

# Powder Metallurgy and Sintered Materials

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### 1. Introduction

Powder metallurgy (PM) as a generic term includes all techniques to produce solid-metal-based products from powders. This involves powder production (for which numerous routes are available), subsequent treatment, and conditioning of the powders, one or more consolidation steps involving application of pressure and temperature (either jointly or in subsequent stages), and a multitude of secondary treatments which can be similar to those applied to wrought metallic products or specific for powder metallurgy [1, 2].

The various production routes are depicted in Figure 1. Numerous options exist to obtain metallic bodies from powders, and a wide variety of products are manufactured through PM today from a wide range of materials [3]. The principal production lines are uniaxial die compaction and sintering as well as metal injection molding (MIM), but the highest growth rates are observed with additive manufacturing, particularly, in its direct variant.

Compared to ingot metallurgy (→ Steel, 2. Crude Steel Production, Chap. 5, Casting and Solidification), the total tonnage of PM products is low; but the added value in PM is typically significantly higher. PM manufacturing is chosen for two groups of products, PM materials and shaped PM components.

For PM materials, the PM route is the best route to obtain products with specific properties. Typical examples are the WC–Co hard metals, which is the PM single product group with the highest turnover; porous self-lubricating bearings, which are inaccessible by classical ingot metallurgy; and refractory metals, which can be produced by ingot metallurgy but with microstructure and properties inferior to those of the equivalent PM products. For the latter, the material and its properties are the main reason for choosing the PM route, and the shape of the product is of secondary importance. PM materials have often simple shapes, such as sheets or bars.

For shaped PM components, complex geometrical shape and precision are the primary

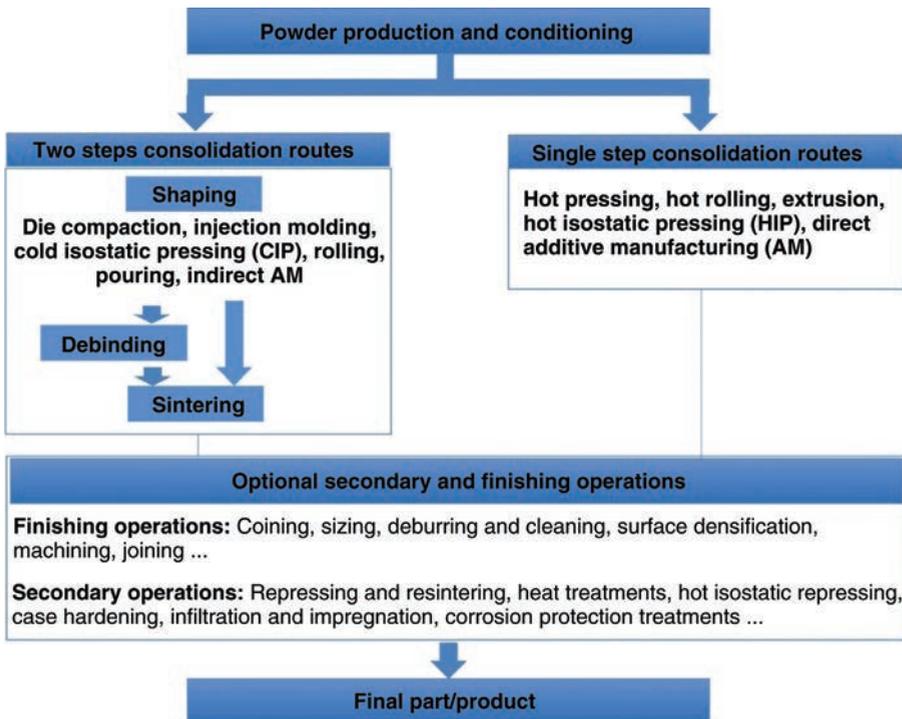


Figure 1. Powder metallurgy production routes

requirements (see, e.g., [4]), whereas some properties, especially mechanical properties, can be inferior to those of, e.g., wrought and machined parts. The main benefit of PM is economical: For large production runs of precision components, PM is frequently more cost-effective than classical metalworking techniques. Its lower material and energy utilization makes PM a “green” technology. Typical examples of PM produced parts are automotive components, especially from engines and transmissions, produced by the press-and-sinter route. Also, for shaped specimens produced by MIM or additive manufacturing, PM offers the chance to overcome shape limitations that hold for other metalworking routes.

### 1.1. Historical Background

Powder metallurgy is usually regarded as a modern metalworking technique, and its main development started in the early 20th century [4, 5]. However, for many centuries, at least until the late middle ages, iron could not be melted, and therefore all iron-based products were obtained by solid-state metallurgy [6, 7], in a variant that was similar to modern powder forging. Reduction of iron ore with charcoal in a bloomery furnace resulted in a porous lump of iron, consisting of metallic particles sintered together and containing slag and coal particles. This lump subsequently had to be hot-worked by the blacksmith to obtain a fully dense metallic product with sufficient strength to be used as a tool or a weapon. Virtually all the elaborate arms and armor displayed in museums have thus been produced by a sort of “powder forging” technique. A particularly spectacular and impressive example of this early technology is the famous Delhi pillar, a column about seven meters tall and weighing six tons, which has been manufactured in the 5th century A.D. [8].

With the emergence of the coke-fired furnace in the 18th century, with much higher output than the old bloomery furnaces, ingot metallurgy dominated, and powder techniques went into oblivion, with some exceptions such as the platinum rouble produced in Russia in the early 19th century. Modern powder metallurgy started with the emergence of the incandescent

lamp with its metal filament; the first osmium wires were produced by C. AUER VON WELSBACH, and they were successfully implemented in large-scale production, by W.D. COOLIDGE who developed the tungsten filament in 1908 [9] (→ Lamps). At that time, melting of W was virtually impossible, and powder metallurgy was the only way to obtain W rods that could be swaged and then drawn to filaments. Through the powder route, also the doping elements were introduced that granted the “non-sag” behavior required for sufficient filament life [10].

The W filament design resulted in another invention highly relevant to PM. The need for drawing dies prompted studies into hard, wear-resistant materials such as carbides. However, the products obtained were too brittle until in 1923 SCHRÖTER and SKAUPY in Berlin combined tungsten carbide with metals of the iron group, particularly cobalt, and sintered it at a temperature at which the metallic binder melted, thus producing the first hard metal [11]. The second innovation by them was the synthesis of the tungsten carbide through solid-state chemistry: They were able to precisely adjust the carbon content to obtain the hexagonal WC phase. A further breakthrough that revolutionized machining was the introduction of hard metal cutting tools by F. KRUPP, Essen, under the brand name Widia, which prompted intense research both on the classical hard metal and such containing also cubic carbides. Further innovations in the hard metal sector were the TiCN-based grades known as cermets and the ultrafine grades which offered improved performance, especially in metal cutting, but also enabled manufacturing of microdrills for electronics, with diameters  $<100\ \mu\text{m}$  [12]. For metal cutting, ceramic coatings were introduced in the 1970s, which greatly improved the productivity, with chemical and physical vapor deposition competing with regard to coating hardness, toughness, and adherence to the hard metal substrate and resulting tool life. For further information on hard metal history and production, see → Hard Materials, Chap. 3. Metallic Hard Materials (Cemented Carbides).

Already in the 1920s, porous self-lubricating bearings were developed that could be impregnated with lubricant, thus enabling maintenance-free operation.

The shaping capabilities of the PM press-and-sinter route, particularly for the large-scale production of precision parts, were recognized in the 1930s when oil-pump gears for cars were made by PM in the United States. Production of multilevel PM parts for firearms was started in Germany during World War II, adapting compacting techniques known for ceramic components to metallic powders [13]. After the war, the demand for automotive applications soared, as did the complexity of the parts produced. Higher requirements towards mechanical performance were met by, e.g., the introduction of special alloyed grades, such as steels prepared from Ni–Cu–Mo diffusion-bonded powders [14] or, later, by Cr and Cr–Mo alloyed types, by combining sintering and heat treatment in the “sinter hardening” process and by locally densifying the porous structure, which process proved to be highly successful especially for gears [15]. For dynamically and/or cyclically loaded components, powder forging, i.e., impact hot consolidation of a porous sintered preform [16], proved to be attractive, e.g., for automotive conrods [17].

The limitations of uniaxial die compaction were overcome by introducing the metal injection molding (MIM) technology in the 1980s. This process combines the shape flexibility of polymer injection molding with the material flexibility of PM [18, 19]. MIM has seen significant growth rates since the 1990s, also because of the moderate investment required for setting up a production line.

The newest PM production route is additive manufacturing (earlier also known as “rapid prototyping”), i.e., the production of complex-shaped specimens from powders by local joining [20]. Two groups of methods can be distinguished, the direct and the indirect ones. In the direct methods, a powder bed is locally melted by a laser or an electron beam to form a solid body. In the indirect methods, an organic binder is used to bond the particles locally together, after which the binder is removed and the assembly is sintered. Both variants have been known since the 1990s, but the direct methods have grown tremendously in importance since ca. 2010, with a resulting increase in powder consumption.

Powder metallurgy, as a particulate technology, will prevail for the production of functional



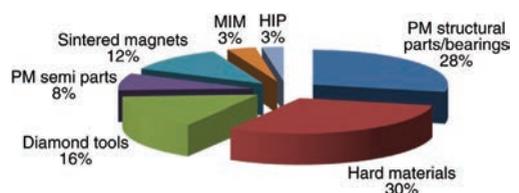
**Figure 2.** European PM production by tonnage (EPMA) in 2016 (total:  $248 \times 10^3$  t)

materials, especially for electrical and electronics applications, such as batteries, capacitors, etc. This will result in a shift from the “shape” aspect of PM to the “material” aspect, although the net-shape capabilities of PM will remain an important asset.

## 1.2. Economic Aspects

PM is a niche technology regarding total tonnage produced. The major tonnage consists of ferrous parts produced by uniaxial die compaction and sintering (Fig. 2), which consume slightly less than  $1 \times 10^6$  t of iron and steel powders annually worldwide [21], as compared to about  $1.6 \times 10^9$  t of crude steel produced through the liquid-metal route [22]. The PM ferrous parts generate an annual turnover of an estimated  $15 \times 10^9$  \$ worldwide. There is a strong dependence on the automotive industry because about 75% of the parts produced end up in cars, especially as components in internal combustion engines and transmissions (e.g., [23]). With regard to the expected changes in car drive systems towards hybrid and electric cars, the PM partsmakers are under considerable pressure to find applications for PM products also in the new car drives.

Regarding turnover, the dominating PM products are hard metal (Fig. 3), generating



**Figure 3.** European PM production by turnover (EPMA) in 2016 (total:  $10.9 \times 10^9$  €)

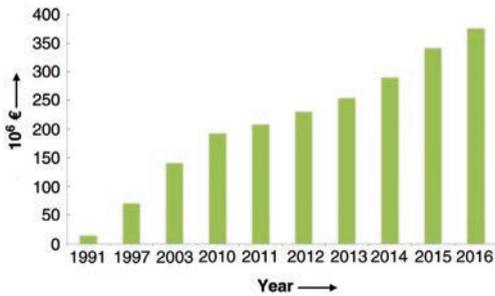


Figure 4. Growth of MIM market in Europe (EPMA)

an estimated turnover of about  $18 \times 10^9$  \$ at an annual tonnage of 75 000 t [12]. Here, metal and wood cutting, rock drilling, and construction are main areas of application. The use of strategic elements such as W and Co occasionally raises environmental concerns towards excessive mining; therefore, systematic recycling of spent tools is proposed.

MIM has encountered stable growth rates since the 1990s [24] (Fig. 4), in part owing to the wide range of applications, from automotive to medical, which make MIM parts less sensitive to economic cycles than pressed and sintered parts. The market is estimated to be about  $1.15\text{--}1.4 \times 10^9$  \$/a [25].

Additive manufacturing has encountered higher growth rates, although from a lower basis. This can be discerned from the numbers of AM equipment sold and in operation (Fig. 5). Medical applications are growing, and the aerospace industry is moving towards the production of components by additive manufacturing, mainly as a consequence of weight reduction possible by employing the unique shaping capabilities of additive manufacturing.

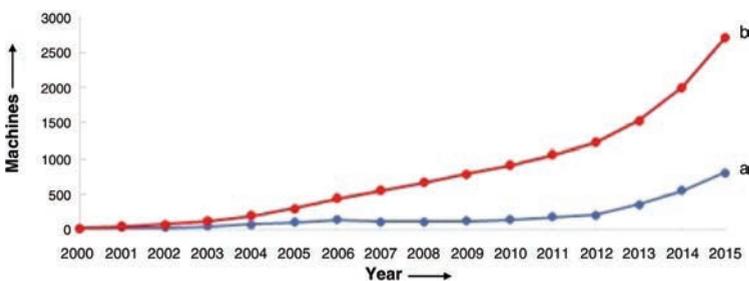


Figure 5. Additive manufacturing (AM) machines sold (a) and in operation (b) worldwide (EPMA)

## 2. Powder Production

The production of powders for PM products can be divided into mechanical and chemical methods. The final properties and the price are strongly dependent on the raw-material cost, the production method (large scale vs. small scale), particle shape, size and distribution, impurities, and oxygen sensitivity [1, 26, 27].

### 2.1. Mechanical Methods

Disintegration of solids (without phase change) and liquids (with phase change) can be applied to produce metal powder.

#### 2.1.1. Disintegration without Phase Change

The production of fine chips by machining techniques such as milling or turning is one of the easiest ways to produce powder, but also one of the most expensive ones because the productivity of these processes is relatively low and the danger of contamination is high. Therefore, it is applied only for producing extremely expensive materials and for special purposes.

**Milling.** The classical approach to break down brittle material is milling in ball mills. The material is stressed by the impact, compression, and shearing of the hard balls, and finally is disintegrated into smaller particles. Brittle materials are more responsive to disintegration, whereas ductile metals respond more to cold welding. The average particle size for most metals produced by milling is  $>100 \mu\text{m}$ , and the average particle size approaches a constant value depending on the ductility of the powder and the processing conditions (especially

temperature). Brittle ceramics or metals may give particle sizes of  $<1\ \mu\text{m}$ . Typical mills are tumbling ball mills, vibratory mills, and attritors [28].

Jet mills are based on the rotating motion of a particle-loaded gas stream at high speed in a round chamber. The high-velocity collision of the particles leads to fragmentation, and the small particles are removed in the center of the chamber whereas large particles are retained in the stream until the desired particle size is reached. The biggest advantage is that the incorporation of impurities is limited because of the absence of milling aids (balls etc.).

The high-energy milling processes such as attritor milling usually require processing in liquids (e.g., 2-propanol) as the temperature management must be improved. This high-energy milling allows refining of the microstructure by frequent fracture and rewelding of the powders, and finally can be used for mechanical alloying, by milling of mixtures of different elemental powders, or the introduction of homogeneous dispersions of fine hard particles ( $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ ) into a metal matrix.

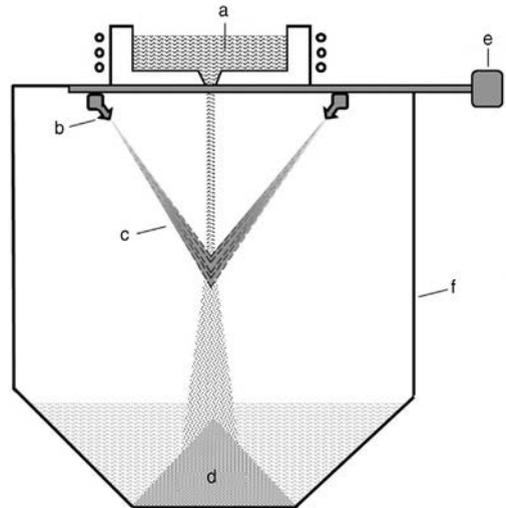
As milling is an energy-intensive process, the costs are high, and the risk of impurities incorporated by wear of the mill and balls is high as well. Therefore, the process is only used if no other large-scale production route for powders is available, as secondary process to obtain defined particle-size distributions, or to break down agglomerates generated by other processes.

The milling process finally leads to an increase of the dislocation density up to  $10^{15}\ \text{m}^{-2}$  and, therefore, reduces the compactibility. In most cases, subsequent heat treatment is necessary to soft-anneal the powders before use.

### 2.1.2. Disintegration with Phase Change

Liquids can be disintegrated by using gases, water, oil, or mechanical dispersion.

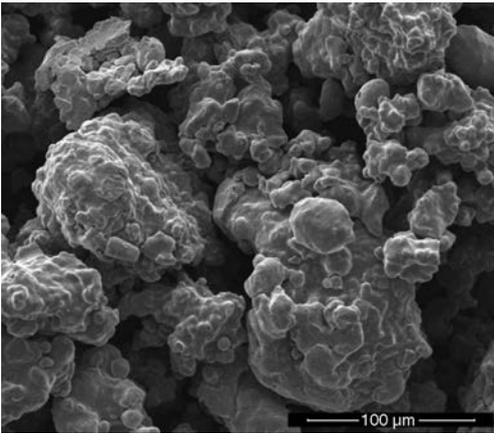
**Atomization.** The water jet process is the most modern and productive way (up to 50 t per batch) to obtain metal powders for PM parts production. Most worldwide shipments of iron and steel powders are produced by the water-atomization technique. The principle of water



**Figure 6.** Principal arrangement of a water atomizer  
a) Melt; b) Jet; c) Water spray; d) Powder; e) Pressure source; f) Chamber

atomization is to disintegrate a free-falling melt stream, supplied from a nozzle in a tundish, by water jets (Fig. 6). The disintegrated melt solidifies immediately, and the surface oxidizes. The powder–water slurry is collected, dried, and subsequently reduced with hydrogen. The freshly reduced powder will slightly sinter to form a sort of cake that is mildly milled before the final treatment of the powders (magnetic separation, screening, and equalizing). The method can be used to produce iron and steel powders (alloyed with Mo, Ni, or Cr), stainless-steel powders, copper, and copper alloys.

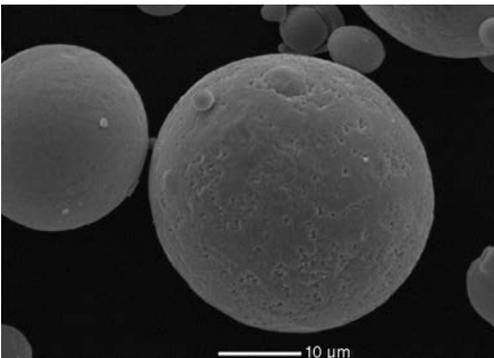
The final powders have an irregular shape that provides good green strength by interlocking of the particles (Fig. 7). The process involves many variables: the temperature and the amount of superheat of the molten material (related to the composition), the water-to-metal ratio (10–15 L per 1 kg of produced powder), the diameter of the molten-metal stream, the geometry of the nozzle (amount of water jets and angle of incidence between water jet and molten metal stream), and the water pressure. The usual pressure of the water jets ( $<15\ \text{MPa}$ ) results in particle sizes of 30–100  $\mu\text{m}$ . High pressure (up to 60 MPa) or special methods are used to produce particle sizes between 3 and 30  $\mu\text{m}$ . The importance of these methods has increased since ca. 2000 because the growing



**Figure 7.** Typical water-atomized powder (ASC 100.29, Höganäs AB)

MIM and additive techniques demand fine powders at acceptable cost [29–31].

Atomization by inert gases is used to produce powders from oxygen-sensitive elements if water atomization is not applicable because of the reactivity of the metals. The typical shape of gas-atomized powders is spherical (Fig. 8), which is needed for applications where high bulk densities and flow rates are required (hot isostatic compaction, MIM, additive manufacturing). The slower cooling rate of 1000 K/s than that of water atomization, in which case 10 000 K/s is possible, allows the droplets to form spheres before solidification. As the energy input of the gas is much lower compared to that of water, the production of fine particles requires special techniques, e.g., by special



**Figure 8.** Typical gas-atomized powder (Böhler S390)

nozzles that allow extremely high gas speeds [32]. Today, the most frequently used gas for atomization is nitrogen, although this gas is, in contrast to argon, not entirely inert. However, the insolubility of argon in metals may lead to porous or hollow spheres which are a drawback because Ar-filled pores cannot be closed at a later stage. In some cases, also air can be used as an atomizing agent, e.g., for aluminum and its alloys (up to the 1980s also for iron and steel).

Oil (also kerosene is reported) atomization requires special safety measures. It has the advantage that the oxidation of the powder surfaces, which is inherent with water atomization, can be avoided, although some carbon pickup may occur.

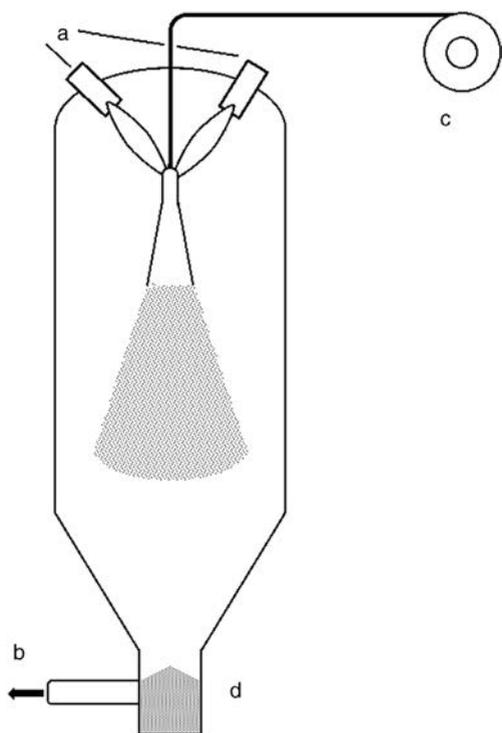
**Special Atomizing Techniques.** Some materials such as titanium and Ti alloys require techniques where the molten metal must not interact with crucibles. The fragmentation by centrifugal forces from a rotating electrode is used to disintegrate the material without contact to a nozzle. The melting of the material is performed by an electric arc or plasma torch on the front surface of the rotating electrode. The centrifugal forces and slow melt supply lead to fine powders with highest purity as the process is performed in argon. The drawback is the low productivity of these methods. The increasing demand for titanium and Ti alloys with highest quality led to plasma atomization in which a metal wire or ingot is introduced into the atomization chamber and molten at the front face by a plasma torch; an argon stream disintegrates the liquid material (Fig. 9).

Inductively coupled plasma methods are also used to transform crushed, atomized, and sponged powders into pore-free spherical powders.

## 2.2. Chemical Methods

### 2.2.1. Reduction with Solids

The classical method of metal powder production is ore reduction (already performed in the early iron age (→ Iron, 1. Fundamentals and Principles of Reduction Processes; → Iron, 2. Blast Furnace Process; → Iron, 4. Smelting Reduction Processes). The starting product is purified iron ore (magnetite,  $\text{Fe}_3\text{O}_4$ ). The

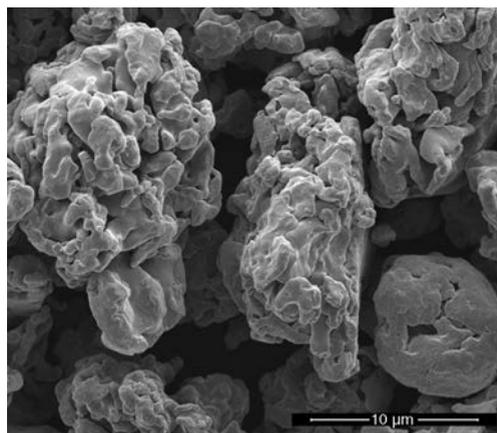


**Figure 9.** Principle of plasma atomization  
a) Plasma torches; b) Vacuum pump; c) Titanium spool; d) Powder collection

milling of this material to fine powders is easy thanks to its brittleness. The material is filled into SiC tubes in close contact to a mixture of coke and limestone (to bond the sulfur from the coke) and then heated to 1200°C in a long (ca. 260 m) kiln furnace. The final reducing agent is carbon monoxide, which reduces the ore to an iron sponge. The sponge is then crushed and screened. A final heat treatment in hydrogen to remove the residual oxygen leads to sponge iron powder with the desired particle size of 40–150 μm. The most pronounced feature of this powder is the internal porosity of the particles, therefore the designation “sponge iron powder” (Fig. 10).

### 2.2.2. Reduction with Gases

For the reduction of ores for which carbon cannot be used because the final carbon content should be extremely low, usually hydrogen is

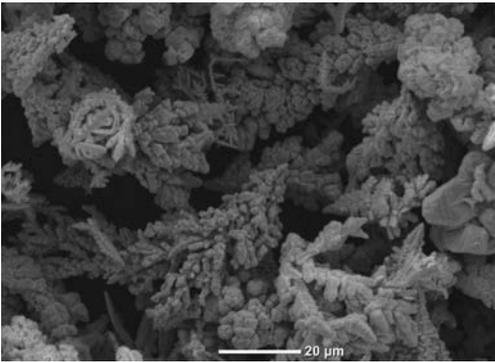


**Figure 10.** Typical sponge-iron powder (NC 100.24, Höganäs AB)

used as reducing agent (→ Nickel, Section 6.4 Hydrogen Reduction to Nickel Powder; → Cobalt and Cobalt Compounds, 5. Cobalt Powders). For iron, this process (Pyron process) is usually economically not competitive; however, it is an easy way for laboratory use. Reduction by hydrogen is the standard process for the production of tungsten and molybdenum from  $\text{WO}_3$  and  $\text{MoO}_3$  (→ Tungsten, Tungsten Alloys, and Tungsten Compounds; → Molybdenum and Molybdenum Compounds, Section 4.5 Production of Molybdenum Metal Powder). Especially for W powders, the powder size can be defined by the height of the  $\text{WO}_3$  bed in the boat. Low filling height leads to extremely fine powder.  $\text{MoO}_3$  is usually reduced in two steps [32, 33]. Ni and Co powders can be reduced from aqueous solutions with pressurized  $\text{H}_2$ .

### 2.2.3. Electrochemical Reduction

The production by electrolysis from aqueous solutions is applicable for copper, iron, nickel, and cobalt (→ Nickel, Section 6.1. Electrorefining), and, due to hydrogen overvoltage, also for Cr and Mn. The process includes the dissolution from the anode and precipitation at the cathode. The particle size, size distribution, and shape are determined by the electrical current density, the temperature, concentration, acidity, and the bath movement. Usually, dendritic powders are desired (Fig. 11). Since the process can



**Figure 11.** Typical electrolytic-copper powder (Cu FM)

also be regarded as a purifying electrolysis, the powders obtained are very clean. The final step is mild grinding and annealing of the powder to remove the strain hardening for sufficient compressibility.

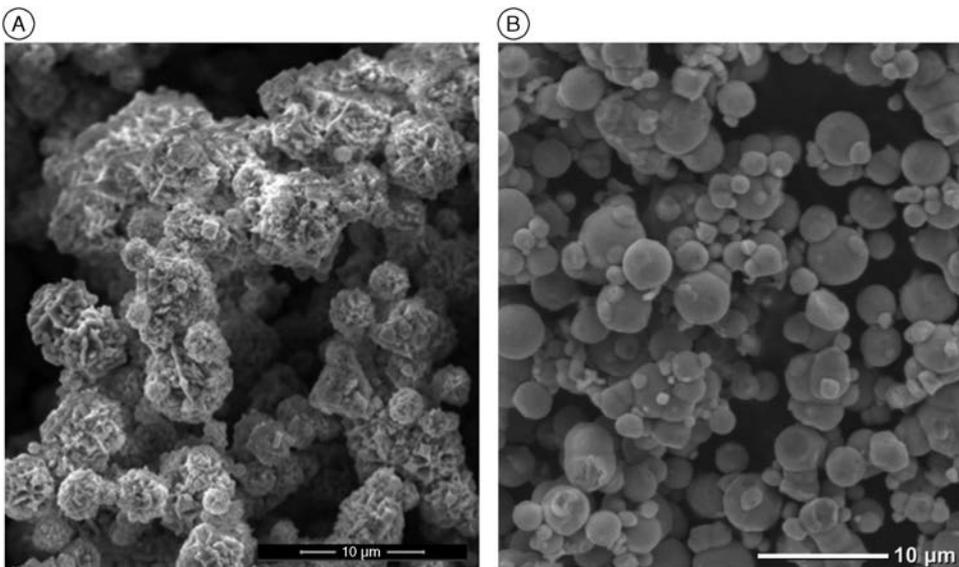
#### 2.2.4. Decomposition of Gases

The carbonyl method is mainly used to produce fine iron and nickel powders (→ Nickel, Section 6.3. Carbonyl Refining). The carbonyls are produced by reaction of

scrap (e.g., Ni-containing Fe alloy) with CO at high pressure (30 MPa) and temperature (200–250°C). The liquid carbonyls are distilled and decomposed at the same pressure range to form mostly fine spherical powder. Ni powders usually have irregular surface compared to Fe powders (Fig. 12). The iron powders incorporate some carbon; to get C-free grades decarburizing anneal is necessary. The powders produced have usually very low contents of metallic impurities. Although the process is energy consuming and involves hazardous chemicals, it is the main production route for Ni powder and iron if the market tolerates high prices for fine powders (MIM).

#### 2.2.5. Reaction with Solids (Carbides)

Carbides (→ Carbides, Chap. 2 Metal-like Carbides of Industrial Importance; → Hard Materials, Chap. 3. Metallic Hard Materials (Cemented Carbides)) as the major raw material for cemented carbides are usually produced by reaction with carbon (soot). WC is produced by intense mixing of tungsten powder with desired particle size (0.5–5 μm) and carbon and subsequent reactive anneal in hydrogen in graphite tube furnaces at 1400–2000°C [34].



**Figure 12.** Typical carbonyl-metal powder  
A) Nickel; B) Iron

TiC, NbC and TaC are produced by direct reduction and carburization from their oxides ( $\text{TiO}_2$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_3$ ) in vacuum at 1700–2300°C. The reaction products are milled to powder in ball mills [35].

### 2.3. Powder Characterization

The different applications for metal powders require the appropriate characterization of physical, chemical, and technological properties.

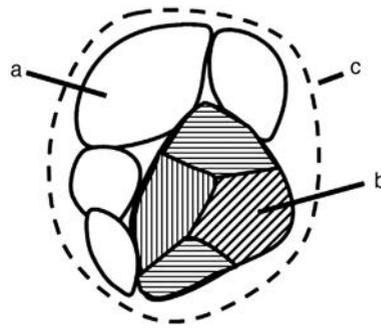
#### 2.3.1. Physical Properties

**Particle-size determination** means the determination of the dimensions of the particle. The determined size depends strongly on the measurement technique, the specific parameter measured, and the particle shape. Different definitions are used. The most important ones are:

- The sieve diameter, which is the width of the minimum square aperture through which the particle will pass in sieve analysis.
- The projected area diameter, which is the diameter of a circle having the same projected area as the particle in random orientation

The most common technique for size determination is laser diffraction, which provides the projected area diameter. The exact size can only be determined by light and scanning electron microscopy.

Most atomization techniques for metal powder provide Gaussian distributions with a linear relationship between the particle size and the cumulative mass fraction if the data are plotted on logarithmic normal probability coordinates [29]. The simplest way for determination of size distribution is sieving in a sieve column with a mesh that decreases from top to the bottom. The method is limited to powders  $>30\ \mu\text{m}$ . For smaller particles, air classification methods can be used. One standard method is to use light scattering by laser diffraction; here, the projected area diameter will be measured. Also, the Fisher sub-size sieve (FSSS) is still a common technique, although the method does not measure any size but a surface area [36]. The



**Figure 13.** Definition of measured entities  
a) Particle; b) Grain; c) Agglomerate

method is based on a pressure drop of a gas passing through a slightly compacted powder bed. Generally, the results obtained differ from method to method.

In most techniques, a spherical or at least equiaxed particle shape is assumed, which means that the interpretation of the results becomes difficult if the particle shape becomes more complex. The shape has eminent influence on the behavior of the powder. EN ISO 3252 [37] describes nine different shapes (acicular, angular, dendritic, fibrous, flaky, granular, irregular, nodular, spheroidal). Furthermore, it is distinguished between “particle,” “grain,” and “agglomerate” (Fig. 13).

#### 2.3.2. Chemical Properties

Two groups of powders are considered with respect to chemical composition. For *elemental powders*, which are usually relatively high-purity materials, chemical analysis concentrates on the impurity content. For prealloyed variants, further attention is given to the alloy composition. For both types of powders, the analysis can be divided into three categories:

1. *Bulk analysis* gives the general chemical composition of the powder. Inductively coupled plasma optical emission or mass spectrometry (ICP–OES, ICP–MS), atomic absorption spectrometry (AAS), and X-ray fluorescence spectrometry (XRF) are used to determine the main constituents and the impurities. If information on the phase distribution is required, X-ray powder diffraction (XRD) is used; if the structural analysis

is performed on the microscale, electron back-scattered diffraction (EBSD) is performed. For interstitial elements such as carbon, hydrogen, nitrogen, and oxygen, special inert-gas fusion and combustion techniques are available.

2. *Surface Analysis*: The large surface area of fine powders requires special techniques to determine the surface composition, which influences the behavior of the powder significantly. X-ray photoelectron spectroscopy (XPS) gives information about the surface composition. Auger electron spectroscopy (AES) provides information about elemental distribution in the first few layers. For microanalysis of surfaces and sections of powders, scanning electron microscopy (SEM) combined with energy dispersive X-ray spectrometry (SEM-EDX) is often used.

### 2.3.3. Technological Properties

The most important technological properties of powders are flow behavior, apparent (bulk) density, compressibility. These properties are usually tested using by methods defined by ISO or ASTM standards.

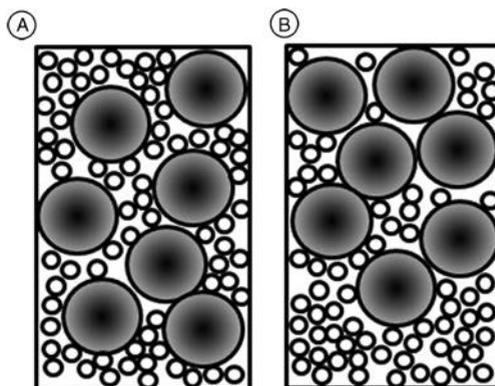
*Flowability*: The method is described in ISO 4490 [38]. The method uses the Hall flowmeter (which is a funnel with 2.5 mm orifice and an opening angle of 60°) and measures the time needed for 50 g of powder to flow through the orifice.

*Apparent density*: The method is described in ISO 3923 part 1 [39]. It measures the mass of powder that has freely flowed through the Hall funnel into a container (25 cm<sup>3</sup>) divided by the volume of a container (25 cm<sup>3</sup>) after removing the excess powder.

Typical values are shown in Table 1. Both apparent density and flow rate are influenced by lubricants and may be used as an indicator for

**Table 1.** Apparent density and flowability of different powder grades

	Apparent density, g/cm <sup>3</sup>	Flow, s/50 g
Spherical (stainless steel)	4–4.5	13–15
Sponge iron	2.3–2.65	29–32
Atomized	3	25



**Figure 14.** Powder mixture  
A) Before segregation; B) After motion-induced segregation

the filling rate and consequently the productivity of the filling process.

In particulate systems such as powder mixes, homogenizing motions equivalent to the molecular diffusion of gases and liquids do not exist. Therefore, the segregation of particles is a phenomenon that strongly influences the processing of the powders. Segregation phenomena in powder mixes are influenced by particle shapes and sizes. The induced movement leads to segregation of large particles, especially when the density of these particles is low, to the top of the mix (Fig. 14)

*Compactibility (compressibility)*: The method is described in ISO 3927 [ISO 3927]. It is characterized by the uniaxial compression of powder in a steel or hard metal die (cylindrical or rectangular) at different pressures (200–800 MPa) and subsequent measurement of the density of the resulting compact. This method is not applicable to powders for hard metals. The main factors that influence compressibility are:

- Compaction pressure
- Particle shape/size
- Particle porosity
- Lubricants/organics content
- Type and powder composition

Another important processing property of powder connected to compressibility is spring-back. It means the elastic (radial and axial)

expansion of a compact after ejection from the compacting die.

*Consistency:* For the serial production of large lots, the “consistency” of the delivered powders regarding all properties is of utmost importance. This means that only powder that provides the same quality in terms of all above cited properties over the entire production period (sometimes years) is applicable without massive adaptation of tooling and all consecutive processes. The consequence is that the major powder manufacturers have adapted their processes in a way that only “synthetic” powder is sold. This means that the produced powder batches are separated in terms of size, chemical composition etc. and then a blend of powder is produced from the fractions that allows the delivery of the same quality over the years. In general, consistency is the most important single property of all industrially used powders.

## 2.4. Conditioning

To proceed the desired composition of an alloy through the powder route, there are in principle five main alloying paths, which holds especially for sintered steels, as depicted in Figure 15 [40].

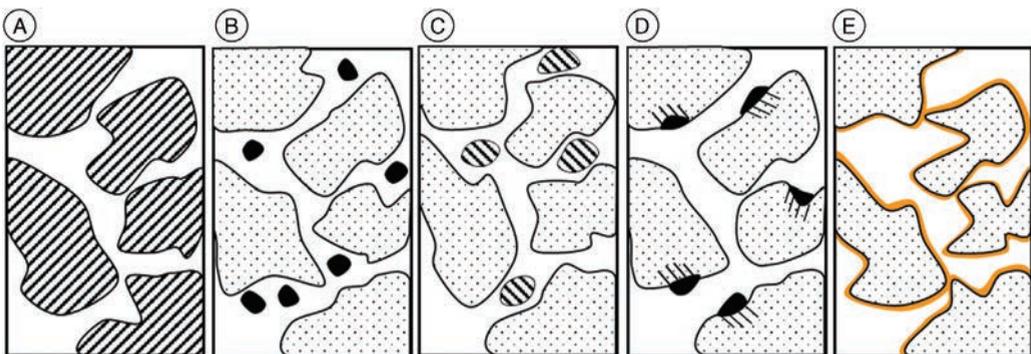
The use of fully prealloyed powders brings advantages in homogeneity but loss in compressibility due to solid-solution strengthening. The complementary attempt is to use mixes of plain powders which eliminates the strengthening effect but may cause risk of segregation and difficulties in alloy element homogeneity.

However, the latter may even be an advantage because it allows producing unique microstructures with defined heterogeneity. Master alloys may be used if the following points apply:

- Complex metallurgical reactions are hard to control
- The costs of elemental powders are extremely high
- The compressibility of the prealloyed variant would suffer too much

Diffusion bonding is extensively used when elemental powder mixes cause problems by segregation effects or health problems (free Ni) [14]. Coated powders offer even better alloy distribution, but are not so easy to produce except some systems (Fe–Cu).

**Milling, Annealing, and Classification.** Some production methods (chemical reduction of ores) provide metal powder cakes that require soft milling to obtain a suitable powder. Mechanical strain hardening during milling operations or uptake of oxygen and humidity during storage or delivery require softening or reduction treatments below the sintering temperature of the powder. Typical reduction temperatures in dry hydrogen for copper, nickel, and iron powder are 150, 650, and 700°C respectively [41]. Classification of the powders is necessary to obtain the desired properties (flowability, filling density, and sintering behavior). Especially, the removal of fine particle sizes in steel powder production is performed.



**Figure 15.** Alloy variants for sintered steels  
A) Prealloyed; B) Powder mixture; C) Master alloy; D) Diffusion bonded; E) Coated

**Addition of Binder and Pressing Aids.** The addition of binders and pressing aids (lubricants) is necessary to provide the desired compaction properties. For uniaxial die compaction, it is necessary to add pressing aids which reduce the friction between the die and the powders [42], to extend tool life, and reduce friction during ejection. Typically, stearates (EBS, Zn stearate or mixtures) are used for ferrous structural parts in contents <1%. For hard metals, paraffin waxes are used in much higher contents up to several weight percent. These paraffins are added in wet mixtures followed by spray drying to form granulates suitable for die compaction. If extrusion techniques are aimed at, the addition of up to 45 vol% of binders (e.g., waxes or different polymer blends) is needed to perform MIM or similar techniques.

**Blending** of powders is performed by dry mixing or mixing of suspensions. Typical blender types are double cones and tumblers. Statistical distribution is not easy to reach sometimes as differences between the powders in size, shape, density etc. can cause inhomogeneity. After mixing, the powders should be handled with special care because demixing can be caused by transport, vibration, or free falling. The ready-to-press mixes provided by the important powder suppliers are specially stabilized by organic additives to avoid these effects during transportation.

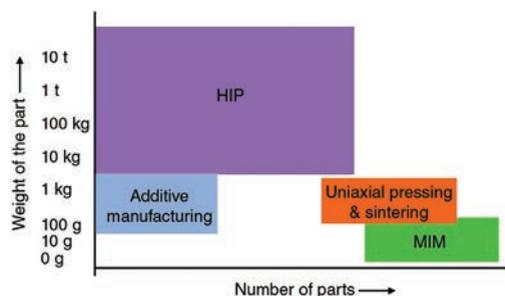
**Agglomeration and Granulation.** Fine powders (micrometer-sized) show inadequate flow behavior. Therefore, the powders are treated to adopt flowability to allow automatic die filling. Flowable powders for hard metals can be produced by agglomeration, spray drying, or granulation.

### 3. Shaping Technologies

Powder metallurgy comprises several processes to consolidate powders into a desired shape with a certain density level. The most common method for shaping PM parts is the uniaxial compaction in rigid dies (die compaction), a cost-effective technique very suitable for the production of large series. In compaction processes, densification and shaping occurs simultaneously, usually providing green compacts

with locally varying density. Densification gradients can be overcome to some extent by isostatic compaction (isostatic pressing) at ambient temperature (cold isostatic compaction, CIP; → Sintered Iron and Steel, 5. Cold Isostatic Pressing) or at elevated temperatures (hot isostatic compaction, HIP; → Sintered Iron and Steel, 6. Hot Isostatic Pressing). There is also the possibility to shape the powders at low pressures by mixing metallic powders with a polymer, and injecting such mix-named feedstock- into a mold (MIM). In some cases—as in the fabrication of filters—pressureless shaping technologies are used, by which the powders are simply poured into molds and sintered (“gravity sintering”). In this latter case, the density can be increased by vibration or during the subsequent sintering. More specific processes are powder forging, extrusion, and rolling. A quickly emerging field is additive manufacturing, which uses metallic powders to build 3D components by adding material layer by layer.

In general, uniaxial die compaction and MIM technologies are employed for large series of small parts, and HIP and additive manufacturing are more suitable for small or medium series (Fig. 16). Additive manufacturing provides great design freedom and is well suited for producing parts of a few grams up to a few kilograms, and HIP allows the production of massive near-net-shape parts. Besides, different techniques can be combined to reach a certain level of performance. For instance, HIP is often used as a complement of other techniques, such as pressureless sintering, to increase the density levels.



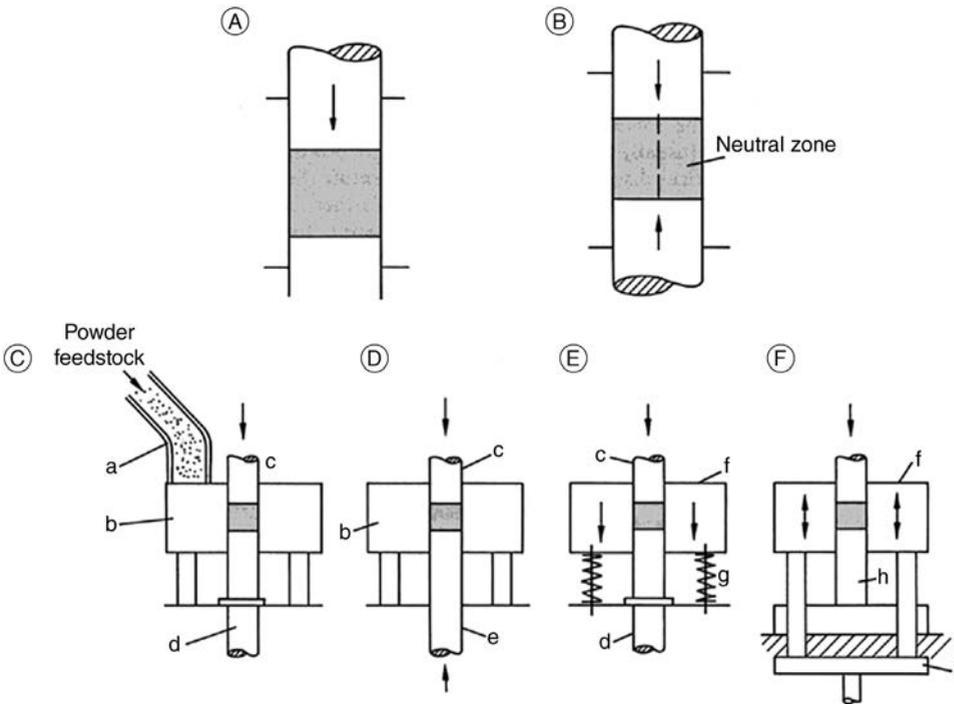
**Figure 16.** Positioning of different PM shaping technologies. Based on information from Olle Grönder [223]

### 3.1. Die Compaction

In terms of mass production and number of parts produced per year, uniaxial die compaction is the dominant technology for shaping metallic powders. Powder particles are consolidated by compaction in a rigid die by the application of pressure through upper and lower punches. The powder is poured in a rigid die cavity, and compaction is achieved by a vertical movement of the upper (Fig. 17A) or upper and lower punches (Fig. 17B) with a fixed (Fig. 17A, B, C, D) or floating die (Fig. 17E, F). Afterwards, the green compact is ejected by pushing the lower punch upwards (Fig. 17C, D, E) or moving the die downwards (Fig. 17F) [43]. Sufficient strength of the compact must be achieved during pressing to withstand ejection forces and handling prior to sintering. Compaction pressures are normally around 150–900 MPa (for ferrous parts usually 400–600 MPa) [43, 44]. In

some cases, pressures around 1000 MPa may be used to reach higher densities and higher levels of performance. Nevertheless, cold pressing cannot result in full density, and some porosity is always left as a consequence of work hardening [45]. An experimental method to attain high density levels is high velocity compaction (HVC), which so far, however, has been applied only to single level parts such as gears [46].

In uniaxial die compaction, the punches move only in the vertical direction. As a consequence of the friction between powder and die walls, the axial stress (stress in the direction of compaction) is larger in the areas of contact with the moving punches than anywhere else. Thus, a density gradient occurs inevitably in the compact, with the highest density next to the moving punch face and the lowest near the fixed punch. Double action pressing (from both sides, Fig. 17B) or the use of a floating die (Fig. 17C) reduces the density gradient by moving the die



**Figure 17.** Uniaxial compaction of metal powder [43]  
 A) Density distribution in the compacted powder bed when upper punch moves, die and lower punch are fixed (case C); B) Density distribution when upper and lower punches move and die is fixed or with floating die if upper punch moves and lower punch is fixed (cases D, E, F); C) Single action pressing; D) Ejection process; E) Floating die process; F) Withdrawal process  
 a) Filling tube; b) Fixed die; c) Upper punch; d) Ejector; e) Lower punch; f) Floating die; g) Spring system; h) Fixed lower punch; i) Withdrawal rods

to compensate the friction effect [42]. In these cases, a neutral zone (zone of lower density) is generated in the center part of the compact.

Friction effects during die compaction are reduced significantly by using lubricants either in powder form (mixed to the metal powder) or applied as a thin coating to the die walls (“die wall lubrication”). Although the amount of lubricant used in lubricated powder mixes is usually below 1 mass%, this is approximately 5% in volume, which means that the maximum density achievable after compaction would not be higher than 95% because the lubricants are virtually incompressible [44]. Die-wall lubrication can be employed as a way to lower the amount of admixed lubricant. However, the practical difficulties of reapplying the lubricant on each die refill is a limitation for large-scale productions.

There are certain shape limitations for uniaxial pressing [47]. Parts with re-entrant angles and with holes at an angle to the vertical direction are generally not produced by die pressing. A critical factor for attaining satisfactory densities and economical processes is the design of ingenious pressing tools [48]

The main advantages of die pressing are the precise dimensional control obtained by pressing in well-defined rigid die cavities, the batch-to-batch consistency and the high rates of production achievable in fully automatized systems.

A variant of the die compaction process is *warm compaction*. In its isothermal variant, both the powder and the pressing tools are preheated to lower the yield strength of the metal, which results in higher density levels [49–51]. Usually, a polymer is used to glue the particles together. The polymer softens or melts with the application of moderate temperatures, reducing considerably the friction forces. Compared to typical powder grades for die compaction, a polymer-coated powder is often used for warm compaction and this can increase the cost significantly (depending on the type of polymer used). Ejection forces vary considerably with the type of polymer selected. Powder and tooling are usually pre-heated to a temperature around 135 to 150°C, and the compaction pressures used are in the range of 700 MPa for steels. Modifications of the die and punches as well as a heater in the powder feed mechanism are required for implementing this technique.

Several press suppliers have developed retro-fitted systems for powder and tool heating that can be implemented to existing presses. Warm compaction allows increasing green densities above 92% relative density, and the high green strength levels achieved facilitate machining of the green compacts. The improvement in mechanical and physical properties has widened the applications of pressed and sintered parts, and components such as helical gears for hand power tools, sprockets, synchronizer rings, and various hubs for automotive applications are produced with this technology. As powder pre-heating is not simple and requires special lubricants, another variant of warm compaction simply uses preheated tools, which is cheaper but results in lower green density levels attained [52].

In *hot pressing* processes, the powder is uniaxially pressed at high temperature, at least above the recrystallization temperature. As compaction and sintering take place simultaneously, the process is also known as pressure sintering. A combination of temperature-induced diffusion and stress at high temperatures causes a time-dependent plastic deformation below the yield strength of the metal [53]. The die is usually made of graphite, also to facilitate induction heating, and the process is often performed in vacuum to avoid contamination of the compact. Maximum temperatures and pressures are around 2200°C and 50 MPa, respectively. Three different types of heating technologies are used: induction heating, indirect resistance heating and field-assisted sintering (FAST)/direct hot pressing [16, 54]. Owing to the rather low productivity and poor dimensional precision, the use of the process is limited. It is, however, widely applied in research and development to investigate innovative compositions. An important application is in the consolidation of diamond–metal cutting tools, for which the high added value compensates the extra costs.

## 3.2. Powder Forging, Extrusion, and Rolling

### 3.2.1. Powder Forging

In powder forging (or sinter forging) a sintered “preform” with a relative density of around

70–85% is processed by hot forging, i.e., impact repressing, in a closed die. Two different processes can be used:

- Sintering a green compact under conventional conditions followed by cooling and new heating to forging temperature
- Directly forging the preform from the sintering temperature

Elimination of oxides during sintering is a critical step for obtaining strong bonding between particles during forging. Low levels of oxygen are particularly important for dynamic properties (i.e., impact and fatigue strength). In the forging step, the compact is initially deformed in the direction of the applied pressure. Once the initial porosity is reduced below about 10%, the material flows also at right angles of the applied pressure. Thus, powder forging provides a combination of densification and flow under uniaxial forces [16]. Depending on the amount of cross flow, the variants are upsetting, which gives lower porosity and better properties but lower dimensional precision, and hot repressing [47].

The high dimensional accuracy obtained, combined with the excellent toughness and fatigue resistance, have proved very useful for the production of powder-forged connecting rods. With a correct preform shape and a well-controlled process, sinter-forged parts present properties comparable to those of forged wrought alloys, or even better because the properties after sinter forging are essentially isotropic [55]. The dimensional and weight accuracy obtained and the high material utilization rate are additional advantages.

### 3.2.2. Powder Extrusion

By powder extrusion, metal powders undergo plastic deformation at ambient or elevated temperatures through an extrusion process that produces a densified and elongated form with structural integrity. Different alternative processes are available depending on the starting material fed in the extruder: loose powder, powder-binder mixes, powder compacts, pre-sintered preforms, etc.

Compaction of loose powders is in most cases facilitated by introducing the powder in

a can made of an easily deformable material (e.g., low-carbon steel). The can is evacuated and sealed, and may be precompact before extrusion. The use of a can allows working with toxic or dangerous materials (e.g., beryllium or uranium), as well as the isolation of sensitive materials from the atmosphere and from extrusion lubricants or other possible contaminants. High extrusion ratios are commonly used (normally above 1:12; for Al 1:16 or higher) which allow obtaining full-density or high-density products. The high shear forces break and disintegrate the surface oxide layers (e.g., of Al or superalloys) facilitating interparticle welding and thus densification [44].

Powder extrusion is normally not used as a final forming process, but it is an important step for processing materials that are difficult to handle because of their toxicity (e.g., beryllium) or the presence of stable surface oxides that inhibit densification of powder compacts (e.g., Al, Ti and their alloys, superalloys, high-speed steels, etc.)

In the production of composite materials, whiskers, particulates, or chopped fibers can be added to the matrix powder, and extrusion serves to align the reinforcing agent as well as to consolidate the product. Multicomponent systems can also be produced by combining in a can solid products and powders.

### 3.2.3. Powder Rolling

Metal powders are fed in a set of compacting rolls to produce strips (preforms) with a high width-to-thickness ratio. The strips can be further processed by sintering and re-rolling to obtain the desired size or the material properties required.

Powder rolling is usually interesting if the metals to be processed are more economically obtained as powder during the extraction process (e.g., Ni). The product from powder rolling does not always show advantages in properties. Special material features are possible with powder rolling, such as the production of porous strips or strips from special materials or alloys that are not easily deformed. In some cases, the strips formed do not present any lamination and are more homogeneous than strips produced by rolling cast billets. Powder rolling can be used to obtain multilayer strips used for instance

in the production of thin-walled sliding bearings [44, 56].

### 3.3. Isostatic Pressing

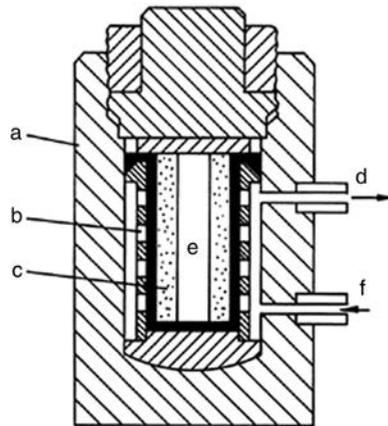
Die pressing results in compacts with heterogeneous density because of the friction between powder particles and between powder and die walls. This can be avoided if the compacting pressure is evenly applied to the powder from all directions (isostatic pressure), which is achieved by placing the powder in a closed flexible mold and introducing the mold in a fluid (liquid or gas) that is afterwards pressurized. The fluid transmits the pressure evenly in all directions through the flexible mold.

As compared to die pressing, isostatic pressing requires lower pressures to achieve a certain density, and the density distribution obtained is more homogeneous. Most of the limitations on mass and dimensions are eliminated due to the homogeneous densification and the elimination of the ejection step. Besides, as no lubricants are needed, contamination is reduced, and it is possible to obtain high and uniform densities. On the other hand, geometrical precision is usually inferior to that of uniaxial die compaction.

#### 3.3.1. Cold Isostatic Pressing (CIP)

In CIP ( $\rightarrow$  Sintered Iron and Steel, 5. Cold Isostatic Pressing), the powder is poured into a flexible mold commonly made of rubber that is then sealed. The filled mold is immersed in a liquid (usually water with some corrosion inhibitors), and the liquid is pumped to high pressure. Pressure is transmitted in all directions from the liquid to the powder through the flexible mold. The process is performed at room temperature, and the pressure applied can be as high as 1500 MPa, but the pressures used in practice are commonly around 200–600 MPa [57].

Two different methods are available: wet-bag CIP and dry-bag CIP. In wet-bag CIP, the mold containing the powder is filled outside the vessel and then immersed into the liquid. Multiple molds can be processed at the same time depending on the size of the pressure vessel. In dry-bag CIP (Fig. 18) the flexible mold is permanently fixed to the pressure vessel, and



**Figure 18.** Simple dry-bag tool for cold isostatic pressing a) Pressure vessel; b) Membrane; c) Powder; d) Pressure outlet; e) Core rod; f) Pressure inlet [43]

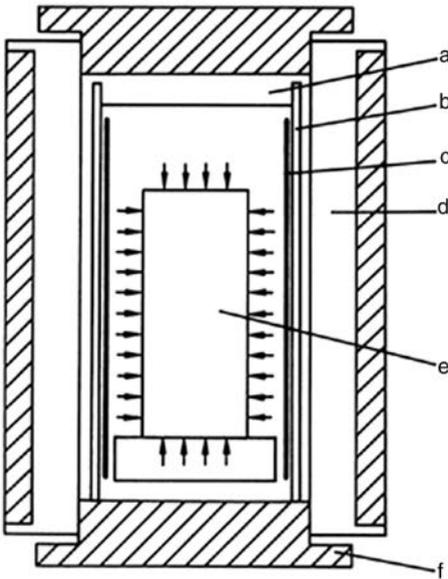
the pressure is transmitted to the mold through a transmission membrane, so the mold remains dry. The cycle times are shorter, and the process can be automatized. Dry-bag CIP is mostly used in ceramic processing, and the main use in metal powders is in the production of filters. This method is suitable for high production rate of small parts, particularly those with a high aspect ratio such as cylinders [43, 58].

The dimensional control is in principle less precise than in uniaxial die pressing—owing to the flexible mold—but some metallic parts can be incorporated to the mold to produce accurate surfaces. Production rates are increased by the automatization of the processes and can be comparable to those of die pressing. Many constraints of die pressing regarding shapes and dimensions can be overcome in CIP (e.g., in the production of long thin-walled cylinders)

CIP has become an essential process step for the production of certain PM materials: molybdenum and tungsten (e.g., in arc furnace melting electrodes), tungsten heavy alloys, hard metal parts (e.g., rollers and dies), high-speed steel semiproducts, and long cylindrical filter elements.

#### 3.3.2. Hot Isostatic Pressing (HIP)

In HIP ( $\rightarrow$  Sintered Iron and Steel, 6. Hot Isostatic Pressing), a gas medium is used to apply isostatic pressure at high temperature to



**Figure 19.** Pressure vessel for hot isostatic compaction  
 a) Isolating lid; b) Isolating mantle; c) Furnace; d) Wire wound pressure vessel; e) Part to be pressed; f) Vessel lid [43]

porous parts, or to a powder that is hermetically sealed in a container that deforms plastically at operation temperature (“canned”). An example of a HIP pressure vessel is shown in Figure 19. The container in this case cannot be of polymeric material because of the high temperatures used in the process. Generally, metallic (low-carbon steel, stainless steel) or even glass containers are used and are referred as “cans”. An inert gas is used to avoid reaction with the material. The gas is usually argon, but other gases such as helium or nitrogen can also be employed. Temperatures are material-dependent and can range from 480°C for aluminum to 1700°C for tungsten powders. This technology is very importantly applied to steel and nickel, with common temperatures between 1100°C and 1250°C. Pressures range from 20 to 300 MPa and are most commonly around 100 MPa. Spherical powders are normally used to achieve higher apparent densities. Avoiding contamination of the powders (e.g., oxidation) is critical for the properties of the HIP components because the contamination affects the formation of strong bonds between particles [59, 60]. Therefore, tool-steel powders are handled in protective atmosphere between

atomization and canning, avoiding exposition to air.

At high temperature, the yield stress of most metals decreases and the gas pressures used are chosen to be higher than the yield point of the material at that temperature. As with hot pressing, densification is typically activated by diffusion and creep processes. The combination of pressure and temperature allows achieving virtually full density at lower pressure than required for CIP and a lower temperature than that required for sintering. As the temperature is reduced, grain growth can be inhibited.

Typically, density levels achieved are between >98% and 100% of the theoretical density. HIP can be used to compact metal powder to fully dense blocks and to densify still porous parts made by casting, pressing and sintering, MIM, additive manufacturing, etc. (if the pores contained are closed). It is also used to join bimetallic components. Modern HIP systems include uniform rapid cooling (URC) systems that allow cooling the part at a controlled rate up to 100°C/min. In this way, heat treatments can be incorporated in a single step, and the cycle times are reduced. Besides, grain growth is restricted and surface contamination can be avoided by using protective gases [61–63].

In spite of the high capital cost required, HIP finds many applications in the production of special PM materials such as high-speed steels, superalloys, and titanium alloys. In the case of hard metals, “sinter-HIP” (→ Section 4.4) has largely replaced HIP. Owing to the properties that can be achieved, many applications are in demanding industry sectors (e.g., aerospace structure and engine parts) and in aggressive environments (e.g., energy, tooling, nuclear, oil, and gas).

### 3.4. Injection Molding

Injection molding is a powder-shaping technology in which metallic powders are mixed with an organic binder to form a “feedstock” that is injected at moderate temperatures into a mold cavity with the required shape (similarly to plastic injection molding, → *Plastics Processing, 1. Processing of Thermoplasts, Section 4.5. Injection Molding*). Afterwards, the binder is

removed through a debinding process, and the remaining powder structure is sintered.

Ideally, very fine powders are used to obtain high and uniform powder loadings in the feedstock and to attain high sintering activity. The amount of binder is typically in the order of 40–50 vol%. The large specific surface area of fine powder particles activates the sintering mechanisms, thus achieving high density levels (usually above 95%). In spite of the large shrinkage, very good dimensional tolerances can be obtained if the powder load in the feedstock is uniform. Critical aspects of this technology are [64]:

- The formulation of a suitable binder that wets the metallic powder particles and forms a uniform mass when mixed with the powder. Besides, it needs to be removable without damaging the powder structure.
- The binder removal process (debinding). Different processes have been developed: heat treatments to decompose and evaporate the binder (thermal debinding), chemical decomposition in a gaseous acid environment at approximately 120°C (catalytic debinding), dissolution in a liquid (solvent debinding), etc. Usually a multi-component binder is used, and different debinding processes are combined to ensure a progressive removal of the binder that keeps the structural integrity of the part. Removal of the most stable binder component, the “backbone” (typically a polyolefin), is always done thermally, in the first stage of sintering. Environmentally friendly water-soluble binders are the newest trends. Debinding is a time-consuming process, and its complexity increases as the thickness of the part increases. Thus, it imposes some limitations on the size and thickness of the parts.

The main advantages of the MIM technology are the possibility to economically produce complex parts from high performance materials in large numbers, the high-density levels and tight tolerances achievable, and the suitability for processing most materials (including special materials such as nickel superalloys, intermetallics, precious metals, refractory metals, and

ceramic-fiber reinforced ceramic composites). In that respect, MIM combines the geometrical flexibility of polymer injection molding with the material flexibility of PM.

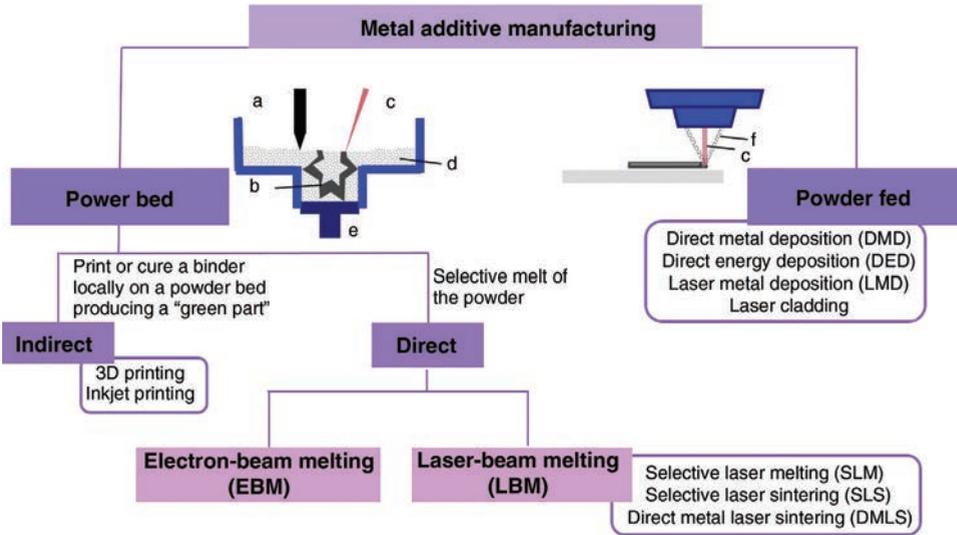
### 3.5. Additive Manufacturing

Additive manufacturing is a technology that allows building parts by the incorporation of material layer upon layer, to achieve a 3D shape. Thus, it is considered an additive technology, in contrast to subtractive technologies such as machining. A digital 3D model is transmitted to a machine that builds the 3D component using different techniques.

The number of technologies available has rapidly increased in recent years, and the different processes can be divided in many ways, e.g., by the energy source used, the starting material (powder, wire, sheets, or liquids), and the way the particles are joined (bonding, melting, etc.). Most additive-manufacturing processes used to build metallic parts are based on the consolidation of powder particles. Figure 20 presents a schematic of the powder-based metal-additive-manufacturing technologies including different terms used to describe the same type of process. A division can be made between *powder-bed* and *powder-fed* technologies [65, 66].

Powder-bed processes rely on the application of a powder layer that is then locally consolidated as a 2D slice either by melting the particles (direct methods) or by bonding them together (indirect method). Then, a second powder layer is applied and consolidated on top of the first one. The process is repeated until the part is fully built, embedded in the powder bed.

In direct technologies, an energy beam (laser or electron beam) is used to selectively melt the powder layer. In laser-beam technologies (direct laser melting, DLM) the laser energy is absorbed by the material, creating a melt pool that solidifies rapidly. Electron-beam process (electron-beam melting, EBM), in contrast, takes place in a vacuum chamber ( $10^{-5}$  hPa or lower). The entire powder bed is heated to an optimum temperature (which depends on the material used) to ensure electrical conductance of the powder bed and avoid charging effects. The parts are then almost free from residual stresses.



**Figure 20.** Additive manufacturing technologies

a) Leveling system; b) Part; c) Beam; d) Powder bed; e) Platform; f) Powder

Indirect technologies print a binder on a powder bed or cure the binder locally, producing a “green part” similar to those of MIM. The green part is subsequently debinded and sintered, and sometimes infiltrated to obtain completely dense materials. This process is known as 3D printing (though 3D printing is a term now also used for DLM and EBM). The technology is more productive than laser-beam melting; it takes place at room temperature and does not require support structures because the part is supported by the powder bed during the building process. As it is virtually isothermal at all stages, distortion and residual stresses are less problematic than with the direct variants.

In powder-fed systems, the powdered material flows through a nozzle and is melted with a beam exactly on the specified surface of the treated part where it solidifies. It offers higher productivity (owing to the high deposition rates), better material utilization, and the ability to produce larger parts than with powder-bed processes. As it allows adding material to an already existing part, it can be used to repair metallic components and to add new functionalities to an existing part with the same or a different material. In contrast, powder-bed techniques are suitable for building high precision

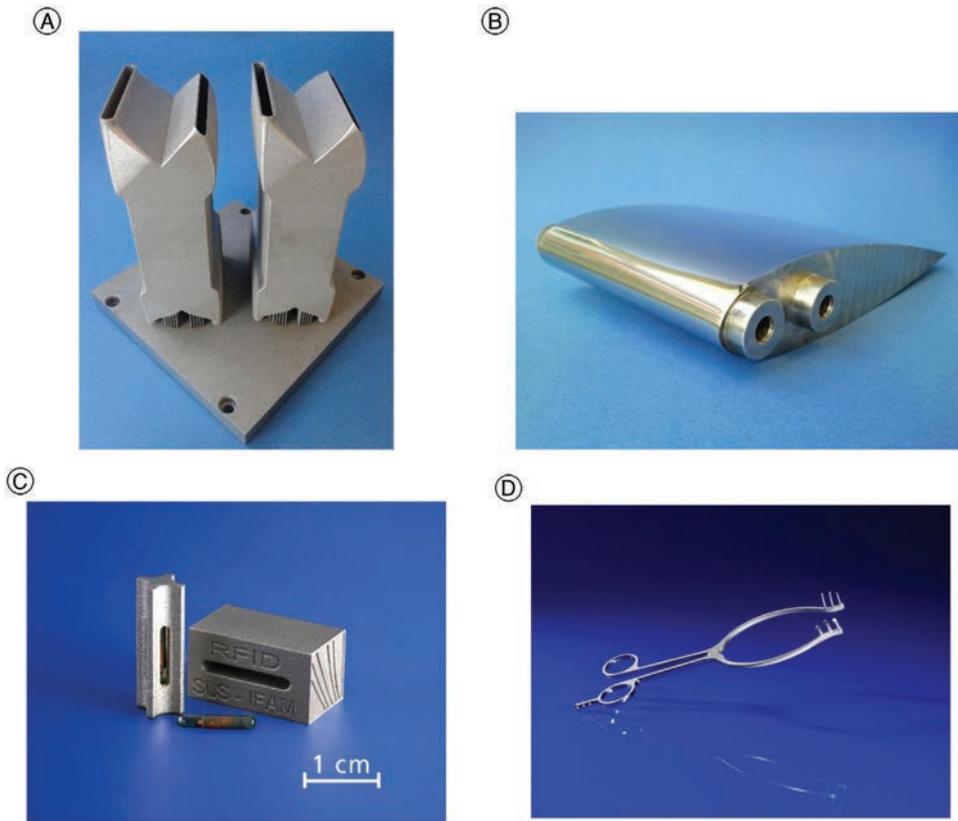
parts and more complex features such as hollow cooling passages that cannot be produced with powder-fed techniques.

Materials commonly used in additive manufacturing are titanium alloys, cobalt–chrome alloys, aluminum, and nickel, and new material compositions suitable for selective melting are investigated. For direct laser melting, gas-atomized particles with size distributions between 10 and 50  $\mu\text{m}$  are preferred. For EBM, coarser fractions up to 150  $\mu\text{m}$  are employed. Spherical shapes are beneficial for powder flowability and allow forming uniform layers in powder-bed systems [66].

Additive manufacturing technologies offer an unrivalled design freedom, combined with the possibility of working with a wide range of materials. Additive manufacturing enables both prototyping and direct manufacturing of complex parts. Applications are found in many different sectors such as aerospace, energy, automotive, medical, tooling, and consumer goods (Fig. 21).

## 4. Sintering

Sintering is the most common thermal consolidation technique in powder metallurgy.



**Figure 21.** Parts produced by additive manufacturing (Fraunhofer IFAM)  
 A) Heat exchanger; B) Wing profile; C) Integrated RFIDs; D) Medical wound spreader

The ISO definition of the term reads: “The thermal treatment of a powder or compact at a temperature below the melting point of the main constituent, for the purpose of increasing its strength by bonding together of the particles” [37].

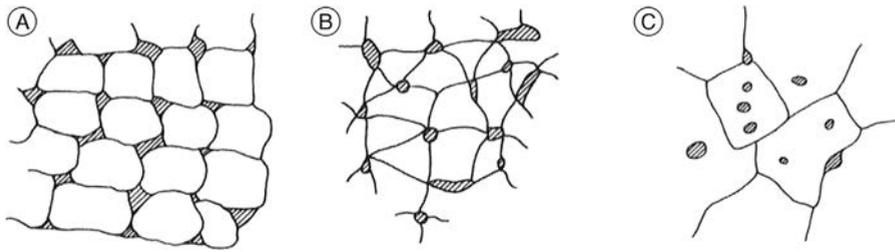
Sintering can be related to the “firing” of ceramics, which has been used for thousands of years. The main difference, however, owes to the fact that metals are typically not in chemical equilibrium at ambient atmosphere; i.e., sintering in air would result in catastrophic oxidation regarding the large specific surface and thus high chemical reactivity of powder-based systems. Therefore, sintering of metallic systems needs protective atmospheres, which has a pronounced impact both on the mechanisms of sintering and on industrial sintering processes.

#### 4.1. Sintering Mechanisms: Solid-State Sintering

Sintering can be performed in different variants, depending on the phases present and the components of which the respective systems consists: solid state, activated, liquid phase (persistent or transient), reactive [67–70].

The most straightforward variant of sintering is solid-state sintering of single component systems. Here, the driving force is elimination of defects among which the surface is dominant; i.e., the disperse system lowers its energy primarily by reducing its surface.

One pronounced difference between dispersed metallic systems and ceramic or polymer systems is the much higher surface energy of metals, which is in the range of  $J/m^2$  whereas it is about 1-2 orders of magnitude lower for



**Figure 22.** Schematic description of the sintering stages in powder compacts [103]  
 A) Green state; B) Open porosity; C) Closed porosity

ceramic systems and even lower for polymers such as PTFE. Therefore, for a given specific surface, the driving force for sintering—as a reduction of surface area—is significantly higher for metals. This is one reason why also coarse-grade metal powders can be sintered whereas for ceramics, fine powders are required and for polymers such as PTFE, external pressure as additional driving force is required. Another consequence of the high surface energy is that reduction of oxidized surface promotes sintering by increasing the energy of the surface and thus the driving force.

This sintering process can be split into different sections [70]:

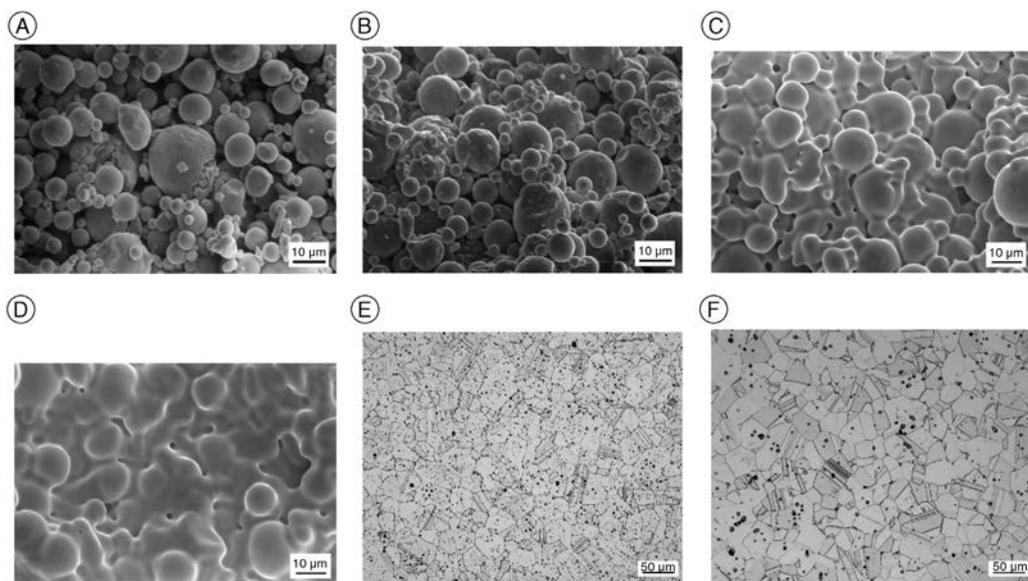
Initially, in the bulk or the pressed (green) state, the particles meet at points or highly deformed pressing contacts (Fig. 22A). In the early stages of sintering, metallic interparticle contacts are formed and grow; the interparticle porosity is still interconnected and open (Fig. 22B). In the later stage, rapid shrinkage occurs; the pores are closed and become isolated against one another (Fig. 22C). In the final stage, any remaining porosity decreases slowly, and grain coarsening occurs because the pores that inhibit grain growth even if scarcely present [71] tend to disappear.

The dominating stage depends on the starting powder used. With fine and highly active starting powders, shrinkage is pronounced, and close to 100% density can be attained. This is the classical sintering process, which is applied, e.g., for MIM [19]. It starts from a relative density of 60%, and about 95–100% density can be obtained after sintering. The sintering results for injection-molded Ti specimens are shown in Figure 23. If coarse powders >40  $\mu\text{m}$  are employed, e.g., for pressed and sintered

ferrous parts or gravity-sintered filters, the sintering process stops at an early stage (Fig. 24B), with hardly any densification (which is undesirable for precision parts because it would tend to adversely affect geometrical precision). In this case, the lowering of the specific surface is attained not through densification, i.e., pore elimination, but by the change of the pore geometry without changing the total porosity. The improvement of the mechanical properties is attained through the increase of the load-bearing cross-section; i.e., the fraction of the specimen taken by metallic bridges, which is, however, lower than the fraction of the metallic phase itself [72]. Although dimensionally stable sintering is aimed at for precision parts, anisotropic density distribution originating from uniaxial compaction must be considered here [73].

For studying the sintering process, model systems have been used, such as the twin-sphere model and the sphere-on-plate model; the parameter investigated is the growth of the neck radius, and capillary forces are driving the process. Different transport mechanisms have been proposed, such as viscous flow or evaporation–condensation, but the main mechanism is diffusion; temperature-dependent surface diffusion, grain boundary diffusion, and bulk diffusion are the dominating mechanisms that transport material.

The role of dislocations has been stressed by SCHATT et al. [70] who proposed that dislocations are ejected from the neck surfaces into the material (“self-activation”), resulting in accelerated mass transport through the dislocation channels and neck growth by mass transport to favorably oriented edge dislocations at the expense of unfavorably oriented



**Figure 23.** Stages of sintering in Ti specimens produced by MIM (Fraunhofer IFAM)

A) Inert-gas-atomized MIM powder; B) Brown (debanded) compact; C) Sintered for 5 min at 1180°C; D) Sintered for 5 min at 1340°C; E) Sintered for 60 min at 1300°C; F) Sintered for 60 min at 1350°C

ones. In contrast, STAAB [74] stated that the high sintering activity is not attributed to dislocations but a consequence of the large specific surface and grain boundary area present when using fine powders, in part combined with crystallographic misfit. In any case, the sphere models are considered to hold for cases when spherical powders have point contacts—such as for gravity-sintered filter materials or MIM specimens—whereas for pressed compacts, the contact areas have been deformed, and in part metallic joints have been formed, as evident from the green strength of the compacts.

In most PM materials, more than one component is contained, and particularly if starting from powder mixes, heterodiffusion and homogenization processes have to be considered. In the case of alloy formation, the driving forces, especially, the mixing entropy, are much higher than those caused by the surface energy, and, therefore, the formation of new pores during mutual diffusion can occur (“Kirkendall effect”). Such phenomena are observed, for example, if Ti–Al mixes are sintered [75], and they are enhanced by exothermic reactions (“reactive sintering”).

In special cases, sintering can be activated by the addition of a small amount of a second

element that is virtually insoluble in the main constituent but has high solubility for this constituent. In this case, a thin layer of the additive is formed on the particle surfaces of the main constituent through which the main constituent can diffuse rapidly, thus enhancing sintering [76]. A typical example is the system W–Ni: whereas for the sintering of plain W to reasonable density levels, 2700°C are required, the addition of 0.3% Ni results in a virtually dense material already at 1400°C [70, 77]. However, by addition of Ni, W also loses its character as high-temperature material, especially, its creep resistance, a phenomenon that underlines the close relationship between creep and sintering.

## 4.2. Liquid Phase Sintering

Even faster sintering can be attained if offering mass transport not through a solid layer but a liquid, the so-called liquid phase sintering [78], which requires two constituents at minimum. Two variants of liquid phase sintering can be distinguished: if at sintering temperature the liquid phase is in chemical equilibrium with the solid phase (which forms the major part

of the system), this is termed *sintering with persistent liquid phase*. The liquid phase enhances material transport and typically also densification; therefore, persistent liquid phase sintering is the process applied if full density is required, such as for hard metals (see Section 6.8) and tungsten heavy alloys (see Section 6.9 and → Tungsten, Tungsten Alloys, and Tungsten Compounds, Section 5.2 Multiple Phase Alloys). An essential criterion is wetting of the solid by the liquid phase [79]. Solubility of the main constituent in the liquid phase usually promotes densification. Densification mechanisms are particle rearrangement, which is supported by the lubricating effect of the liquid phase, as well as solution–reprecipitation processes that change the shape of the solid phase towards higher packing density [80, 81]. Grain growth depends on the interfacial energy of solid–liquid; it is very pronounced in the system W–Ni but much less so in hard metals in which low-energy WC surfaces are formed. However, with ultrafine hard metal grades, grain growth stabilizers have to be added to retain the submicron microstructure [82].

Classical sintering with persistent liquid phase occurs in powder mixes, such as W–Ni or WC–Co, in which an additive metal generates the liquid phase. A special variant is the *supersolidus liquid phase sintering* in which a prealloyed powder is used that is heated above the solidus temperature, thus generating a liquid phase from within the powder particles [79, 83]. This very homogeneously distributed melt results in enhanced material transport and densification within a narrow temperature range, as used, e. g., for sintering of high-speed steels. For some Al alloys, the *hetero supersolidus liquid phase sintering* has been developed. In this case, a prealloyed powder is mixed with plain Al, and sintering is performed such that the supersolidus melt is generated in the alloy powders; however, this results in pronounced densification of the entire powder compact [84].

In the above cases, the liquid phase is in equilibrium with the solid one, and the system is comparable to an ingot in the intermediate cooling range. However, a powder compact can be prepared to be in full chemical inequilibrium if it, for example, consists of mixed elemental powders although the composition is such that from the phase diagram a solid solution is

predicted. In this case, during sintering, also homogenization must take place, which may occur through solid-state sintering. If, however, the melting point of the minor constituent is below the sintering temperature or if a low-melting eutectic is formed [85], a liquid phase is formed that is not thermodynamically stable but rapidly disappears, forming a solid solution [86]. This liquid phase is called “transient,” and *transient liquid phase sintering* is a common process, for example, with sintered steels, the most widely used steel grade for precision parts, Fe–Cu–C, is sintered in such a way. This type of sintering has the advantage that it does not result in densification but, in contrast, slight swelling is observed—frequently called “copper swelling” [87, 88]—, which is used in industrial practice to compensate for the natural shrinkage of pressed compacts; thus, net dimensional change  $+/-0$  can be established. The second benefit of the transient liquid phase is enhanced distribution and homogenization of the alloy elements, which improves the mechanical properties, as shown not only for Fe–Cu–C but also for steels alloyed with Mo, Cr, and W [89]. Regarding the reaction with the base metal, “non dissolutive” and “dissolutive” liquid phases can be differentiated [90]: the former remaining liquid for considerable time and usually filling the pore network of the base compact whereas the dissolutive liquids solidify by reaction with the matrix metal, thus choking the pores. This latter effect is less welcome for sintering because it inhibits homogenization, but can be useful for sinter brazing (Chap. 5). With non dissolutive liquid phases, the rapid distribution of the liquid phase in the pores of the matrix results in the formation of pores at the sites of the original alloy powder particles [85, 86]. These “secondary” pores may be similar in size to the particles, as such as for Fe–Cu, or considerably larger, such as for Fe–Mo–C, and have to be considered especially with regard to fatigue properties because larger secondary pores may act as crack initiation sites [91]. Therefore, using fine alloy powders is recommended, and agglomeration of alloy element particles must be avoided.

In some systems, transient and persistent liquid phases have to be combined, such as for sintering of Al–Cu based systems: here, first, transient liquid phase is required to crack the oxide layers covering the Al powder particles

and to enable formation of stable metallic bridges [92, 93]. The driving force is the formation of the solid solution, i.e., it is an entropy-driven process. Subsequently, the temperature is raised further to cause formation of a persistent liquid phase that enhances shrinkage, thus eliminating the swelling caused by the transient liquid phase.

### 4.3. Chemical Aspects of Sintering

Most metals—except Au and the platinum group metals—are thermodynamically unstable in air. They can be stored in ambient atmosphere because the reaction towards equilibrium, oxidation, is kinetically inhibited. However, at higher temperatures, the reaction will occur, and therefore any heat treatment of disperse metallic systems—bulk powder or compacts—including sintering must be performed in protective atmosphere that may either be inert or reducing.

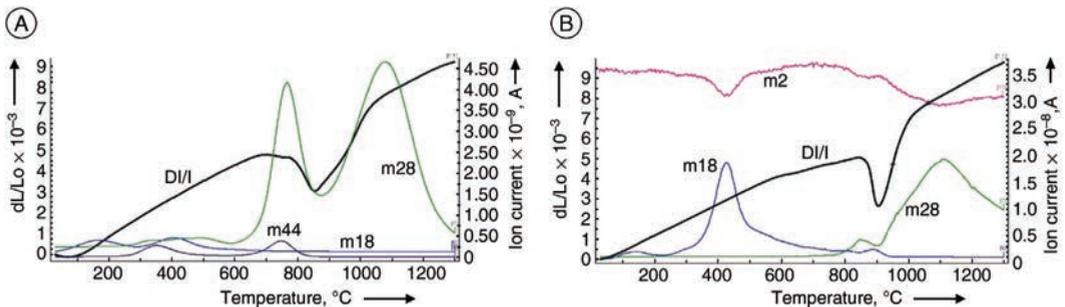
Furthermore, all metal powders that have ever been exposed to air are covered by surface layers consisting of oxides, hydroxides, and adsorbed gases. These layers are usually unwelcome because they lower the surface energy and thus the driving force and also inhibit transport processes. In some cases, they are, however, necessary for safety reasons because fine Al or Fe powders that are not protected by oxides are pyrophoric and thus a safety hazard.

Nevertheless, such oxidic surface layers tend to inhibit the sintering processes, the more, the more stable they are. Therefore, the removal of

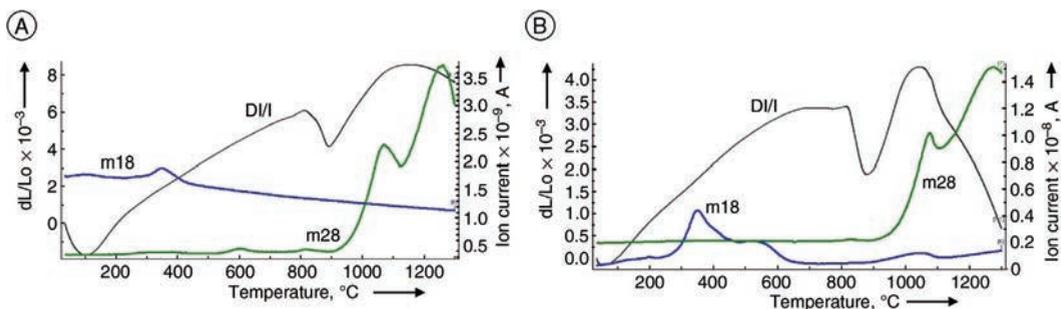
the layers in the early stages of sintering is necessary to ensure successful sintering.

Except for aluminum, in which case the oxide is thermodynamically very stable and the melting point and thus the maximum sintering temperature are low, and for Ti, in which case O is dissolved in the lattice at higher temperatures, most oxide layers covering powder particles can be reduced during sintering [88]. The most common reducing agents are constituents of the sintering atmosphere, usually hydrogen, or of the specimen itself, typically carbon. Generally, higher sintering temperatures are required to reduce more stable oxides [94, 95]. From a thermodynamic point of view, at lower temperature,  $H_2$  is the stronger reducing agent than C or CO, and at high temperatures, C is the strongest reducing agent because the Gibbs free energy of CO formation becomes more negative with increasing temperature whereas that of  $H_2O$  becomes less negative. This means that in a system in which both  $H_2$  and C are present, stable oxides that require high temperatures for their reduction are reduced carbothermally despite the presence of  $H_2$ . A special sort of reduction occurs for systems containing elements with widely differing oxygen affinity. Here, oxygen transfer can occur from the matrix to alloy elements with higher oxygen affinity, the “internal getter” effect [96, 97], which is a metallothermic reduction process within the powder compact.

Examples are given in Figure 24 and 25, which depict thermoanalytical and mass-spectrometry graphs for the sintering of Fe–C and Fe–Cr–Mo–C in inert (Ar) vs. reducing ( $H_2$ )



**Figure 24.** Degassing during sintering of powder compacts Fe–0.5%C observed by dilatometry and mass spectrometry  
A) Inert atmosphere (Ar); B) Reducing atmosphere ( $H_2$ )  
 $m_2 = H_2$ ;  $m_{18} = H_2O$ ;  $m_{28} = CO$ ;  $m_{44} = CO_2$



**Figure 25.** Degassing during sintering of powder compacts Fe-3%Cr-0.5%Mo-0.5%C observed by dilatometry and mass spectrometry

A) Inert atmosphere (Ar); B) Reducing atmosphere ( $H_2$ )  
 $m_2 = H_2$ ;  $m_{18} = H_2O$ ;  $m_{28} = CO$ ;  $m_{44} = CO_2$

atmosphere [94]. Sintering in  $H_2$  results in an  $m_{18} = H_2O$  degassing peak at about  $400^\circ C$  that is markedly more pronounced with Fe-C, but even for this material and more pronounced for Fe-Cr-Mo-C, the major reduction process occurs at  $T > 900^\circ C$  through the formation of  $m_{28} = CO$ , i.e., through carbothermal reduction. In inert atmosphere, only the carbothermal process is observed, and two distinct  $m_{28}$  peaks are recorded for both materials. However, the peaks differ in their temperature as those for the Cr-Mo alloy steel are observed at higher temperature, which agrees with the presence of more stable oxides.

Carbothermal reduction means loss of carbon, which is not crucial for sintered steels as long as it is reasonably controllable. With hard metals, in contrast, carbon control is one of the most decisive factors because the useful carbon “window” for the two-phase material WC-Co is narrow, and exceeding this range towards low C or high C results in useless products (see Section 6.7). Because of the close interaction between carbon and oxygen, carbon control also means oxygen control, and the oxygen content of the starting powders must be considered when defining the composition of the hard metal powder mix, especially the amount of C added to compensate for C burn-off during the reduction.

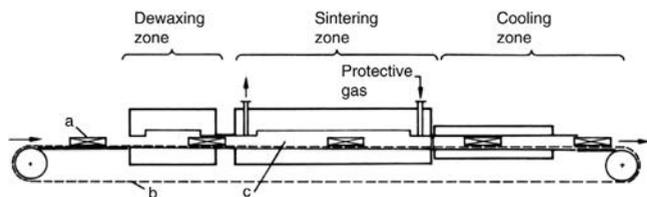
#### 4.4. Sintering Practice

The furnaces used for industrial manufacturing of PM products differ depending on what is to

be produced. Continuous or batch-type furnaces may be used [98, 99], and the operating temperature may vary as well as the type and purity of the atmosphere. Regarding the temperature, it may vary from about  $600^\circ C$  for Al base components,  $800\text{--}900^\circ C$  for Cu alloys,  $1120\text{--}1280^\circ C$  for ferrous parts, and around  $1400^\circ C$  for hard metals with up to  $2800^\circ C$  for sintering of tungsten. In any case, the energy efficiency becomes increasingly important (e.g., [100].)

For the mass production of ferrous precision parts, continuous furnaces are employed [98], in which the specimens to be sintered are transported through a heated tunnel split into different sections. In the first section, operating at temperatures in the range of  $600\text{--}800^\circ C$ , the pressing lubricant is removed; in the second section, the sintering process is performed. Then, a carbon restoration zone may follow and/or a rapid cooling zone in which the components are quenched by a flow of cold nitrogen. In all furnaces, complete cooling is afforded in a cooling tunnel, still under protective atmosphere.

The furnace types used are mostly mesh belt furnaces (Fig. 26) that may be electrically or gas heated and operate at temperature of  $1150^\circ C$  maximum because at higher temperatures, the belt life tends to decrease dramatically. The furnaces are open at both ends, with flame curtains offering some protection against the intrusion of oxygen into the sintering zone. Nevertheless, the atmosphere purity in mesh belt furnaces is moderate. If higher temperatures are required, walking beam furnaces



**Figure 26.** Schematic of mesh belt furnace used for sintering of ferrous precision parts  
a) Sintering tray, b) Conveyor belt, c) Furnace muffle [136]

are employed with locks at both ends. These furnaces are electrically heated, usually with Mo elements, can be operated at up to 1400°C, and offer better atmosphere quality, but are significantly more expensive and typically do not afford rapid cooling facilities. Special types such as roller hearth furnaces have been brought into service in some cases.

For hard metals and refractory metals, of which markedly lower tonnages are produced, batch-type furnaces are used. Sintering of hard metals has traditionally been performed in vacuum because this “atmosphere” makes carbon control easier, and electrically heated furnaces with graphite heating elements are employed. The “sinter-HIP” variant has become standard in which the major part of the sintering process is performed in vacuum, and in the final stage of isothermal sintering, Ar pressure of typically about 70 bar is applied to eliminate the last remaining pores. The furnaces thus not only have to be gas-tight, but they are pressure vessels that fulfil special safety criteria and undergo regular inspections.

For sintering of refractory metals, batch-type furnaces with metallic heating elements are used that operate in vacuum or hydrogen. The same holds for MIM components for which the temperatures are typically lower; for stainless steels 1350°C is a common temperature. Occasionally, continuous furnaces are used for MIM production if the production volumes are sufficiently high to justify the higher investment cost and the inevitable loss of flexibility.

#### 4.5. Sintering Atmospheres

Sintering of metallic systems requires a protective atmosphere to prevent oxidation [98]. In addition to avoiding unwelcome reactions, the

atmosphere should also remove reaction products, e.g., from dewaxing or from reduction of the “natural” oxides present on the powder surfaces [101]. For the removal of reaction products, it should be considered that the atmosphere flow is usually laminar, i.e., the products, esp. evaporated lubricants, are removed rather slowly.

Regarding oxygen, the atmospheres may be inert or reducing; there is also the option of carburizing or decarburizing atmospheres. In some cases, as with stainless steels or soft magnetic materials, also nitriding effects should be considered. Because of the high impact of the carbon content on the properties of steels, carbon control has become an increasingly crucial task with these materials [102] whereas for WC-Co hard metals, it has always been the key to success (see Section 6.7).

For ferrous products, synthetic N<sub>2</sub>-H<sub>2</sub> mixes have been well established, mostly from cryogenic gases of high purity. For safety reasons, the H<sub>2</sub> content is usually kept at 10% maximum. The oxygen potential (frequently expressed as dew point) should be sufficiently low, to avoid surface decarburization or, if alloy elements with high oxygen affinity are present, also oxygen pickup. As the crucial parameter for oxidation is the H<sub>2</sub>O/H<sub>2</sub> ratio, at lower H<sub>2</sub> contents also the dew point should be sufficiently low. For mass production in belt furnaces, endogas is preferred, an atmosphere of roughly 40% N<sub>2</sub>-40% H<sub>2</sub>-20% CO with some CO<sub>2</sub> and H<sub>2</sub>O produced by the endothermic reaction between methane and air at low CH<sub>4</sub>/air ratios. By adjusting the ratio, the carbon potential, i.e., the carbon content in the sintered specimens that is in equilibrium with the atmosphere, can be adjusted. However, the carbon content holds only for a given temperature; at lower temperature, e.g., during cooling, for the

same composition of the atmosphere, higher C levels are attained.

Dissociated ammonia was popular in early sintering processes because of the easy storage and transport of  $\text{NH}_3$ , but it has been superseded by the  $\text{N}_2$ - $\text{H}_2$  mixes, at least in industrialized countries. Plain  $\text{N}_2$  is the standard atmosphere for sintering of Al in which case defined reactivity is necessary to overcome the passivating effect of the oxide layers [103–106].

Plain  $\text{H}_2$  is used, e.g., for sintering of refractory metals in which nitrogen might pose problems; in this case the higher costs are regarded as acceptable. However, the risk of hydrogen embrittlement should be considered. Vacuum is the standard atmosphere for hard metals, but also for highly reactive metals such as Ti for which the main goal is to lower any oxygen pickup during processing as much as possible. Theoretically, also high-purity Ar might serve the purpose, but Ar is insoluble in metals, and thus any Ar trapped in closed pores remains there, inhibiting further densification. This is a problem with additive manufacturing through direct laser melting because this process is performed in Ar atmosphere, and Ar-filled pores are difficult to remove even by hot isostatic pressing. For vacuum sintering, also the vapor pressure of the elements present in the specimens must be considered; and in liquid phase sintering, too low pressures may result in the evaporation of the liquid-forming additive. Backfilling the vacuum furnace with some mbar of high purity gas may be helpful here.

## 5. Secondary and Finishing Operations

Even though PM is considered as a near-net-shape technology, in many cases, PM-components require features and properties that cannot be achieved simply by sintering. For instance, supplementary operations may be used to reproduce complex shapes, achieve closer tolerances, improve mechanical properties, or protect against corrosion. In spite of the increase in cost caused by secondary operations, often the final products are still economical compared to those from competing technologies.

Some of the secondary operations described in this section are specific for PM parts (such as the steam treatment and the infiltration with metals or polymers), but most of the operations are commonly used also in non-PM parts. However, some specific requirements must be considered for PM parts because of the limitations imposed by the peculiar characteristics of the PM materials, particularly porosity.

### 5.1. Deburring and Cleaning

PM parts are often subjected to deburring processes to remove burrs, sharp edges, or surface irregularities resulting from compaction or machining operations. It is possible to carry out deburring in bulk by tumbling or shot blasting (hitting by abrasive media in compressed air), or on a unit basis using processes such as brushing, polishing, and electrolytic deburring. A common practice consists of tumbling PM parts in a liquid medium with abrasive particles by using rotating barrels (barreling) or vibrating tubs (vibratory deburring). As a consequence of the penetration of liquids in the surface porosity, corrosion problems may arise. Thus, corrosion inhibitors should be added to the liquid media. In some cases, the parts are resin- or oil-impregnated to minimize water absorption during the deburring process.

Parts may be cleaned to remove surface contaminants from the production process (such as shop oils, grease, oil, and lubricants). Cleaning operations are diverse and depend on the specifications and the type of pollutants that the part may contain. For ultrasonic cleaning, the parts are placed in a tank and agitated with ultrasonic waves that are able to shake the contaminants trapped in the pores. Electrolytic-alkaline cleaning reduces the risks of corrosion as the parts are immersed in a strong alkaline solution. Through electrolysis, the parts are cleaned and the oxides or nonmetallic coatings are removed.

### 5.2. Repressing, Sizing, and Coining

*Repressing* is sometimes used to increase the density of a compacted and then presintered part, before the final sintering process. For ferrous components, it allows achieving a

high level of density and mechanical properties, whereby using standard pressing loads. The plastic deformation imposed during repressing operations is substantial (from 5 to 20%) and the forces required are comparable to those used during the initial pressing operation. As the repressing tool can be designed simpler than that for powder pressing, even higher loads may be applied.

**Sizing** is also a repressing process, but the aim is to improve geometrical precision. It requires only moderate forces as usually only slight deformations are needed (below 5%)—at least if the hardness of the as-sintered part is not too high (typically below 200 HV). For an as-sintered ferrous part, the accuracy in the dimensions is typically 0.004 mm per mm in parallel to the pressing direction, and 0.002 mm per mm within certain angles from the pressing direction. The tolerances and properties achievable after sizing depend on the material (Table 2 [107]), and closer tolerances are attained with softer materials [108].

**Coining** is a repressing operation in which plastic deformations are intermediate between repressing and sizing. The process has a double purpose: reduce dimensional variability and increase density. The considerable strain hardening achieved with this process causes an increase in tensile strength and hardness and a decrease in elongation. This process can also be used to imprint the faces in contact with the punches.

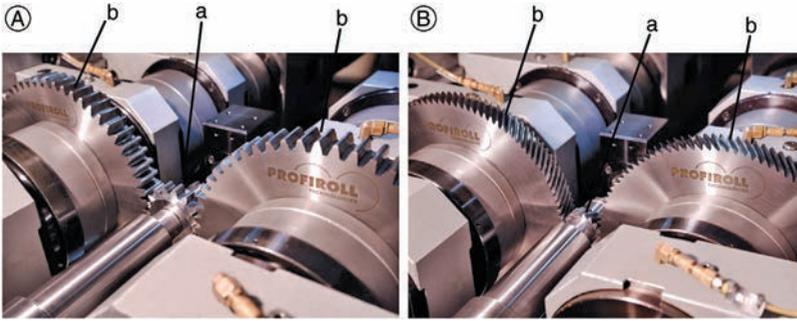
### 5.3. Local Surface Densification Techniques

As the mechanical performance of components is determined to a large extent by the structure and properties of the surface, a promising method to widen the capabilities of PM parts consists in developing techniques to increase the density of near-surface areas, which are frequently the mechanically loaded zones. In porous components, superficial plastic deformation brings out a density increase in surface and near-surface regions, creates residual compressive stresses, and provides work hardening in the deformed layer. Thus, a surface layer of controlled plastic deformation can dramatically improve fatigue properties in PM components [109].

An important method for increasing the fatigue life of PM components is *shot peening*, a cold working process in which small spherical media (metallic, glass, or ceramic particles) are used to impact the surface of a part with enough energy to cause plastic deformation. A compressive residual stress layer is formed in the surface, and the mechanical properties in this layer are modified by the effect of strain hardening. In porous PM materials, it has an additional effect because plastic deformation induces surface densification by closing smaller pores and reducing the size of larger pores [110, 111]. Fatigue and contact fatigue resistance can be increased by up to 25%, and the resistance to surface damage is also significantly enhanced [110, 112].

**Table 2.** Tolerances attainable as-sintered and as-sized, respectively, in different sintered-steel grades [107]

Designation DIN 30910	C, mass %	Cu, mass %	Ni, mass %	Cr, mass %	Mo, mass %	Fe, mass %	Density, g/cm <sup>3</sup>	Sintered at °C	Hardness HB	IT sintered	IT sized
C00	<0.3	<1.0				balance	6.4–6.8	1120	>35	9	5–6
C10	<0.3	1–3				balance	6.4–6.8	1120	>40	9	6
D10	<0.3	1–3				balance	6.8–7.2	1120	>50	9	6
E10	<0.3	1–3				balance	>7.2	1120	>80	9–10	7
C11	0.4–1.5	1–3				balance	6.4–6.8	1120	>85	9	7
D11	0.4–1.5	1–3				balance	6.8–7.2	1120	>100	9	7–8
D30	<0.3	1–3	1–2		0.3–0.8	balance	6.8–7.2	1120	>80	9	7
D30	<0.3	1–3	1–2		0.4–0.8	balance	6.8–7.2	1250	>80	10	7
D39	0.3–0.6	1–3	1–2		0.4–0.8	balance	6.8–7.2	1120	>140	9	8
D39	0.3–0.6	1–3	1–2		0.4–0.8	balance	6.8–7.2	1250	>160	10	
D39	0.3–0.6	1–3	2–5		0.4–0.8	balance	6.8–7.2	1250	>160	10	
C40	<0.08		10–14	16–19	2–4	balance	6.4–6.8	1140	>100	10–11	7
D40	<0.08		10–14	16–19	2–4	balance	6.8–7.2	1140	>130	10–11	8



**Figure 27.** Gear rolling process on gears (Höganäs AB, Profiroll Technologies)

A) Spur gear; B) Helical gear

a) Worked piece; b) Rolling tools

Another effective method for increasing the density precisely in those areas where it is required is *surface cold rolling*. A PM preform with a controlled amount of excess material on the profile is rolled with a meshing rolling tool (see Fig. 27). Local densification is created in the surface layer of the rolled profile. This method was originally used for PM bearing races, and then has been used for treating the tooth profiles of both straight spur gears and helical gears [113–116]. Surface cold rolling applied to gears (also called *gear rolling*) improves tooth bend fatigue strength, surface contact fatigue strength and pitting wear resistance. Such densified surface improves the response of PM parts to carburizing treatments.

## 5.4. Machining

Machining operations are often needed to incorporate geometrical features that cannot be reproduced during pressing (e.g., transversal bores or re-entrants at an angle to the pressing direction). In some cases, it is simply more economical to introduce such features with a machining operation.

Machining parameters for PM parts are different from those of cast or wrought components. Machinability of PM parts is affected by their complex property profile (density, chemical composition, microstructure, additives, etc.). The inherent porosity affects chip formation, thermal conductivity, cutting temperature, bulk strength of the workpiece, cutting forces, and the characteristics of the surface generated after machining [117]. Typically, machining

becomes more difficult with higher porosity levels and with heterogeneous microstructures. A technique specific for PM is green machining in which pressed but not yet (fully) sintered parts are machined; this requires, however, a certain level of green strength, attained, e.g., by warm compaction or presintering [109].

It has not been possible yet to establish a relationship between the specifications of a PM material and its machinability. Several methods can be used to determine empirically the machinability of PM materials by correlating a certain level of tool wear with parameters such as: the PM material, additives, cutting conditions, etc [117]. Most data about machinability of PM steels are based on the “drilling test” as it is relatively inexpensive, fast, and reproducible. This test evaluates machinability by the number of holes that can be drilled before the drill breaks down (or before reaching a certain edge wear) [118, 119].

Machinability of PM parts can be improved by incorporating certain additives in the powder mix prior to compaction (lead, copper, graphite, sulfur, or a metal sulfide such as manganese sulfide). Also, infiltration with low-melting-point metals or impregnation of the porosity with polymer is a common practice to improve machinability [117, 118].

PM parts can be machined using traditional technologies such as drilling, turning, milling, tapping, grinding, honing, and lapping. Guidelines can be found, e.g., in [120]. Grinding is a very common finishing operation as it allows adjusting the required size with tolerances of few micrometers. During grinding, metal chips from the PM workpiece are detached in contact

with the grinding wheel. Conventional grinding materials are SiC and Al<sub>2</sub>O<sub>3</sub> (suitable for low alloyed PM steels). CBN grinding wheels can be used for PM high speed steels, and for hard metals, diamond wheels are most commonly used for grinding [117].

## 5.5. Joining

Some of the limitations in the geometries achievable with powder metallurgy techniques can be overcome by joining different sintered parts, or a sintered part with another part produced through a different technique. However, some factors should be considered when joining PM parts [121–124]. Porosity affects thermal conductivity and thus expansion as well as thermal conductivity and thus hardenability. As porosity may trap impurities that could seriously damage the properties of the joint (e.g., residual lubricants, machining coolants, quench oils, etc.), it is important to thoroughly clean the parts before joining.

Low density PM parts are preferably joined using solid-state processes such as brazing, diffusion bonding, shrink fitting or techniques as adhesive bonding. Parts with higher densities can be welded using fusion based processes [124, 125].

**Welding.** (→ Welding and Cutting) Most of the conventional welding methods can also be used for PM parts. In general, low heating input is recommended for porous materials and, if needed, any steam treatment or heat treatment should be performed after joining. Thermal stresses in the heat affected zone (HAZ) can result in cracks due to the porosity. Any given welding process needs to be optimized for each specific PM components considering factors such as porosity, chemical composition, impurity level, ductility and toughness, residual stresses and distortion, welding metal and HAZ cracking. Typical welding techniques used for PM materials are arc welding, laser welding, electrobeam welding, resistance projection welding, and friction welding. Arc welding is often avoided because it can result in pore coalescence. Laser and electrobeam melting provide low heating inputs that minimize distortions. The disadvantage is the rapid thermal

cycling that may result in cracking. Friction welding is a remarkable welding technique for PM material as it promotes porosity closure and oxide layers breakage in the weld interface.

**Brazing** (→ Soldering and Brazing) consists of assembling the parts to be joined in the desired position and insert a brazing powder between them. During heating, the brazing powder melts and infiltrates the components. The most practical way of applying the brazing powder is in the form of a green compact with the required shape and weight. The brazing alloy must be conveniently designed to avoid the absorption of the brazing liquid in the adjacent pores, which would leave insufficient material in the joint. Reactive fillers that rapidly solidify when entering the pores, by uptake of Fe or diffusion of filler components into the matrix, are therefore used [126,127]. Simultaneous sintering and joining can be carried out, and the process is adaptable to mass production.

**Diffusion bonding** is based on the interdiffusion between two parts in contact. Interdiffusion can be promoted by locating a bonding material that, upon heating, creates a small amount of liquid phase between the parts to be joined. Another possibility is to use HIP in which case the simultaneous application of temperature and pressure promotes inter-diffusion. A variant that is frequently used is *sinter bonding* in which green components of dissimilar materials are assembled before sintering. During the sintering cycle differences in dimensional changes between both components are used to generate a solid metallic bond. The components are thus bonded by mechanical interlocking and alloy diffusion. The strength of the joint can be increased by infiltrating one of the parts with Cu that, during sintering, acts as a braze in the joint.

**Shrink fit/press fit** consist of heating or cooling one of the parts to be joined before assembling. When the temperature equalizes, the differences in thermal expansion provide an effective fit. This joining technology is limited to certain geometries and alloy compositions and might not be suitable for applications that require gas/liquid tightness, good performance at high temperature, or specific operating conditions with demanding levels of structural integrity. For

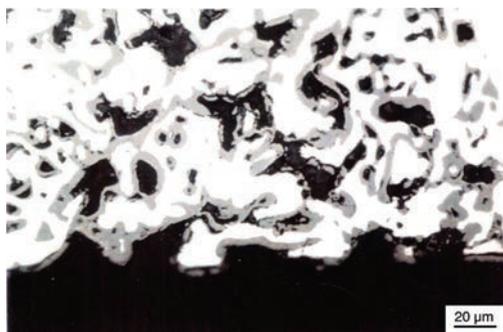
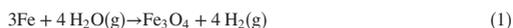
those applications in which this technology is suitable, it represents a cost effective joining technique that provides joints with considerably good strength.

**Adhesive Bonding.** In some cases, PM parts can simply be joined by gluing, and the inherent porosity can be advantageously used to hold the adhesive in place providing high bond strengths. Care must be taken to avoid that the adhesive is drained by the porosity. Adhesive bonding allows joining thin and thick parts, thus complex shapes can be obtained. High temperature performing adhesives are developed to overcome poor resistance at elevated temperature in this type of joint. In any case there is virtually no thermal loading on the joining partners, with resulting good geometrical precision.

## 5.6. Surface Treatments

The aim of chemical modifications of the surface is usually to improve corrosion behavior or wear resistance.

**Steam treatment** process is frequently performed on ferrous materials to improve their corrosion resistance and/or to seal the surface porosity, thus avoiding liquid or gas penetration. The part is exposed to overheated steam at temperatures in the range of 430–590°C for 1–4 h. As a consequence of the reaction with the steam (Eq. 1), a well adhering blue-gray oxide (magnetite  $\text{Fe}_3\text{O}_4$ ) is formed on the surface of open porosity (Fig. 28):



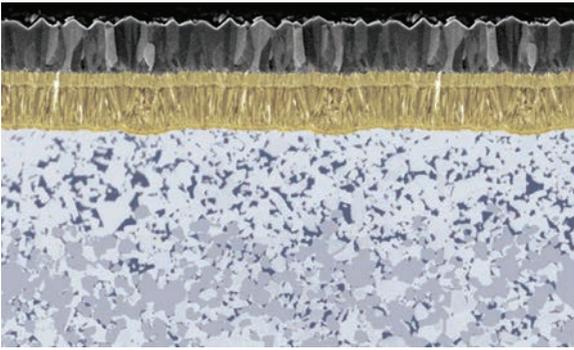
**Figure 28.** Typical microstructure after steam treatment

Temperature and composition of the atmosphere must be carefully controlled to ensure the formation of magnetite  $\text{Fe}_3\text{O}_4$  and not wuestite  $\text{Fe}_{1-x}\text{O}$  or hematite  $\text{Fe}_2\text{O}_3$  because the latter oxides present poor adhesive properties and do not provide corrosion resistance. Oxide thickness and penetration of the oxide in the part are determined by the treatment conditions, the density of the material, the type of base powder used, and previous operations that could close surface porosity. Due to the formation of the oxide, compressive stress is increased on the surface. As a general rule, apparent hardness is increased (improving abrasive and adhesive wear resistance) and tensile strength can be slightly increased or decreased depending on the thickness of the oxide formed [128, 129]. Steam treatment might be followed by plating, or by dipping in oil to enhance the blue-gray color and further increase corrosion resistance.

**Plating** is performed on sintered parts in the same way as in wrought or cast materials. However, in PM parts, the surface open porosity must be closed or sealed before plating (e.g., by resin impregnation). During plating, metals such as Cu, Ni, Cd, Zn, and Cr are deposited galvanically on the surface.

**Coatings** are applied to a large percentage of hard metal cutting-tool inserts. Typically, chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes are used to deposit ceramic layers of  $\text{TiC}$ ,  $\text{TiN}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiAlN}$ , etc. In coated inserts, the role of the hard metal changes. The coating withstands the erosion from the machined material, and the hard metal acts as a support for the coating, providing rigidity, toughness, good thermal properties, and allowing good adhesion of the deposited layer. Once the coating is eroded off as a consequence of the abrasion, the cutting performance of the insert is that of the uncoated material. Improved performance is obtained by the combination of several thin coating layers in the so called multilayer coatings (Fig. 29) [11, 130, 131].

**Infiltration and impregnation** processes are used to fill the open porosity present in a sintered part. Sealing the open porosity provides some increase in mechanical properties,



**Figure 29.** TiCN–Al<sub>2</sub>O<sub>3</sub> multilayer CVD coating on gradient-cemented carbide substrate (Sandvik Coromant R&D Stockholm)

prevents the entry of corrosive electrolytes during plating, improves pressure-tightness, and has a positive effect on machinability. The term infiltration is used if metals with a lower melting point or interval than the base metal are used as fillers, and impregnation is used when the infiltrant is an organic compound (oil or polymers).

Infiltration does not require any applied pressure, but the metallic infiltrant must present good wetting on the metallic substrate to be able to enter the pores by capillary action. Besides, low solubility of the base metal in the liquid infiltrant is desirable to avoid excessive erosion of the surface. Infiltration can also be used to make composite electrical contact materials such as W/Cu and Mo/Ag, in which case the low melting point metal is infiltrated on a porous sintered W or Mo body (see Section 6.8).

Vacuum processing is typically used to impregnate PM parts. An outstanding application is in self-lubricated bearings. PM bearing parts are impregnated with oil which during operation provides lubrication between bearing and shaft, thus rendering external lubrication unnecessary.

## 5.7. Heat and Thermochemical Treatments

In ferrous parts, properties such as hardness and strength can be improved by heat treatments. In PM materials, thermal conductivity is reduced as a consequence of the porosity

[132], and the parts may crack when quenched too rapidly. Whereas in conventional wrought steels, plain water or water and brine are used as quenching media, PM parts are normally quenched in oil or gas to avoid penetration of water, brine or salt baths in the pores that could cause severe corrosion. Besides, heating must typically be carried out in protective atmosphere.

**Sinter hardening** is a process that combines sintering with a gas quench treatment within one run and is therefore highly economical. At the transition between the high temperature furnace zone and the cooling zone of the furnace, a quench unit is installed in which the parts are cooled with cold N<sub>2</sub> gas, with typically linearized cooling rates of up to 3 K/s attained.

**Induction hardening** allows performing a heat treatment only in certain areas of the part surface. Before quenching, the part is heated for a few seconds in an induction coil that must be specially adapted to the shape of the component. The depth of the hardened case can be controlled by modifying the frequency of the alternating current in the coil (higher frequencies give thinner heated zones).

Case hardening treatments are relatively inexpensive and simple processes for increasing surface wear resistance and mechanical properties (fatigue). The chemical composition of the surface is modified by the local diffusion of carbon (carburizing), nitrogen (nitriding), or both (carbonitriding /nitrocarburizing), and the part is subsequently quenched.

As the reactive gases can penetrate the open and interconnected porosity of PM materials, fast pick-up of carbon and/or nitrogen occurs during the treatment, increasing the risk of through hardening. Care must be taken to achieve even penetration depths and narrow hardness transition zones.

**Carburizing** is carried out at temperatures in the range of 820–920°C in a carburizing atmosphere (e.g., endogas, 40%N<sub>2</sub>–40%H<sub>2</sub>–20%CO<sub>2</sub>). To obtain a better control of the carburized layer, especially with locally densified parts, *low-pressure carburizing* is employed. Low-pressure carburizing is carried out in a vacuum furnace in which hydrocarbon gases (such as acetylene or propane) are pulsed in well-defined periods of time. The temperature, number, and length of the pulses, and the time allowed between pulses for carbon diffusion determine the case depth. The process is usually combined with high-pressure gas quenching [133]. As quenching can be carried out in a protective atmosphere, this process is particularly suitable for materials with a high oxygen affinity [134, 135]. Low-pressure carburizing yields case depths that are almost independent of the porosity and therefore is well suited for surface-densified gears.

**Nitriding** consists of heating the part in a nitrogenous atmosphere (e.g., ammonia or nitrogen). In gas nitriding, ammonia dissociates into hydrogen and nascent (atomic) nitrogen catalyzed by the Fe surface. Low processing temperatures are used, within the ferrite range, and the parts need not be quenched. Thus, drastic volume changes can be avoided; however, there

is the risk of through-nitriding. *Plasma nitriding* is increasingly used because it minimizes distortion and provides better control and high-quality layers, with nitriding limited to the surface area.

Carbonitriding and nitrocarburizing introduce both carbon and nitrogen, giving emphasis to carburizing/nitriding, respectively. The processes differ mainly in the process temperature (lower for nitrocarburizing) and in the composition of the atmosphere. Carbonitriding makes use of the fact that nitrogen stabilizes austenite and increases steel hardenability, thus this treatment is commonly used in low alloy or unalloyed steels.

## 6. Materials and Products

### 6.1. Precision Parts

#### 6.1.1. Low-Alloyed Steel Parts

The classical compositions of low-alloyed steel parts are listed in Table 3. Compared to wrought steels, alloying elements with high affinity to oxygen such as chromium, vanadium, and manganese is avoided because sintering of the listed compositions, containing Cu, Ni, and Mo, is performed in atmospheres of rather moderate purity (high dew points), for example, in belt furnaces run in endogas atmospheres. In contrast, alloying elements such as Cu and especially P are common in the production of low-alloyed-steel precision parts because the risk of grain-boundary embrittlement due to segregation is much lower with sintered than with wrought steels. The system

**Table 3.** Composition (in wt%) and mechanical properties\* of typical ferrous PM steels according to DIN 30 910-4 [DIN 30910-4]

Composition	Symbol	X = C $\rho = 6.4\text{--}6.8 \text{ g/cm}^3$		X = D $\rho = 6.8\text{--}6.8 \text{ g/cm}^3$		X = E $\rho = 7.2 \text{ g/cm}^3$		
		Sint-	$R_m, \text{ N/mm}^2$	A, %	$R_m, \text{ N/mm}^2$	A, %	$R_m, \text{ N/mm}^2$	A, %
Fe	X 00		130	4	190	10	260	18
Fe-C <sub>(0.3-0.6)</sub>	X 01		260	3	320	3		
Fe-Cu <sub>(1-5)</sub>	X 10		230	3	300	6	400	12
Fe-Cu <sub>(1-5)</sub> -C <sub>(0.4-1.5)</sub>	X 11		460	2	570	2		
Fe-Cu <sub>(1-5)</sub> -Ni <sub>(1-5)</sub> -Mo <sub>(&lt;0.8)</sub>	X 30		390	2	510	3	680	5
Fe-P <sub>(0.3-0.6)</sub>	X 35		310	11	330	12		
Fe-Cu <sub>(1-5)</sub> -P <sub>(0.3-0.6)</sub>	X 36		360	5	380	6		
Fe-Cu <sub>(1-3)</sub> -Ni <sub>(1-5)</sub> -Mo <sub>(&lt;0.8)</sub> -C <sub>(0.3-0.6)</sub>	X 39		520	1	600	2		

\*  $\rho$  = density,  $R_m$  = ultimate tensile strength, A = elongation

Fe–Cu offers the possibility of sintering with intermediate liquid phase, which leads to a slight swelling effect [88] which can be controlled by the amounts of copper and carbon. This swelling effect can compensate for the shrinkage caused during the isothermal sintering and finally lead to extremely precise products. Furthermore, copper acts as a solid solution and precipitation hardener [136, 137] and nickel improves toughness. Due to safety regulations concerning nickel, this element is only introduced as diffusion-alloyed powder (Distaloy type). Carbon-containing variants (Fe–Cu–C and Fe–Cu–Ni–C) are stronger than Fe–C steels, but require precise carbon control during sintering.

Since the 2000s, chromium- and manganese-prealloyed steels have been introduced into precision parts production because the control of the sintering atmosphere has been improved with the ability of better furnaces [138] and the need to substitute the alloying

element nickel, which has hazardous properties. The manganese- and chromium-prealloyed steels materials offer extraordinary properties (hardenability), but exhibit higher shrinkage than the classical elemental mixtures. Importantly, sintering (and posttreatment) in endogas atmospheres is not possible because of oxidation. Furthermore, high-temperature sintering, which means sintering temperatures above the usual 1120°C, is extremely beneficial, but requires different furnace concepts, as the usual belt furnaces cannot be operated at these temperature levels without causing extremely short belt or retort life [139].

Many of these modern structural parts, especially gears for valve drive, need secondary operations such as densification of the gear surfaces with consecutive thermochemical treatment to improve rolling contact and root-bending fatigue strength [140]. Some examples of structural parts are shown in Figure 30.



**Figure 30.** Typical low-alloyed structural parts

A) Chain sprocket (Miba Sinter Austria); B) Dog ring (Miba Sinter Austria); C) Shock-absorber component (PMG Füssen); D) Helical gear (PMG Füssen); E) Synchronizer hub (GKN Sinter Metals Engineering); F) Rotor pump components (GKN Sinter Metals Engineering)

### 6.1.2. High-Alloyed Corrosion-Resistant Steel Parts

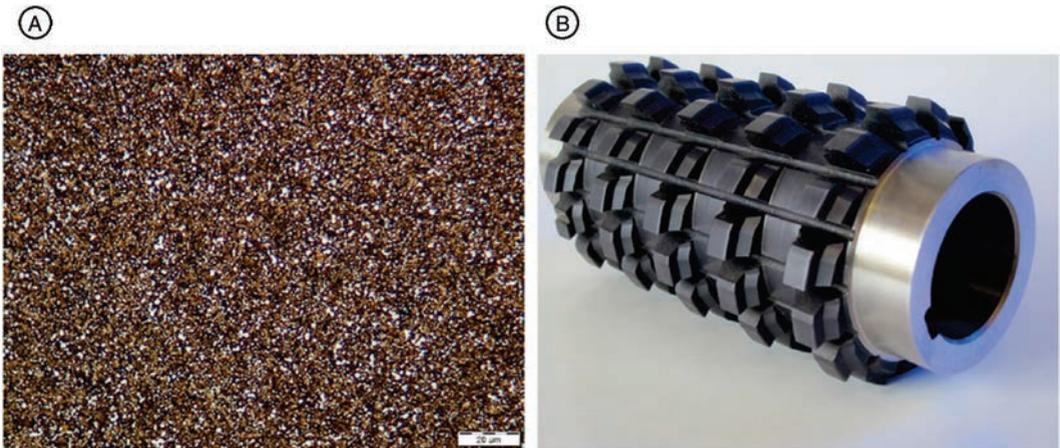
If corrosion resistance for precision parts is required, parts are made of austenitic, martensitic, or duplex stainless steels. The high alloy element content requires the usage of, usually water-atomized, prealloyed powders. All these powders suffer of poor compressibility because of the high alloy content. Although, e.g., austenitic grades are rather soft materials, the compressibility is low because of the solid-solution and work-hardening effects. This means that press-and-sinter products from these materials are usually in the density range of about  $6.5 \text{ g/cm}^3$ , which diminishes corrosion resistance. If better corrosion resistance is required, the parts are typically resin-impregnated.

The compositions used are close to those of cast and wrought steels (e.g., 304L, 316L (austenitic), 410L, 430L (ferritic), 2205 (duplex), and martensitic grades (400 series with higher C content; 0.1–0.5 wt%). The corrosion resistance of all these steels depends on a natural layer of  $\text{Cr}_2\text{O}_3$  on the surface which is immediately formed by the contact with air if the free chromium content is above 12 wt%. For austenitic grades, nickel is added (6–22 wt%), and for duplex steels a combination of ferrite and austenite is balanced which offers excellent corrosion resistance and high strength. The presence of chromium in solid solution is essential for corrosion resistance; therefore, for ferritic, austenitic, and duplex grades, the carbon content has to be controlled carefully to avoid chromium carbide precipitation, which would cause intergranular corrosion. Especially the dewaxing process is critical for avoiding carbon pickup. However, the corrosion resistant chromium oxide layer must be removed during sintering to enable the formation of metallic contacts, usually through reduction by dry hydrogen (dew point  $< -40^\circ\text{C}$ ) at high sintering temperatures. Usually, nitrogen as sintering atmosphere is avoided because of the nitride formation that would lower the corrosion resistance [141]. For martensitic steels, the carbon needed for hardening must be overcompensated for by additional chromium, and heat treatment is performed to avoid the formation of Cr carbides.

Metal-injection molding has extended the application of corrosion-resistant steels to small and complex parts for automotive and medical applications and consumer products. About 50% of all MIM products are from stainless steel. The main difference of these products, apart from complex shape, is the almost full density and closed porosity, which is reached by the MIM process using extremely fine powders.

### 6.2. Tool Steels

Tool steels are hard, tough, and wear-resistant high-alloyed ferrous alloys with varying composition that determines the application. Applications are cold work tools (e.g., for pressing dies and punches), hot work tools (e.g., for injection molding inserts) and high-speed steels for highest operating temperatures [142]. The main alloying elements are tungsten, molybdenum, chromium, vanadium, cobalt, and sufficient carbon to form carbides. The powder metallurgical production route offers the possibility to avoid the brittle carbide network usually developed in the cast ingots during solidification. After hot working processes, the microstructure of the ingot metallurgy (IM) tool steels show inhomogeneously distributed carbides, typically as stringers, which finally causes anisotropic properties. The maximum alloying content of the IM material is limited by the hot workability of the alloys, which is not a limit for PM variants. The ASEA-Stora process for PM tool steels [143] includes gas atomization (in  $\text{N}_2$  atmosphere) resulting in tool-steel powder with homogeneous microstructure and very fine carbide precipitates, filling in steel containers, hot degassing (if the powder ever was in contact with air), gas-tight sealing of the evacuated container, and hot isostatic pressing typically at 100 MPa and  $1100^\circ\text{C}$ . By this process, the top-quality tool steels are produced with homogeneous and isotropic microstructure (Fig. 31A) and therefore isotropic properties that are significantly better than those of IM grades. The technique completely avoids carbide segregation, and therefore the billets could be used directly without hot working. However, the usual hot forming processes can be used to produce the desired shapes (rods, billets,



**Figure 31.** PM tool steel (Böhler Edelstahl)  
A) Typical microstructure, Murakami etched; B) Hob cutter

blanks). Typical products are hob cutters (Fig. 31B), pressing dies and punches with extremely high demands on uniformity, stability during the hardening process (extremely low distortion). Since PM tool steels are significantly more expensive than IM grades, typical applications are tools for which shaping is very demanding, and longer tool life therefore justifies higher material cost.

To produce small tool steel parts with complex shape in high quantities, conventional pressing combined with supersolidus liquid phase sintering in vacuum is used [67]. Here, the sintering temperature is of crucial importance: At too high temperatures, too much liquid phase is formed and the parts lose their shape and become brittle whereas too low sintering temperatures lead to insufficient densification. The sintering temperature has to be kept within a few degrees at around 1240°C (depending of the material), and the corresponding carbon content must be carefully controlled to produce full-density parts without distortion [45].

### 6.3. Electrical Contact Materials

If electrical power or information are transmitted, the electrical current has to pass through numerous devices and components that are joined together directly or via wires and leads. From the generator to the consumer or from the sender to the receiver, about 1000 contact points

are passed, ca. 100 of them are switching contacts. The purpose of a switch is to turn the current on and off reliably, to conduct the current without a minimum of loss when switched on, and to insulate the current paths from one another when switched off. The range of currents to be switched starts at a few milliamperes up to 100 000 A in the case of unfavorable shortcuts in power-supply network.

In power engineering, silver-based composite material produced by PM is used [144–146]. Precious metals are used in communication and information technology owing to their high corrosion resistance.

Switching contacts must fulfil numerous requirements depending on the operation:

During make operation an arc may be formed as the switch is partly reopened by springback of the contacts, called bouncing. This arc heats the contact surfaces and may finally lead to welding of the contact when final closing is achieved. Therefore, the welding tendency of the contacts has to be minimized.

In current carrying, usually the contacts touch each other only at a few single points causing electrical contact resistance and finally heat at the contact points. The goal is to minimize the contact resistance and therefore the heating effect.

During break operation, an arc is formed at the contact component, which causes high thermal loading of the contact material surface. For long service life, the contact material should have low erosion rate by this arc.

### 6.3.1. Contact Materials for Low-Voltage Switchgear

Base material for low voltage switching is silver due to its high electrical conductivity and its chemical stability against the surrounding atmosphere, which is commonly air [146]. Silver does not form nonconducting oxides, but plain silver is only used to a small extent. Silver alloys or silver based-composite materials produced by PM are used to withstand the mechanical loads during switching to reach sufficient wear resistance, suppress the welding tendency, and to assist arc migration and extinction.

There are four groups of contact materials for air-switching devices:

1. Silver and silver alloys
2. Silver-metal composites
3. Silver-metal oxide composites
4. Silver-graphite composites

*Silver and silver alloys* are produced by conventional techniques, but the use in power engineering is limited due to the welding tendency. They have largely been replaced by particle reinforced silver composites.

*Silver-metal composites* are mainly produced by the PM route. The main material in this group is silver nickel (10–40 wt% Ni). Nickel is insoluble in silver; therefore, the only production route is PM by extrusion. The main advantage is low contact resistance and simple processability. The typical area of operations is conducting currents <100 A. Typical applications are switches for which higher erosion resistance is needed and the higher contact resistance by the formed nonconducting erosion products is compensated by sufficient contact forces.

*Silver-metal oxide composites* (Ag–SnO<sub>2</sub>, Ag–CdO, and Ag–ZnO) have reached outstanding relevance owing to their longer service life caused by the higher welding resistance at higher currents. They can withstand high current peaks during make operation in engines, capacitors, and lamps.

Silver-cadmium oxide was developed in the early 1950s for applications in the current range from 30 A to several kA. Production routes are internal oxidation of molten alloy or powder

route by extrusion. The substitution of the toxic CdO by the more environmentally compatible silver-tin oxide (2–14 wt% SnO<sub>2</sub>) material is favored by the higher erosion resistance, lower welding tendency, and lower tendency of material migration in DC operation. Additions (<1 wt%) of various other metal oxides such as, WO<sub>3</sub>, MoO<sub>3</sub>, CuO, Bi<sub>2</sub>O<sub>3</sub> are effective during the switching operation at the contact area molten silver-oxide particle. Silver-zinc oxide (6–10 wt% ZnO) is a cost-effective alternative to silver-tin oxide in certain applications.

*Silver-graphite composites* (2–5 wt% C) have the highest welding resistance but rather low erosion resistance owing to the sensitivity of graphite to air. Extrusion technique is used for compaction of the material and for orientation of the graphite particles. For improvement of the erosion resistance, graphite flakes can be partly substituted by graphite fibers. Main applications are switches with the highest safety requirements, e.g., automatic circuit breakers in power switches and power circuit breakers that must still be able to switch off reliably in the event of malfunction. As graphite burns in air, AgC has limited service life. Therefore, AgC can only be used in devices to fulfil protective functions when switching operations are rarely occurring.

The optimal material combination for a certain application can only be found by comprehensive switching tests, as the materials behave very differently depending on the applied loads. Material tables roughly classify the material by the type of load. Classifications by welding tendency during make operation and break erosion is shown in Table 4 [146].

The erosion behavior of the materials differs widely in different current ranges. Table 5 gives the optimal switching current ranges for the

**Table 4.** Contact material with increasing welding tendency

AgC	3–5% C
AgSnO <sub>2</sub>	8–12% SnO <sub>2</sub>
AgCdO	10–15% CdO
AgZnO	6–8% ZnO
AgNi	10–40% Ni
AgCu	Hard silver with 3% Cu
AgNi	Fine-grained silver with 0.15% Ni
Cu	Electrolytic copper
Ag	Fine silver

**Table 5.** Optimal switching current ranges [146]

10–1000 A	AgNi
100–3000 A	AgCdO
200–5000 A	AgSnO <sub>2</sub>
3000–5000 A	AgZnO
>5000 A	AgW, AgWC

materials. The limits between the current ranges are flexible because the erosion behavior is not only influenced by the current but also by the design of the switching device.

The PM production routes of contact materials are:

**Extrusion:** After mixing of the powders, cold isostatic pressing to form billets and presintering are performed. After extrusion of the billets rectangular profiles and wires are produced.

**Pressing and sintering:** Powder mixes are uniaxially pressed and sintered. To reach the desired densities, repressing is necessary.

### 6.3.2. Contact Materials for High-Voltage Switchgear

In the medium voltage range up to 40 kV, vacuum switches are used (vacuum  $<10^{-4}$  hPa). In the absence of ionizable gases, the arc consists exclusively of the molten and evaporated material of the contacts. The contact material for these kind of switches is CuCr (see also Section 6.9). The production route for Cr  $>45\%$  is sintering of a Cr skeleton that is infiltrated by liquid copper. Chromium contents of 25–40 wt% guarantee a satisfactory combination of high welding resistance, high breaking capacity, and low contact heating. These materials can be produced by the press-and-sinter route.

For switching operations with currents up to 100 kA, WCu or WAg composites have to be used under oil, SF<sub>6</sub>, and in air.

## 6.4. Magnetic Materials

Industrially used magnetic materials are usually ferromagnetic or ferrimagnetic (ferrites). They can be divided into two groups:

*Soft magnetic materials:* they are easily magnetized and de-magnetized, which means that they show a narrow but tall hysteresis loop. Magnetism is almost zero after removing the external magnetic field. They are used to guide or amplify magnetic flux.

*Hard magnetic materials* are characterized by high remanence  $B_r$  (tesla), coercive force  $H_{CJ}$ , and induction  $H_{CB}$ , and high energy product  $BH_{max}$  (kJ/m<sup>3</sup>). They show broad and tall hysteresis loops; therefore, the material remains magnetized without external field and can be used as a source of magnetic field. Sintered materials are listed in Table 6

The PM production route becomes economical if complex shapes are required, as in some cases all machining operations can be eliminated which saves a substantial amount of costs. MIM offers another option to produce even more complex shaped magnetic parts, especially when molding can be performed in magnetic fields to favorably orient the particles already in the green compact [147, 148]

### 6.4.1. Soft Magnets

The width of the hysteresis loop of soft magnetic material is caused by the motion of the Bloch walls (boundaries of finite thickness

**Table 6.** Soft and permanent magnetic sintered material and composites [149]

Material type	Soft magnetic material	Permanent magnets (energy density, kJ/m <sup>3</sup> )	
		Classical	Modern
Metals	Fe, FeP, FeSi	Steel (3), AlNiCo (40)	SmCo <sub>5</sub> (160)
	FeNi, CoFe	CrCoFe (40)	Nd <sub>2</sub> Fe <sub>14</sub> B (240)
	NiFeMo	Sm <sub>2</sub> (Co, Cu, Fe, Zr) <sub>17</sub> (200)	
Ceramics	MnZn ferrites		Ba hexaferrites (30)
	NiZn ferrites		Sr hexaferrites (30)
Composites	Resin and inorganic bonded Fe, NiFe,	Resin bonded AlNiCo	Resin bonded ferrites, SmCo <sub>5</sub> , Nd <sub>2</sub> Fe <sub>14</sub> B
	SiFe powder (crystalline, amorphous) cores and parts	Resin bonded Sm <sub>2</sub> (Co, Cu, Fe, Zr) <sub>17</sub>	

between Weiss domains with different directions of magnetization). This motion is hindered by every structure in the material (e.g., nonmagnetic inclusions, segregations, grain boundaries, pores or local lattice distortions) in size comparable to the Bloch walls ( $0.12\ \mu\text{m}$ ) by a sort of pinning effect. Therefore, soft magnetic material should be single phase, of high purity, low porosity (at least rounded porosity), and large grain size [149]. The advantage of PM materials is based on their homogeneity, near-net-shaping capability, and the small amount of scrap (which is especially important for the materials with high alloying cost).

Most common PM materials are plain iron, in the best case sintered at high temperatures in  $\text{H}_2$  to form large grains, rounded porosity, and high density. This effect can be supported by the addition of 0.45 wt% P, which is known to be a sintering accelerator for iron by stabilizing bcc iron, but does not compromise the magnetic properties. Typical products are ABS sensor rings, contactors for industrial equipment, and poles for electric machines, starters dynamos etc. (Fig. 32).

Other soft PM material are  $\text{Fe}_3\text{Si}$  (at frequencies  $>1\ \text{Hz}$  the permeability is higher than with  $\text{Fe}_{0.45}\text{P}$ ),  $\text{NiFe}$  (50–80% Ni), which has the lowest saturation induction, and  $\text{CoFe}$  (35 wt% Co) with the highest saturation induction. Especially for  $\text{NiFe}$  and  $\text{CoFe}$ , PM production is competitive because of the possibility to produce complex shapes without material waste.

For conventional PM magnetic materials, higher frequencies lead to deterioration of the magnetic properties, especially energy losses caused by eddy current formation. Classical counteraction is to use laminated stacks. If



**Figure 32.** Pulse sensors (Fe and  $\text{Fe}_{0.45}\text{P}$ ) (AMES Sintered metallic components)



**Figure 33.** SMC components (AMES Sintered metallic components)

iron powder particles are insulated against on another by organic, inorganic ore mixed coatings the same effect is achieved. The material is called SMC (soft magnetic composite). These materials are not sintered, only cured or annealed at temperatures below  $500^\circ\text{C}$ , and the final strength levels are low. The insulating nonmagnetic phase reduces saturation induction and permeability, but at higher frequency ( $>100\ \text{Hz}$ ), permeability is higher than for plain iron, and eddy current losses are low. Typical products are stators and rotors for electric motors (Fig. 33). As the strength of the material is so low, recycling of the material (and separation from copper wires) is much easier than with laminated stacks [150, 151].

#### 6.4.2. Permanent Magnets

In modern permanent magnets (e.g.,  $\text{SmCo}_5$ ), extremely high crystal anisotropy is the basis of the superior permanent magnetic properties. This crystallographic texture cannot be produced by PM, these structures must be obtained by directional solidification. Therefore, the fraction of classical permanent magnets (e.g.,  $\text{AlNiCo}$ ) produced by PM is decreasing.

The most important modern permanent magnet materials are strontium and barium ferrites,  $\text{SmCo}_5$  [152] and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  [153]. The so-called superhard magnets provide extraordinarily high energy densities. The basic requirements (high saturation polarization and sufficiently high Curie temperatures) can only be fulfilled by rare earth transition-metal magnets. The basic microstructure of these materials is complex: it has to provide defect-free grains

of ferromagnetic phase to avoid local decrease of the anisotropy, combined with impurities or nonferromagnetic phases at the grain boundaries to prevent magnetic domain walls and flux fields from crossing the boundaries. Finally, the grains have to be well-aligned to optimize the total magnetic moment.

The production route consists of crushing and milling the melted material into monocrystalline powders (3–4  $\mu\text{m}$ ), compaction in a strong magnetic field to orient the particles (die compaction or CIP), and liquid phase sintering to full density. Special heat treatment to optimize the microstructure, shaping operations (cutting and finishing), and final magnetization are needed to finalize the product. Complications arise from the material having to be sintered to full density without grain coarsening. Careful control of the sintering atmosphere is essential because of the oxygen sensitivity of neodymium. Unfortunately, the usual reduction processes cannot be performed within the sintering window, therefore the oxygen content of the starting material and oxidation during the whole processing must be kept to a minimum, to prevent the depletion of the alloy of the rare earth component which would result in unfavourable magnetic properties. The major drawbacks of these super magnets are their brittleness, corrosion sensitivity, and the rather low Curie temperature (250–310°C).

Resin-bounded hard magnets have significantly lower magnetic properties, but they also offer manifold benefits like easier production, close tolerances, and low brittleness.

## 6.5. Cu and Cu Alloys

→ Copper, → Copper Alloys. Cu has a very high electrical and thermal conductivity under standard conditions (second of all metals, after silver). The combination of these properties with its ductility and corrosion resistance makes it very suitable for the production of electrical and electronic components in which conductivity is an essential attribute. The application of PM for the production of Cu structural parts allows reducing machining operations and production costs, while achieving the required level of properties. With

nearly full density PM parts, the physical and mechanical properties are comparable with those of cast and wrought Cu materials. PM manufacturing of Cu and Cu alloys is also supported by the low oxygen affinity of the elements which lowers the purity requirements of the sintering atmosphere.

Cu powders are commercially available with purities above 99%. Powder purity is an important characteristic because the impurities present in solid solution have a detrimental effect on conductivity. In addition, electrical properties of PM Cu parts are directly related to porosity. After standard pressing and sintering conditions, conductivities of 80–95% IACS. (International Annealed Copper Standard) can be reached. If higher conductivities are required, the density must be increased, e.g., through additional operations such as double-pressing double-sintering, or forging. PM copper parts are mainly used in electrical and electronic applications thanks to their excellent electrical conductivity. Some typical applications of PM Cu parts are twist-type electrical plugs, nose cones, shading coils, commutator rings, and contacts

Different methods can be used to produce Cu and Cu-alloyed powders, and the most important ones are atomization, oxide reduction, hydrometallurgy, and electrolysis. All these methods can provide Cu powders with purity of 99% or above. Copper alloys are produced using either mixes of elemental powders or prealloyed powders. The major Cu alloys produced by PM are bronze, brass, and nickel-silver. PM bronze (Cu–10 wt% Sn) is mostly produced from mixes of elemental Cu and Sn powders. In cast bronzes, it is difficult to avoid interdendritic interconnected porosity occurring as a consequence of the wide solidification range of the alloy, and the isolated porosity typical of PM bronze parts is an advantage. PM brass are Cu–Zn alloys with Zn contents ranging from 10 to 30 wt%; sintering of brass is, however, tricky because of the high vapor pressure of Zn [154]. Nickel silver has a nominal composition Cu–18Zn–18Ni and has properties similar to brass but with improved corrosion resistance and a silvery-gray color. Around 1–2 wt% Pb may be added to brass or nickel-silver alloys to improve machinability. While brass and nickel-silver alloys are most commonly

used in self-lubricating bearings, they are also frequently selected for structural applications where strength, corrosion resistance and appearance are important.

To improve the mechanical properties especially at high temperatures, oxide dispersion hardening (ODS) can be applied, with the nm-size dispersoids typically consisting of  $\text{Al}_2\text{O}_3$ . Its production can be performed through internal oxidation, i.e., exposing a Cu–Al powder to oxidizing conditions [155]. Oxygen is dissolved in the Cu matrix and precipitates Al as fine  $\text{Al}_2\text{O}_3$ . An alternative route is reaction milling, i.e., mechanical alloying of Cu, Al, and CuO powders [156]. In both cases, consolidation is performed by extrusion. ODS Cu is employed, e.g., for resistance welding electrodes and sliding electrical contacts such as pantograph strips.

A key feature of using PM for the production of Cu and its alloys is the ability of this technique to produce porous metallic parts in which the level of porosity as well as the shape and size distribution of pores are controlled. Important applications of parts with controlled porosity are self-lubricated bearings and the low-density materials used for the production of filters (Fig. 34).

*Self-lubricated bearings* are a very remarkable application of PM that consumes a major proportion of the Cu powder production. In self-lubricated bearings, the interconnected porosity of the PM part is intentionally kept around 10–30 vol% to store lubricant. During rotation of the shaft, friction increases the temperature,

and the lubricant is drawn out of the pores by capillary forces, supplying a continuous lubricating film. When rotation stops, the bearing cools down and the lubricant is withdrawn into the porosity by capillary action. As the process is reversible, the need for periodic external lubrication is eliminated. The most widely used material is bronze Cu–10 wt% Sn, often with addition of 0.5–2% graphite depending on the application. For applications that do not require a high level of performance, iron base and iron bronze compositions can be used, providing lower cost but also inferior corrosion properties. Self-lubricated bearings are produced by conventional press and sinter techniques. Both prealloyed and elemental powder mixes are used. In Cu-base bearings, low compaction pressures are applied (100–400 MPa), and sintering is carried out for short periods (about 3–8 min) at temperatures of 750–900°C. Bearings are usually sized after sintering, to obtain the required dimensional accuracy. Sizing conditions need to be carefully chosen to avoid closing the porosity in the bore.

In the production of *PM filters*, tin bronze is the material most commonly used, but also nickel silver, Cu–Ni–Sn, Ni-base alloys, and stainless steels are sometimes employed. Filters are a special application of PM in which the ability of the technique to provide close control of the amount, shape, and size of porosity, is successfully used. The properties of the filters are controlled through parameters such as the powder shape, particle size, and size distribution. For filters gravity sintered in molds,



**Figure 34.** PM Cu alloy parts (AMES Sintered metallic components)  
A) Bearings; B) Filters

spherical powders with a narrow particle size range are often used to have a close control on the pore size and permeability. PM filters can be applied for filtering solid particles, but also for separating air from liquids or mixtures of liquids. In this latter case, separation is based on the ability of certain liquids to wet the pore surfaces and thus pass through the interconnected porosity. Apart from filtering, PM filters are also used for sound damping and as flame arresters.

## 6.6. Al and Al Alloys

→ Aluminum; → Aluminum Alloys. Aluminum offers attractive properties for applications in which weight reduction is targeted for. It combines low density ( $2.7 \text{ g/cm}^3$ ) with good corrosion resistance, high electrical and thermal conductivity, and acceptable/good strength. The possibility to obtain near-net-shape parts makes Al PM competitive with other production methods that require expensive finishing operations. Conventional pressing and sintering is a cost-effective process that can produce high volumes of complex Al components [157, 158].

Sintering of PM Al parts is, however, challenging. The protective oxide layer covering the surface of metallic powders hinders the sintering mechanisms. This oxide is thermodynamically very stable and cannot be reduced by conventional means [159, 160]. To enable sintering the oxide layer must be reduced or at least disrupted. Different mechanisms have been used with that purpose: cracking during heating [159], disruption through the application of plastic deformation [161], formation of a liquid phase [162, 163], or through the addition of Mg [83, 164]. Magnesium has a double effect: On one hand, it acts as an oxygen getter and locally decreases the oxygen partial pressure of the atmosphere, and on the other hand, Mg reacts with aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and forms MgO or the spinel  $\text{MgAl}_2\text{O}_4$ . The change in volume caused by the transformation of the oxide contributes in cracking in the oxide layer [84, 158]. In most cases, sintering of Al is performed in the presence of a liquid phase, and the disruption of the oxide allows penetration of the liquid that wets the underlying metal and eventually causes breakage of the oxide layer [93]. The fragments

of the oxide layers, however, remain within the sintering contacts, and, therefore, especially the ductility of pressed and sintered alloys is usually inferior to that of wrought products.

### 6.6.1. Conventional Pressed and Sintered Aluminum Alloys

PM Al parts are commonly used for structural applications that require a lightweight material. Moreover, the excellent corrosion resistance and cost efficiency makes Al-PM very attractive for the automotive sector, where it has potential for replacing cast aluminum or PM ferrous parts.

Aluminum powders are mostly obtained by air atomization. Alloys are produced using mixes of Al powder with elemental alloying elements (such as Cu, Mg, Zn and Si), or with binary pre-alloyed powders with compositions near eutectic ( $\text{AlSi}_{12}$ ,  $\text{AlMg}_{50}$ ). Also, mixes of Al powders with master alloy powders containing all alloying elements provide good sintering response [84]. During processing, the low yield strength of Al powders enables the use of moderate compaction pressures (200–400 MPa) while achieving green densities of 90–95%. Lubrication (about 1.5 wt% admixed) is required during pressing, and it is very important to completely remove the lubricant before sintering because carbonaceous species interfere with sintering. This happens in pressed parts and still more in injection molded ones [165].

Sintering is usually performed at temperatures between 570 and 620°C in inert atmosphere. The highest as-sintered mechanical properties are achieved by sintering in dry nitrogen. Liquid phase sintering is commonly used, and due to the influence of the solid/liquid fraction on dimensional stability, a tight control of the sintering temperature is required.

Postsintering operations such as resin impregnation, chemical polishing, anodizing, and coloring can be performed on PM Al parts. Besides, as in the case of wrought Al alloys, PM Al parts can be strengthened by precipitation hardening. As liquid phase sintering is performed closely below the liquidus temperature of the material, as-sintered dimensional stability is at best moderate, and, therefore, sizing is standard with PM Al parts. In part, this also results in higher density, especially if done

immediately after rapid cooling from sintering/solution treatment; then artificial aging will follow [157].

One of the most successful applications of PM Al alloys within the automotive market is in camshaft bearing caps. The near-net-shape capability of the PM process and the self-lubricating effect of the porosity, together with a significant cost reduction (up to 50% depending on the part complexity) are the drivers for this application. Another example of a quite successful application is the fabrication of connecting rods, where the use of Al PM has allowed a reduction in weight with an increase in fatigue strength as compared with the forged material. The high thermal conductivity of Al also makes it very suitable for manufacturing heat sinks, with the high coefficient of thermal expansion of Al compensated by reinforcing the Al with SiC particles.

### 6.6.2. High-Performance Aluminum Alloys

Production of Al parts using PM technologies offers the possibility of refining the microstructure to obtain structures and compositions that cannot be achieved with other techniques [166]. Microstructural refinement can be obtained by using techniques such as rapid solidification or dispersion hardening.

*Rapid solidification* is a powder production method in which significant undercooling of the molten metals or alloys is imposed typically by atomization, melt spinning, or planar-flow casting. It provides powders with very fine microstructures and extends the solubility of alloying elements in aluminum, enabling precipitation hardening with phases that are much less sensitive to overaging than the phases from conventional elements such as Cu, Mg or Zn. This is because of the very low solubility of the alloy elements (e.g., Fe, Ce, V) in solid Al. Thus, the temperature range of applications is significantly extended compared to conventional 2xxx or 7xxx type alloys.

*Dispersion hardening* offers still better high temperature strength; it is generally achieved by using high-energy milling. Insoluble nm-sized dispersoids (oxides and carbides), can be used as reinforcements for producing high performance materials. Dispersion of carbides and fine oxides stabilizes fine-grained

microstructures [167]. Besides, mechanical alloying can also be used to increase solubility limits achieving systems with anomalous supersaturation of alloying elements (e.g., Al-Fe, Al-Ni, Al-Cr, Al-Ti). High-performance Al PM materials provide improved high-temperature creep resistance, fracture toughness, fatigue life, high specific stiffness, and corrosion resistance.

## 6.7. Ti and Ti Alloys

→ Titanium, Titanium Alloys, and Titanium Compounds. Titanium alloys offer an excellent combination of mechanical properties and low density ( $4.5 \text{ g/cm}^3$ ) with an outstanding corrosion behavior that is very attractive for highly demanding sectors such as the aerospace industry. It is thus not surprising that most of the research carried out in the area of PM Ti alloys is focused on the system Ti-6Al-4V, which is the most common aerospace titanium alloy. The main advantage of using PM for the production of Ti parts is in the net-shape capability of this processing route. Not only is Ti an expensive raw material, but also the cost of machining a component easily doubles the cost of the component. Hence, the more efficient use of material through the PM approach is a primary advantage [168–173]. However, because of the large specific surface of powders and powder compacts, interstitial control during processing is essential, with particular regard to the oxygen content, because Ti absorbs O in the lattice at elevated temperature (as it does with C, N, and H), and oxygen once absorbed cannot be removed any more.

Production of Ti alloys by PM usually follows two different approaches: the *blended elemental method* (BE) and the *prealloyed* technique (PA). BE approach consists on mixing fine elemental Ti powders (usually obtained as byproducts of the Hunter or Kroll reduction processes [173]) with a master alloy powder containing all the alloying elements. Elemental mixes are generally shaped by die pressing or CIP and then sintered at 1150–1320°C in vacuum. Avoiding contamination is critical because it seriously damages the performance of PM Ti parts, especially the ductility. Following the

processing route described, densities around 99% can be obtained (which would be considered as full density in many PM materials such as e.g., ferrous alloys), but for Ti alloys 1% residual porosity is enough to degrade fatigue and fracture properties [168]. By selecting the proper powders and suitable combinations of compaction techniques (CIP and HIP) and sintering parameters, fully dense BE parts can be obtained with static properties comparable to those of wrought materials [169]. With the PA approach, a fully prealloyed powder presenting the desired final composition is used. Prealloyed powders are typically produced by crucible-less gas atomization, or with the plasma rotating electrode process (PREP), with which powder cleanliness is a major concern. Powders are generally processed by using HIP to obtain full density products. Also here, low levels of contamination are critical to avoid substantial loss of inherent properties, particularly fatigue properties [170, 172]. Both approaches (BE and PA) are in use by the industry. While BE is mostly used to produce low cost parts that do not have high requirements in terms of fatigue properties, PA—with a higher production cost—is normally used to obtain demanding components with high requirements of mechanical properties and particularly with good fatigue performance.

PM Ti alloys have an important potential of growth through approaches such as MIM and additive manufacturing [169, 174–176]:

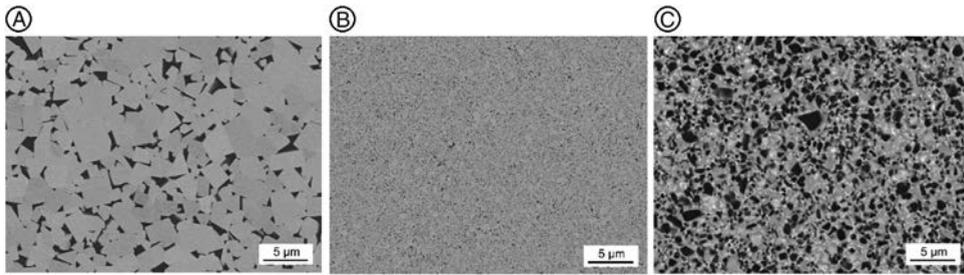
MIM is a very attractive processing technique for Ti parts, as it gives the possibility to perform large series of very complex parts with high material utilization rate and low production costs. A major technological challenge is however the high affinity of Ti for carbon and oxygen and the strong detrimental influence of these elements on the mechanical properties of Ti PM parts. The binder composition and the removal of the organic binder used in the MIM process are critical, because Ti has also a high tendency to absorb carbon. Hence, the growth of Ti MIM will be critically influenced by the successful development of low cost spherical powders as well as effective feedstock compositions and debinding processes [176]. Ti MIM is applied for the production of medical implants, where the good corrosion resistance and biocompatibility are a great asset. Further

applications are in the aerospace and in the consumer industry (for instance in the production of watch cases).

Additive manufacturing (AM) of Ti PM parts also offers a very high growth potential since it gives the possibility to produce cost effective near net shape parts with features impossible to obtain with any other techniques, and can also be used for repairing damaged parts [173, 177]. Through a correct understanding of the AM process, knowledge of the alloy phase transformations and control of the processing parameters, AM can provide tailored microstructures and properties. The challenge presented by the high reactivity of Ti powders can be overcome by the use of inert chamber processing, Ar for direct laser melting (which, however, may result in Ar-filled pores) and vacuum in electron-beam melting. AM Ti parts are mainly used in aerospace and medical industries. The most significant disadvantage is the need for high-cost spherical powders. However, recent studies show the possibility of producing Ti PM parts from lower cost angular powders [178, 179].

## 6.8. Hardphase-Based Materials

As PM offers the chance to combine very dissimilar materials, it is the primary production route for tool materials based on hard phases. The main group of such materials contains WC as the hard phase, combined with binders from the Fe group of metals. They are commonly known as *hard metals* or *cemented carbides* [180–183] (→ Carbides, Chap. 2 Metal-like Carbides of Industrial Importance). Hard metals are the most important tool materials in service today and are available in a wide variety of compositions [184], depending on the respective application: turning, milling or drilling of metals and of wood, stone, and concrete cutting, rock drilling etc. [185, 186]. A second group of tool materials are *cermets* (ceramic–metal composites) which are based on TiCN and contain similar binders as WC based hard metals. Whereas WC–Co hard metals are fairly metallic because WC has a relatively high thermal and electrical conductivity, the cermets are more ceramic-like, which means higher hot hardness but also lower conductivity and toughness. The materials also differ in microstructure: while



**Figure 35.** Microstructures of carbide-based PM cutting materials (Ceratzit Luxembourg)  
 A) WC–Co hard metal, coarse grade; B) WC–Co hard metal, ultrafine grade; C) TiCN-based cermet

WC–Co hard metals are characterized by a WC skeleton that consists of angular WC grains with low-energy surfaces (Fig. 35A), in the cermets the hard phase grains are more rounded and exhibit a typical core-rim structure with concentration gradients within the individual grains (Fig. 35B).

WC–Co-based hard metals are available in numerous different grades. One crucial parameter is the binder content, which controls the toughness of the material. Metal cutting grades have typically lower binder content, for turning about 6 mass% and for interrupted cutting, such as milling, in the range of 10%. Rock-drilling and stone- and concrete-cutting grades, which need higher toughness, are frequently more binder-rich. For special applications, *binderless hard metals* are employed that are made, e.g., by pressure-assisted sintering [183]. The second relevant parameter is the WC grain size, which may vary from <200 nm up to >20 μm. Ultrafine and fine grades are used in metal cutting or for special drills used in the electronics industry [12, 187, 188], and coarse grades are employed in rock drilling etc. To increase the hot hardness, the addition of cubic carbides such as TiC, NbC, and TaC is beneficial, and such grades are used mainly in metal machining. Also, the composition of the binder may vary. WC–Co proved to be the optimum regarding properties, but just this combination is harmful as fine powder or grinding dust, resulting in the so-called “hard metal (lung) disease” [189, 190]. Addition of further elements, such as Ni or Fe, was found to lower the health hazard, but sintering and carbon control are trickier here [191–193]. Binders containing Cr improve the corrosion resistance of hard metals which is desirable for some

applications. Also, Mn containing binders have been studied [82]; here the high vapor pressure of Mn is a challenge.

A very important parameter for WC–Co is the carbon content. The two-phase field WC–Co is relatively narrow regarding the useful carbon interval, especially for low binder grades. If the carbon content is set too high, free carbon is present in the microstructure, which adversely affects the properties; at too low C levels, brittle  $\eta$ -carbides  $(\text{Co}, \text{W})_6\text{C}$  or  $(\text{Co}, \text{W})_{12}\text{C}$  are formed which strongly decrease the toughness [182].

Manufacturing of hard metal tools can be done following different routes. At first, the powders are intensely mixed, which is done either by ball milling or attritor milling, typically in a milling fluid, a hydrocarbon or also water. Pressing aids or plasticizers are added if appropriate. Then, the slurry is granulated, usually by spray drying. For cutting inserts, the granulate is uniaxially die compacted; for larger blocks, cold isostatic pressing is done. Drills are mostly produced by extrusion of a powder mix with plasticizer; usually longitudinal bores are co-extruded through which drilling fluid can be piped during operation of the drill. Small tools with complex shapes can also be produced by powder injection molding. Before sintering, the organic components have to be removed, by lubricant burnout in the die-compacted parts and by debinding with extruded or MIM specimens. Sintering is done in vacuum, mostly following the sinter-HIP route, i.e., vacuum sintering with application of 70–100 bar Ar pressure in the final stage, to close the few remaining pores. Oxygen removal is a crucial step because it affects also the carbon content, with C the

only reducing agent available. Typically, the oxide layers covering the WC particles are reduced at about 700°C, above which temperature sintering starts, discernible through densification. Except for very coarse grades, most of the densification occurs through solid state sintering, i.e. below the eutectic temperature; nevertheless, liquid phase sintering is essential to obtain the final density as well as the typical hard metal microstructure with resulting optimum combination of hardness and toughness. For coarse and medium hard metal grades, grain growth during liquid phase sintering is not an item, whereas for fine and ultrafine grades, with WC grain size well below 1  $\mu\text{m}$ , grain growth inhibitors, typically VC or  $\text{Cr}_3\text{C}_2$ , have to be added to stabilize the fine microstructure [82].

For metal cutting, hard metals are typically coated by chemical (CVD) or physical (PVD) vapor deposition of ceramic layers such as TiC, TiN,  $\text{Al}_2\text{O}_3$ , TiAlN, etc. Usually numerous thin layers of different hard phases are deposited, resulting in multilayer coatings. PVD can be done at lower temperatures than CVD and results in more favorable residual stresses, but CVD results in more regular coating of all surfaces. For both coating techniques, suitable preparation of the hard metal surface is essential.

Cermets are manufactured in a similar way; here, however, the balance between C and N in the carbonitride can be used to shift the C–N ratio in a desired way, producing graded microstructures near the surface that in some cases can eliminate the need for coatings [194].

A special type of ceramic–metal composites are the TiC-reinforced steel grades commercially available as *Ferro-Titanit* [195]. Here the hard phase content is significantly lower than in hard metals, but the steel matrix can be suitably heat treated, which results in interesting property profiles for niche applications.

A further commercially highly important group of PM materials are diamond–metal composites widely used for cutting of rocks and concrete [196]. Typically, a low amount—in the range of 5 vol%—of diamond grit with a few 100  $\mu\text{m}$  diameter is contained in a metallic matrix that may be bronze-, Co-, or Fe-based and may be reinforced by hard phases. The metal–diamond mix is consolidated either by die compacting with subsequent pressureless

sintering or by hot pressing, for which the consolidation parameters are selected such as to avoid undesired interaction between diamond and matrix, such as dissolution or graphitization.

Diamond grade as well as binder composition and microstructure have to be carefully chosen for the respective material to be cut—concrete, limestone, granite, etc.: the diamond grains should be well bonded to the matrix as long as they are sharp-edged and cut well; as soon as the edges are blunted, the grains should break out of the matrix, and the metal phase should be worn such that other, new and sharp-edged diamond grains are exposed. Too high wear means unnecessary low tool life whereas too low wear results in rubbing of the tool against the workpiece without cutting and thus just in waste of energy. Therefore, the metallic binders are usually complex systems that contain carefully balanced phases to grant optimum cutting performance.

## 6.9. Refractory Metals

### 6.9.1. Monolithic Refractory Metals

Refractory metals were the first to be processed at the beginning of modern powder metallurgy in the early 20th century because at that time it was not possible to melt them, particularly W with its very high melting point of  $>3400^\circ\text{C}$  [9, 181]. This incentive does not hold any more, but nevertheless for the refractory metals W, Mo, Ta, and Cr, and to some extent also Nb, PM continues to be the dominant production route [33, 197]. The main reason is that ingot metallurgy results in coarse microstructure and in brittle behavior while PM enables attaining fine, regular microstructure that is well suited for subsequent deformation processes. Furthermore, PM offers the chance to eliminate an inherent weakness especially of W and Mo, the tendency to grain coarsening and resulting embrittlement during high temperature applications. The PM manufacturing route enables the introduction of finely dispersed second phases that inhibit grain growth, thus stabilizing the microstructure and the mechanical behavior. Typical dispersoids are TiC, ZrC, HfC, and  $\text{La}_2\text{O}_3$ .  $\text{ThO}_2$  was also used, e.g., in welding

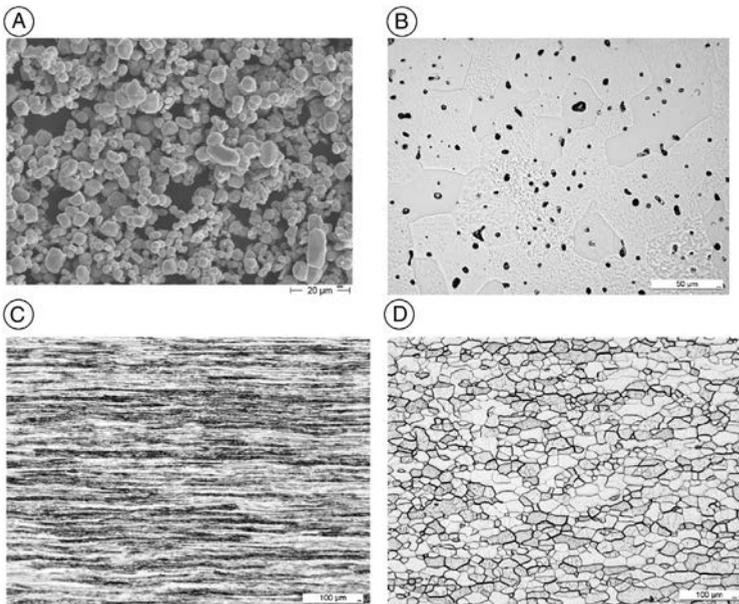
electrodes, but is no longer permitted because of radioactivity. For lamp filaments of the *nonsag* grades [198], fine bubbles (<100 nm) filled with K vapor serve the same purpose, particularly, by forcing grain growth parallel to the wire axis, resulting in elongated interlocking grains which structure results in high creep resistance (i.e., the nonsag behavior).

Refractory metals are usually manufactured as semifinished products, as sheet, bar, or wire. Production starts from oxides that in case of Mo and W are reduced in hydrogen atmosphere to obtain metal powders <10  $\mu\text{m}$ . For Ta and Nb, metallothermic reduction with Na is done or fused salt electrolysis, and Cr powder is produced by electrolysis from aqueous chromate solutions with subsequent milling of the Cr flakes. Dispersoids or their precursors are either added already to the oxide or to the metal powder, and homogeneous distribution is essential here. Consolidation is done mostly by CIP with stepwise sintering in  $\text{H}_2$  (Mo, W) or vacuum (Ta), and the removal of interstitials, especially O, is essential here. After sintering, some closed porosity is usually left in the compacts that is then eliminated by subsequent hot working such as rolling or wire drawing (Fig. 36).

Refractory metals are marketed as semifinished products, but also as final products with defined shape, and a multitude of different components is available from a limited number of suppliers. Mo and W are used for high-temperature applications in nonoxidizing environment, such as furnace heating elements and radiation shield, X-ray anodes—mostly from W–Re alloys—welding electrodes, and, especially Mo, as sputter targets for PVD coatings in the electronics industry. For applications in oxidizing environment, protective coatings have been developed [199]. Ta finds its main applications in corrosion-resistant components for the chemical industry as well as in capacitors. Cr is employed in interconnects for fuel cells, and these components are net-shape manufactured by the press-and sinter route.

### 6.9.2. Two-Phase Refractory Metals

Tungsten is the heaviest commercially affordable metal, with a density of  $19.3 \text{ g/cm}^3$ . However, it is relatively brittle and poorly machinable. To circumvent this, W base pseudoalloys with Ni and Fe, Cu, Co, the so-called tungsten heavy alloys can be used [200]



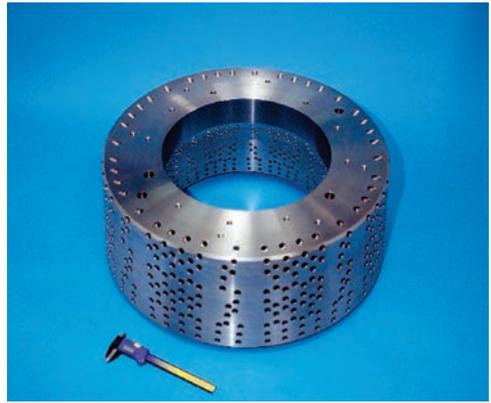
**Figure 36.** Molybdenum in different states of PM production (Plansee SE)  
A) Powder; B) Section of sintered Mo; C) Sintered and hot-rolled; D) Hot-rolled and annealed

(→ Tungsten, Tungsten Alloys, and Tungsten Compounds, Section 5.2 Multiple Phase Alloys). These materials contain 90 to 96 mass% W and typically Ni and Fe in a ratio of 2:1; if paramagnetism is required, Ni–Cu binders are used.

Manufacturing follows the classical PM route: the starting powders, typically  $<10\ \mu\text{m}$ , are mixed, cold compacted—mostly isostatically—, occasionally also through MIM, and then sintered in flowing  $\text{H}_2$  at temperatures at which the binder melts and forms a persistent liquid phase, for W–Ni–Fe heavy alloys in the range of 1460–1500°C. This results in virtually dense materials that contain roughly spherical W grains of 50–80  $\mu\text{m}$  diameter cemented together by an austenitic Ni–Fe–W matrix. This combination of strong W and ductile austenite results in excellent property profiles. A degassing treatment in vacuum removes the dissolved hydrogen, thus further improving the ductility.

These heavy alloys offer density levels of 17.0–18.5  $\text{g}/\text{cm}^3$  and, after degassing heat treatment, a tensile strength of 900–1000 MPa and elongation to fracture of 20–40%; they are, however, sensitive to embrittlement by atmospheric constituents and trace impurities [201–204]. The strength can be increased up to 1400 MPa, e.g., by swaging. A further benefit of the heavy alloys is their excellent machinability. They are not really high-temperature materials, as is plain W, but are employed if high density is required together with excellent mechanical properties, such as in balancing weights or low-vibration shafts. Also, radiation shields are made from heavy alloys that offer much better antifire protection than, e.g., lead (Fig. 37). A major proportion of heavy alloys are used in defence, for antitank projectiles, so-called penetrators.

Another type of W-base pseudoalloys are of W–Cu type, occasionally also W–Ag. They are used, e.g., as high-power contact materials in which the excellent conductivity of Cu is combined with the high arc resistance of W. Such contacts W–10–30%Cu are typically employed in SF6-insulated switches with maximum switching capacity. They are characterized by a “penetration microstructure,” i.e., two continuous phases are intensely intertwined. Such contacts are usually manufactured by first



**Figure 37.** W heavy alloy collimator for radiotherapy; mass ca. 2 t (Plansee SE)

producing a porous W body that is presintered. The W body is then inserted into a mold and infiltrated with liquid Cu, the melt penetrating the pores of the W skeleton. After solidification, the remaining Cu forms the basis for the switch and serves as the connector. As an alternative, also liquid phase sintering is possible, usually enhanced by a small amount of Ni added (Figure 38).

A further application of W–Cu and Mo–Cu are heat sinks and housings for power electronics [205, 206] that spread the heat generated in microprocessors to prevent overheating. In this case, the interesting properties are high thermal conductivity and a coefficient of thermal expansion that is not too far off that of the Si which forms the base of the microprocessor, to minimize thermally induced stresses during



**Figure 38.** W–Cu tipped high-power electrical contacts (Plansee SE)

operation. Such heat sinks can be manufactured by the press-and-sinter route or also by MIM, and, typically, composite powders are used to enhance the sintering activity. Also for highly loaded components in fusion reactors, W–Cu materials with graded structures are tested [207].

For medium voltages and currents, typically up to 70 kV and 30 kA, vacuum switches are employed that are equipped with Cu–Cr contact materials [208]. These contacts are frequently made by ingot metallurgy, but also PM is employed, typically the press-and-sinter route, which is able to generate net-shape contact geometries. Compositions may vary from Cu–25%Cr to Cu–50%Cr. A major requirement is the absence of interstitial elements that might form gases during operation since in such switches high vacuum must be maintained for at least 30 years.

## 6.10. PM Superalloys

Superalloys are metallic materials that retain significant strength up to temperatures close to the solidus and are chemically stable in heavily oxidizing and corrosive atmospheres. Typical examples are the turbines in jet engines [209, 210]. For superalloy components, especially for aerospace applications, the PM route is attractive both regarding the material aspect and the shaping capabilities as recognized quite early [211, 212]. As a consequence of the very high cooling rates during powder production by atomizing, segregation, which is a problem in ingot metallurgy (IM) production, can be largely suppressed, the PM route thus offering extremely homogeneous, virtually segregation-free microstructure [213]. In that respect, PM superalloys are similar to PM tool and high-speed steels. Furthermore, enhancing the high-temperature properties by dispersion strengthening is possible only via the PM route.

Superalloys are expensive also from the material aspect because they are based on Ni, in part Co, and containing further costly alloy elements. Furthermore, they are difficult to machine, and therefore the net shaping consolidation techniques offered by PM are welcome [213–215] because they avoid the extensive machining operations required for ingot

metallurgy products, with resulting poor fly-to-buy ratio. For these reasons, PM manufacturing of components for turbines, particularly turbine disks, has been investigated quite early [216] (the most highly loaded components of a jet engine, the single-crystal blades in the high-pressure section of the turbine, are produced by investment casting). For PM superalloy components, the route by inert-gas atomization and HIP using suitably shaped capsules is mostly chosen. After HIP and removal of the capsules by machining or chemical etching, only some finish machining is required, thus eliminating most of the usual machining operations and dramatically reducing the amount of expensive scrap. Extrusion of the HIPed billets helps in decreasing the size of defects contained [210], but at the expense of net-shape capability. Further production routes are MIM and, most recently, additive manufacturing.

Singular defects, particularly, nonmetallic inclusions, and their effect on fatigue properties are critical factors. Especially for rapidly rotating superalloy components such as turbine disks, the reliability is an essential question, and here PM products have been regarded with some scepticism, despite systematic studies on the effect of inclusion that have significantly improved knowledge on the correlations between defects and fatigue in general [217]. The problem has been countered by the use of fine starting powder grades because in powders screened to <100  $\mu\text{m}$ , in part even <50  $\mu\text{m}$ , no larger defects can be present. For manufacturing of superalloy parts by powder injection molding, interstitial control, especially regarding debinding, is a crucial item [218]; also here, however, control of inclusions is essential [219].

The first PM Ni-base superalloys were more or less PM variants of conventional wrought grades. Later, compositions that are inaccessible by ingot metallurgy were obtained (Table 7) [220]; however, the limit regarding alloying content was set by the requirements towards defect tolerance [221].

Another group of superalloys that are inaccessible by IM are the dispersion-strengthened grades [156, 222]. These materials are commonly produced by a relatively laborious process, including attritor milling, CIP/HIP, and extrusion, and frequently a defined recrystallization treatment is done to obtain

**Table 7.** Composition of Ni-base PM superalloys [195]

Element	Alloy designation					
	Rene 95	Rene 88DT	Astroloy	MERL76	IN-100	IN-18
C	0.06	0.03	0.02	0.02	0.07	0.02
Cr	13	16	14.5	12.4	12.5	11.5
Co	7	13	16.5	18.5	18.5	15.7
Mo	3.5	4.0	5–0	3.2	3.2	6.5
W	3.5	4.0	–	–	–	–
Ti	2.5	3.7	3.5	5.0	4.4	4.35
Al	3.5	2.0	4.0	4.3	5.0	4.35
B	0.007	0.015	0.03	0.02	0.02	0.02
Zr	0.005	0.03	0.06	0.05	0.06	0.03
Other	Nb 3.5	Nb 0.7	–	Nb 1.65	V 0.8	Hf 0.5

elongated, coarse-grained microstructure for high creep resistance. Here, both austenitic grades (PM1000, PM3030) and ferritic grades (PM2000) were produced, of which the grade PM2000 (Fe-20Cr-6Al-0.5Y<sub>2</sub>O<sub>3</sub>) is attractive from the property profile. However, the production was stopped around 2006, and the similar dispersion-strengthened ferritic (Fe–Cr–Al-based) PM superalloys Kanthal APM and AMPT have entered the market, which are manufactured by the more economical HIP route and offer excellent high temperature strength, particularly the AMPT grade, and resistance to oxidation, with service temperatures in air of up to >1400°C given by the manufacturer [195]. These superalloys are not so much used in aerospace applications but for industrial applications such as furnace technology and in glassmaking.

## 7. Acknowledgements

The authors wish to thank the following companies, institutions, and persons for their support: AMES—Sintered metallic components, Barcelona, Spain; Boehlerit GmbH, Kapfenberg, Austria; Ceratizit Luxembourg S.a.r.l., Mamer, Luxembourg; European Powder Metallurgy Association (EPMA), Shrewsbury, UK; Fraunhofer-IFAM, Bremen, Germany; Höganäs AB Sweden; Prof. Gerhard Leichtfried, Innsbruck, Austria; MIBA Sinter Austria GmbH, Vorchdorf, Austria; Plansee SE, Reutte, Austria; Profiroll Technologies GmbH, Bad Dübren, Germany; Sandvik Coromant Co.,

Stockholm, Sweden; Prof. Wolf-Dieter Schubert, Vienna, Austria

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