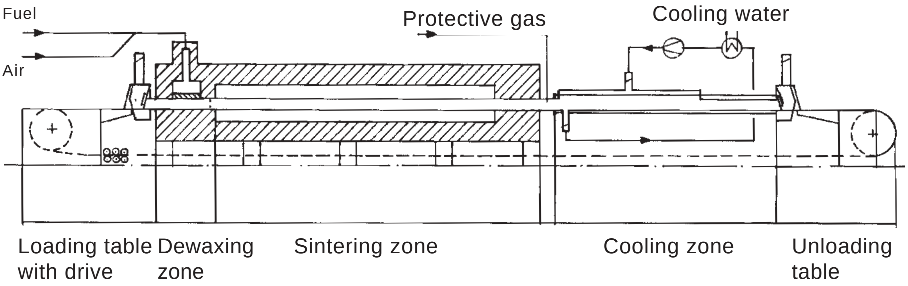


**Fig. 6.17** Schematic of a conveyor belt sintering furnace.

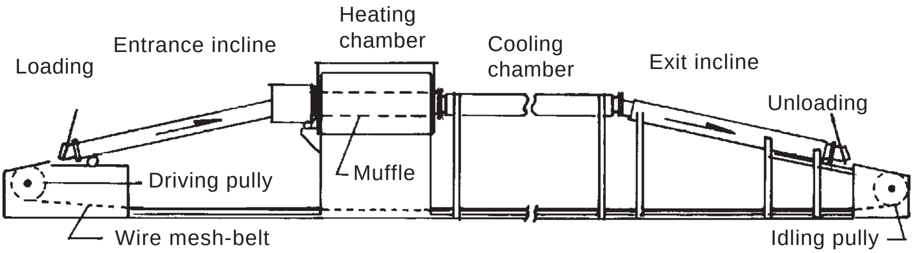


**Fig. 6.18** Section through a humpback mesh-belt furnace; belt drive and take up mechanisms omitted.[3]

– the mesh-belt conveyor
– the roller hearth type
– the pusher-type
– the walking beam type.

**Mesh-belt furnaces,** shown schematically in Fig.6.17, have an endless woven belt generally made of a nickel-base heat resistant alloy wire which runs over large motor-driven drums at the ends of the furnace. Inside the furnace it slides over the refractory hearth in the hot zone. The green compacts to be sintered can be put directly on the belt or they can be put on heat resistant trays. The doors in such furnaces are open and the furnace, therefore, requires large amounts of protective atmosphere. A modified mesh-belt furnace is a humpback furnace (Fig.6.18). These have inclined entrance and exit zones with the heating and cooling chamber at an elevated level. They are used for sintering materials, such as aluminium alloys and stainless steels, which require particularly dry atmospheres. Sintering atmospheres high in hydrogen have tendency to rise because of their low density and their contamination in such types of furnaces is naturally prevented.

The increasing demand for sintered products has resulted in a greater need for higher mesh-belt furnace performance, in conjunction with the requirement for cost efficient sintering. Conventional conveyor belt furnaces which can transport greater quantities without increasing their surface heat losses have a lower specific energy requirement. Assuming that the dwell time at the required sintering temperature must not drop below a specified value, such improvements can only be achieved by increasing the heat up speed and the belt load. The overall furnace length is determined by the section lengths required for heat up and for holding at sintering temperature. If it is possible to accelerate heat up whilst achieving complete lubricant burn-off, the length by this furnace section can be reduced. In one of the furnaces this aspect has been introduced, where the green compacts are heated with a high energy density by vertically impacting, high velocity protective gas jets distributed evenly over the conveyor belt width.[8] The intensive contact of the parts with the heating gas provides for a rapid heating dewaxing and burning off of the lubricant. The temperature in the rapid heating zone is kept constant by continuously adjusting the burner output.

The sintering zone proper is heated electrically by free radiating resistance heaters. These heaters are installed above and below the conveyor belt at right angles to the transport direction. This ensures uniform temperature distribution over the belt width. They can be replaced individually during belt operation. Several heating zones ensure that the desired temperature profile is maintained over the entire furnace length. The built in gas generation in the furnace provides lower investment costs, the low operating costs and the less required space. The protective gas composition can be adjusted between that one of exogas and that one of endogas. In the cooling zone, the sintered parts are cooled by circulating gas. The protective gas passes in a closed cycle via a water cooler. Regardless of the conveyor belt loading, the quantity of protective gas at the furnace outlet is kept constant via a control loop. This device permits a considerable reduction in the overall plant length. The flow of protective gas from the muffle of the sintering zone into the dewaxing zone makes it possible to have different protective gas atmosphere in the dewaxing and sintering zones.

In **roller hearth furnaces** one has a hearth in the hot zone of the furnace which consists of a series of parallel rollers made of a heat resistant alloy. The green compacts are placed on trays that are conveyed through the three zones by riding on driven rolls. For a given length the roller hearth method can allow much higher loading than the mesh-belt technique, but the maximum sintering temperature is still 1150°C. The charge and discharge doors are operated automatically and open only when a tray of work is charged or discharged. This reduces the quantity of atmosphere consumed and minimizes heat losses.

The **pusher-type sintering furnace** is suited for sintering metal parts that load too heavily for the mesh-belt type, and where the production rate does not warrant the roller hearth furnace. In case the sintering tempera-

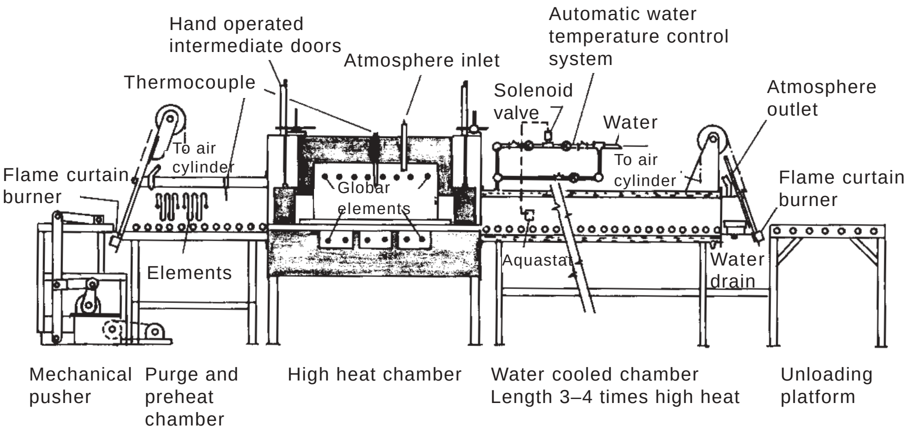


**Fig. 6.19** Longitudinal section of mechanical pusher furnace.

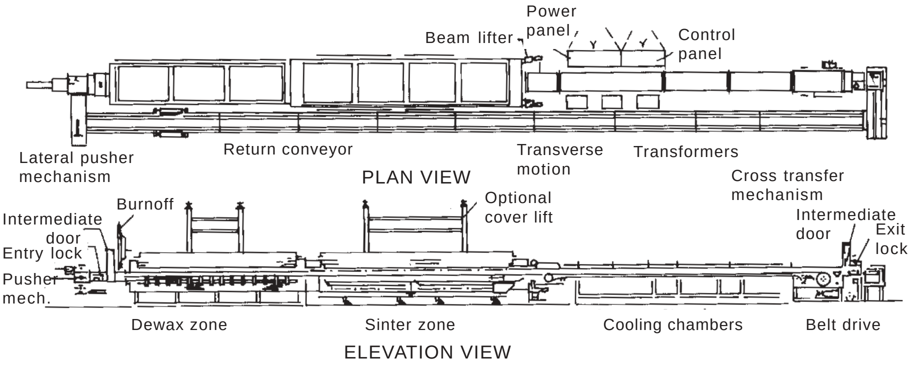


**Fig. 6.20** Diagram of a walking beam sintering furnace illustrating cross transfers and return conveyor for automated operation.

ture is high, say up to 1650°C, such a furnace is suited, because mesh-belt and rollers are ineffective. Mechanical or hydraulic pusher furnaces are available for high outputs. Generally, two types of pushing mechanisms are used, one being the intermittent pusher mechanism, while the other continuous stoker pusher-type. A typical pusher furnace is shown in Figure 6.19. The intermittent pusher-type is generally used for most common metals, while the continuous stoker pusher-type more often used for carbides. Smaller furnaces are often manually stoked.

**Walking beam types** of continuous sintering furnaces were first developed in Germany for use at high temperatures as much as 1800°C, depending on the compatibility of the atmosphere and the heating element used. At high temperatures (>1150°C) mesh-belt furnaces commonly used in industry cannot operate due to limitations of both the alloy wire belt and heating chamber length. The amount of production weight that can be conveyed safely through the furnace is practically unlimited. In these furnaces boats or trays are conveyed by a mechanism which periodically lifts them, advances them a short distance and then lets them settle back on a ceramic ledge. The part of the lifting mechanism heated to the furnace temperature is made of refractory. A typical furnace is schematically shown in Fig.6.20. It illustrates a furnace with cross transfers and return conveyor that provides fully automatic operation. This particular system consists of an entry lock chamber with an intermediate door, a preheat or dewaxing zone, a sintering zone, cooling chambers, an exit lock chamber with intermediate doors, cross transfer mechanisms, and a return conveyor system. In this system, three means of transport are provided. A pusher mechanism which pushes the workload tray through a muffled preheat or dewaxing zone, a walking beam mechanism to transport the trays throughout the high heat sintering zone, and a cooling chamber consisting of a conveyer belt drive system. The three methods of conveying the workload throughout the furnace is used to provide a closed system, so atmosphere consumption will be considerably reduced.[9]

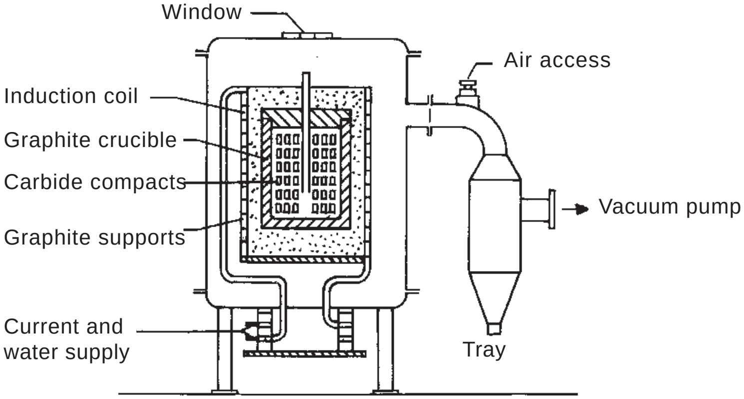


**Fig. 6.21** Schematic of vacuum furnace for sintering cemented carbides.[3]

### 6.10.3 Vacuum Furnaces

Vacuum furnaces are generally of batch type, but new developments in continuous vacuum furnaces have also been made, in which they incorporate burn-off chambers, vacuum locks and cooling zones through which the compacts are conveyed continuously. However it may be mentioned that the batch type furnaces offer better control of the sintering cycle than continuous furnace.

A typical vacuum sintering furnace for cemented carbide parts is shown in Fig.6.21. Because it is relatively easy to obtain high temperatures and to control the sintering environment in vacuum furnaces, they have almost completely replaced atmosphere sintering furnaces for hard metal processing. Resistance furnaces are getting more and more common over induction furnaces on a first cost basis, particularly when the work zone size is

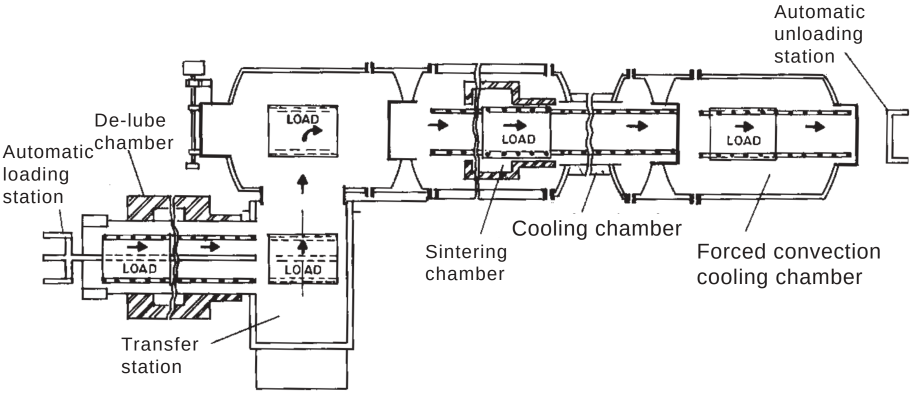


**Fig. 6.22** A typical continuous vacuum sintering furnace.

increased. The vacuum pumping system is generally continually connected to the furnace chamber during the entire cycle (except during cooling) to pump away any out gassing or products of reaction. Because excessive paraffin may destroy the lubricating effect of the vacuum pump oil, effective condensing systems are necessary to trap the vapour before it reaches the pump. Pumping equipment usually includes a Roots blower backed with a mechanical vacuum pump. Operating pressures range from 1 torr to 10 millitorr.

A typical continuous vacuum sintering furnace is shown in Fig.6.22, which consists of an external loading table followed by an atmosphere presinter chamber, a transfer tunnel, an 'atmosphere to vacuum' vestibule section followed by the heating chamber, vacuum cooling chamber, combination fan cooling and vacuum to atmosphere vestibule, and a two tray loading table.[10] A typical furnace of this type will accommodate trays 450 mm wide × 600 mm long with up to 230 mm working height. The heating elements is manufactured from solid graphite in the vacuum section and metallic alloy in the presinter section. The vacuum section is capable of operating up to 1400°C at a vacuum level of 500 µm. The gross output of a typical unit is 250 kg·h$^{-1}$.

**Table 6.5** Furnace heating elements and uses

| Element | Max temperature, °C | Atmosphere |
|---|---|---|
| nichrome (Ni–Cr) | 1150 | 1, 2, 3, 4, 5, 6 |
| kanthal (Fe–Cr–Al–Co) | 1300 | 1, 3, 4, 6 |
| super kanthal ($MoSi_2$) | 1800 | 1, 3 |
| silicon carbide (SiC) | 1250<br>1600 | 1, 2, 3, 5, 6<br>1, 3 |
| platinum | 1500 | 1, 3, 4 |
| molybdenum | 1800<br>2200 | 2, 3, 4, 5, 6<br>4 |
| tantalum | 1900<br>2400 | 3, 4<br>4 |
| tungsten | 1900<br>2600 | 2, 3, 4<br>4 |
| graphite | 2000<br>3000 | 3, 4, 5<br>3, 4 |

Atmosphere key: 1 is oxidizing, 2 is reducing, 3 is inert, 4 is vacuum, 5 is carburizing, 6 is decarburising.

### *6.10.4 Electric Furnace Heating Elements*

Electric heating elements in sintering furnaces may be:

(a) base-metal nickel–chromium alloys, (b) nonmetallic heating elements SiC, $MoSi_2$ or graphite and (c) refractory metal heating elements, Mo or W. Graphite and refractory metal heating elements are used almost exclusively in vacuum furnaces. Wrong selection of heating element, particularly with reference to furnace atmosphere, can cause very high furnace maintenance. A mere comparison in hours for the same resistor in commercial furnaces operated at the same temperature would not give a true picture of the action of different atmospheres. Table 6.5 gives a summary of maximum temperature and atmospheres, where each type of the elements can be used. The life of a resistance material depends not only on the furnace atmosphere but also on many other working conditions i.e. watt-density loading, cross-sectional area, operating temperature, frequency of switching the current on and off, support of the resistor in the furnace, physical shape and design of the resistor.

Resistance temperatures are always higher than furnace control temperatures. When the furnace is operated close to the maximum temperature, the watt density loading must be lower and more conservative.

## 6.11 Sintering Zones

A conventional sintering furnace can be divided into three distinct zones. They are (Fig.6.15):

1. Burn-off and entrance zone
2. High temperature sintering zone
3. Cooling zone.

### *6.11.1 Burn-Off and Entrance Zone*

The zone of the furnace is designated to heat the green compacts rather slowly to a moderate temperature in the order of 450°C. The main function of this burn-off zone is the volatilizing and elimination of the admixed lubricant. A slow heating rate is necessary to avoid excessive pressures within the compact and possible expansion and fracture. The length of this zone must be sufficient to allow complete elimination of the lubricant before the compacts enter the high temperature zone. The metal (for example zinc from zinc stearate) and the carbon after the breakdown of the hydrocarbons resulting from the volatilizing of the lubricant can deposit on the furnace heating element and promote premature failure. Such deposits on refractory walls and cooling zones lead to poor heat transfer. On the other hand the compacts may be subjected to discoloration and possible undesirable chemical reactions.

The flow of the atmosphere is important in expelling the lubricant vapours. For this, sufficient atmosphere gas must be provided, and the flow directed so the vapours are discharged toward the furnace entrance and not into the high heat zone. The burn-off zone is sometimes separated with an air gap, using a flame curtain before the high heat zone.

During vacuum sintering metallic stearates are not used and instead stearic acid or a wax compound is used. Other wise the furnace and vacuum pumps get contaminated. For batch type vacuum furnaces, the burn-off is best accomplished in a separate protective atmosphere oven at about 450°C.

### *6.11.2 High Temperature Zone*

In this zone the actual sintering of the compacts takes place. It must be properly heated so that the desired temperature is reached and of sufficient length so that enough time at temperature is attained to achieve the necessary end properties in the sintered parts. The lengths of the burn-off and high temperature zones are usually about equal. Because of the necessity of having a reducing atmosphere present during sintering a gas tight muffle is utilized. However, heating through a muffle is less efficient than having the heating elements exposed to the atmosphere and furnace chamber.

### *6.11.3 Cooling Zone*

The cooling zone often consists of a short insulated section and a relatively long water jacketed section. The former cools down the parts from the high sintering temperature to a lower one at slow rate so as to avoid thermal shock in the compacts and the furnace. The latter provides cooling to a temperature low enough to prevent oxidation of the material upon exposure to the air. Since the cooling rate is rather slow at the low temperature range, fans are used in the cooling chambers to help cool by circulating the atmosphere over the work. However, care must be taken, so that air is not sucked into the cooling chamber when the doors are opened.

Automatic water temperature control on cooling chambers is desirable to ensure that it does not get too cold or too hot. In case it is below the dew point of the atmosphere, water gets condensed on the chamber walls and parts may get oxidized. To compensate automatically for varying loads, automatic flow control of the water is introduced.

### References

1. J.S. Hirschhorn, Introduction to Powder Metallurgy, American Powder Metallurgy Institute, Princeton, 1969.
2. R.M. German, Powder Metallurgy Science, 2nd edition, MPIF, Princeton, 1994.
3. F.V. Lenel, Powder Metallurgy Principles and Applications, MPIF, Princeton, 1980.
4. R.M. German, Liquid Phase Sintering, Plenum Press, N.Y., 1985.
5. M.B. Waldron and B.L. Daniell, Sintering, Heyden & Son, London, 1978, p.44.
6. S. Bradbury (Ed.), Powder Metallurgy Equipment Manual, Metal Powder Industries Federation, Princeton, 1986.
7. H. Nayar, Heat Treating, March–April, 1988.
8. Anonymous, *Metal Powder Report*, **36,** No.1, 1981, 27.
9. J.W. Boswell, Industrial Heating, Jan., 1988.
10. G.P.Read, *Powder Metallurgy*, **26**,1983, 37.

# 7 HOT CONSOLIDATION

Hot consolidation methods are applied to obtain fully dense metal powder compacts with controlled microstructures. This encompasses many diverse operations, including uniaxial hot pressing and pressure sintering, hot isostatic pressing, hot extrusion and hot forging. The present chapter describes these processes.

## 7.1 Hot Pressing

Hot pressing is a suitable method for densifying materials with poor sintering behaviour. This technique, which combines powder pressing and sintering into one single operation, offers many advantages over conventional powder consolidation. By simultaneous application of temperature and pressure, it is feasible to achieve near theoretical density in a wide range of hard to work materials. As the resistance of metal particles to plastic deformation decreases rapidly with increase in temperature, much lower pressures are required for consolidation by hot pressing. Further, densification by hot pressing is relatively less sensitive to powder characteristics – shape, size and size distribution which are important in cold pressing and sintering. Hot pressing parameters pressure, temperature, time and the working atmosphere largely control the properties of compacts. High speed tool steels, super alloys, beryllium and the refractory metals are particularly amenable to hot pressing. Hot pressing is perhaps the only method of producing dense fine grained shapes of materials such as pure carbides, nitrides and borides which are otherwise difficult to sinter due to the lack of adequate atomic mobility at the sintering temperature.

The various steps involved in the hot pressing procedure are as follows:

1. Powder or a cold compacted preform is placed into the die mould;
2. The mould is heated either by resistance or by induction method to a predetermined temperature;
3. The powder in the die cavity is then pressurised;
4. The temperature is steadily increased during compacting until a maximum required temperature is reached;
5. Compacting pressure and temperature are maintained for a dwell time and
6. The mould is cooled slowly, under pressure, to a temperature at which oxidation of the material would not occur.

There are many variations on the general procedure given above. In

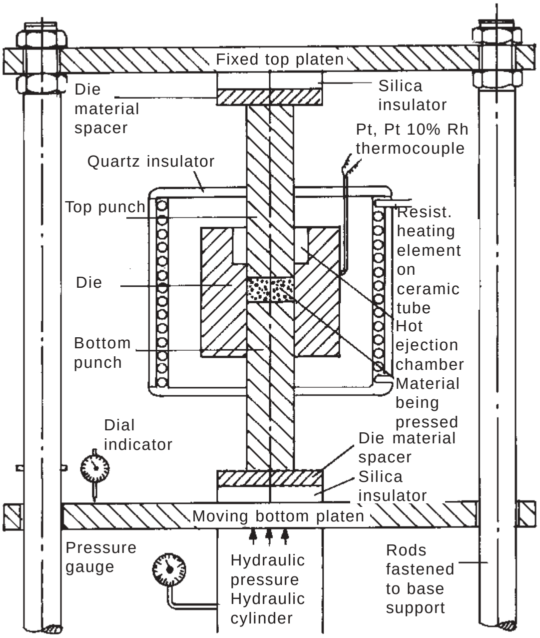


**Fig. 7.1** Schematic design of hot pressing unit.

many cases it is preferable to apply a nominal pressure or even the maximum required compacting pressure before the initiation of consolidation cycle. This is particularly true in case of reactive hot pressing.

Many oxide and carbide ceramics can be hot pressed using graphite dies in the open atmosphere. However, the die life is limited due to severe oxidation at temperatures above 500°C. Hot compacting of refractory and reactive metal powders demands inert atmosphere or vacuum. In place of inert gas, vacuum for hot pressing offers additional advantages of removing air from the powder body (thus eliminating the possibility of air entrapment) and also degassing it during the initial heating up of the pressing cycle. This would enhance the activity of the powder and thus help in sintering. Figure 7.1 gives a schematic design of a hot pressing unit.

Philips Research Laboratory during 1960’s developed a continuous hot pressing technique, in which the upper punch exerts a force on the bottom punch is continuously lowered by means of a spindle mechanism. A water cooled upper punch is used, which means that the upper part of material remains unsintered. Figure 7.2 shows a schematic presentation of the pressure–time relationship, which shows that the process operates on a stick slip process. As a result of the fact that the material sticks to the wall; the pressure difference over the sintering material increases until this value has become large enough for the material to slip free from the wall. The speed of the process is limited by the low heat conductivity of the ceramic powder. The product is, thus, a bar and the firm extensively used it for ferrite consoli-

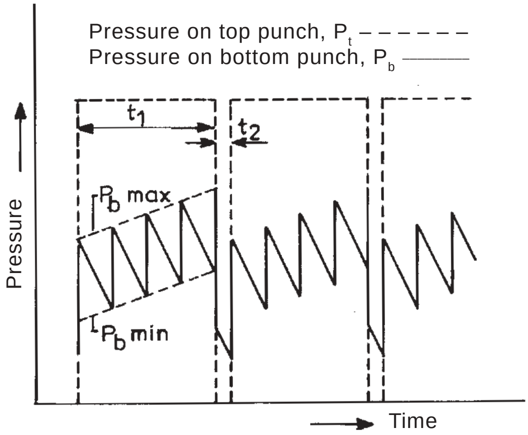


**Fig. 7.2** Schematic presentation of the pressure–time relation during continuous hot pressing.

dation, where fully reacted products have to be used to take full advantage of the special features of the continuous hot pressing.[5]

While graphite is the most common die material, other ceramics and refractory metals have also been used on a limited scale.

Graphite is available in many grades, differing in density, strength, thermal and electrical properties. Its strength increases with temperature up to about 2500°C beyond which it falls. Its strength at 2500°C is almost twice that at room temperature. A low thermal expansion coefficient, ease of machining and low cost make it a nearly ideal choice for die material.

Oxide ceramic dies are promising for hot pressing in oxidizing atmosphere. High density alumina can be operated up to 40 hot pressing cycles, provided extreme care is taken in alignment and rate of loading and heating.

The carbides have been tried is hot pressing die materials on a limited scale. The machining of these materials is difficult and expensive. Titanium boride although showing excellent high temperature strength and increase in strength with temperature, (flexural strength of 240 MPa (35 000 psi) at RT and 414 MPa (60 000 psi) at 1600°C), is used only to a limited extent because of difficulty in machining. The refractory metals tungsten and molybdenum have been used as die materials but creep of the metals at high temperatures limits their usefulness.

A number of different kinds of die washes, coating, spacers, liners and sleeves have been employed to overcome or decrease the die compact interaction and thus decrease contamination and facilitate ejection of the final compact. Die washers such as $B_4N$ and $Al_2O_3$, liners or spacers of foliated graphite and punch coatings such as pyrolytic graphite have been used to prevent interaction between the materials being pressed and the graphite die parts. Foils of noble or refractory metal (e.g. Pt, W, Mo, Ta) and spacers of refractory compounds, such as SiC and refractory oxides, such as $ZrO_2$, have also been used for the same purpose.

Induction heating is most commonly employed for heating the graphite die tooling. Heating by radiation from resistance heating elements facilitates closer control of temperature. However, the maximum temperature attainable by indirect resistance heating is limited to about 1800°C.

Earlier hot pressing was primarily employed to improve the densification of some metal and metal bonded carbide cutting tools. At present hot pressing as a fabrication process, has been finding increasing use in the ceramic industry for the preparation of materials having improved properties through the control of composition, microstructure and density. Hot pressing has also been employed in the fabrication of various high temperature components, multiphase ceramics, ceramic–metal systems and pressure bonding. Tungsten, tungsten base alloys, dispersion strengthened aluminium and copper base alloys, super alloys and beryllium metal have also been consolidated by vacuum hot pressing for many years.

## 7.2 Hot Isostatic Pressing

The aim of the process is to compact materials that would not otherwise compact even at considerably higher pressures, or to combine the pressing and sintering operations in one step. The pressure medium used is an inert gas. Heat is applied by an internal furnace in the pressure vessel. In most cases the powder or workpiece is encapsulated in a gastight material, which

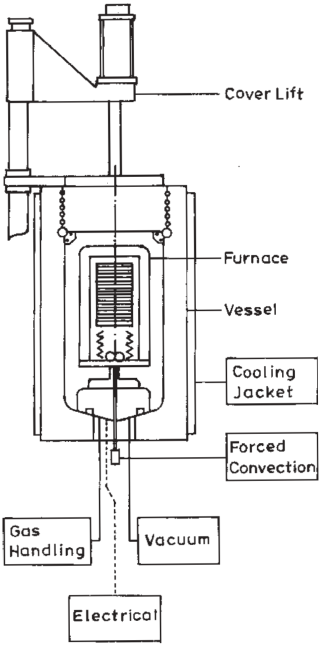


**Fig. 7.3** HIP-system diagram.

can withstand the pressure and temperature and which does not react with the powder. Typical temperatures are 1000–1750$^{o}$C and typical pressures 100 to 320 MPa (1000–3200 bar).

### 7.2.1 Equipment

A HIP system usually consists of five major components: pressure vessel, internal furnace, gas handling, electrical and auxiliary systems (Fig.7.3).

1. **Pressure Vessel**: The pressure vessel in a HIP system contains the high temperature furnace and retains the high pressure gas. Most HIP vessels have threaded closures. The sealing of the gas in the vessel is done with elastomer 0 rings since the vessel temperature is kept below 250$^{o}$C. The ASME Code section VIII, Division 2 requires a minimum 3:1 safety factor of stress versus tensile strength. The quality assurance of a vessel after installation is very important regardless of the type, size, design and stress analysis.

2. **Furnace**: There are following types of furnaces: radiation furnace, natural convection furnaces and forced convection furnaces. There are several advantages to using a convection furnaces. The workpiece is not exposed to direct radiation from heater elements. Heating elements are not susceptible to damage by the load/unload process. Most common heating elements are graphite, molybdenum and nickel/chrome. As the pressure vessel is designed as a 'cold wall vessel', a thermal barrier is used, which prevents hot gas penetration to the inside vessel wall.

3. **Gas Handling**: Most systems use argon as the pressurizing medium. Gas pressures can be achieved with a compressor by thermal expansion. Gas purity is very important. Gas with 50 ppm total impurities is acceptable to prevent premature furnace failure, but can be harmful to superalloys or titanium which require less then 5 ppm total impurities.

4. **Controls**: This can be done in three levels; viz. relay, programmable (Level I), mini- and microcomputer (Level II) and total computer supervision (Level III).

5. **Auxiliary Systems**: These include a cooling system, vacuum system, material handling with workpiece fixtures and facilities subsystems including exhaust fans, oxygen monitoring equipment and cranes.

### 7.2.2 HIP Variables

The following are the HIP system variables:

- Workpiece configuration (powder, compact, bonding, etc.).
- Shape, size, density, thermal characteristic, and number of work pieces processed per year.
- Hot or cold loading/unloading.
- Type of fixturing: manual or automatic workpiece loading unloading.
- Method of loading/unloading into/from vessel with crane or automatic jib.
- Maximum pressure and temperature.

– Maximum tolerable temperature uniformity during steady state, heating and cooling.

– Maximum heating and cooling rates during transients. Is rapid quenching of workpiece required for optimum property recovery?

– Type of cycle: (i) pressurize cold, then heat; (ii) pressurise and heat simultaneously; (iii) heat first at vacuum or low pressure then pressurise.

– Maximum time at steady state.

– Desired cycle time.

– Minimum required gas purity for workpiece.

– Levels I, II or III electrical control.

– Utility requirements: electrical, water, air or gas.

– Shutdown modes: preventive maintenance, quality assurance, power failure etc.

– Room size for equipment pit for vessel (water table) and barricading, crane for loading/unloading etc.

– Amortisation time of equipment (life of vessel and other components).

– Applicable codes ASME, ASA, ASTM, ASM, IEEE, NEC, NEMA, OSHA and other codes.

– Requirements of insurance carrier, local safety codes, seismic etc.

– Cost effectiveness: cycle cost versus loading efficiency.

### *7.2.3 HIP Economics*

Equipment cost depends on the system component size. The size of the equipment influences installation and building cost as well as operational cost. Workpiece volume, higher pressures (200 MPa) and temperature (2200°C) increase the cost of the HIP System. Table 7.1 illustrates the HIP'ing cost as a function of equipment size.

**Table 7.1** TOLL HIP'ing costs as a function of equipment size for several existing installations at 1200°C

| Vessel dimensions | A | B | C | D | E |
|---|---|---|---|---|---|
| Diameter (cm) | 15.2 | 25.4 | 50.8 | 86.6 | 102.0 |
| Volume ($m^3$) | 0.0092 | 0.0386 | 0.308 | 0.639 | 2.08 |
| Cost estimates | | | | | |
| $ per cycle* | 800 | 1,700 | 3,500 | 3,500 | 7,500 |
| $ per $cm^3$ | 0.087 | 0.044 | 0.0114 | 0.0055 | 0.0036 |
| $ per kg** | | | | | |
| 20% packing efficiency | 54.30 | 27.50 | 7.13 | 3.43 | 2.26 |
| 50% packing efficiency | 21.70 | 11.00 | 2.85 | 1.37 | 0.90 |
| 70% packing efficiency | 15.50 | 7.86 | 2.04 | 0.98 | 0.64 |

*Based on 710 cycles/month. Cycle costs obtained from toll HIP'ers.

**Based on a density of 8 g/$cm^3$.

### *7.2.4 HIP Applications*

HIP'ing P/M parts has the demonstrated potential to produce 100 percent dense high performance alloy parts on a consistent basis. Thus, the application of P/M are now possible where residual porosity can not be tolerated because of its adverse effect on key properties such as:

- Surface finish
- Corrosion resistance
- Fatigue resistance
- Impact strength
- Ultimate tensile strength
- Yield strength
- Elongation

HIP has many applications, but in the context of powder metallurgy, it has two applications, namely the densification of cemented carbides and consolidation of metal/ceramic powders.

### *7.2.5 Sinter HIP or Overpressure Sintering*

The widespread application of HIP is restricted by two factors:

- Lack of HIP equipment capable of necessary high temperature.
- The difficulty in containerizing the green powder compact.

It was felt that by introducing containerless HIP'ing a higher throughput of as much as 50–90 percent can be achieved as compared to containerized parts. Furthermore, it is difficult to always assure that containers are fully sealed with no pinholes. The major benefit in combining sintering with the introduction of gas at the end of the sinter cycle for HIP'ing. This eliminates one major piece of equipment, reduces materials handling, provides greater control of the process, and saves energy and labour costs. This process is particularly useful for cemented carbides, superalloy and ceramic products where the HIP'ing is used extensively. The sinter HIP eliminates the need for reheating the product to solidus temperature a second time, which risks abnormal grain growth. The HIP'ing pressure is rather low in the range 6–10 MPa as compared to the classical HIP'ing, since the material structures are soft in the sintered condition. Moreover, the formation of cobalt lakes in sintered cemented carbide is prevented. Figure 7.4 shows a typical cycle for cemented carbide.

## 7.3 Spark Sintering

Spark sintering combines electrical energy and mechanical pressure to convert metal powder into a solid part of desired configuration and density.[4] It is performed in air, vacuum or inert atmosphere using graphite or other specially developed materials for tooling. Powder is fed into the cavity of a punch and die assembly. The powders used are usually electrically conductive, however nonconductive mixtures also can be used. High density electrical energy – moderately high frequency AC and DC combined – is passed through the powder while compacting it at relatively low pressures. Using

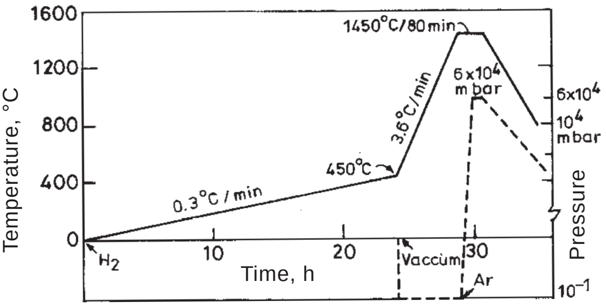


**Fig. 7.4** Typical hydrogen dewaxing and overpressure sintering cycle of WC–6Co cemented carbide.

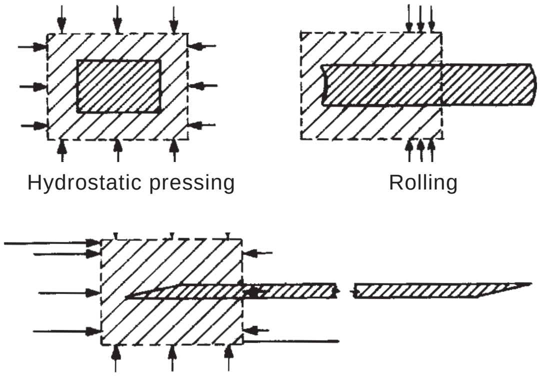

Hydrostatic pressing
Rolling
Extrusion

**Fig. 7.5** Forces and deformation of powders in hydrostatic pressing in rolling and in extrusion.[1]

both AC and DC energy simultaneously, accelerates and augments particle to particle bonding, which in turn promotes more uniform part density. At the end of the densification cycle, power is turned off, but pressure is maintained for some time while the part cools. The die stays relatively cold during this type of hot pressing. Time for the entire operation ranges for seconds to minutes depending on the material, part size, configuration, tooling and equipment capacity. This method was originally introduced by Lockheed Missiles & Space Co for the production of several beryllium components. This required considerably less material and less subsequent machining than if it were machined from hot pressed blocks.

## 7.4 Powder Extrusion

In extrusion, large hydrostatic compression forces occur and a unidirectional force component makes the compact flow through the die (Fig.7.5). Frictional forces produce a shear component which results in a characteristic shear pattern in the extruded metal. Figure 7.6 shows the three basic meth-

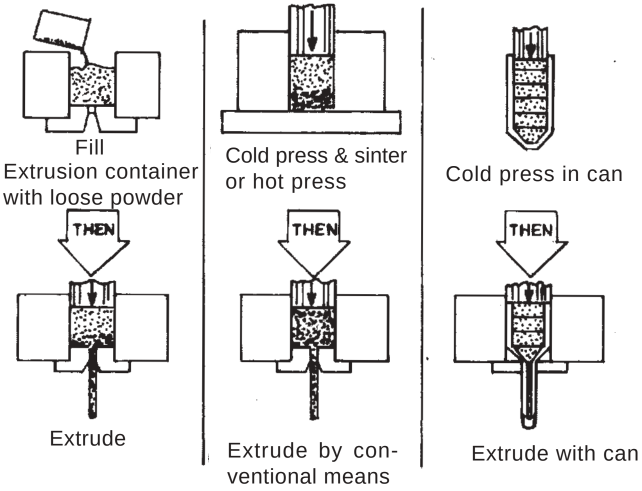


**Fig. 7.6** Three hot extrusion methods.[1]

ods of hot extrusion of metal powders. In the first method loose powder is placed into the heated extrusion container and extruded directly through the die. This method has been developed for the extrusion of certain magnesium alloys powders. In the second method, the powder is cold compacted and then hot pressed. The hot pressed compact is then extruded as per conventional method. Aluminium alloys powder billets are extruded by this method. In the third method, the metal powders are placed into a metallic capsule or 'can', heated and extruded with the can. A green metal powder compact may be canned or the powder may be cold pressed into metal can under moderate pressure. The can is out gassed by evacuation at room or elevated temperature and sealed off before can and powder are heated for extrusion. To prevent turbulent flow during extrusion, the end of the can is conical and fits into an extrusion die with a conical opening. To avoid folding, when the powder in the can is not packed very densely, a penetrator ram may be used as shown in Fig.7.7. The material of the can, in such cases should have:

1. The same stiffness at the extrusion temperature as the powder to be extruded.

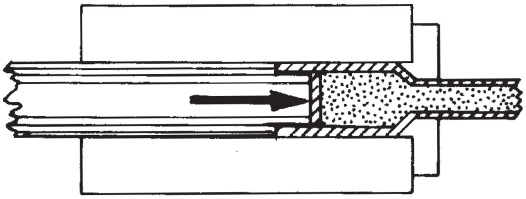


**Fig. 7.7** Penetrator technique in powder extrusion to avoid folding.

2. No reaction with the powder

3. Possibility to get removed by etching or mechanical stripping.

Copper and low carbon steel are most commonly used can material. Hot extrusion of powders encapsulated in cans was first developed for consolidating beryllium powder and powders of dispersions of fissile material in a matrix of zirconium and stainless steel. The method has been almost universally used for copper- and nickel-based dispersion-strengthened alloys. A hot extrusion process for producing seamless tubing from stainless steel powder was developed in Sweden.[6]

Negm and Davies [13] extensively studied the high speed hot extrusion of iron powder preforms using a petro-forge machine, having a velocity range, at impact, of 4–5 m/s. The slow speed forward and backward extrusions were also carried out on a 2000 kN eccentric press (velocity 0.2 – 0.25 m/s). The variables involved were initial density, sintering and extruding temperature, sintering time and area reduction ratio. The extrusion pressures were found to be higher at high speed than at slow speed. The difference in forward extrusion was approximately 7% and in backward extrusion approximately 25 %. The average final density in high speed was found more than that of slow speed for both forward and backward extrusion. The optimum sintering temperature/time for iron preform was 1100°C for 15 min. To avoid cracking in both forward and backward extrusion, it was noticed that there was a lower limit of the average final density of about 7.7 g/cm$^3$, below that limit, it would be difficult to extrude successfully. This final density was achieved by a suitable combination of initial density and reduction ratio. The portion extruded at the earlier stage had a comparatively low density, but other portions had a constant higher density. In high speed extrusion, the hardness distribution was more uniform and a somewhat greater general level of hardness was obtained when compared with slow speed extrusion.

## 7.5 Powder Forging

Powder forging can be broadly classified into two classes – (*i*) conventional powder forging and (*ii*) preform powder forging. The conventional forging as applied to original compacting of loose powder consists of 'canning' the powder in some type of metal container. Once the powder is within such an enclosure it can be evacuated and, eventually, the assembly is treated in a conventional forging press. After forging, the can material may be removed by chemical or mechanical means. The resulting compact can have a very high density and may require no sintering if the powder was heated prior to the forging step.

Powder preform forging is a combination of powder metallurgy and forging. Powder used for preform forging are essentially those used for conventional powder metallurgy practice. Powder preform forging processes have developed along two distinct lines;

(1) Compression of a preform very similar in cross section to the final

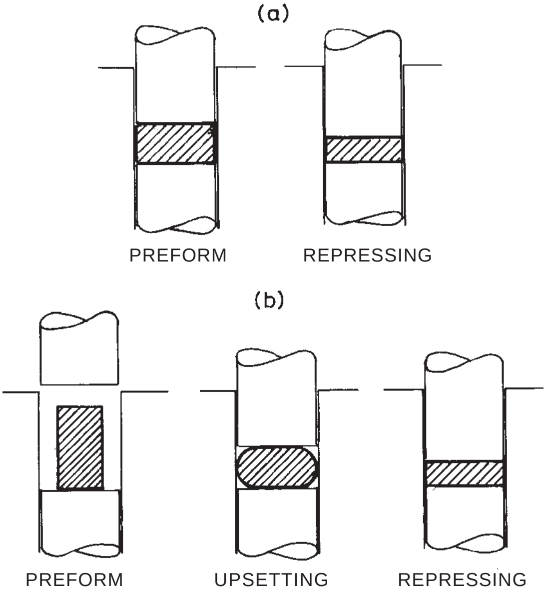


**Fig. 7.8** (a) Schematic diagram of hot repressing. (b) Forging in a confined die showing upsetting and repressing modes.

part (Fig.7.8a). This is known as hot repressing.

(2) Compression of a preform of relatively simple shape into a part having a much different shape (Fig.7.8b). This is similar to true forging.

The first involves densification with little or no lateral flow, while the second achieves densification and shape change simultaneously through a large degree of plastic deformation and lateral flow. In true forging, the associated lateral flow subjects the pores to a combination of normal pressure and shear (Fig.7.9). This shearing action aids the normal pressure in closing up pores and lower pressures are required for densification of the material. In addition, the shearing action increases the bond strength between opposite sides of collapsed pores, which enhances the soundness of the metallurgical structure. The lateral flow during forging involves a period of deformation in which the expanding vertical surfaces are free and tensile stresses can develop, leading to fracture. This is designated in Fig.7.9 as the upsetting stage. The likelihood of fracture increases as the amount of lateral flow before reaching the die side walls increases. In case of hot repressing fracture is prevented, since the preform is initially in contact with the die side walls and tensile stresses do not occur. Rational design of preforms involves specification of the shape and dimensions such that the deformation during forging is sufficient to achieve full density and a sound metallurgical structure, but less than the amount at which fracture occurs.

Forging of powder preforms have following advantages:[7]

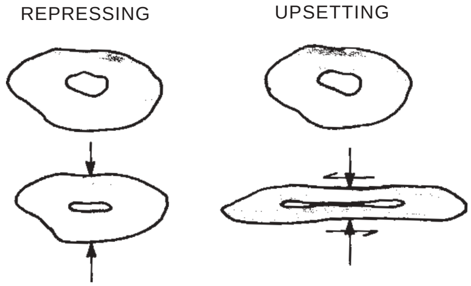


**Fig. 7.9** Pore closure by: (a) prepressing (b) upsetting (lateral flow).

– High production rates

– No waste of materials as usually associated with more conventional production methods

– Elimination of much or all finish machining

– Good surface finish

– Ability to form quite complex components in one finishing operation

– Randomly oriented fine grain structure

– Equiaxed orientation of physical properties

– Forging costs are lower than in conventional forging

– Lower forging load.

The powder forging process is suitable for the manufacture of wide range of parts and competes with sintering in the area of longer sintered parts and with forgings over the small to medium–large range. While comparing the route by which traditionally forged and powder preform forged components are made, it is clear that whilst the basic number of production stages are similar, the number of actual forging steps varies significantly. In conventional forging the heated bar or billet stock is subjected to a number of forging blows in a series of dies to develop the final shape with transfer from one die to the next. With preform forging, however, a fully formed component can be produced with one forging stroke only, in one set of closed dies with an attendant reduction in actual forging cost and a greater improvement in press utilization. In its relatively low density condition at forging temperature, the preform starts to plastically deform under relatively low forging loads. As the density approaches nearer to the 100% value so the required forging load increases. A great deal of the final forged shape is developed during the early stages of forming when the loads required are relatively low. By the end of the forging stroke when the load requirement is at its maximum, most shape detail has been achieved and the last stages are simply hot compacting involving relatively little plastic flow. In cases in which the preform has a form which corresponds closely to the finished part, hot working is essentially simple compacting involving very little lateral metal flow.

### 7.5.1. Preform Manufacturing and Forging

**Powder Blending**: The conventional use of powder blending is mixing the alloy ingredients and the lubricant. The alloy ingredients introduce chemical heterogeneity into the finished part because the powders can never be mixed ideally and the sintering is not sufficient to permit complete interdifusion of the different elements. The lubricant decreases die wear, makes ejection of the part easier and acts to distribute the pressure throughout the part while it is being pressed. After pressing of the part, the lubricant must be removed, which poses many problems. If the green parts are larger or dense, complete lubricant removal becomes extremely difficult and the entrapped lubricant either remains as an impurity in the part or erupts during sintering to cause defects in the parts.

**Preform Compacting**: The design of the powder preform depends very much on the process. The preform design, i.e. its size, shape, weight, density and design tolerances, limits the methods that can be used to manufacture it. Preform weight control and speed of die cavity filling are critical production factors. Coarse, dense, regular shaped powders would be easier to densify than fine, porous irregular powders and provided their lower green strength and sintering activity could be tolerated, they would be more desirable for both the preform compacting and preform forging operations. Preform density and density distribution becomes more important as the complexity of the part increases. On complex parts it is necessary to have the correct mass distribution in the preform to ensure proper metal flow during forming. Improper mass distribution could result in low density in some areas and overloading of tooling in other areas.

**Preform Sintering:** Preform sintering is carried out after preform compacting and before the forging operation. The sintered preforms are then normally cooled to room temperature and reheated to the forging temperature. In case of alloy steels, the prevention of oxidation is a serious matter. An alloying element in dilute solution is more difficult to oxidize than if it existed as the pure metal or as a rich master alloy. It would be, therefore, easier to prevent oxidation in the prealloyed powders rather than mixtures of elemental powders. All the details and precautions described in the chapter on sintering are valid for preform sintering as well.

**Preform Forging**: The deformability and the oxidation characteristics of the preform are important for forging operation. The deformability of a preform is a function of many variables, e.g. forging temperature, preform design and the composition and characteristics of the powder constituting the preform. In general, the highly alloyed preforms would be more difficult to deform. As for as oxidation control of the preform is concerned, carbon-containing preform coatings are very common. The lower the density of the preform, the more serious the oxidation problem becomes. Oxidation, in general, becomes worse with increasing time and temperature of exposure although the oxides become less stable and carbon more protective towards the metal as the temperature is raised.

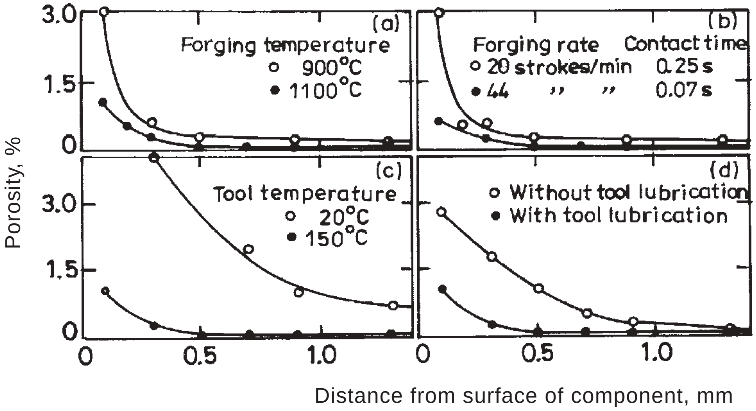


**Fig.7.10** Influence of processing parameters on components surface porosity.[16]

Figure 7.10 illustrates the influence of processing parameters like forging temperature, and speed, tool temperature and tool lubrication on the surface porosity of forged structural parts.[16] The surface porosity originates as a result of the rapid cooling of the surface zones of the preform when in contact with the forging tool and the resulting reduced forgeability in those zones. Only the optimization and strict control of all these sintering parameters yield flawless powder forgings.

Figure 7.11 shows the effect of forging in steel temperature on total carbon, dissolved carbon and total oxygen content.[8] It is evident that a temperature above 1120°C is required to dissolve admixed graphite into solution as well as decrease the oxygen content. However, it is worth mentioning that this figure applies only to powder forging using the single heat method.

As already been indicated earlier forging temperature has an adverse effect on surface decarburization and surface oxidation.

Once the part is hot forged, the ejection of part from the dies is important. The force required to eject the part from the forge die is dependent

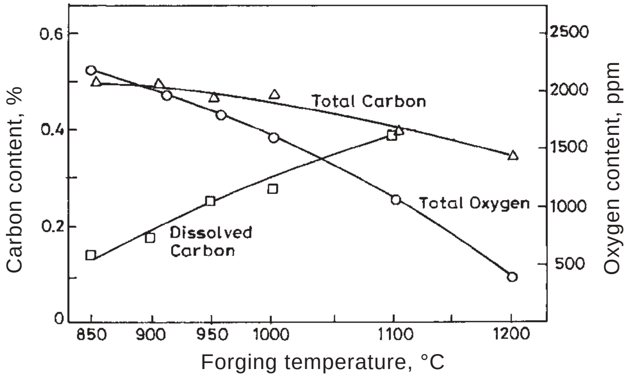
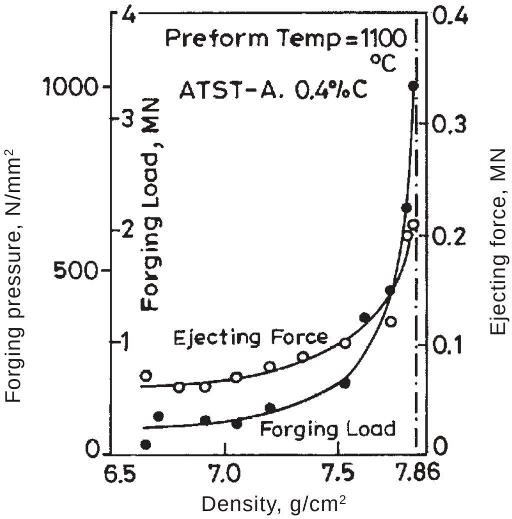


**Fig. 7.11** Effect of forging temperature on oxygen and carbon content in steel.[15]



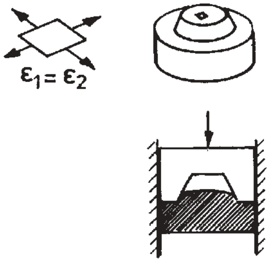


**Fig. 7.12** Forging pressure and ejecting force as a function of residual porosity.[15]
**Fig. 7.13** (right) Schematic of hub extrusion indicating tensile strain at top free surface.

on both the preform temperature and the density of the part. In general, the ejection force decreases with elevated temperature. Figure 7.12 shows the dramatic increase in forging tonnage applied and die ejection force required as full density is achieved. Forging die life can be prolonged by keeping both forging pressure and ejection force as low as possible. Since the latter two variables increase exponentially as zero porosity is reached, it is worthwhile to consider whether a totally pore free material is essential for the application in question.

Hot forging of preforms often involves not only upsetting, but also extrusion. A typical example is that of hub-extrusion (Fig.7.13). The top surface of the hub is a free surface which under goes bulging and tensile strains. Free surface fracture occurs on this surface when the strains reach the critical amount for fracture. These strains may be altered by changing the draft angle of the hub or by using a preform that partially fills the hub section of the die. Not only free surface fractures, but also contact surface fracture may occur during extrusion forging of a hub on a cylinder. Suh and Kuhn[11] analyzed in depth the conditions under which such cracks will be found and how they may be eliminated by design changes. A typical example of preform design could be understood from the case study for differential pinion gear (Fig.7.14), in which the preform is flat topped with a bevelled bottom surface. When this preform is forged, cracks are developed in the partially formed gear during tooth formation. These cracks are closed up in the final stages of the forging stroke as the material is pressed against the die surface. However, oxidation of the crack surface and trapping of lubricant in the cracks may lead to structural weakness of the tooth surfaces. Kuhn[12] proposed a modification of the preform contour involving

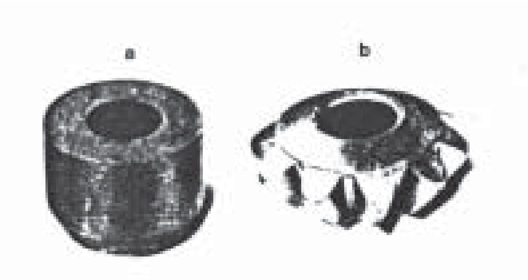


**Fig. 7.14** Differential pinion gear, preform and forging (a) sintered preform, (b) finished part.

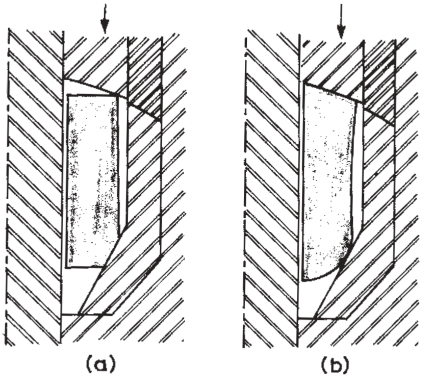


**Fig. 7.15** Longitudinal section view of preforms and tooling for forging pinion gear: (a) original preform which leads to crack formation at teeth (Fig.7.14); (b) modified preform which lead to defect free gears.

a slightly tapered top surface and a rounded instead of a bevelled bottom surface (Fig.7.15).

### *7.5.2. Heat Treatment and Machining*

In general, standard heat treatment is used for the powder forged parts. The microstructures and properties of powder forged parts, no doubt , differ slightly from parts produced from conventional wrought steels. Most powder forged parts require only minimal machining or grinding. In cutting operations the powder forged parts in general exhibit more consistent behaviour than ingot metallurgy parts, because the finely dispersed inclusions in the former yield short chips rather than long continuous chips.

### *7.5.3 Mechanical Properties of Preform Forged Alloys*

The mechanical properties of the forged parts are influenced by forging parameters such as forging temperature, forging pressure, preform chilling by tooling, speed of the press, amount of lateral flow during forging and chemical composition. Full density is desired to achieve the maximum material prop-

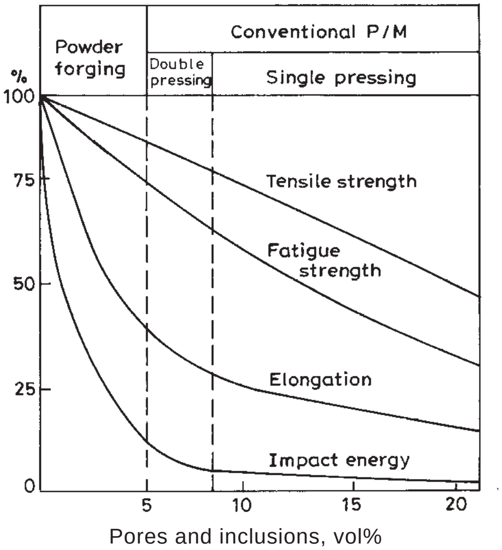


**Fig. 7.16** Mechanical properties in % of values at full density.[15]

erties. Figure 7.16 illustrates the effect of density on mechanical properties. Any residual porosity results in marked decrease in tensile and fatigue properties as well as impact strength. In general, higher forming temperature and less preform chilling enhances the densification of the forged part and consequently increases mechanical properties. Mechanical properties in general and dynamic properties in particular are strongly influenced by the oxygen level of the forged part. The lower oxygen level of the forged part, promotes better dynamic mechanical properties. This is due to the fact that better metallurgical bonding between particles results during forging. In contrast to the tensile properties, the dynamic properties are extremely sensitive to material impurities like inclusions and voids. Generally, the powder forged dynamic properties lie between the longitudinal and transverse values of wrought steels of equivalent hardenability (Fig.7.17). There are also indications that these properties are sensitive to the degree of deformation given to the preform to reach its final density. The amount of lateral flow is particularly important for dynamic properties such as fatigue and impact strength. Such properties get improved with increasing lateral flow because of the extensive particle shearing caused by lateral flow.

Tables 7.2 and 7.3 give some typical steel compositions and their mechanical properties after powder forging.

Powder forgings have yield strengths at least equal to wrought steels of the same chemical composition. Cases have been made that the finer grain size of powder forging increases these properties. Studies have shown that increasing porosity from 0% to 5% decreases tensile strength by 35%. Ductility shows greater sensitivity yet, to structural defects such as porosity, notches or inclusions.

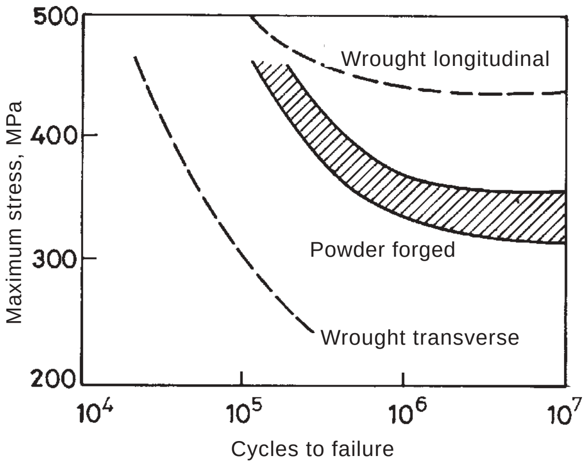


**Fig. 7.17** Fatigue behaviour of powder forged steel in comparison with wrought material.[16]

**Table 7.2** Chemical composition (mass %) of common powder forged steels

| Material | C* | Mn | Cr | Ni | Mo | S | Cu |
|---|---|---|---|---|---|---|---|
| Sint F 30 | 0.2-0.6 | 0.3-0.4 | 0.15-0.25 | 0.25-0.40 | 0.3-0.4 | <0.025 | - |
| Sint F 31 | 0.2-0.6 | 0.2-0.3 | <0.1 | 1.8-2.0 | 0.5-0.6 | <0.02 | - |
| Toyota/Ford | 0.4-0.8 | - | - | - | - |  | 2-3 |

*The carbon content is adjusted according to heat treatment required e.g. to 0.2 for case hardening heat treatment, to 0.6 for quenching and tempering

**Table 7.3** Static and dynamic mechanical properties of common powder forged steels (in the forging state)

| Material | Sint F30 | Sint F30* | Sint F31 | Toyota/Ford |
|---|---|---|---|---|
| Content S (mass -%) | <0.025 | 0.2 | <0.02 | <0.02 |
| Content C (mass - %) | 0.6 | 0.6 | 0.2 | 0.67 |
| Tensile Strength (N/mm$^2$) | 1010 | 910 | 760 | 985 |
| Yield Strength (N/mm$^2$) | 675 | 620 | 530 | 875 |
| Elongation (%) | 11 | 9 | 18 | 10 |
| Fatigue Strength (N/mm$^2$) | 340 | 335 | 290 | 460 |

*Increased sulphur content

Table 7.4 gives a comparison of powder forging with other competing forming processes.[9] Since powder forging is a relatively high cost process, the considerations affecting its choice will rest to a large extent with the cost of subsequent operations.

**Table 7.4** Comparison of powder preform forging with competing technologies

| Process | Powder preform forging | Sintering | Die forging | Cold forging | Precision casting |
|---|---|---|---|---|---|
| Part weight, kg | 0.1-5 | 0.01-1 | 0.05-1000 | 0.01-35 | 0.1-10 |
| Height/dia | ≤ 1 | ≤ 1 | not limited | not limited | not limited |
| Shape | No large variations in cross-section, openings limited | No large variations in cross-section, openings limited | Any, openings limited | Mostly of rotational symmetry | Any, any openings possible |
| Material utilization, % | 100 | 100 | 50-70 | 95-100 | 70-90 |
| Tolerances | IT 8-10 | IT 6-8 | IT 13-15 | IT 7-9 | IT 8-10 |
| Surface roughness, μm | 5-30 | 1-30 | 30-100 | 1-10 | 10-30 |
| Production begins to become economical at number of parts (for 0.5 kg/part) | 20000 | 5000 | 1000 | 5000 | 2000 |
| Main goal | High strength, no machining | Moderate strength, porous materials, no machining | High strength, machining to final shape | High strength, minimal machining | Intermediate strength, minimal machining |
| Cost of one production unit (sintering = 100%) | 250 | 100 | 150 | 150 | 100 |
| Possibilities for automation | Good | Good | Limited | Very good | Limited |

As per price applicable in 1977.

## 7.6 Spray Deposition/Forming

In all spray deposition/forming processes from the melt the first objective is to atomize the liquid metal into small liquid particles generally having a mean diameter between 100 and 200 μm. The liquid particles are propelled rapidly towards the substrate surface either by a high speed stream of gas or by centrifugal force. As the particles move towards the substrate they become spherical in form and also cool in flight by radiation and convection. But it is important that they reach the substrate whilst still fully liquid or at least mostly liquid. The liquid particles flatten on the substrate to form adherent splats which deposit on one another, thus building up a substantial layer. The splats cool extremely rapidly at speeds up to $10^6$ °C $s^{-1}$, because of the thinness of the splat and the excellent contact with the cool substrate. Typical splats are 10–20 μm thick and 500–1000 μm in length.

Surface preparation of the substrate is an important feature of spray forming processes. A very rough surface causes mechanical interlocking making the subsequent removal difficult. On the other hand, deposition on very smooth surface leads to serious difficulties giving rise to porous non adherent coating. The success of spray forming lies in the fact that each deposited particles should splat at its point of impact and stay exactly in its original position.

The integrity of spray deposits is greatly influenced by the entrained or adsorbed oxygen in the form of air or oxygen containing compounds. Although all commercially used metals can form undesirable oxides, it is particularly difficult when the molten metal contains aluminium, chromium or titanium. The metal oxide so formed even very small in quantity, is significant in preventing the effective welding of one splat to the next during deposition.

The spray deposited mass is subjected to subsequent treatment such as rolling, pressing, forging or machining. Hot rolling or forging has the advantage of closing any residual porosity and modifying the internal structure as well as giving a more acceptable external surface. Hot rolling has the additional advantage that it can be operated continuously or semi continuously. A wide range of metals and alloys has been made by spray rolling including aluminium and its alloys, copper and copper base alloys, some super plastic zinc base alloys and various steels. The product after hot rolling is of fine grain size and generally shows a much finer structure in terms of unabsorbed or insoluble constituents. The mechanical properties of the products are at least equal and often superior to conventional materials.

Osprey Ltd (United Kingdom) has done pioneering work on spray forging of metal powders.[14] The process is first to make a preform by atomising molten metal with an inert gas and spray depositing into an open mould. The deposit fills the mould replicating exactly the mould surface. The operation is continued until the mould is sufficiently filled when the atomization is either stopped or is transferred to another mould. The mould cavity is shaped in such a way that the preform can readily be separated from it. After separation, the preform is reheated to the forging temperature, transferred to a press and forged hot usually in a single operation. Figure 7.18 illustrates schematically the process. The advantages of spray forging compared with conventional processing are:

– operating directly from the melt

– a single forging operation from a sprayed preform.

– zero segregation and very fine microstructure leading to good ductility and toughness.

The spray process is used to produce a wide variety of preform shapes and sizes. Typical preform shapes are tubes, rings, cylinders, disks or simple billet. Size is dictated by economics, with the melt facility, atomizer and

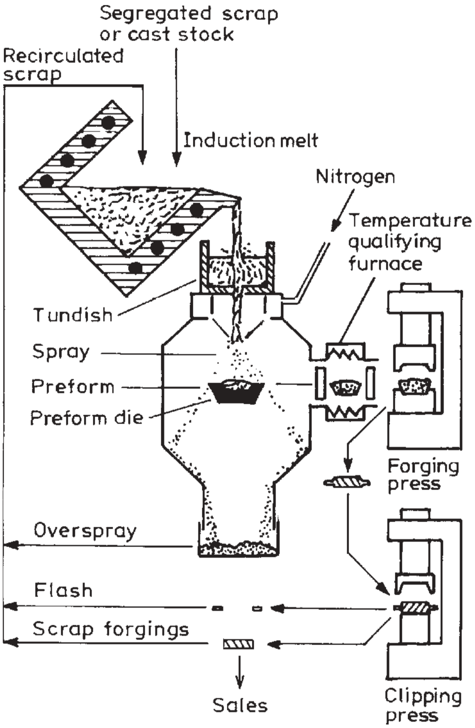


**Fig. 7.18** Osprey process for production of parts from spray formed preform.

inert chamber size for a particular product line. The largest preform sized produced weighed 540 kg. Typical deposition rates range from 10 to 50 kg/min.

## References

1. F.V. Lenel, Powder Metallurgy: Principles Properties and Applications, Metal Powder Industries Federation, Princeton, 1980, p. 156.
2. Metals Handbook, Vol.7, Ninth Ed. American Society for Metals International, Ohio, 1984, p. 401.
3. W.D. Jones, Fundamental Principles of Powder Metallurgy, Edward Arnold, London, 1960.
4. R.W. Boesel, N.I. Jacobson, I.S. Yoshioka, Materials Engineering, October 1969.
5. A.L. Stuits and J.G.M. De Lau, In Advances in Ceramic Processing', Ed. P. Vincenzini, National Research Council Research Lab. for Ceramics Technology, Faenza 1978, p. 166.
6. C. Aslund, Preprints 5th European Symposium on Powder Metallurgy, Stockholm, Vol.I, Jernkontoret, Stockholm, 1978, 278.
7. H.H. Hausner and M.K.Mal, Handbook of Powder Metallurgy, 2nd edition, Chemical Publishing Co. Inc, New York, 1984.
8. G. Bockstiegel and M. Stromgren, Hoganas Automatic P/M forging systems, Concept and Application, SAE Tech Paper, Feb. 1979, p.6.
9. L. Larason,M. Stromgren and K. Svartstrom, Proceedings of PM 84, Toronto, MPIF, Princeton, 1984.
10. F. Hanejko, In Progress in P/M' **33**, 1977, p. 16–17.
11. S.K. Suh and H.A. Kuhn, In ' Modern Developments in Powder Metallurgy' Vol.5,Ed.

H.H. Hausner and P.W. Taubenblat, MPIF, Princeton, 1977, p. 407.

12. H.A. Kuhn, In ‘Powder Metallurgy Processing’, Ed. H.A. Kuhn and A. Lawley, Academic Press, N.Y., 1978, p.99.
13. M. Negm and R. Davies, In Proceedings of the 15th International Machine Tool Design and Research Conference’, Ed. S.A. Tobias and F. Koenigsberger, MacMillan Press Ltd., London, 1975, p. 637.
14. A.G.Leatham, A.J.W. Ogilvy, P.F. Chesney and O.H. Metalmann, In ‘Modern Developments in Powder Metallurgy’, Compiled by P.U. Gummeson and D.A. Gustafson, Metal Powder Industries Federation, Princeton, N.J. **19**, 1988, p. 475.
15. T.G.Grady, *J. Materials Shaping Technology*, 1989, 7, 105–111.
16. W.J. Huppmann, *Powder Metallurgy International*, **24**, No.3, 1992, 186.

# 8 SECONDARY TREATMENTS

In practice, P/M components may require closer tolerances, increased mechanical properties and features not possible by simply sintering. Most of the operations that accomplish these processes are performed on P/M components in the same manner as on cast or wrought components. However, porosity frequently imposes limitations on some secondary operations.

In this chapter various types of secondary post consolidation treatments are described. Even though such treatments increase the cost, in a very large number of cases the process can prove economical in comparison to other competing technologies.

## 8.1 Machining

Sintered parts do have some porosity and it is, therefore, necessary to differentiate their machining behaviour from those of fully dense wrought products. The major differences are, as follows:

(*i*) when a porous metal is machined, the depth of work hardening is more important than for the wrought metal, as in case of former, pores create stress concentration.

(*ii*) The temperature at the tool end causes oxidation of the pore surface.

(*iii*) The surface porosity enhances tool vibration, which is submitted to fatigue.

Pleney and Eudier[1] have elegantly summarized various stages of tool wear. The stages are:

- Adhesion wear of tool
- Influence of the oxidation of parts
- Tool oxidation
- Tool wear by fatigue.

Although P/M parts are often specified because machining operations can be eliminated, in some cases it is more economical to leave certain part details desired for machining, rather than to incorporate them in the pressed configuration. Parts made by P/M techniques generally require machining methods that differ from those used for wrought or cast parts of similar composition because of the inherent porosity of P/M parts. The following are some of the causes of machining problems in P/M parts:

(*i*) Pores may be closed by smearing of the metal surface.

(*ii*) Cutting fluids may cause difficulties by entering the parts.

(*iii*) Parts may become charged with abrasives when ground; honed or lapped.

Variations in machinability may be caused by differences in sintering conditions and by different alloy compositions. In steels the degree of surface carburization or decarburization would have significant effect on machinability. Machinability will also be affected if the parts are either over or under sintered. As parts increase in density, they begin to approach the same machinability as wrought and cast parts. This is due to the fact that porosity simulates a series of interrupted cuts. To partially eliminate or minimize this, many ferrous parts are copper infiltrated to fill the pores or impregnated with a polyester resin or wax. Pearson[2] described various, additives like sulphur, copper, lead, bronze, phosphorus and molydisulphide to iron powder to obtain better machinability. Any addition to an iron mix which will have a hardening effect on the matrix will improve machinability. Copper improves the surface finish and also gives longer tool life. Sulphur in the form of iron sulphide improves tool life. Manganese in the form of manganese sulphide acts as a chip breaker and gives a smooth surface finish, but at the same time tends to decrease the tool life. With quantities between 0.3 and 0.5 % MnS, the wear is reduced by a factor between 5 and 20 and hence the solid lubricant addition can be decreased by 0.2–0.3 %. Phosphorus has the general effect of decreasing tool life, although smoother surface finishes can be obtained at faster machining rates.

The machining of sintered stainless steel parts is more difficult than machining wrought stainless steel parts. Poor machinability of stainless steel can be attributed to carbide precipitation resulting from improper sintering.

Aluminium sintered parts of more than 95 % theoretical density do not pose much machining problem. However improper lubricant removal before sintering or excessive aluminium oxide in the powder may deteriorate machinability.

In case of sintered bronze, widely used as porous bearing, it is essential to maintain good surface finish without closing the surface porosity. Care must be made to minimize the number of machining operations. Sharpest possible cutting tools must be used and it must be seen that the tool have good surface finish free from the ‘saw tooth’ effect. Light cuts, no greater than 0.38 mm, may be used. It is difficult to mill, drill or thread sintered bronze and maintain surface porosity. Grinding is definitely not recommended because of the extreme tendency to close the surface pores.

## Machining Practice

**Turning and Boring**: Carbide tools with sharp nose point have been found to be best for such operations. Table 8.1 gives some typical data for turning of sintered steels.[8]

**Drilling**: Carbide or high speed steel drills with a low right hand helix angle prevent the drill from digging in the cutting edges should also be dubbed to reduce the axial rake.

**Table 8.1** Machining data for the turning of sintered steels

| Material | Carbide grade | Cutting speed, m/min | Feed rate, mm | | Depth of cut, mm | | Angle of attack, *l* | | Rake angle |
|---|---|---|---|---|---|---|---|---|---|
| | | | coarse mach. | fine mach. | coarse mach. | fine mach. | coarse mach. | fine mach. | |
| All sintered materials | K01 | min. | max. | max. | max. | max. | 6–10 | 6–20 | 5–10 |
| | K10 | 150 | 0.3 | 0.1 | 3 | 0.3 | | | |
| | P10 | | | | | | | | |

*l* – for soft materials the higher angle of attack within the limit is reccomended.

**Tapping**: Spiral pointed taps are most desirable because they throw the chips ahead and prevent them from driving into the pores.

**Milling**: Milling is generally difficult because of the tendency of the material to smear. To minimize the smearing, it is recommended that dead sharp helical tool cutters with an axial rake be used so that the chips are sheared on an angle.

**Shaping:** Shaping is very similar to turning or boring in that a single point tool is employed.

**Reaming:** It is satisfactory for structural parts. However, it is not recommended if porosity is to be maintained because of the tendency to smear the bearing surface.

**Burnishing**: Ball sizing or burnishing of holes maintains open pores, providing that proper sintered dimensions are held.

**Broaching**: Broaching is not recommended if porosity is to be maintained. Standard draw broaching is recommended to obtain best tolerances and finish.

**Grinding, Honing and Lapping**: These operations are usually a finishing operation for heat treated materials; and only a small degree of pore closure occurs.

In case of doubts, the standard machining charts for cast or wrought parts of the same composition be referred and the recommended speed be increased by 10%.

Another solution to easy machining is to machine the parts after a presintering operation at a low temperature (850–950°C for steels). The parts are than sintered and eventually sized.

## 8.2 Impregnation

Controlled porosity permits powder metallurgical parts to be impregnated with oils or resins. In the former the lubricant oil is filled in the interconnected pores, which imparts lubricating function to bearings and mechanical parts subject to wear such as cams, gears and connecting rods. The choice of lubricant is a factor controlling the functionality of the system. Parts to be impregnated may be simply submerged in an oil bath for several

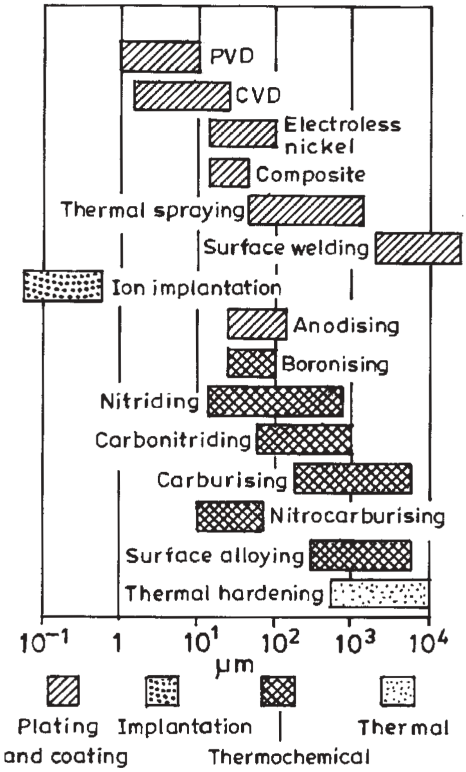


**Fig. 8.1** Typical thickness of surface engineered layers.[14]

hours. Reasonably good impregnation can be obtained if the oil temperature is maintained at about 80°C. The best results are obtained with vacuum impregnation. In this process, the parts to be impregnated with oil are placed in a basket in a vacuum chamber. After the air in the chamber and the parts have been evacuated, the chamber is flooded with oil. Next, the chamber is returned to atmospheric pressure, the oil drained from the chamber and the surfaces of the parts. Gas bubbles formation may pose a serious problem in the complete pore filling. The formation of such gas bubbles can be due to:

– dissolved gases in the oil
– gases formed by chemical reaction
– dissolved gases in the sintered material.

In case of resin impregnation, most of the interconnected pores are filled with resins, usually polyesters of the thermosetting type. This process greatly improves the machinability of P/M parts by filling the pores and increasing the density. One drawback is that machined plastic impregnated parts cannot be heat treated. The process takes place in suitable vacuum chamber. The greatest potential for impregnated P/M parts is for pressure tight components such as valves, pumps, meters, compressors, brake pistons and hydraulic systems.[10]

The problem posed by the presence of pores in parts to be plated are eliminated by resin impregnation. Some P/M parts which are subjected to such treatments include gun components, pole pieces, decorative automotive parts and outboard motor parts.[10] Filling the parts with hardened resin prevents entrapment of other fluids which would later leach out and ruin surface finishes. Related benefits include improved structural strength, and internal corrosion is virtually eliminated.

## 8.3 Surface Engineering

The first step in selecting a surface modification treatment for a P/M part irrespective of its density is to determine the surface and substrate engineering property requirements, such as:

- abrasion wear resistance under conditions of low or high compression loading
- resistance to scuffing and seizure
- bending or torsional fatigue strength
- rolling contact fatigue
- resistance to case cracking (surface collapse)
- resistance to corrosion.

The thickness of the engineered surface can vary from several millimetres for weld overlays to a few micrometers of physical or chemical vapour deposited coatings, while the depth of surface modification induced by ion implantation is $< 0.1$ µm (Fig.8.1).

Table 8.2 summarises some of the typical surface treatment methods applied

**Table 8.2** Typical PM components surface engineered to improve specific properties

| Component | Material | Key property | Surface treatment |
|---|---|---|---|
| Injection moulded computer parts | 2% Ni/Fe | High load carrying capacity<br>High cycle fatigue | Carburizing |
| Cold forming tool | ASP23 | Abrasive wear resistance | TiN–TiC CVD coating |
| Heavy duty transmission components | Cr/Mn steel | Rolling contact fatigue | Vacuum carburized |
| Shock absorbers | Sintered Fe | Friction | Steam treatment |
| Gearbox synchromesh ring | Sintered Fe | Localized friction | Induction hardening |
| Precision gears | Sintered low alloy iron | Good tribological properties fatigue strength | Plasma nitriding |
| Automotive lock assembly fasteners | | 400–800 h<br>5 % NaCl salt spray corrosion resistance | Zn coatings |
| Bevel gears | Powder forged alloy steels | Increased fatigue life | Shot peening |

on a wide range of P/M parts either fully dense or porous.

In the following sections some major surface modification methods have been highlighted. Thermochemical methods have been separately described in the section ‘Heat Treatment’.

### *8.3.1 Steam Treatment*

It is commonly used to improve the wear properties of ferrous P/M components and additionally provides improved corrosion resistance. During the process, all exposed surfaces, interior and exterior, are coated with a hard black magnetic iron oxide $Fe_3O_4$. The parts are first of all made free from oil or grease and subsequently placed in a forced convection furnace. Parts are first heated to 370°C to drive off moisture. Steam is then introduced into the furnace to purge the air from the furnace. The temperature is then raised to 510–540°C, when iron combines with the oxygen in the steam to form magnetite. The hydrogen from water is given off to the furnace atmosphere. Care should be taken that steam does not come in contact with the parts before the temperature is reached to 100°C. Otherwise the parts get rusted. After the steam treatment the parts are immersed in oil to help both corrosion and wear resistance. The thickness of oxide layer is limited and does not exceed 10 μm.

Steam treatment increases resistance to compression stresses and considerable increase in hardness. Very limited dimensional changes, compared to traditional hardening or case hardening heat treatments, and much reduced warpage because of the low temperature of the treatment result. However the only negative effect is on toughness, which gets lowered, particularly in parts with low relative density.

For iron copper and iron–copper–carbon the steam treatment is always combined with some age-hardening.

Figure 8.2 illustrates the variation in weight increase with respect to steam treatment period. At the beginning the slope is high, because the oxide formation happens on extended surfaces. When the smallest pore sections start to close, the slope becomes that typical of oxidation of non porous materials. The rate of layer growth decreases with time, as a consequence of a continuous increase offered by the formed oxide layer to the migration of iron and oxygen atoms.

### *8.3.2 Coating*

Coatings are useful because they can impart surface properties which cannot be produced in the body of a structure. Because of inter connected porosity in sintered parts, surfaces are exposed to environment. Therefore, sintered products are more susceptible to corrosion damage than are their cast or machined counterparts. One of the common method is to plate a sacrificial metal, e.g. zinc, to a part which had been first sealed with a resin or other filler. Serma Tel Inc.[13] of USA developed an aluminium filled ceramic coating which eliminates the need for impregnation, and offers bet-

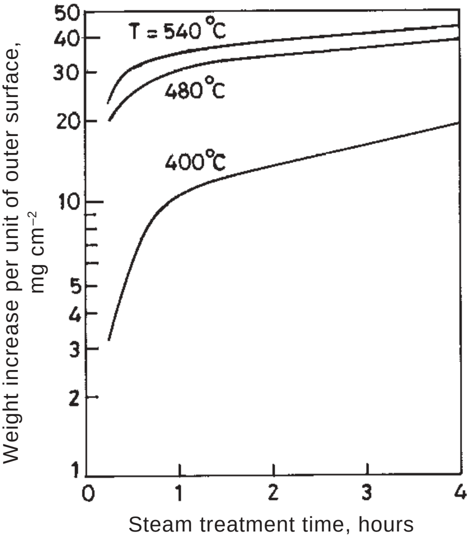


**Fig. 8.2** Effect of steam treatment time on the weight gain of a ferrous part at different temperatures.

ter corrosion resistance than zinc over a wider range of operating environment. The coating material is a slurry comprising aluminium powder in an acidic water based binder. The viscosity of the liquid is low so that the coating may be sprayed using conventional equipment. Small P/M parts is generally coated using the 'dip/spin' process. In this process, batches of parts are immersed in a coating, lifted from the liquid and spun at high speed (700–1500 rpm) so that any excess liquid is thrown from the part by centrifugal force.

Powder metallurgy components can be electroplated with the same metals as cast and wrought components. For this, the P/M component should have porosity sealed to avoid entrapment of plating solutions in the pores. Copper, nickel, chromium, zinc and cadmium plating are commonly used. Electroless nickel plating can also be used. Acid copper plating generally gives the best result on P/M components because of its excellent throwing power. Nickel, applied either alone or over a copper base, is used to increase wear resistance and to provide a bright corrosion resistant surface. Chromium plating is done for either decorative or wear resistant applications. Cadmium plates faster and has greater throwing power than zinc. To plate a part having more than 10% porosity, it is important to first impregnate the pores with a resin or close them by peening the surface to exclude the plating salts from the pores of the part. Full details of various electroplating practices are given elsewhere.[7]

The organic metallic zinc coatings, commercially available in the UK under the trade names of Deltatone and Dacromet, involve the application of a coating of bichromated zinc flakes. The components are dipped in a mixture of the zinc flakes with an epoxy resin and subsequently dried at

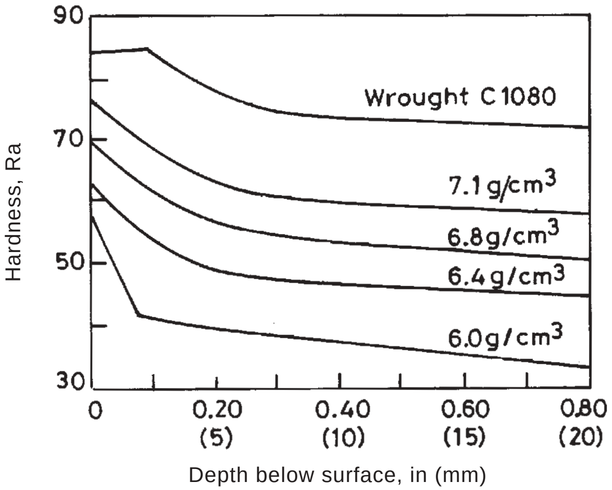


**Fig. 8.3** Effect of density on the hardenability of SAE 1080 steel.[3]

140°C. Such coatings can resist corrosion for up to 800 hours in a salt spray environment. The coatings also have the advantage – this being an electroless process – that it is impossible to incur hydrogen embrittlement effects of the substrate material.

## 8.4 Heat Treatment

Heat treatment of P/M parts is an important secondary operation. With emergence of high compressibility powders, the role of heat treatment in enhancing properties of P/M alloys has been still better appreciated. As density approaches theoretical as in P/M forging, compression residual stress patterns similar to those in wrought steels are created. This improves properties like fatigue strength, impact strength and hardenability.

### *8.4.1 Hardenability*

The response of a metal to heat treatment depends on its thermal conductivity which in turn is dependent upon surface area. In wrought alloys because of highest weight to volume ratio, heating and cooling rates are fast. In low density P/M alloys, the slow heat removal inhibits the hardenability and slack quenching or shallow hardening results. Figure 8.3 shows the hardenability response of SAE 1080 steel. This illustrates the poor thermal conductivity of low density parts. As quenched surface hardness decreases with density, and depth of hardening drops off.

Various methods of heating may be used to austenitize sintered parts, including induction heating, the only limitation being in the use of salt baths. Quenching is usually done in oil. Hardening is generally followed by tempering at such a temperature as to obtain the correct balance between hardness, strength and toughness. The normal tempering range is 150–650°C depending

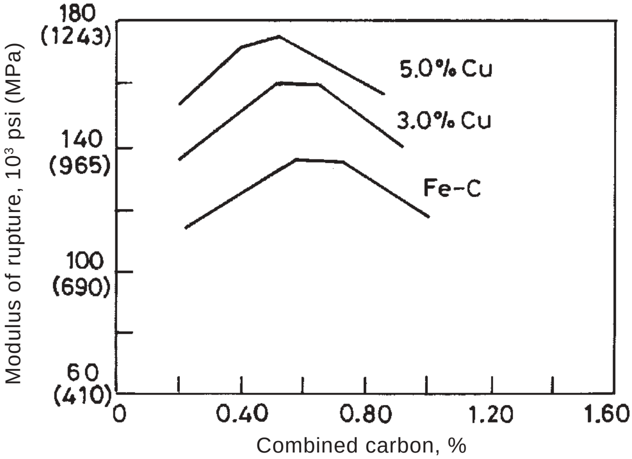


**Fig. 8.4** Effect of carbon and copper additions on heat treated strength of sintered steel.[3]

on the properties desired. The disadvantage of oil for quenching, is that it is less severe than brine or water, which means that one must quench from a higher temperature to get equivalent hardening. However in a way, it is advantageous, as it reduces the amount of distortion and possibility of cracking.

In sintered steels the most common alloying elements are carbon and nickel. Addition of copper increases both hardness and tensile strength in the sintered condition. The effect of copper addition in relation to combined carbon content is shown in Fig.8.4. Increasing nickel content significantly increases heat treated tensile strength. However, this benefit begins to taper off when the addition exceeds 2%.[3]

The heating atmosphere is significant in controlling the end properties of P/M steels. Most heat treating is done in an endothermic atmosphere which contains approximately 20 CO, 35 $H_2$, 0.3 $CH_4$ and balance $N_2$. Usually other gases are added to adjust the carbon potential to meet requirements for a part. Nitrogen-based atmospheres are also getting popular, which gives better part uniformity.[4]

A distinctive feature in sintered steel is that by varying the cooling rate of the steel in the cooling zone of the mesh-belt continuous furnace, a wide range of microstructure could be achieved. Lindskog[5] discussed how the mechanical properties of steel could be enhanced from the present 0.05 to 2°C/s range to perhaps 5°C/s. This would of course involve new furnace designs. The effect would be highly dependent on the shape and size of the P/M parts.

The specific surface of the iron powder used for developing sintered steels is also important, as it can be seen that both the strength and the martensite contents are linear functions of the specific surface[6] (Fig.8.5). This infers that surface diffusion plays a prominent role in distributing the alloying elements in steel, particularly nickel.

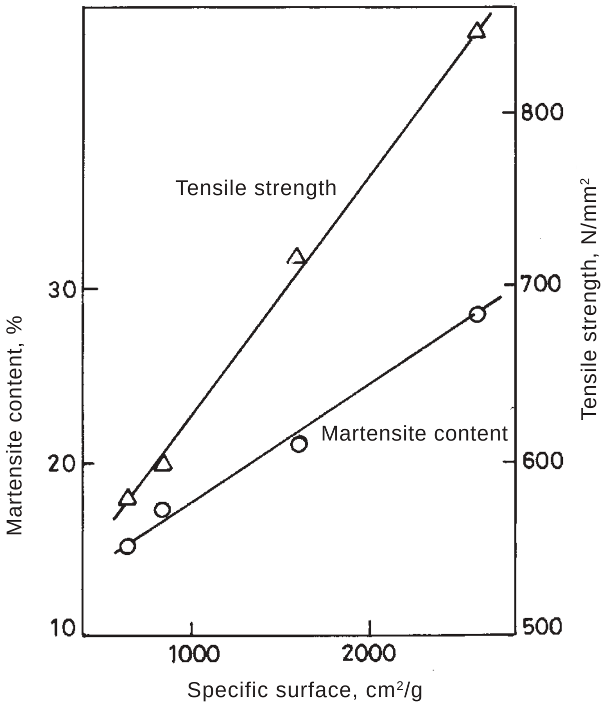


**Fig. 8.5** Tensile strength and martensite/bainite content versus the specific surface of the base iron powder for material with composition 1.75% Ni, 1.5% Cu, 0.5% Mo, 0.5% C at a density of ~ 7.0 g/cm$^3$. Sintered for 1 hour at 1120°C.[6]

### 8.4.2 Case Hardening

Under similar carburizing conditions, the diffusion depths in steels are much deeper when the porosity level is higher and are in any case far above those found in wrought steels. Carbon and nitrogen are the most common case hardening elements. For P/M steels, classical gas carburizing atmospheres or carbonitriding are adopted. Figure 8.6 illustrates a typical case depth variation in C1018 steel. It is obvious that lower is the sintered density, the greater the case depth. This is due to the greater amount of porosity, which allows for greater gas penetration. It can be concluded that it is difficult to achieve maximum physical properties in low density parts. With the deep carbon penetration in the case of low densities, the core properties would be approximately the same as the case properties.

The case hardening operation is invariably followed by oil quenching and tempering. This is done in order to reduce internal stresses and improve the toughness.

The carbonitriding process is a modification of the straight gas carburizing process in that anhydrous ammonia is added to the atmosphere of the furnace along with the hydrocarbon gas and endothermic gas.[7] At the carburizing temperature, the ammonia dissociates into hydrogen and nitrogen with some of the nitrogen combining with the iron and the hydrogen

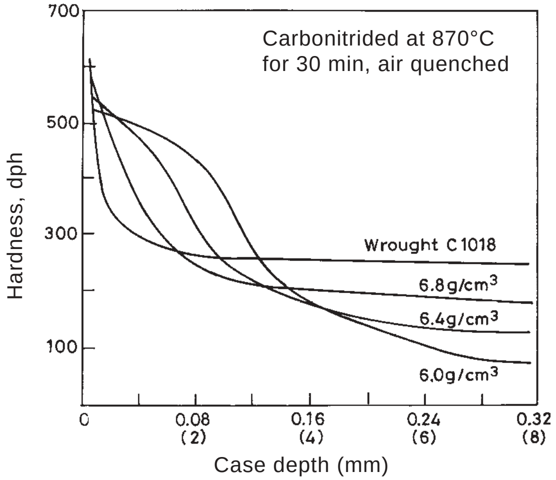


**Fig. 8.6** Effect of density on the case depth of carbonitrided P/M steel (mm).[3]

being given off to the furnace atmosphere. The higher the carburizing temperature, the less nitrogen will be taken into the part. In general, where light case depths of extremely hard surfaces are desired, carbonitriding is the most desired practice.

With the advent of glow discharge plasma surface engineering, an environmentally harmless technology has been introduced. Plasma nitriding is the most developed of the plasma thermochemical treatments and is used quite extensively for P/M components. Figure 8.7 shows such a microprocessor-controlled modular unit.

### *8.4.3 Age Hardening*

Age hardening or precipitation hardening is an important heat treatment for many aluminium alloys. Similarly parts made from iron and copper or iron, carbon and copper can be age hardened, since the solubility of copper in iron decreases with temperature. In 85Fe–15Cu alloy, the tensile strength can be raised as much as 170 N/mm$^2$ by the precipitation hardening process. Sintered aluminium alloys after solution hardening are invariably subjected to sizing prior to ageing treatment. Most of the sintering furnaces for aluminium alloy parts include provision for quenching as well. This avoids an additional solution treatment in a separate furnace thus offering energy efficiency.

## 8.5 Joining

All major joining processes can be equally applied to sintered products. Powder metallurgy itself makes it possible to obtain complex shapes, and hence the joining operation is not met very frequently. Sometimes the very presence of pores in sintered parts may pose problems during joining for

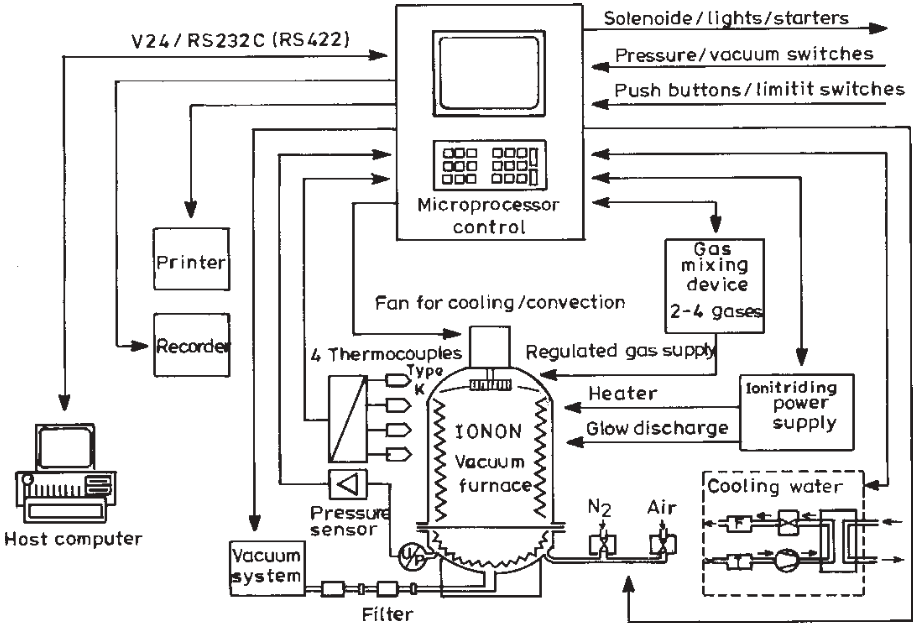


**Fig. 8.7** Layout of multi-functional plasma nitriding installation.[14]

example, brazing is unsuitable because the molten brazing alloy prefers to infiltrate the pores by capillary action. However, in case of necessity the parts to be joined should first be infiltrated using an alloy with melting point equal to or higher than that of the brazing alloy, or to use an excess of brazing material to infiltrate the pores during the joining process.

As far as welding of P/M parts is concerned, most conventional welding methods (TIG, MIG, electron beam, resistance, projection and friction) are used. There are no special technological problems in joining sintered to wrought steel parts so long as the joints are correctly dimensioned and the operational parameters of the welding process are well selected. Best welding results for P/M steels are achieved when the component density is 6.8 g/cm$^3$ (88% of theoretical density) or higher and carbon content is held to the minimum practical for the application. Higher densities yield greater weld strengths while higher carbon levels tend to make welds more brittle.

Another method for joining is equivalent to ‘shrink’ fit by using two materials with different growth characteristics during sintering. P/M parts can be also joined during the infiltration process by assembling the component parts and infiltrating the assembly during sintering. Hausner[11] introduced the concept of sinter-welding, which consisted of joining two metal parts by inserting a suitable powder of the same metal between the parts to be joined, and then hot pressing the assembly in a suitable atmosphere. Hausner further modified the process to what was called as ‘activated sinter welding’, in which the reactive metal hydride decomposition and hot pressing were combined.[12]

## References

1. L. Pleney and M. Eudier, In ‘Powder Metallurgy 1986 : State of the Art’ Ed. W.J. Huppmann, W.A. Kaysser and G. Petzow, Verlag Schmid, Freiburg, 1986, p.123.
2. G.L. Pearson, In ‘Source Book on Powder Metallurgy’, Ed.S. Bradbury, ASM International, Materials Park, Ohio, 1979, p.273.
3. H. Ferguson, Heat Treating, May, 1984, 34.
4. P. Johnson, W. Q. Judge and H.S. Nayar, Heat Treating, May 1985, 34.
5. P. Lindskog, In ‘Powder Metallurgy Promises and Problems’, Materiaux et Techniques, Paris, 1975, p.66.
6. P. Lindskog, In ‘P/M Conference Karlovy Vary, 1970’, The Institute of Experimental Metallurgy of the Slovak Academy of Science, Kosice, (Slovakia), 1970, p.333.
7. S. Bradbury (Ed)., Powder Metallurgy Equipment Manual, 3rd Edition, Metal Powder Industries Federation, Princeton, 1986, p.170.
8. General Guidelines for the machining of sintered materials, Hoganas AB Report 77-14, 1977, p.3.
9. W.J. Huppmann and G.T. Brown; *Powder Metallurgy*, 1978, No.2, 105.
10. Source Book on Powder Metallurgy, Ed. S. Bradbury, ASM, Ohio, 1979, p.245.
11. H.H. Hausner, ‘Powder Metallurgy in Nuclear Reactor Construction’, International Atomic Energy Agency, Vienna, 1961.
12. H.H. Hausner, In ‘Sintered Metal Ceramic Composites’, (Ed. G.S. Upadhyaya), Elsevier Science Publishers, Amsterdam, 1984, p.121.
13. B.G. McMordie, ‘Further Developments in Coatings for P/M Parts’, Sermatel Inc Brochure.
14. T. Bell, *Materials and Design*, Vol.13, No.3, 1992, 139.

# 9

# POWDER INJECTION MOULDING

The potential of powder injection moulding (PIM) for cost effectively forming small, complex, precision parts is finding application in the markets of fire arms, business machines and printers, hand tools, aircraft, automotive, ordnance, medical and dental, cameras and controls. The process is finding acceptance on a part by part basis, and is expected to penetrate almost all market segments in competition with investment castings.

Powder injection moulding process is similar to plastic injection moulding, with the difference that the polymer is filled with dispersed metallic or ceramic powders. This technology permits production of stronger, more uniform and more complex P/M parts. The process has virtually unlimited possibilities of low cost, three-dimensional design features and the ability to handle very fine metal powders than enable sintering to high densities, conferring high ductility and strength to the finished parts. PIM becomes more attractive when compared with other manufacturing techniques for medium to high volume production of small parts. The process is economical when intricate three-dimensional details in the part need to be introduced. Pressure die casting can produce the same shapes and details as PIM, but not in comparable materials – low alloy steels, stainless steel, magnetic alloys, nickel alloys, tool steels, etc. Investment casting no doubt covers a wide range of alloys than are currently available for PIM, the latter is particularly useful for fine details such as blind holes, recesses, sharp edges and internal or external threads.

A general flow chart illustrating the steps of the PIM process is shown in Fig.9.1.

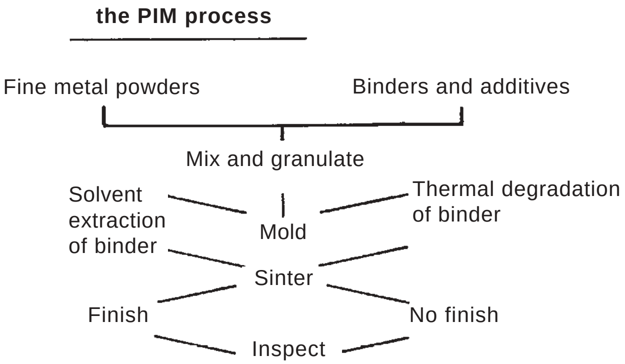


**Fig. 9.1** Flow diagram of the PIM process.

The process steps involved in injection moulding are:

- Selection and production of metal powders.
- Mixing
- Moulding
- Debinding
- Sintering

## 9.1 Selection of Metal Powders and Binders

The major P/M fabrication techniques are mechanical, chemical and atomization. The detailed fundamentals have been described in earlier chapters. Typical powder sizes used for injection moulding are in the range of 0.5–20 µm, in contrast to the relatively coarse free-flowing powders having particle sizes greater than 40 µm used in conventional P/M. Because of fine particle size, the initial density of PIM powder is low and non uniform within a poured mass.

In PIM spherical particles are desirable rather than the irregular particles used in conventional P/M. Because of this, gas atomization of the melt is preferred. Because of the wide size distribution of the atomized powder, the proportion of fine powder is rather small, making the powder costly on a weight basis. The carbonyl method for producing iron and nickel fine powders is very useful in case of PIM. In case of refractory metal powders, hydrogen reduction gives rise to reasonably fine size powders. Because of fine size the storing of the powder must be done with due care in order to prevent oxidation.

Polymeric binders are mostly used. The binder system could contain several components and are normally classified as major binders, minor binders and processing aids. High-molecular weight polymers as as polypropylene, low-density polyethylene, ethylene vinyl acetate and low-molecular weight waxes have been used as major binders. Minor additives are mainly used to control the viscosity of the powder–polymer blend. Processing aids are minor additives that act as surfactants to the powder and improve the wetting characteristics between powder and binder during compounding control. The exact compositions are still proprietary in nature. These binders are generally thermoplastic ones, but a thermosetting system (epoxy resin + paraffin wax + butyl stearate) has also been used. Although thermosetting binders offer an advantage in shape retention but generally prove difficult to control in practice.

Table 9.1 shows the main binder systems used for powder injection moulding.

## 9.2 Mixing

The feedstock must perform like a stable thermoplastic during the moulding process. The thermoplastic binder system used must be stable and repeatable. Because the green part undergoes considerable shrinkage, the volume ratio of binder to fine powder must be held within a tight tolerance. The

**Table 9.1**

**Binder systems**

| | | |
|---|---|---|
| Thermoplastic binders | main ingredient:<br>polymer backbone:<br>additives (surfactants): | Paraffin/microcrystalline/carnauba/bees-wax, vegetable/peanut oil, acetanilide, antipyrine, naphthalene<br>PE, PP, PS, PA, PE-VA, PE-A, PP-A, PBMA-E-VA<br>stearic/oleic acid and esters thereof, phthalic acid esters |
| Duroplastic binders | main ingredient:<br>additives | epoxy resin, furan resin<br>waxes, surfactants |
| Gellation binders | main ingredient:<br>polymer backbone:<br>additives: | water<br>methyl cellulose, agar<br>glycerin, boric acid |
| Freeze-drying binders | main ingredient:<br>additives: | water, aniline<br>paraffin wax |
| Polymer binder | main ingredient:<br>additives: | polyoxymethylene<br>proprietary |

(From: Metal Injection Moulding Brochure, European Powder Metallurgy Association, Shrewsbury, UK, reprinted with permission)

goals in mixing are to coat the particles with the binder, to break up agglomerates and to attain uniform distributions of binder and particle size throughout the feed stock. For thermoplastic binders, mixing is performed at an intermediate temperature, where shearing is predominant.

In general procedure, the binder is placed in a temperature controlled mixer and heated to its melting temperature. The blended metal powder is added to the molten binder and mixed for a prescribed period to achieve a uniform blend. The mixture is than cooled and removed from the mixer. The feed stock mass can be extruded and cut into pellets for ease in feeding into the moulding machine. Throughout mixing, special care is needed to maintain a repeatable mixture. Weighing and temperature control must be precise, since small change gives rise to variations in final dimensions after sintering. The common mixers used for mixing dry powders are not useful in the preparation of PIM feed stock, as the binder components require shear to cause molecular scale thinning and dispersal between the particles.

Figure 9.2 shows schematically a batch-type double planetary mixer.

There are two reasons for pelletizing or granulating PIM feedstock. The first is to prepare easily transported clusters of powder and binder, while the second is to incorporate recycled material back into the moulding process. In some cases, the mixing and moulding equipment are combined and the

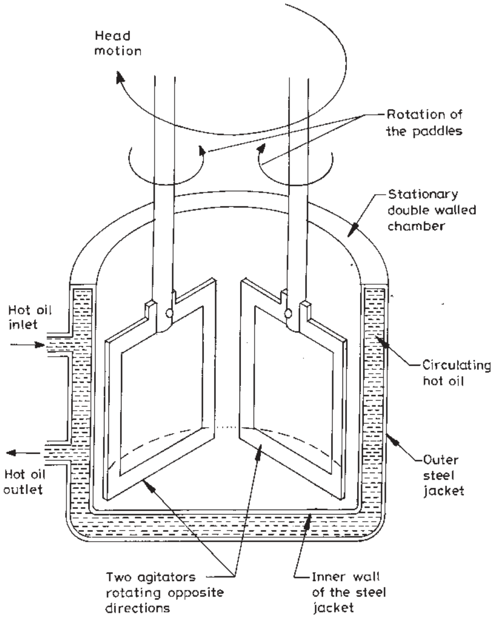


**Fig. 9.2** Schematic illustration of a batch-type double planetary mixer (reprinted with permission from Advances in Particulate Materials, Animesh Bose, Butterworth Heinemann, Newton, MA, USA, 1995).

pelletization step can be avoided. The powder binder mixture can be mixed with a solvent to lower the viscosity. This slurry can be used to form agglomerates using rotary dryers, spray dryers or disc pelletizers.

## 9.3 Moulding

Moulding consists of heating the feedstock pellets to a sufficiently high temperature such that they are melted, then forcing this melt into a cavity where it cools and assumes the compact shape. The purpose is to attain the desired shape free of voids or other defects and with a homogeneous distribution of powder.

During solidification of a moulding, a solid layer forms at the mould surface immediately after injection. Shrinkgae occurs which the thickness of this layer continues to increase. The static hold pressure continues to compensate for shrinkage by filling the mould cavity until the centre of the sprue solidifies. The control of shrinkage and the internal stresses during solidification by keeping the sprue molten is vital for the production of void and crack-free large mouldings with thick central sections.

There are three types of moulding machines: reciprocating screw, hydraulic plunger and pneumatic. The most commonly used is horizontal reciprocating screw inside a heated barrel, which has adequate control. The details of such machine is described adequately by German.[1] After the mould is filled, heat is extracted from the feedstock through the die. Finally, the cavity is opened to eject the hardened compact. The presence of a high solids content raises the viscosity, requiring high pressures during moulding. High packing pressure can result in the compact sticking to the die wall with severe ejection problems.

In brief, moulding parameters are highly dependent on particle characteristics, binder formulation, feedstock viscosity, tool design and machine operating conditions.[2] The probability of defects and the presence of distortion in sintering is highly dependent on the moulding step.

## 9.4 Debinding

The most common debinding techniques depend on the basic processes, which include combinations such as solvent extraction and evaporation or wicking and evaporation. Thermal debinding is the most widely used in practice. Failure to remove the binder before sintering results in compact cracking. The important feature is that the binder must be extracted from the pores as a fluid (liquid or vapour) without distorting or contaminating the compact.

The batch process of debinding has greater flexibility but lower productivity. Figure 9.3 shows a batch system for thermal debinding, which consists of a retort that holds the compacts and atmospheres and various controls for temperature, time, pressure and atmosphere. Thermal debinding is carried out in either vacuum or an atmosphere of air, hydrogen, nitrogen–hydrogen, hydrogen–argon or nitrogen–hydrogen–water. Debinding in air is cheap and efficient but will oxidize a metallic part and create subsequent problems in sintering. Protective atmosphere with proper control of dew point and carbon potential is therefore desirable.

The results on decarburizing low-carbon ferrous compacts during debinding under hydrogen were reported in Ref. 5. The purpose was to produce high-performance PIM soft magnetic components. The debonding at 700°C in hydrogen (dew point –20°C) resulted in compacts of less than 0.05% carbon.

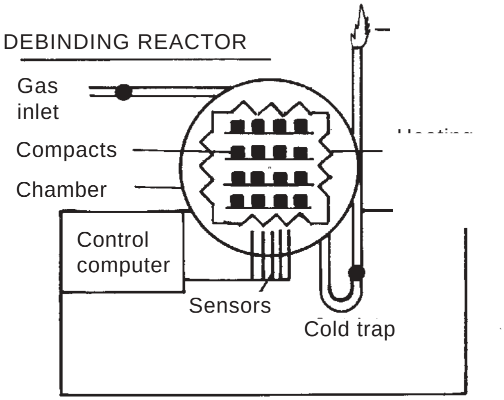


**Fig. 9.2** A batch debinding system (schematic view).[1] (reprinted with permission from Powder Injection Moulding, MPIF, Princeton, NJ, USA, 1990).

**Table 9.2** Some typical sintering schedules[1]

| Material | Sintering aids | Particle size, µm | Atmos-phere* | Dew point, °C | Heating rate, K/min | Hold temp., °C | Max. temp., °C | Time, min |
|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | MgO | 0.3 | H | | 10 | | 1600 | 240 |
| 316L | | 15 | V, H | –40 | 5–10 | 1000 | 1360 | 90 |
| SiC | B, C | 0.2 | A, V | | 10–50 | 1700 | 2100 | 60 |
| $Si_3N_4$ | $Y_2O_3$ | 0.5 | N | –40 | 10 | | 1750 | 120 |
| Ti | $TiH_2$ | 30 | V | | 10 | 600 | 1300 | 60 |
| Steel | | 4 | A, H | –20 | 15 | 870 | 1250 | 60 |
| W–Ni–Fe | | 3 | H | 10 | 5–10 | 1000 | 1500 | 30 |
| WC–Co | VC | 0.5 | V | | 2–10 | 700 | 1400 | 60 |
| $ZrO_2$ | $Y_2O_3$ | 0.4 | A, V | | 5 | | 1450 | 90 |

* V is vacuum, H is hydrogen, N is nitrogen, A is argon

As already indicated earlier debinding if not properly done, gives rise to a number of defects and problems. These include the loss of the compact shape through distortion, slumping or warping, as well as the formation of surface pits, discoloured spots and internal cracks.[1,3] Figure 9.4 shows several such defects in a cross-sectional compact. Thorough description on this aspect can be had from the monograph by German.[1]

## 9.5 Sintering

The basic and applied aspects of sintering has already been described in Chapter 6. It must be clearly understood that sintering cannot correct defects introduced in earlier steps such as mixing, moulding or debinding. Sintering

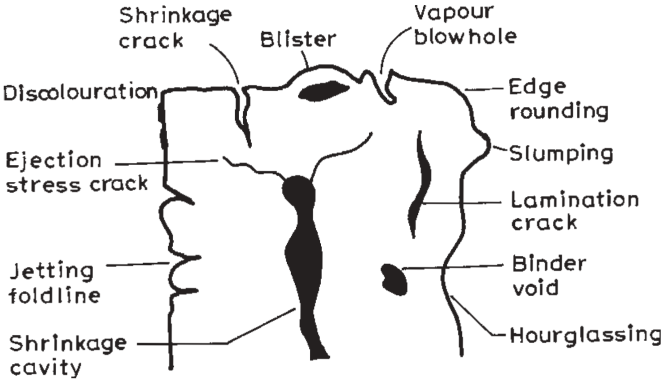


**Fig. 9.4** Possible defects in a PIM compact that might be observed after debinding.[1](reprinted with permission from Powder Injection Moulding, MPIF, Princeton, NJ, USA, 1990).

behaviour is dependent on several factors, including powder packing density, compact thickness, binder contamination, powder oxidation, particle size, sintering aid and heating rate. However, in general, PIM sintering occurs at higher temperatures where densification is more likely to occur. Table 9.2 illustrates some typical sintering schedules of some of the important metal and ceramic systems.[1]

Postsintering treatments are similar to those described in Chapter 8. The main concerns with PIM materials are removal of the residual porosity by techniques such as hot isostatic pressing or infiltration.

## 9.6 Design Aspects of PIM

The following features would suffice the practical ranges for various design characteristics.[4]

**Size Range**: PIM processing is best suited for relatively small parts. The lower limit of size is determined only by the limitations of the injection moulding process itself. Part as small as 6.4×2.5×1.3 mm are economically feasible. The upper limit of the part size is established by processing economics. As part size increases, the powder cost becomes a significant percentage of the overall cost. Dimensions up to 150 mm are possible.

**Section Thickness**: The part thickness must be kept relatively low in order to remove binders efficiently. Minimum wall thickness is about 0.5 mm which makes the process very competitive for producing thin walled parts. Parts normally have a ruling section of less than 10 mm.

**Weight Range**: Part weights typically range from 0.1 g to 150 g. However, the process is most economical for parts in the range 1 to 20 g. Parts are made today up to 240 g.[6]

**Density**: The density of the parts is generally greater than 94 % of full density. Depending on the material and processing schedule, densities approaching theoretical may be obtained. Full density can however, be achieved through subsequent HIP treatment. Porosity in PIM parts are almost completely closed. Interconnected porosity amounts to typically less than 0.2%. Unlike conventional P/M parts, PIM parts cannot be oil impregnated or metal infiltrated because the interconnected porosity is too low. PIM parts can be case hardened to closely controlled case depths equivalent to wrought material.

**Tolerances**: PIM parts normally require a dimensional tolerance of ±0.3 percent. As part size decreases, increasingly tighter total tolerances can be achieved as would be expected. It is possible to improve general tolerances somewhat with tighter process controls, but this may reduce efficiency and increase costs. Extremely tight tolerances may have to be obtained through machining.

**Surface Finish**: Surface finish of PIM parts is approximately 32 rms. The degree of surface smoothness is very must dependent on the sintering operation and is relatively independent of the powder particle size and finish of the mould cavities.

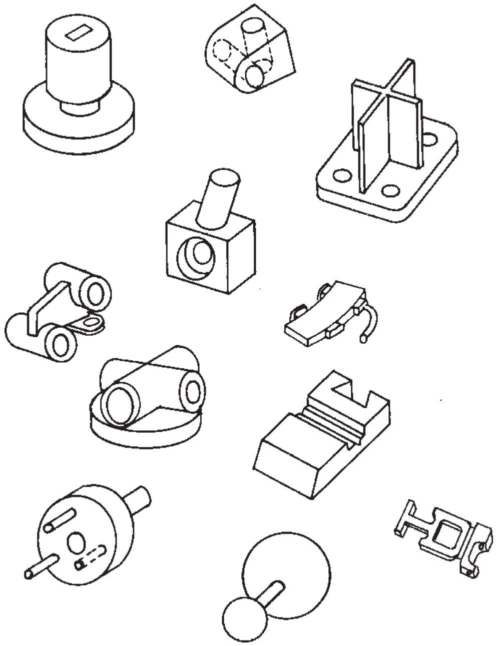


**Fig. 9.5** Sketches of some viable component geometries for powder injection moulding.[1] (reprinted with permission from Powder Injection Moulding, MPIF, Princeton, NJ, USA, 1990).

**Part Complexity**: Because the metal–polymer feedstock can fill nearly any volume, complex geometries can be created. Hence, the more complex the part, the economical advantage PIM process has. For example, external threads can be moulded directly into the part although an allowance must usually be made for parting lines. While internal threads can also be directly formed, it is often more economical to thread in a subsequent tapping operation. Complex internal diameters or cavities are difficult to form, where undercuts prevent the tool member from being withdrawn.

Figure 9.5 shows a number of viable geometries, illustrating the possible combination of holes, pins, fins, slots, grooves, arms etc.[1]

**Other Features**: Gates, parting lines and knockout or ejection pin marks are present in PIM parts and design of parts should take them into consideration. For example, flats can be built into parts in the areas of parting lines, particularly on contours or external threads. The areas around the pins may be recessed, if burrs caused by knock out pins are the problems.

## References

1. R.M. German, Powder Injection Moulding, Metal Powder Industries Federation, Princeton, 1990.
2. A.R. Erickson and R.E. Weich Jr., In ‘ Metals Handbook’, Vol.7, Ninth Edition, Ameri-

can Society for Materials International, Materials Park, OH, 1984, pp. 485.
3. J.G. Zhang, M.J. Edirisinghe and J.P.G. Evans, *Industrial Ceramics*, Vol.9, No.2, 1989, 72.
4. J.R. Merher, ‘ Overview of Metal Injection Moulding’, paper presented at Seminar on ‘Metal Injection Moulding’, held at 1988 International P/M Conference, Orlando, MPIF, Princeton.
5. T. Kohno, Industrial heating, Vol. 45, No. 5, 45 (1997).
6. D.G. White, Int. J. Powder Met., Vol. 33, No. 5, 45 (1997).

# 10 QUALITY CONTROL OF POWDER METALLURGY MATERIALS

The quality and reliability of a P/M part like any other engineering component must be defined as a basic part of the specification of the product. Many aspects of quality and reliability can be expressed in objective and measurable terms but certain aspects will always be subjective and based on user's opinion. Quality can be achieved at three stages in the life of a product. These are (1) at the design stage, (2) at the manufacturing stage and (3) at the service stage. Variation in the quality of manufactured parts is inevitable and decisions must therefore be made about the standards of quality and reliability which will be achieved and the cost which will be incurred in meeting these standards.

Some of the specific quality aspects of manufacturing planning include:

- Choice of machines, processes and tools capable of holding the tolerances.
- Choice of instruments of an accuracy adequate to control the processes.
- Planning the flow of manufacturing information and inspection criteria.
- Planning of process quality controls.

Quality control can be carried out at three stages. The first stage involves ensuring that raw materials are to the standards specified. The second stage involves checking the manufacture of components as they are being made within the company's own manufacturing organization. Finally, completed products can be tested in the operating environment to ensure that they are able to perform to specification.

## 10.1 Sampling

The sampling aspect of sintered products must be dealt with in the same way an any other industrial product. Care must be taken to choose sampling procedures and acceptable quality levels in a way which takes cost into account.

Before putting any sampling plan into action, the supplier and user must agree on the following points:[1]

- The properties to be inspected, their values and relative tolerance ranges.

– The methods of measurement for each of the properties to be inspected.

– Sampling plans and the acceptance or rejection criteria for the lots supplied.

When there is no interaction between different testing procedures more than one type of test may be carried out on the same test specimen, for example density, hardness, metallographic examination etc.

## 10.2 Density

In general, the density achieved in sintered products is between 70 and 95 % of the fully dense wrought products, depending on the production technology in use and the type of application.

Pores are of two types: (a) interconnected and (b) closed or isolated. In the first case the pores are connected with each other along the particle junctions. The pores are consequently irregular, unless the particles are initially spherical. Such pores can remain as low as 5% of total porosity. The latter types of pores, i.e. closed pores, are pronounced when total porosity is low (< 5%). They are often, but not necessarily, spherical.

The sintered density determination is carried out following the procedures of ISO standard 2738. This is valid both for dry parts and for parts that have been impregnated with oil. In case parts have been impregnated with thermosetting polymers, the true density is obtained graphically (Fig.10.1). This allows the calculation of the unknown density by determining the density of the part examined and assuming a degree of impregnation equal to 0.8. As most impregnating resins have a density of between 1 and 1.3, two straight lines have been drawn on the diagram delin-

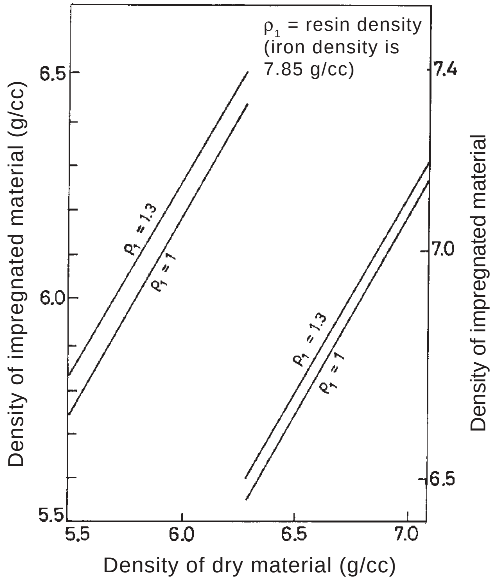


**Fig. 10.1** True density of resin-impregnated parts.[1]

eating the two limits of the band; intermediate points may be obtained by interpolation.

The density may be calculated by the oil impregnation method, the formula being:

$$D = \frac{A}{B - C} \ (\mathrm{g/cm^3})$$

where $A$ is the mass of the unimpregnated part in air, g; $B$ is the mass of the part after impregnating with the oil, g; $C$ is the mass of the impregnated part in water, g. Either of two procedures may be used for oil impregnation:

1. The specimen is immersed for 4 hours minimum in oil 'Saybolt Universal' at 380°C held at a temperature of 82 ± 4°C and then cooled to room temperature.

2. The pressure over the specimen immersed in oil at room temperature is reduced to a maximum of 50 mm Hg pressure for 30 minutes. The specimen then remains immersed in oil at atmospheric pressure for 10 minutes.

The amount of interconnected porosity ($P$ in %) can be calculated as follows:

$$P = \frac{B - A}{(B - C)S} \times 100$$

where $A$ is the mass of the lubricant-free sample, g; $B$ is the mass of the oil impregnated sample, g; $C$ is the mass of the oil impregnated sample immersed in water, g; $S$ is the specific gravity of the impregnant at test temperature. All the masses are determined to the nearest 0.1%.

## 10.3 Mechanical Properties

The Metal Powder Industries Federation (MPIF) of USA has adopted the concept of minimum strength values for P/M materials for use in a structural application.[8] It may be noticed that the P/M process offers equivalent minimum tensile strength values over a wide range of materials. It is seen as an advantage of the process that equivalent strengths can be developed by varying chemical composition, particle character, density and/or processing techniques.

The material may be specified as the basis of properties obtained in test samples made under similar condition, but it is understood that the properties of sintered parts may not be identical to the testpieces because of shape effects. The test methods and instrumentation used are similar to those used for wrought products. The various national and international standards have been limited to standardizing the types of testpieces.[1] A brief description of various common mechanical properties is given as follows:

### *10.3.1 Hardness*

Like density, the hardness value has great importance and provides indications of the mechanical behaviour of sintered products. The indentation hardness of a sintered material is also strongly affected by its density because voids in the structure of a material do not contribute to the support of indenter. The indentation of a porous material should be considered in apparent hardness. The ISO standard on apparent hardness recommends Vickers as the reference method but allows Brinell and Rockwell methods as alternatives. It forbids direct conversion from one hardness scale to another. Though it is possible to compare one hardness scale with another provided both tests have been done on the products concerned, there are practical shortcomings in the tests currently specified. In Vickers and Brinell tests, surface preparation is critical, the tests are slow and require both visual judgement and use of a conversion table. Furthermore automation is not practical.

The Rockwell test, on the other hand, uses heavy loads of 60–150 kg which are less responsive to the metallurgical structure of the material than density variations. In addition the test is insensitive in the most common hardness ranges used in sintered metals. A possible alternative is the superficial Rockwell test using a 15 kg load. Apart from testing procedures, there are problems associated in measuring true hardness of a multi-component system. For example, the porosity may be filled by a softer or harder material than the skeleton material, and at times the true hardness may not be an indication of functional parameters, such as abrasion wear. In order to avoid such complexities, the best thing is to express true hardness for a ‘specific constituent’. This is determined by microhardness testers utilizing Knoop or diamond pyramid hardness indentors. It measures the true hardness of the structure by eliminating the effect of porosity, and this is a measure of resistance to wear. Care should be taken in converting Knoop or Rockwell hardness value because the usual conversion chart is based on a 500 g load, while the recommended load for a P/M material is 100 g. In case the indentor strikes a pore, the diamond mark will exhibit curved edges and reading must be discarded. Since the data tend to be scattered compared to fully dense material, it is recommended that 5 to 10 indentations be made, anomalous readings discarded and an average taken of the remainder.

### *10.3.2 Tensile Strength*

The tensile properties of sintered products are directly influenced by porosity. Due to presence of porosity, the tensile properties are somewhat lower than those of wrought materials of the same composition and structure. For sintered materials machined test pieces are almost never used and test pieces are invariably obtained by pressing and sintering. Figure 10.2 illustrates a typical MPIF testpiece for tensile properties evaluation. With sintered materials care should be taken with their storage before testing because their

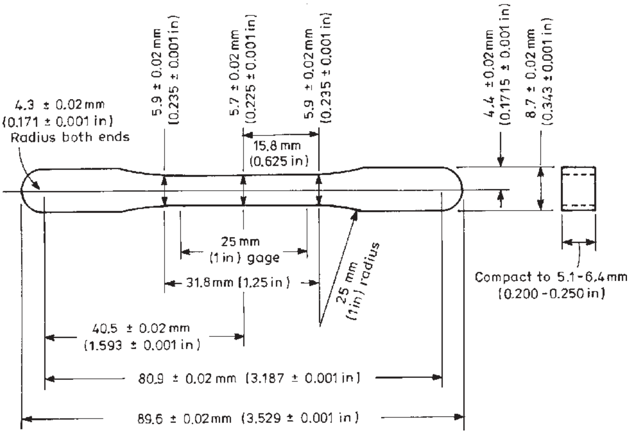


**Fig. 10.2** MPIF tensile test piece dimensions.

interconnected porosity may give rise to internal corrosion. In the case of fully dense materials like P/M forged, the machined test pieces may be used.

Porosity has a more pronounced effect on ductility than on strength. A pore content of a few percent can be rather detrimental to ductility. However, production variables, particularly in sintering, also have a significant effect on ductility, so that the ductility of similar materials of the same porosity but of different origins, may differ widely.[2]

### *10.3.3 Transverse Rupture Strength (Bending Strength)*

This test is applicable only to materials of negligible ductility. The width and thickness of the specimens are measured accurately. The specimens are then broken in the testing fixture shown in Fig.10.3. In this fixture, the specimen is supported by two hard metal or hardened steel rods at 25.40 mm centres and another rod presses at the centre of the specimen. The test is performed in a universal testing machine and the breaking load recorded. The modulus of rupture is calculated as follows:

$$S = \frac{3PL}{2t^2W}$$

where $S$ is the modulus of rupture, N/mm$^2$; $P$ is the breaking load, N; $L$ is the distance between the supporting rods (25 ± 0.2 mm); $t$ is the thickness of the specimen, mm; $W$ is the width of the specimen, mm.

At least five determinations should be made and the result is expressed as the arithmetic mean rounded up to the nearest 10. This test is very significant for cemented carbides.

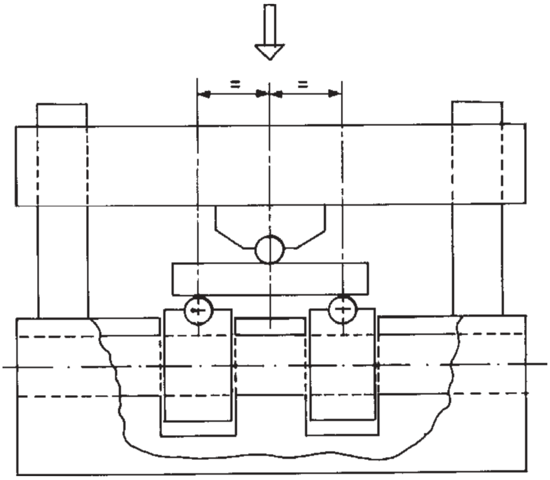


**Fig. 10.3** Test fixture for transverse rupture strength.[1]

### 10.3.4 Toughness

The standard impact tests are of very limited value to the application engineers in the area of sintered products. There are, thus, the following two classes of test:

(a) Measurement of energy absorbed when a test piece is fractured by the application of an impact force, for example, the Charpy or Izod test.

(b) Measurement of resistance to crack propagation under non-dynamic conditions of stress, for example, the fracture toughness test.

The impact tests have major drawbacks. Firstly, the result obtained is purely comparative and cannot be used as a design parameter. Secondly, the values obtained when testing a sintered product is very low, inaccurate and hard to reproduce. On the other hand, the fracture toughness test offers many advantages. The value obtained is quantitative assessment of the toughness of the material which can be used as a design parameter. In most of the cases for the range of materials covered by powder metallurgy (excepting fully dense sinter forgings) it is not necessary to induce an initial crack by fatigue stresses, and a suitable machined notch is adequate. In conclusion, the validity of applying fracture toughness testing in a given sintered product is established if it meets the following criteria:

(a) The shape and size of the test pieces must ensure plain strain during the three-point bending.

(b) An accurate method of measuring load and crack opening displacement (COD) must be employed.

(c) It must be established by testing that the measured stress intensity factor ($K_Q$) is in fact equivalent to the critical or minimum fracture toughness ($K_{IC}$) for each type or range of materials considered.

The test consists of a three-point slow bend test similar to that used for measuring transverse rupture strength. The toughness $K_Q$ is calculated from:

$$K_Q = \frac{P_Q}{BW^{1/2}} Y$$

where $P_Q$ is the fracture load, $Y$ the is geometrical factor, $B$ is the specimen thickness, and $W$ is the specimen width.

Provided plane-strain conditions apply (largely determined by correct specimen geometry), then

$$K_Q = K_{IC}$$

Testpieces for the impact test are generally obtained by pressing and sintering. The die cavity has a rectangular section of dimensions 55×10 mm and preferably made of cemented carbide. The thickness of the testpiece must be 10 mm with a tolerance of ±0.2 mm on both the dimensions of the cross section. If the sintered materials are particularly tough it is possible to make standard U- or V-notches as with wrought materials. The pressing direction must be noted on the test pieces as the direction of impact must be perpendicular to it. Impact tests are carried out with standard Charpy or Izod methods.

### *10.3.5 Fatigue Properties*

The influence of porosity is more important in fatigue tests than in other mechanical tests. The kind of test piece used for the tensile test after pressing and sintering, as shown in Fig.10.2, may also be used for reverse bend or tension–compression fatigue tests.

Fatigue tests are important after surface treatment, hardening and nitriding of sintered steels. All such treatments raise the fatigue limit, as in pore-free materials. Above the fatigue limit microcracks are initiated at pores and inclusions and linked together to form the final crack, which generally gives in a mixed transgranular–intergranular manner.

## 10.4 Fracture

Fracture in sintered materials may involve similar mechanisms known in wrought materials. As inclusions and cavities are important in ductile fracture, the porosity in the sintered materials controls fracture and is responsible for its early onset. As sintered materials generally contain relatively large volume of coarse pores, localized internal necking is able to start at relatively low plastic strains. The large pores lead to high stress concentrations, thus accelerating the spread of fracture. The real sintered materials are, therefore, more complex in the stress strain response; their behaviour depends on the work hardening characteristics of the matrix and on the pore size distribution and shape. Intergranular and cleavage fractures are less common than ductile failures, although intergranular fracture may occur in sintered parts at interparticle necks which may be imperfectly bonded, e.g. due to segregation of impurities at the interface. The pulling out of particles from a fracture surface, may be an indication of intergranular fracture. For more details one may follow the monograph by Haynes.[2]

## 10.5 Roughness

The roughness of sintered parts is governed by the successive operations the material is subjected to. In the powder pressing stage, it is influenced by the wear of the dies. In the sintering stage the governing factors are the lubricant burn off and the reduction of any oxide on the powder surface. During the sizing operation the surface condition of tools is important. The roughness would be different if measured on the surfaces normal to the pressing direction or on surfaces parallel to it.

Conventional profilometer readings give an erroneous impression of surface finish for sintered parts, because a different surface condition exists from that found on the machined or ground surfaces of wrought materials. Conventional readings (RMS) take into account the peaks and valleys of machined surfaces, while P/M parts have a series of very smooth surfaces which are interrupted with varying size pores. A chisel stylus is preferred for P/M parts because it bridges the negative gaps caused by the pores and will still measure any protrusions on the surface of the part.

## 10.6 Electrical Resistivity

Electrical conductivity is an important property for evaluating the performance of electric contact materials, which are often prepared by powder metallurgy route. The contact area and, thus, electrical resistivity is affected by several factors, including oxide films, lubricant, compacting pressure, sintering parameters as well as powder characteristics. The physical properties of the metal concerned will also have to be considered. For measurement of electrical resistivity a Kelvin double bridge set up is useful. Spring loaded knife edge contacts are required with side feeding of the current. The potential difference is then measured across two points within the length of the compact. The width and thickness of the specimens are measured as well as their resistance and the apparent resistivity ($\rho$) found from the equation:

$$\rho = \frac{RA}{L}$$

Another method is based on eddy current principles and the instrument is designated primarily to measure the electrical conductivity of non-ferromagnetic specimens having a flat surface larger then 2 mm diameter, and thickness greater than about 0.3 cm. A single probe or test coil carrying 50 000 c/s a.c. frequency is placed on the specimen and the electrical conductivity is found by adjusting a calibrated dial to bring a galvanometer deflection to zero. This operation compares the impedance of the probe with that of a standard coil inside the instrument case. Before use, the electrical circuits must be adjusted by using two specimens of known conductivities. The conductivity reading obtained is not affected by surface roughness or surface films provided the probe is no where more than 0.1 mm from the specimen surface. Since the area covered by the probe is only about 3 $cm^2$, the instrument is useful for detecting inhomogeneities, segregation and small surface cracks in flat strips obtained after powder roll compacting.

## 10.7 Magnetic Properties

The important nondestructive quality test in wide spread use for ferrous alloys and cemented carbides is the analysis of magnetic properties. Magnetic properties are affected by the presence of pores because of:

– a lower quantity of magnetically active material per unit of volume

– an alteration in the distribution of magnetic flux.

In addition to above the pore size and shape and their distribution along the flux path must be taken into account.

Magnetic properties measurement devices for soft magnetic materials permit two types of test pieces: ring or bars. In the former, the closed ring test pieces, square in section, are obtained directly by pressing and sintering, so as to have uniform section in all directions with minimum variation in density. In such type of test direct magnetizing current may be used with a stabilized generator and a ballistic galvanometer to measure the induction. Induction and density are correlated in linear mode, while there is a less evident correlation between the maximum permeability or coercive force and the sintering conditions.

In the latter case, i.e. bar test pieces, the method is used less frequently because of the lack of accuracy of the method of measuring the circuit. The bars are inserted in a core or yoke, which is a part of the measuring circuit. They must be straight with a constant cross-section along their whole length. Both types of test pieces ring or bar must be deburred before winding and their dimensions checked.

In case of hard magnetic materials, unlike soft magnets, magnetic tests are carried out directly on the sintered parts, as long as their dimensions are compatible with the instrument, the shape is cylindrical or parallelopiped and the flux is in the direction of the axis. In case the part is of complex shape, it is necessary to make it of constant cross-section in the direction of the flux. The main features of such a magnet are obtained from the demagnetization curve traced on the second quadrant of the graph of the hysteresis cycle. The test piece is placed between the poles of an electromagnet in which a direct amount of variable intensity and sign is fed. The field is measured with a Hall probe and gaussmeter while induction is measured with a coil wound around the sample and an integrating fluxmeter. Such measurements are helpful in relating composition and any heat treatment on the permanent magnets. In the case of cemented carbides, because the factors influencing coercive force are complex and interactive, the test is employed to indicate departure from a norm, rather than to determine absolute values of cobalt content, grain size or carbon deficiency. When both cobalt content and grain size for a particular grade are controlled within reasonable limits, test can give a clear indication of carbon deficiency and the consequential presence of the embrittling eta-phase.

## 10.8 Metallography

Metallographic study of sintered products is essential to study the type and morphology of pores which affect various properties. Metallographic preparation of such material can lead to changes in the specimen surface which can cause erroneous interpretation of the microstructure. Some examples of such changes are:[3]

- Partial closing of pores by plastic deformation during grinding
- Break out of material around pore
- Closing of pores with grinding debris
- Rounding of pore edges

The preparation sequence of metallographic specimens of porous materials may be described as follows:

**Sample Preparation:** An abrasive cut off wheel with water as coolant may be used for sectioning purpose. Thorough rinsing with water must be carried out in order to remove any cutting debris. Specimen mounting can be done as usual practice.

**Grinding:** This can be done using SiC paper of 220 grit size using water as a coolant or an automatic grinding wheel. A speed of 300 rpm with a load of 90, 60 and 30 N is used for three grinding steps. After the grinding operation, the specimens are ultrasonically cleaned in alcohol bath.

**Impregnation:** The process is necessary to seal the open porosity of the specimen so that abrasives, water and etchants are not entrapped later on. If the specimen is not moisture free, ‘bleeding out’ during etching may occur which causes staining of the surface. Vacuum impregnation is carried out with epoxy resin.

**Regrinding:** After impregnation, regrinding is carried out on 500 and 1000 grit silicon carbide paper.

**Polishing:** This operation is generally carried out with 6, 3 and 1 µm diamond polishing spray on an automatic wheel using a load of 90, 60 and 30 N for one minute each. Polishing on a cloth with a suspension of alumina may also be carried out. In unetched condition total porosity, pore size and shape, nonmetallic inclusions, additions like manganese sulphide for improved machinability, undissolved alloying elements, etc., may be observed.

**Etching:** Etching is generally performed by immersion. This facilitates study of homogeneity of alloying, grain size and the presence of different phases.

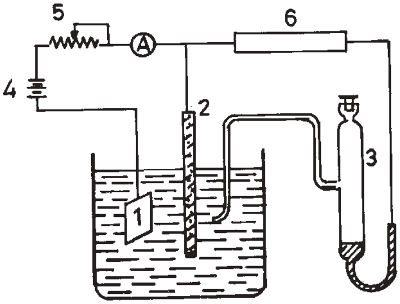


**Fig. 10.4** Schematic diagram of apparatus for measuring polarization.[13]

Various metallographic atlases[1,4–6] are available for comparing the sintered alloy's microstructures.

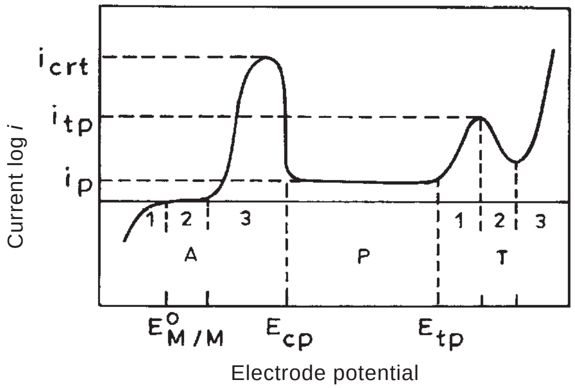
## 10.9 Corrosion Resistance

All corrosion consists essentially of reactions between a solid phase and its environment.

One of the most popular test methods for corrosion study is the weight loss method where the weight of the specimen is semi-continuously recorded when corroding in a test solution. This method is, however, not applicable when testing passive alloys, say stainless steels, as the degree of weight loss is near the vanishing point.

Another method consists of measuring and interpreting polarization curves. The specimen to be investigated (2) is connected as electrode into an electrolytic circuit together with a platinum electrodes (1) (Fig.10.4). The solution usually contains N $H_2SO_4$ and has to be entirely free of oxygen or reducible ions. The idea is to change the potential of the specimen electrode from negative to positive values and in the same time to record both the electrode potential and the current density values. These operations are done with a potentiostat and from these measurements the polarization curve is constructed (Fig.10.5).

The polarization curve and the coordinate represent a kind of plot which describes the electrochemical activity, i.e. the corrosion behaviour of the material as a function of its potential in solution. All current values above the zero line represent anodic current densities, i.e. corrosion currents. Values below the zero line represent corresponding cathodic current densities, i.e. mainly the rate of hydrogen evolution on the material surface. At all potentials left from $E_R$ the current is cathodic, when the potential changes from $E_R$ to more positive values the metal turns anodic, i.e. it begins to dissolve with a rate proportional to the anodic current density. When the current density reaches the value of $i_p$ (passivation current density), it suddenly drops to extremely low values $i_{kp}$, which remains approximately constant through the passive region. Thus, the lower the passivation current density the easier



$E^{o}_{M/M}$ – Initial electrode potential
$E_{cp}$ – Potential for complete protection
$E_{tp}$ – Potential for start of transpassive range
$i_p$ – Current in passive state
$i_{tp}$ – Critical current for transpassive range
$i_{crt}$ – Critical current for attaining passivity

**Fig. 10.5** Typical polarization curve.[13]

the passivation of the metal and the lower the passive current density the more stable the passive state.

Figure 10.6 illustrates some polarization curves from 316L stainless steel sintered to different densities. It is clear that the higher the density the lower the passive current density but at the same time there are only small differences in the passivation current densities.

## 10.10 Quality Control of Sintered Products - Some Case Studies

Sintered products are often used to replace traditional metals for cost saving or technical improvement or ideally both. In either case it is necessary to quantify the service parameters in terms of physical, mechanical, and chemical properties. Moreover, while dealing with sintered products, one must emphasize the need for function awareness when specifying any material. Unfortunately, in powder metallurgy industry there is not much record of past failures which may help in selecting a material that will satisfactorily perform a particular function. To simplify the matter, the first thing is to define the function of the component and develop functional tests which will determine whether the part will do the job. This brings out the importance of differentiating between material tests and product tests. The former provides information about the properties of the material of a test piece in relation to its intended applications. The product tests, however, specifically check the immediate fitness for service of the product and the batch from which it has been drawn.

A detailed analysis of the quality control aspect has been reported by Upadhyaya[12] elsewhere.

Some factors which may handicap the quality of sintered products may be:

(1) Testing and inspection procedures which do not realistically reflect actual use situation, e.g. particle size yield in floor screening by vibroscreens vs. the laboratory routine screening.

(2) Arbitrary material substitution by the purchasing or manufacturing departments, without adequate engineering evaluation. This is very important in case of tool material selection for complex P/M parts.

(3) Crash design revisions to incorporate new features in existing designs with minimum tooling changes. Here a prototype development can help considerably in building up confidence.

(4) Failure to apply the same evaluation methods to purchased components or powders as are applied to internally manufactured ones.

(5) Failure to anticipate misapplication of the product by the user, for example in selecting the proper grade of cemented carbide for different cutting purposes.

(6) Too little consideration given to the wide variations in the physical and intellectual abilities of customers.

(7) Interpretation of the statistical quality control function as absolute quality assurance rather than a basis for action.

(8) Inadequate advice to the user of safety procedures related to the product. For example iron base metal powder sintered bearings are more suitable for higher loads and slower speeds than copper base bearings.

(9) The P/M process allows considerable cost variation if specific part requirements are not clear. Such a situation would consequently bring forth a considerable quality variation too. For widely different costs; there may be various reasons such as (1) revision of tolerance (2) difference in

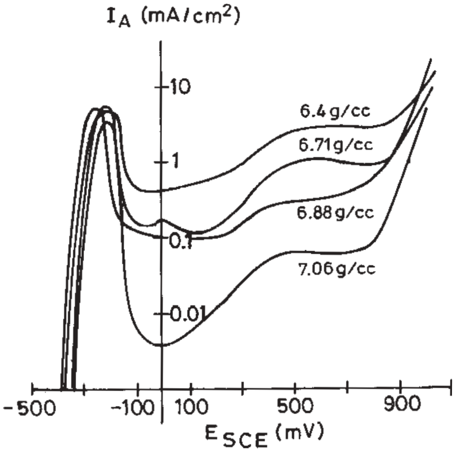


**Fig.10.6** Some polarization curves for sintered 316L stainless steel.[13]

manufacturing practices (3) introduction of supplementary processes such as repressing etc. and (4) lack of any specified minimum density. In brief, gross differences in quality may lead to a serious misunderstanding of requirements. A tendency for reduced manufacturing cost and increased short time profit is another handicap in P/M part quality.

In the following sections, the testing and quality control of some typical sintered parts have been described.

### *10.10.1 Filters*

For filters, the following functional performances are evaluated:

- geometric characteristics
- fluid permeability
- filtration threshold

While most tests of different porous P/M parts are similar, thus far no standard test fixture has been established in the industry. It is important for each test procedure to be worked out jointly between supplier and customer. Fluid permeability tests may be carried out with a simple instrument, for example the type shown schematically in Fig.10.7 which conforms to the MPIF standard 39–68. The filtration threshold is measured by the bubble test method, following the procedures of ISO standard 4003. Chemical composition of the filter material is an additional check, when there is onset of corrosion during operation.

### *10.10.2 Porous Bearings*

Porous bearings or self-lubricating bearings are those which retain a considerable amount of lubricant in their pores. This lubricant comes out of the pores and provides a film between shaft and bearing when the shaft

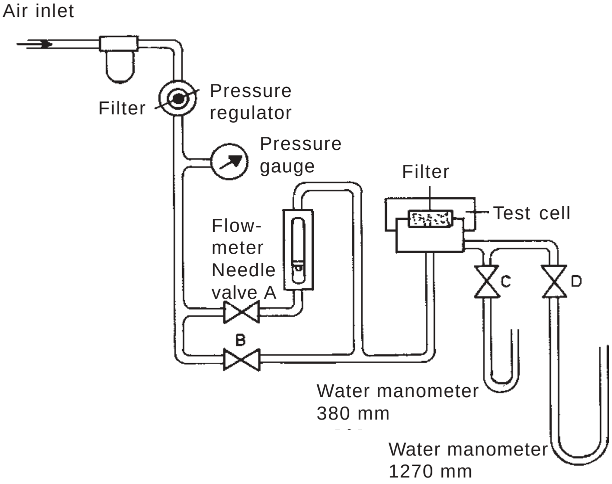


**Fig.10.7** Instrument for permeability control.[1]

begins to turn. The copper-base bearings having either a copper–tin bronze or a copper–tin–lead bronze composition may be considered for general purpose use. They are used where load on the projected area of the bearing does not exceed 58.6 MN/$m^2$ and velocities are medium or high. Iron-base metal powder sintered bearings are supplied in a variety of compositions, such as plain iron, iron–carbon and iron–copper. They are more suitable for higher loads and slower speeds than copper-base bearings. They are not as corrosion resistant as bronze bearings and require more lubrications. The major material properties to be specified in the case of porous bearings are adequate porosity, pore size distribution and adequate strength. The quality of oil is also an important factor, since it affects the performance of the bearing more than the material of which it is made. Porosity in terms of interconnected void space should not be less than 18% in case of such bearings. In addition, radial crushing strength should not be less than the value calculated by:

$$P = \frac{KLT^2}{D - T}$$

where $P$ is the radial crushing load, kg; $K$ is the strength constant for the grade and type specified; $L$ is the length of the bearing, cm; $T$ is the wall thickness of the bearing, cm; $D$ is the outside diameter of the bearing, cm.

Radial crushing strength is determined by compressing the test specimens between two flat surfaces at a ‘no load’ speed of 2.5 mm/min the direction of the load being normal to the longitudinal axis of the specimen. The point at which the load drops due to the first cracks is considered the crushing strength. This test is applied to plain cylindrical bearings; flanged bearings are tested by cutting off the flange and compressing the two sections separately.

### *10.10.3 Structural Parts*

As an illustration component testing of some of the structural P/M parts is given below:[9]

(a) Baulk ring in automotive gear box – The test is done to determine bursting load. A typical burst load for a baulk ring is 1.5 tonnes at which there is an adequate safety margin for actual service.

(b) Timing-chain sprocket – Such sprockets are used to drive the chain which conveys motion from an engine crankshaft to the camshaft. The test comprises loading an individual tooth and measure the torque to cause failure.

(c) Bevel gear – The gear is placed in mesh with a solid fixed gear in the jig and 2.7 kg (6 lb) weight is dropped from a height of 230 mm on to a collar which is located into the root of one of the bevel gear teeth. The teeth around the gear, which can be checked individually, must withstand this impact of 6 Nm without breaking.

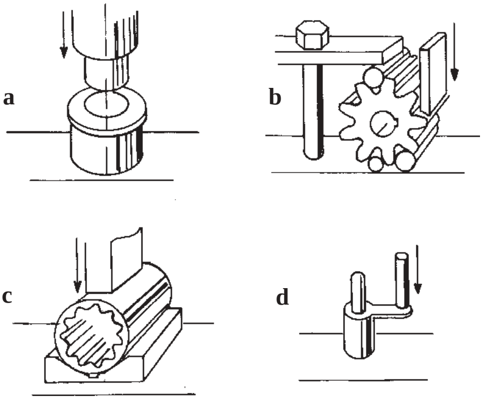


**Fig.10.8** Some typical breaking test modes for (a) cup type component; (b) gear; (c) tubular component; (d) lever type component.[14]

(d) Car seat belt latch and cog – In this test, the latch and cog are placed in the jig and subjected to a torque load of 135.6 Nm.

(e) Differential Pinion – Eloff and Wilcox[7] described in detail the impact fatigue and differential fatigue testings for differential pinions. In the impact fatigue testing a 90 N hammer is dropped onto the striker initially from a height of 15 cm. For each successive blow, the drop height is increased by 2.54 cm until failure occurs. While the data from the type of test was somewhat difficult to treat statistically, the advantage of this test is that only a few blows (less than 50%) were required to fail the pinion. Differential fatigue testing differs from impact fatigue testing in that it is primarily a running test and during each revolution of the pinion member, all possible loading positions are encountered. Consequently, by maintaining constant applied torque to the differential gear set, the maximum bending stress in the root fillet of a pinion tooth is always obtained and the test becomes insensitive to tooth load height position. One major disadvantage of the method is, however, that two pinion members and side gear members are required to make up the differential assembly for one test.

Figure 10.8 (a–d) illustrates some examples for the structural part testing fixtures.[14]

### *10.10.4 Cemented Carbides*

There is a large extent of ignorance on the part of customers of cemented carbides as to what in fact they really need. The customer of cemented carbides are interested in ‘service’. Most of the properties measured are those which, assist in controlling the quality of hard metal during manufacture, for example, hardness, density, transverse rupture strength, coercive force etc. However, the direct relationship of these properties with application of these hard metal is still far distant. Basically, there are three major difficulties in the evaluation of hard metals.[10] The causes of such difficulties are:

(a) The material is basically brittle which introduces a psychological barrier in the mind of designers. The very first question arises as how to measure brittleness. No notch test or impact test is of any value because they lack sensitivity for this type of material. The transverse rupture test is too, not very accurate for hardmetal owing to the very high scatter experienced in the results of such a test.

(b) The materials are applied in extreme conditions of temperature, pressure or time. These are difficult to describe and investigate.

(c) In the case of light machining applications wear resistance could roughly be related to hardness. Wear in case of hard metal is rather a collective term, which signifies such categories like erosion, frittering, oxidation, corrosion, and the most important of all – diffusion wear. In other words to measure wear resistance in hard metals as a ‘single’ property is at present an impossible proposition.

## References

1. E. Mosca, Powder Metallurgy Criteria for design and inspection, Mechanical Metallurgical and Allied Manufactures Association, Turin (Italy), 1984, p.67.
2. R. Haynes, The mechanical behaviour of sintered metals, Freund Publishing House, London, 1981.
3. W.Schatt, Pulvermetallurgie, Sinter und Verbundwerkstoffe, 2nd Edition, VEB Deutscher Verlag Fur Grundsstoff- industrie, Leipzig, 1985.
4. W.J. Huppmann and K. Dalal, Metallographic Atlas of Powder Metallurgy, Verlag Schmid Gmbh, Freiburg, 1986.
5. James Marsden, In ‘Source Book on Powder Metallurgy, Ed. S. Bradbury, ASM International Materials Park, OH, 1979, p.403.
6. A. Stosuy, ibid, p 419.
7. P.C. Eloff and L.E. Wilcox, Ibid, p.298.
8. Materials Standards for P/M Structural Parts’, (MPIF Standard 35), 1984–85 Edition, Metal Powder Industries Federation, Princeton.
9. J.W. Lennox, *Powder Metallurgy*, 19, No.2, 1976, 96.
10. E. Lardner, *Powder Metallurgy*, 19, No.2, 1976, 104.
11. T.M. Cadle, *Powder Metallurgy*, 19, No.2, 1976, 89.
12. G.S. Upadhyaya, *Indian Standards Institution Bulletin*, Vol.29, No.1, 1977, 354–56.
13. I.A. White, In ‘Stainless Steel P/M Seminar’, Michigan, February, 1965, Hoganas Corporation, Riverton, p.47.
14. Hoganas Iron Powder Handbook, Hoganas AB, Sweden, 1957.

# Index