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Faculty of Metallurgy and Materials Engineering



POWDER METALLURGY

(university textbook)

Kateřina Skotnicová, Miroslav Kursá, Ivo Szurman

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1. INTRODUCTION



Study time: 2 hours



Objective

- The history of powder metallurgy
- Advantages and limits of powder metallurgy



Lecture

Powder metallurgy deals with a technical manufacture of powder metals, metalloids, metal alloys or compounds and their processing to a finished product shape without melting-down their main components. Powder metallurgy includes also a manufacture and processing of nonmetal powders to products, which exhibit metallic properties, such as iron oxide based magnetic materials – the so-called ferrites, sintered corundum for machining and forming, some types of semiconductors etc.

From the historical point of view, powder metallurgy (PM) has been the world's oldest kind of metallurgy, which has been proved by archaeological discoveries from different parts of the world. For example, powdered gold was used by Incas for jewelry making and iron powder was known to Egyptians as early as 3000 years B.C. Daggers decorated with granulated gold were found in a tomb of the Egyptian pharaoh Tutankhamun (Fig. 1.1), who lived in the 14th century B.C. These ornamental (decorative) powders of gold, silver, copper and other metals were made by grinding particles of these metals or amalgams in a special mortar. Mercury evaporated while heating an amalgam and the obtained powders were used for a manufacture of pigments. Powders were also prepared by mechanical pulverizing in water or by reduction of oxides. The manufacture of iron components was wide-spread around 800 – 600 B.C. in Greece. Later on the metallic iron was used to make weapons. At those times, the compaction of several pieces of a sponge iron into demanded shapes by forging was the only way to make needed objects of iron. The sponge iron was prepared by reduction of an iron ore using charcoal. Most of products made this way were limited in size of pieces weighing several kilograms. An interesting historical artefact is a non-rusting iron pillar in Delhi (Fig. 1.2), which was erected by king Chandragupta II around 375 – 414 B.C. The pillar of 7.21m in height, 0.41 m in a diameter and more than 6 tons in weight is a testimony of craftsmanship of medieval India's blacksmiths. It was probably made by forging hot pieces of reduced iron obtained by direct reduction of iron oxides without melting. It has attracted a great attention by the fact that it has remained in a good state for 1600 years without a more serious detriment caused for example by a corrosion due to the rainy weather in Delhi. This phenomenon has been explained by a high content of phosphorus in iron, which reacted with iron, air humidity and oxygen and thus a coating was formed, protecting the pillar against corrosion over the course of centuries. Powder metallurgy principles were also used by Arabians and Germans around 1000 A.D. to make high quality swords of iron powder. These methods for iron and steel making through powder metallurgy were replaced by smelted iron metallurgy accompanied with a development of high-temperature furnaces for iron and steel reduction and processing in the 17th and 18th century.

Powder metallurgy started to be used in a larger extent at the turn of the 19th and 20th century, namely for industrial making of metals with a high melting point temperature – tungsten (3422°C) and molybdenum (2623 °C), for which no suitable melting equipment existed. Thomas Edison's invention of the light bulb in October 1879 essentially contributed to the development of tungsten powder metallurgy for a manufacture of filaments. The first filaments for electric lamps were based on

osmium, carbon and tantalum, however, they were very brittle. It was tungsten with its high melting point temperature and favourable electrical properties which appeared the most suitable material for the manufacture of the filaments. A great advancement was achieved through a development in the tungsten filament manufacture by drawing at room temperature, which was patented by W. D. Coolidge in 1909. He found out that the application of a sufficiently high temperature of sintering and subsequent forging led to a significant increase in the tungsten ductility, enabling its drawing to wire at room temperature. Further, it was also possible to form filaments as threads of very small diameters which improved the effectiveness of filaments in light bulbs significantly.

In the early 20th century the first sintered metal-carbon based compounds started to be produced commercially, featuring high electrical conductivity of copper (or silver) and excellent lubricating properties of graphite. A development of these materials was connected with the development of the technology of machines and equipment, such as dynamos and electric power engines. Since 1920, further composite materials started to be developed known under the name “hardmetals or cemented (sintered) carbides”. Their main application has been a manufacture of high wear resistant tools. After 1930, a manufacture of sintered materials with controlled porosity began – self-lubricating bearings, membranes, metallic filters etc. After the World War II, the attention started to be paid to bearings and friction materials based on iron and bronze, usually containing nonmetallic additions. These are metal-oxide based composites, the so-called cermets, used for special high-temperature purposes. In the 70s the development of the second generation cermets featuring finer and more uniform structure began. These were based on the use of special alloys based on a metallic binder and non-oxide material, such as carbides, borides, nitrides and their mixed phases. The follow-up development involved a manufacture of contact and electrode materials, a wide range of electric and magnetic materials and finally the use of powder metallurgy for production of special components as a competitive process to the conventional methods of casting, processing and machining.

Powder metallurgy advantages

Powder metallurgy products have been used above all in the automotive industry, engineering industry, aircraft industry, medicine, oil industry etc. In practice, the PM technology can be successfully applied to a manufacture of components from all typical metal materials. This also enables to make components of very complicated shapes, often without a necessity of final machining which brings-in considerable material as well as energy savings. In many cases properties of a material manufactured using the PM technology surpasses an adequate material made with the use of a different technology. These are e.g. hard (the so-called high-speed) steels for machining, some aluminium alloys, sliding materials, magnetic materials etc. The ability to combine alloys which could be produced only with difficulties or could not be produced at all using the conventional casting metallurgy allows obtaining almost any material with combined or new properties. This characteristic is particularly useful for components with:

- very different melting temperatures,
- a limited mutual solubility in a liquid state,
- very different densities.

Other advantages of powder metallurgy

- A possibility to manufacture new materials based on a combination of metal and nonmetal compounds and on a combination of elements which cannot be made by different methods.
- Narrow dimensional tolerances without costly secondary operations.
- Pores can be infiltrated by other metals to achieve improvement in special properties and weight by as much as 100 %.
- Porosity regulation also enables to make components such as self-lubricating bearings and surfaces, sintered metal filters, catalyzer balls etc.
- In a manufacture of components the proportion of waste is less than 4 %.

- Raw materials are easily available and cheap.
- Each duplicate of a component is precise and unchanged.
- A possibility to make high wear resistant surfaces.
- A less number of complex operations needed to obtain a finished component Components are chemically homogenous.
- A higher production efficiency in comparison with most machining methods.
- A short time of preparation from a design to a finished component.
- Components for magnetic applications, as well as permanent magnets for electromagnets, can be manufactured in any shape and any magnetic quality.
- A possibility to join two kinds of different materials, which allows successful and economically profitable solution of a problem of creating different functions within various parts of one component (e.g. a joint of ferromagnetic steel with non-ferromagnetic materials based on copper).



Fig. 1.1 Two daggers found in King Tutankhamun's tomb: one with a gold blade, and one of smelted iron [1].



Fig. 1.2 Non-rusting iron pillar in Delhi [2].

Limitations of powder metallurgy:

1. *A product shape and size* – a shape is defined by possibilities of the pressing (moulding) technology, a product size depends on a maximum pressing power of the equipment and principles of pressure propagation in powder.
2. *A sintered product density* – it is very difficult to reach a volume weight almost identical with density of a metal or an alloy manufactured by casting.

**Summary of terms****Powder metallurgy****History of powder metallurgy****Iron sponge****Questions to the topic**

- 1.1. Which are the main advantages and limits of powder metallurgy?
- 1.2. Which types of materials can be prepared by powder metallurgy?
- 1.3. What are the main applications for PM components?

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2. POWDER METAL PRODUCTION TECHNOLOGY



Study time: 6 hours



Objective

- Overview of production methods of powder materials
- Principles of powder production techniques
- Characterization of particle shape and morphology depending on the production technique



Lecture

A production method for powder materials affects their physical and technological properties considerably. Almost all materials can be manufactured in a form of powder, but a choice of the manufacturing technology depends on the material specific properties. There are four basic manufacturing processes:

1. Mechanical
2. Physical-mechanical
3. Chemical
4. Physical-chemical

Except these basic methods, other special technologies are used for certain types of materials. Formation of powder requires supplying a material with energy needed for creating a new surface area. The process efficiency, energetic capacity, the initial material type, possible sources of contamination etc. are important characteristics. For example, when disintegrating 1 m^3 of metal to particles of $1 \mu\text{m}$, around $2 \cdot 10^{18}$ of spherical particles with a surface area of c. $6 \cdot 10^6 \text{ m}^2$ can originate. The energy needed for creation of such an area of a surface is great and is defined by the process efficiency. The choice of the manufacturing technology depends on economic aspects, demanded resulting characteristics of the powder and the particular application type.

2.1 Grinding and milling

2.1.1 Qualitative changes occurring during disintegrating

The mechanical crushing principle lies in a transfer of the mechanical motion energy onto the disintegrated material. This energy causes the mechanical stress in crystals which, regarding to the material physical properties, results in the material disintegration. The dimension reduction process in the solid state is then based on the fracture mechanism: nucleation and crack propagation, followed by a fracture accompanied by a formation of new surfaces. An increase of the specific surface of particles and a decrease of the surface roughness leads to an increase of capillary forces in the powder volume, which is characterized as the geometric activity. In metal powders the regions with strong discontinuities occur, where attractive forces of structural elements of the matter (atoms, ions, molecules) are off balance, and thus significant structure failures emerge. Therefore the surface is a place of occurrence of free energy (related to an area) which is the larger the more structural elements surrounded only by a small number of neighbours are on the surface. The size and energetic state of the powder material surface imply the amount of the total surface energy and this, compared to

compact materials, results in the higher reaction ability – the structure activity. Imperfections in powder particles, which can partly protrude to their surface, can also contribute to the structure activity. Both the influences are stronger and stronger with a decreasing size of powders. A lattice deformation and an increasing density of vacancies, interstitions and dislocations give rise to internal stresses, resulting in an increase of a number of grain boundaries. The internal stresses and particularly dislocations and structure boundaries, which remain effective up to high temperatures, are of a considerable significance for sintering and they allow further compaction of a porous material.

The following belong among the basic mechanical disintegration processes: impact, shear, wear and pressure (Fig. 2.1). An impact includes a fast stroke of a material, which leads to a crack origination and the ensuing dimension reduction. A wear is applied to the dimension reduction of particles through a friction motion, while a shear forms a cleavage fracture. For powder making, the mentioned disintegrating mechanisms are often combined and they are characterized by an irregular shape.

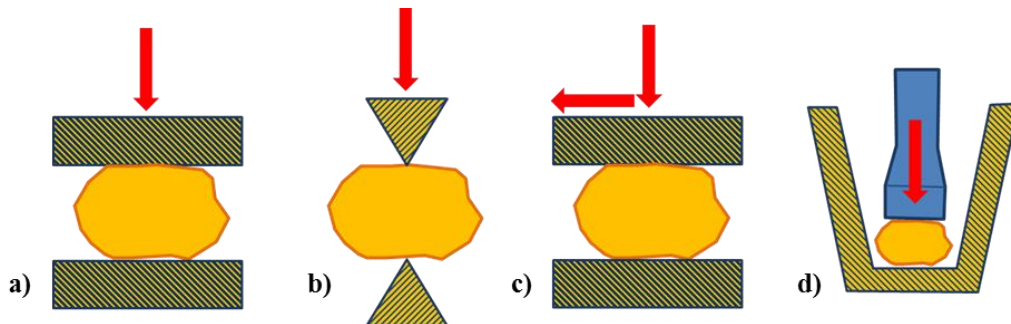


Fig. 2.1 Basic disintegration procedures: a) pressure, b) shear, c) wear, d) impact.

A limited minimal particle size, which can be obtained, depends both on the mechanical process conditions and on properties of the material itself. This grinding and milling balance was found out for many metal and nonmetal powders and ranges between 0.1 up to 1 μm . It has been explained by several independent processes:

- In a solid material, the bonds are not the same in the entire volume, but a certain spectrum of bonds depends on types and a concentration of imperfections. These imperfections can be of macro, micro or atom extent. Only poorer bonds can be disturbed by mechanical ways and a further dimension reduction of small particles is very complicated.
- The smaller particles, the more difficult the application of necessary shear stresses on each particle and to reach the fracture.
- Small particles feature higher surface activity than larger particles, therefore re-bonding can occur more probably.

2.1.2 Grinding

To grind a sintered sponge metal from reduction and electrolytic processes, jaw and hammer crushers are used above all. Grinding in a jaw crusher is performed between a fixed jaw and a moving one (Fig. 2. 2) and represents the first stage of disintegration, where a coarse powder is obtained. This is subsequently milled to a final product in some type of a mill. In a hammer grinder the material is crushed using an impact of hammers attached on a rotor.

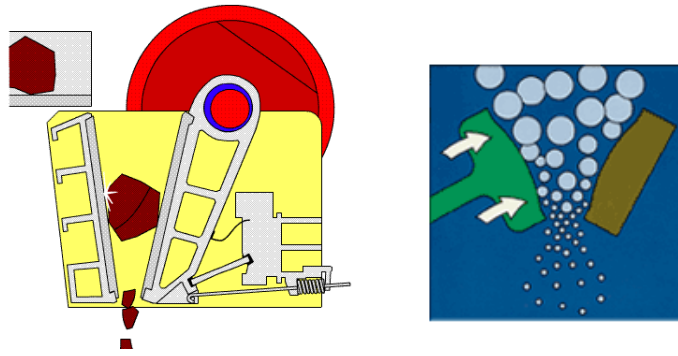


Fig. 2.2 Jaw crusher principle [4].

2.1.3 Milling

The simplest device is a ball mill where milling is performed by mechanical impacts of hard milling objects carried up by a rotary motion of a drum onto the disintegrated powder. The milling objects, balls, rollers or rods inserted into the milling drums, are manufactured from unalloyed and stainless steel, pottery, agate, hardmetal etc. depending on hardness, milling capability and demanded cleanliness of powders. Milling can be carried out dry or wet, whereas the application of a suitable surface active liquid makes the disintegration easier. The work needed for the disintegration can be formulated as follows:

$$\Delta A = \Delta S \cdot \gamma$$

where ΔS – enlargement of a surface area (m^2) and γ – surface stress (N/m)

Surge stress σ needed to disintegrate a brittle material when milling depends on a structure of imperfections and susceptibility to the crack propagation:

$$\sigma = (2 E \cdot r / D)^{1/2}$$

where E – Young's modulus; r – a radius of a tip of an existing crack or defect; D – a particle size

In wet milling the liquid prevents the formation of larger secondary particles and, moreover, a decrease of the γ value occurs as a result of the liquid adsorption on the particles' surface. By this a necessary output of the aggregate can be decreased or fineness of particles can be enhanced. For very intensive grinding the so-called attritors are used (Fig. 2. 3), where a motion of the milled material (grist) and milling balls is achieved by a agitating element and circulation pump providing a circulation of the liquid with powder. The disintegration is carried out by friction between the grist and milling balls.

To determine relative energy needed for milling the given powder material type of an initial granularity D_p (m) to the final size D_k (m), the empirical relationship may be utilized:

$$W = g \cdot (D_k^{-a} - D_p^{-a})$$

where g is a constant depending on the material, mill design and milling conditions. The exponent a ranges from 1 to 2. The energy needed for the powder refinement changes with a relative change of the particle dimensions. A milling time depends on the output, particle size change, milling medium, mill rotational speed. Milling is not too advisable for malleable metals, because they are very difficult to disintegrate and their bonding occurs, which reduces the process effectiveness.

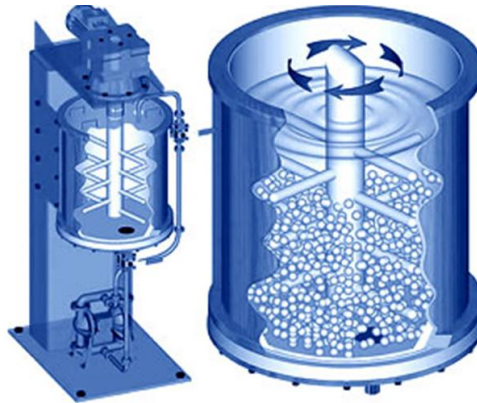


Fig. 2.3 Attritor for intensive material milling [5].

2.1.4 Mechanical alloying

The so-called attritor mill is used for mechanical alloying. A production of composites with a controlled uniform distribution of the second phase in the metallic matrix is its principle. The process allows a development of special microstructures important for achieving favourable high-temperature mechanical properties. For example, materials dispersion hardened by oxides feature high-temperature creep resistance. The mechanical alloying principle is depicted in Fig. 2.4. The process consists in a long-time milling of a powder mixture containing a formable matrix as the main component.

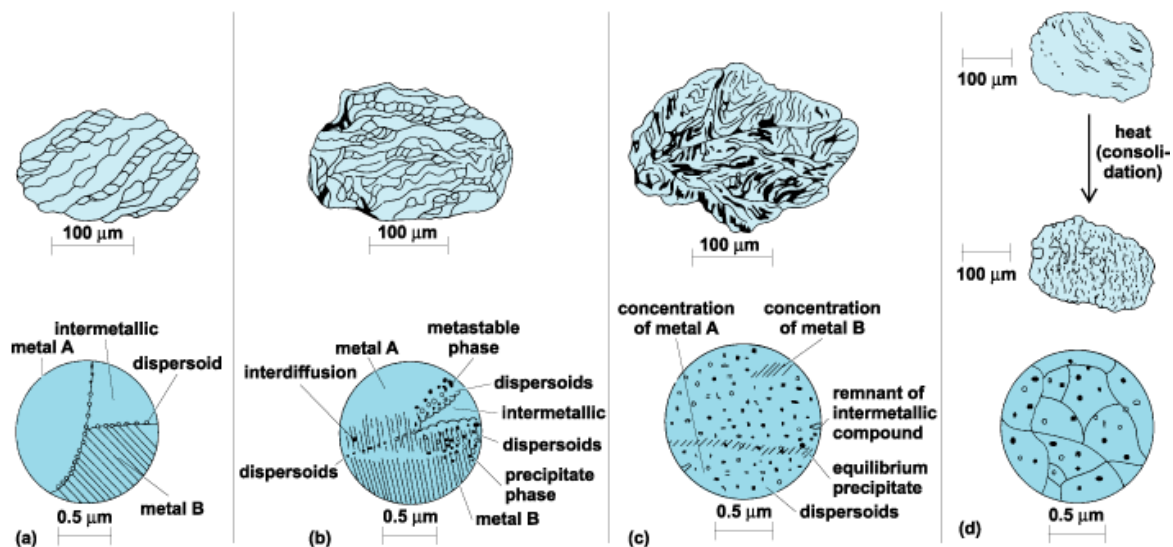


Fig. 2.4 Mechanical alloying principle: a) intensive cold-welding; b) fracture (shattering); c) consolidation of the cold-welding; d) the end of the process [6].

The result of the intensive high-energetic interaction between the balls and the powder is that the formable phase is subjected to the continuous cycle of plastic deformation, fracture and re-joining (re-welding), while fine dispersoids are gradually implemented into its volume. This means that alloying is a result of a repeating fracture and cold welding of particles of particular components. Using this process, metastable materials in the nanometric range as well as amorphous powders can be prepared. High-energetic milling can also induce chemical reactions, e.g. when preparing magnetic oxide-metal nanocomposites by mechanically induced reactions between a metal oxide and a more reactive metal.

2.2 Physical-mechanical production methods

These methods of a manufacture of powder metals and alloys include above all spraying or atomization of melts, the principle of which lies in application of a pressure gas, a fluid jet or centrifugal forces on molten metal (Fig. 2.5). Formed drops solidify subsequently due to rapid cooling-down in the spraying medium. Properties of the obtained particles (size, shape, morphology, structure...) are determined by many factors and their mutual combinations:

- the melt temperature;
- the melt viscosity and surface stress;
- cooling conditions;
- atomization conditions.

Various shapes of atomized particles are documented in Figs. 2.6 and 2.7. The higher the melt overheating and mechanical energy applied on the melt, the larger the proportion of the fine powder. The powder size is reduced with the increasing melt temperature, i.e. with the decreasing viscosity. The melt surface stress, and thus also a shape of originating particles, can be influenced in the preparation by additives such as B, P, etc. These additives in a larger amount can change even the melt viscosity significantly.

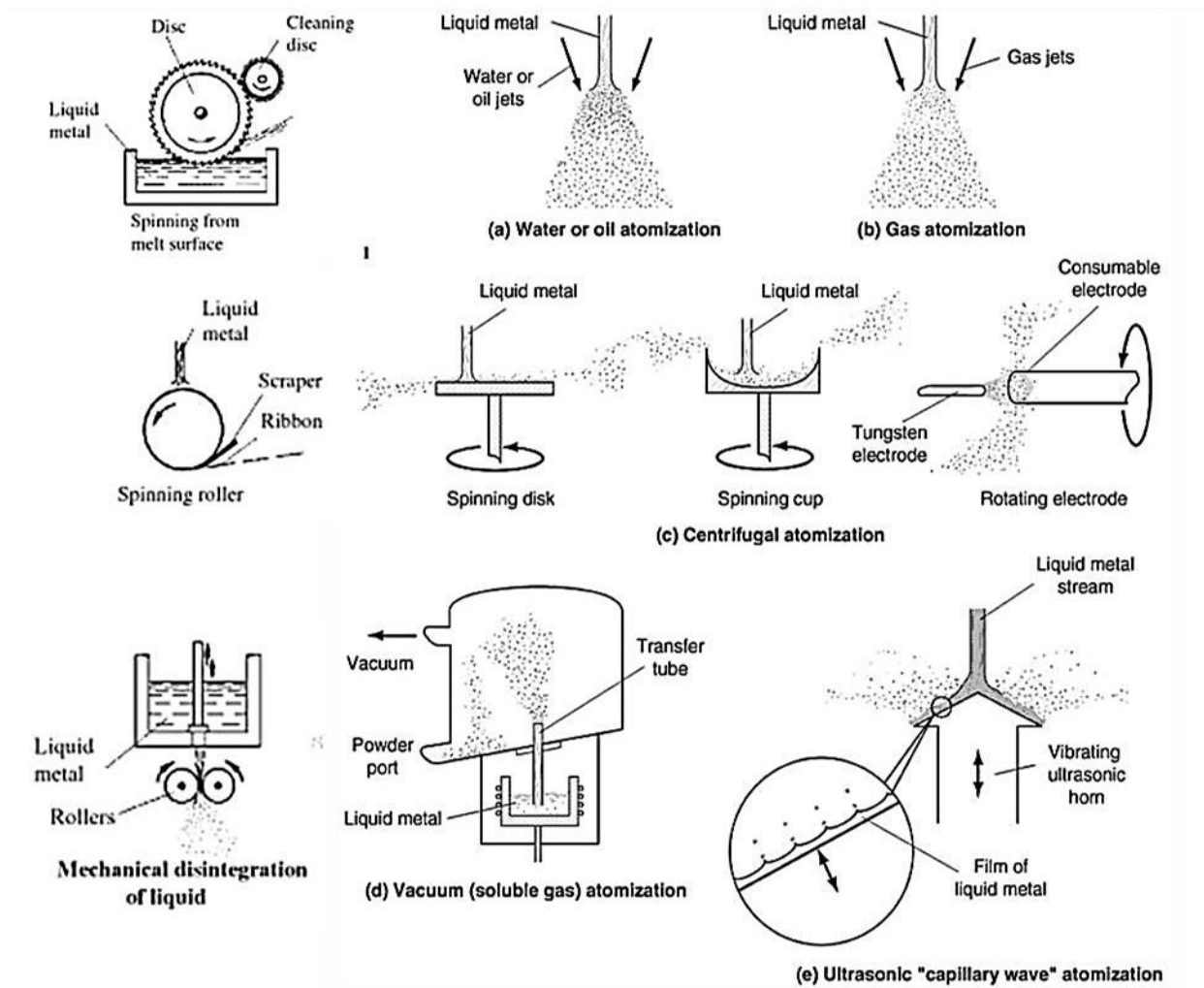


Fig. 2.5 Schematic depiction of possible methods of the melt atomization [7].

The rapid melt cooling allows obtaining a fine and homogenous distribution of particular components of an alloy in particles; otherwise they would segregate intensely by reason of a different weight, e.g. Fe-Pb, Cu-Pb based alloys etc. Another advantage is preventing a formation of coarse-grained structure components (precipitates) which would be formed during a slow cooling-down. For example, these are various types of carbides in high-speed steels.

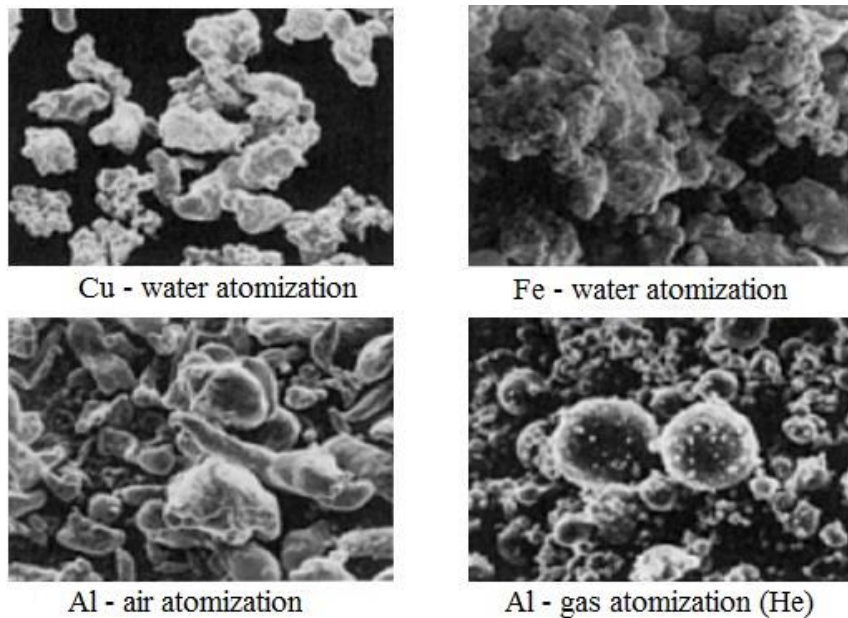


Fig. 2.6 A shape and a structure of particles obtained by various methods of the melt atomization [7].

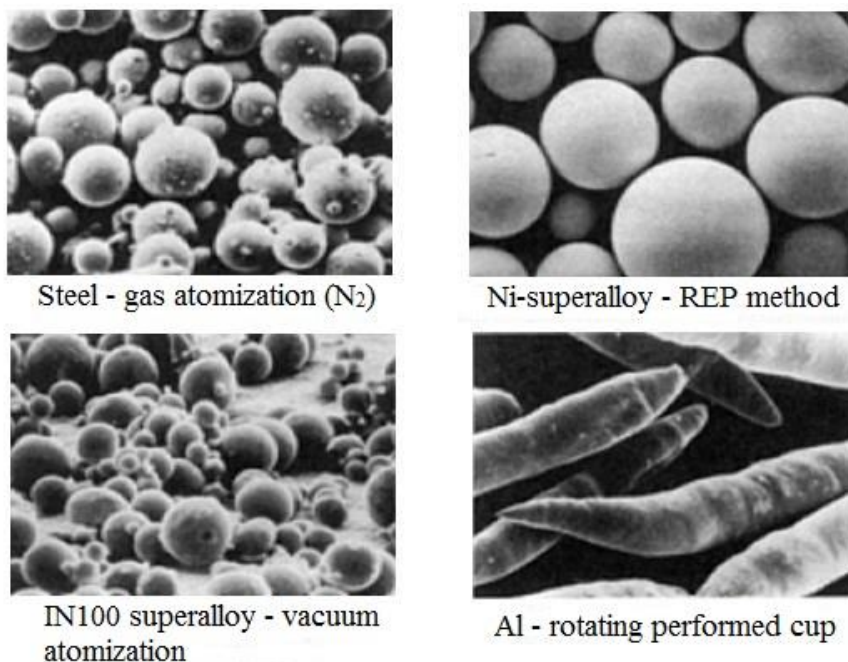


Fig. 2.7 A shape and a structure of particles obtained by various methods of the melt atomization [7].

2.2.1 Water atomization

A melt stream gets “splintered” by a water jet. The process of water atomizing of melts features high density of the spraying medium (water), high cooling speed and vapour formation in a

point of water and melt contact (Fig. 2.8). The high water density $\rho_{\text{H}_2\text{O}} \approx 10^3 \rho_{\text{air}}$ leads to a significant increase of momentum ($p = mv$) and kinetic energy ($E_k = mv^2/2$) of the medium. Compared to other methods, the water atomization is economically more profitable on the ground of a low price of the spraying medium (water) and very high productivity which can be up to 30 t/h. The obtained particles are characterized by an irregular shape and the relatively high oxygen content. Therefore, e.g. when making powder aluminium, considering its tendency to spontaneous ignition it is more suitable to apply an inert gas spraying (nitrogen, argon). Key parameters of the water atomization process and a basic configuration of water nozzles are shown in Fig. 2.9 and 2.10.

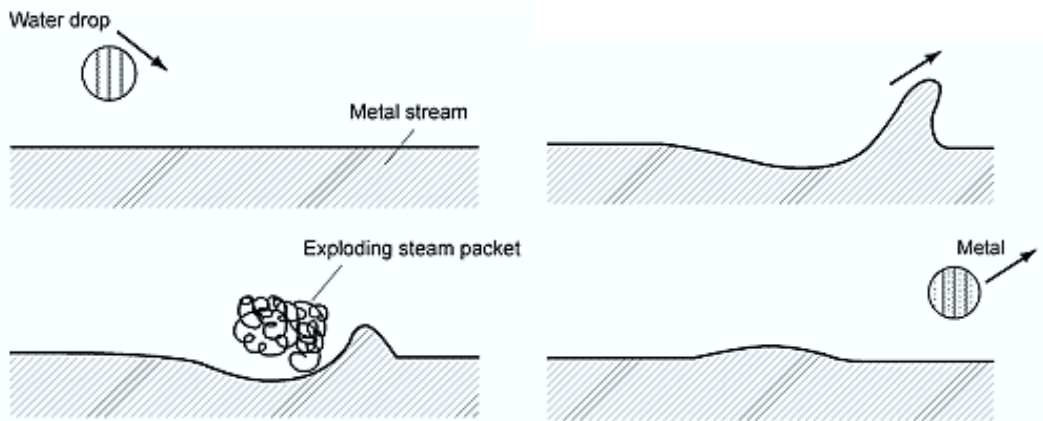


Fig. 2.8 Metal drop formation mechanism during the process of the water atomization of melts [7].

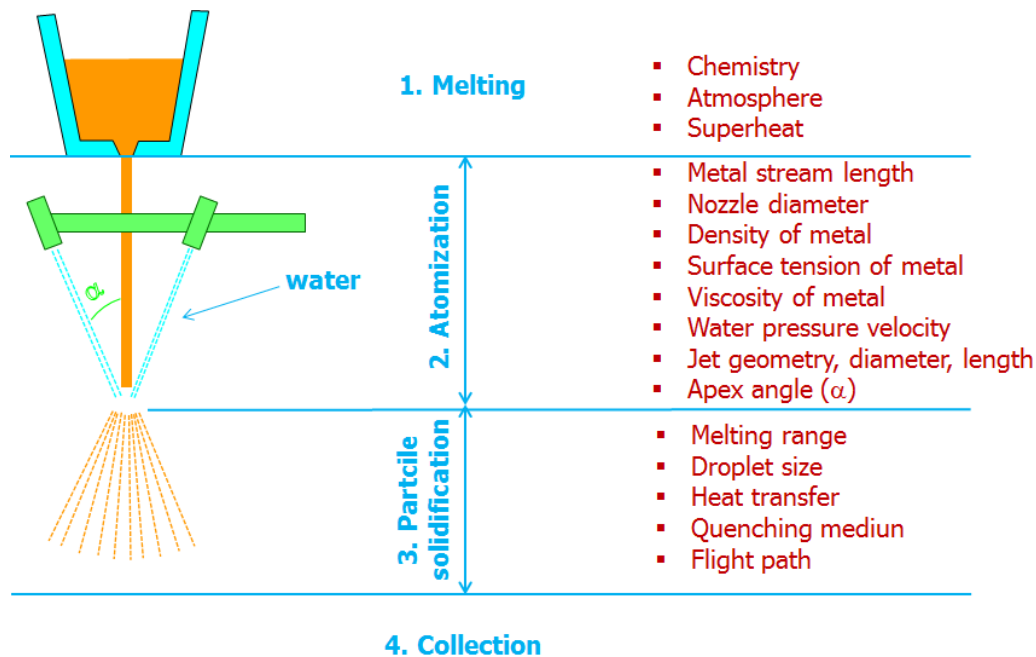


Fig. 2.9 Key parameters of the process of the water atomization of melts.

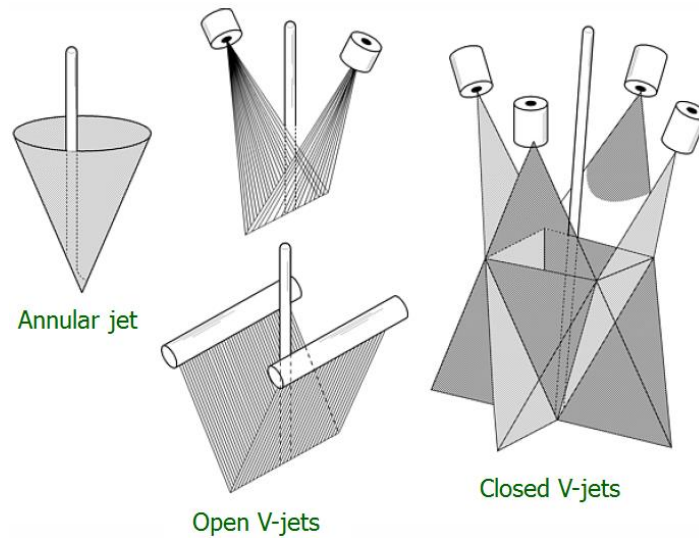


Fig. 2.10 Basic configuration of water nozzles [7].

2.2.2 Gas atomization

A principle of the gas atomization (Fig. 2. 11) is the melt stream disintegration by air, nitrogen, helium or argon flowing from the nozzles under pressure. This method is preferably used for a manufacture of nickel-based superalloy powders and many other high alloyed materials. The resulting characteristics of the powder are given by many process parameters, such as the gas type, residual atmosphere, melting temperature and viscosity, alloy type, melt charging velocity, gas pressure, gas speed and viscosity, nozzle geometry and gas temperature. The main advantage of the gas atomization of melts is the production homogeneity and good properties of the powder resulting from the spherical shape.

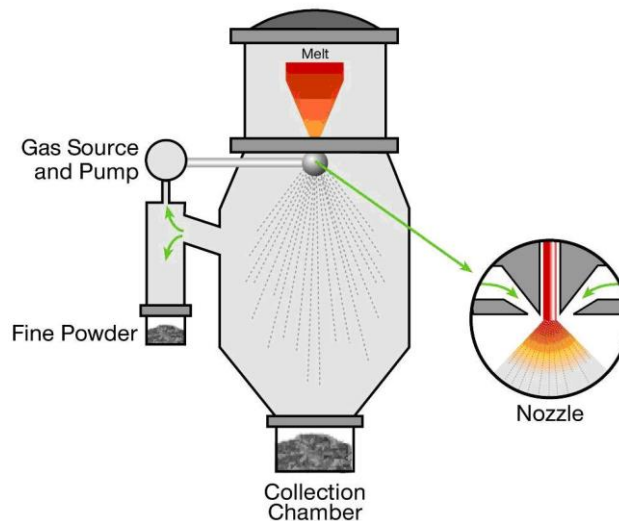


Fig. 2.11 Gas atomization principle [8].

The drop formation mechanism during the gas atomization process, determined by Dombrowski and Johns, occurs in three phases – see Fig. 2.12. In the first phase the formation of sinusoidal waves rapidly increasing their amplitude on a melt layer occurs. In the second phase these waves are smashed and melt ligaments are formed, being subsequently disintegrated into individual drops and spheroidized in the third phase.

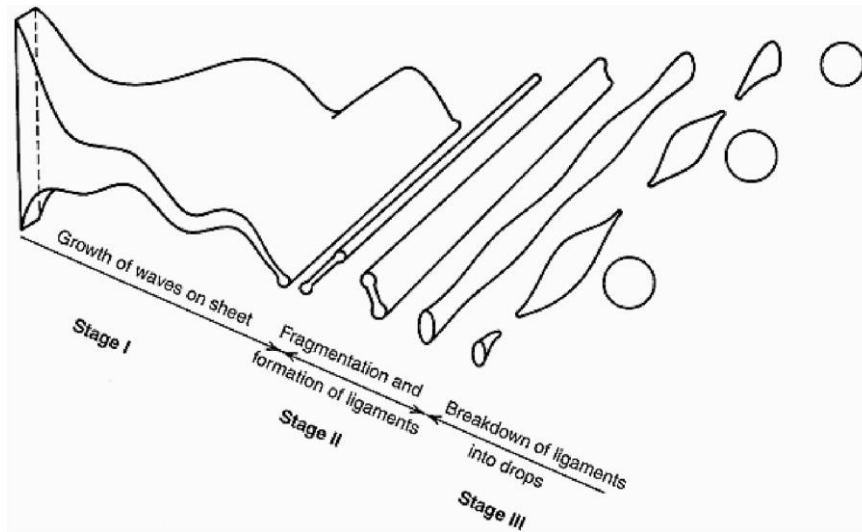


Fig. 2.12 The drop formation mechanism during the gas atomization process [7].

A mean size of powder particles obtained from the gas atomization ranges between 20 up to 300 μm . The particle shape is usually spherical (globular) or near-spherical. Irregular shapes of particles can be formed only in systems where the reactions between a gas and a molten metal lead to a formation of surface layers (for instance the air atomization of aluminium).

The air atomization of melts is applied for a manufacture of iron powder using the RZ (Roheisen-Zunder) method. This is a metal granulation method where molten cast iron containing 3 – 4 % C is sprayed into fine particles by application of a compressed air flow and individual particles oxidize on the surface. A carbon content in the particle volume and oxygen amount on its surface have to be regulated by the process conditions, so that their fusion occurs during annealing at 800°C – 1100 °C temperature, while creating CO and the resulting product does not contain oxygen and carbon anymore. The powder obtained is characterized by excellent compressibility.

There are lots of construction solutions for the gas atomization equipment. In principle, there are three types according to the nozzle configuration: 1. free fall, 2. enclosed, 3. internal mixing – the gas and molten metal get mixed before the inlet into the atomization chamber (Fig. 2. 13).

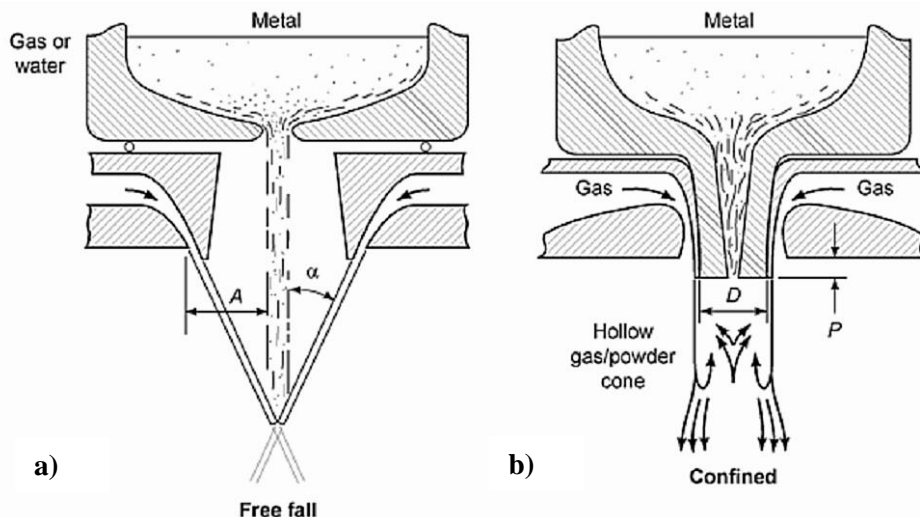


Fig. 2.13 Gas atomization equipment configuration: a) free fall (water, gas) – a molten metal stream flows-out from a funnel and falls down 100 – 200 mm by acting of the gravitation force into the atomization chamber, where it is sprayed by a gas (or water); b) – enclosed nozzles [7].

2.2.3 Centrifugal atomization

The melt atomization methods using the centrifugal force can be divided to one-stage and two-stage processes. The basic methods using the one-stage process include the Rotation Electrode Process (REP) and the Plasma Rotating Electrode Process (PREP). The REP method comprises an apparatus where two electrodes are placed – an anode of the appropriate alloy of which the powder is made and a tungsten cathode. By applying a voltage, an arc occurs between the electrodes and the alloy electrode surface becomes smelted. By rotating this electrode (1000 to 20000 rpm) the smelted metal drops are sprayed inside a tank which has a cooled outer surface. The PREP method principle is similar, but a helium plasma arc is excited between the alloy metal anode and the water-cooled tungsten cathode, which smelts the anode surface and due to the centrifugal forces the melt drops are separated. The electrode, which rotates at the speed up to 15000 rpm, has to meet strict requirements for stability, homogeneity and surface quality. The advantage of this method is achieving a high purity product and the fact that the melt is not in a contact with a ceramic crucible and a supporting plate. Therefore it is used e.g. for making the powder of titanium and its alloys, with regard to its corrosion behavior in the liquid phase.

The two-stage process involves melting of the given metal or alloy (for instance with the help of the induction heating in a melting crucible) and the melt disintegration with the aid of a quickly rotating cooled wheel, disc or crucible separately in two steps. A problem in the two-stage process is a transmission of the high rotational speeds to the melt. This atomization method is used for a manufacture of powders of aluminium, titanium alloys, superalloys and high-melting point metals.

At relatively low rotational speeds and low velocity of the melt charging, the melt disintegration occurs through the direct drop formation mechanism (DDF) – see Fig. 2. 14. When the centrifugal force and the surface stress are in equilibrium, a growth of “protrusions” occurs on the edge of the electrode or the disc, from which primary particles are emitted as soon as the surface stress is lower than the centrifugal force. For a short time, these particles are connected to the edge by a thin strip of the melt, which is then also emitted as a secondary particle. The particle size distribution then features a bimodal character. At higher melt charging speeds, a “protrusion” extends to a ligament which is disintegrated to a chain of many particles by the ligament disintegration mechanism (LD). The amount of secondary particles increases continuously along with the melt charging (feeding) velocity. At high melt charging velocities a thin film is formed on the edge of the disc, from which drops are emitted directly through the film disintegration mechanism (FD). A diameter of melt drops reduces with an increase of the rotational speed, the melt density and a decrease of the melt feeding velocity. The particles exhibit a spherical shape.



Fig. 2.14 Melt disintegration mechanisms during the centrifugal force atomization [9].

An advantage of the centrifugal force melt atomization is obtaining a narrow particle-size distribution. For the one-stage process, a mean particle size ranges between 150 to 250 μm . For the two-stage process, where rotational speeds up to 25000 rpm may be applied, a mean particle size 80 to 90 μm can be obtained.

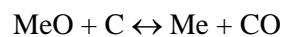
2.3 Chemical production methods

2.3.1 Reduction of metal compounds

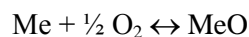
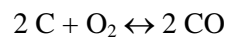
Reduction of metal compounds using a solid or gaseous reducing agent represents one of the most significant methods of powder metal making. Metal contamination with slag, which occurs in the melting process, is eliminated during reduction in the solid phase. However, the obtained metal powder needs to be further refined by mechanical, magnetic or chemical procedures.

Further, for reduction processes applies that initial materials have to feature adequate dispersiveness, so that thermodynamically passable reactions can run effectively and in an actual time. In solid phase – gas reactions (including oxidation-reduction reactions with carbon) the rate of diffusion of the reducing gas in oxide is considerably accelerated, and subsequently also an offtake of reaction products (mostly gaseous) through the metal layer.

Carbon and hydrogen are the main reducing agents, either in the elementary form or in the form of their compounds and mixtures - CH₄, CO, cracked NH₃, etc. As reduction processes take place mostly at elevated temperatures (≥ 800 °C), at which the equilibrium is on the part of CO origination, the summary reduction reaction can be generally expressed as follows:



Partial reaction:



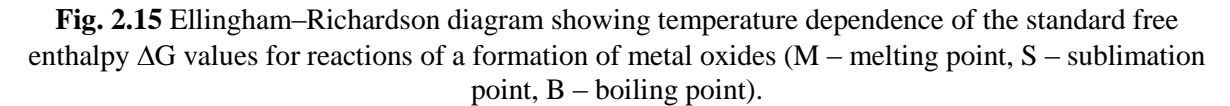
Equilibrium constant of the reaction:

$$K_a = \frac{a_{\text{Me}} \cdot a_{\text{CO}}}{a_{\text{MeO}} \cdot a_{\text{C}}}; K_p = p_{\text{CO}}$$

Under a boundary condition, the activity of the solid mutually insoluble components equals $a = 1$ and the activity of CO vapour phase corresponds to the partial pressure p_{CO} . The thermodynamic data for the most important reactions of metal oxides with carbon is shown in the so-called Ellingham–Richardson diagram in Fig. 2. 15, which makes possible to assess practicability of the course of the reaction at the chosen temperature.

Using a gas for the metal compound reduction is not as effective as for carbon, because free enthalpy of $\Delta G_{\text{H}_2\text{O}}$ and ΔG_{CO_2} is quite low. Therefore only oxides of relatively noble metals can be reduced using CO. In the case of H₂ the reduction conditions can be improved by taking-off reaction products and using a well-dried gas, enabling to keep the $p_{\text{H}_2\text{O}}/p_{\text{H}_2}$ ratio on a low level. General principles of the reduction of metals oxides by hydrogen include the following:

- A higher temperature and longer reduction time results in a formation of larger particles with a smaller specific surface and a lower content of residual oxygen. Sintering of powder material may occur.
- A lower temperature and shorter reduction time results in a formation of small particles with a larger specific surface and a higher content of residual oxygen. A formation of pyrophoric powder may occur.
- A high hydrogen flow rate with a low dew-point results in high reduction rate, low content of residual oxygen and preventing re-oxidation of reduced powder during cooling-down.



Reduction processes are used to produce more than one half of the world production of iron powder for powder metallurgy applications. The input raw materials for its manufacture are iron oxides which are used especially in a form of ores or scales. They are usually reduced using solid (coke, furnace black) or gaseous (CO , CH_4 ...) reducing agents.

$$\text{MeO} + \text{CO} \leftrightarrow \text{Me} + \text{CO}_2$$

Except this main reaction, side reactions, such as carburization of iron, formation of Fe_3C carbides, etc. can occur, however, they are insignificant for the particular reduction processes.

As a matter of fact, when reducing Fe_3O_4 using CO at temperatures $< 650^\circ\text{C}$, no reaction between Fe_3O_4 and CO occurs. Also, on the ground of the temperature dependence of the reaction



the equilibrium shifting to the benefit of CO only occurs from temperatures of 700 °C, which explains the high reduction capacity of carbon at higher temperatures (Fig. 2. 16).

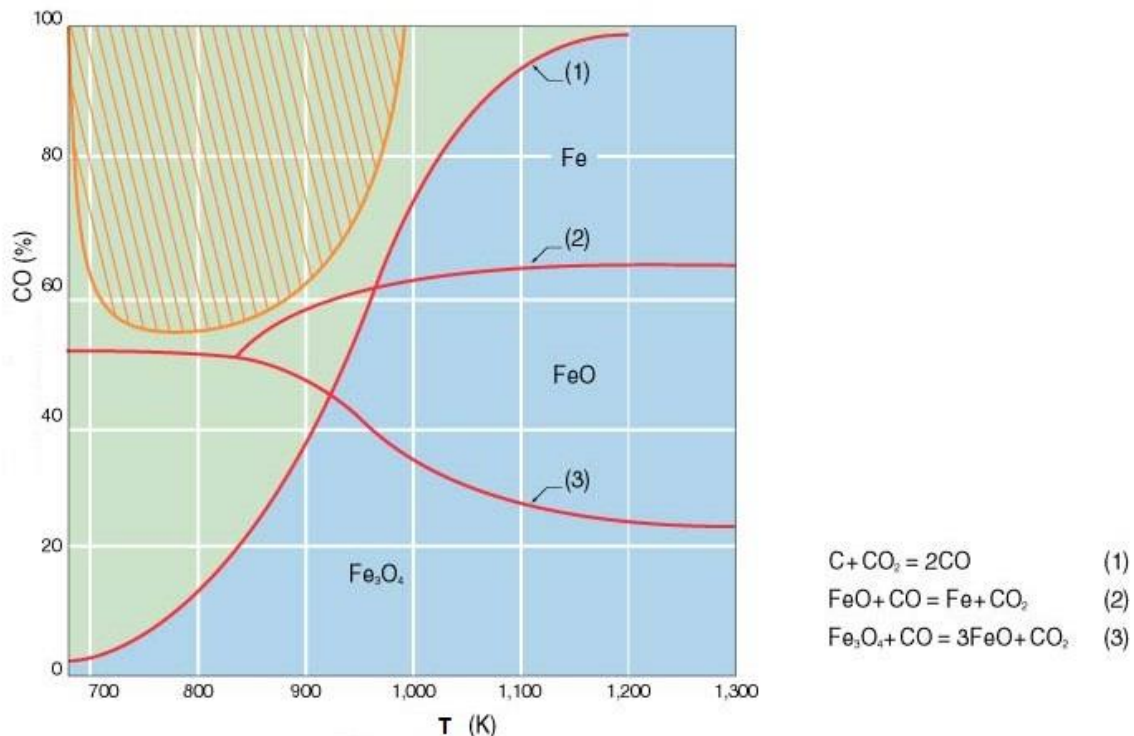


Fig. 2.16 Equilibrium curves for reduction of metal oxides by carbon depending on temperature [10].

The direct reduction only takes place, when particles of a reduced oxide are in the direct contact with a deoxidizing agent. The reduction by carbon monoxide, the gaseous deoxidizing agent, – the so-called indirect reduction – runs substantially faster than the reduction by solid carbon, because the reduction gas both envelopes particles to be reduced, and penetrates in their pores. In this reduction CO is consumed, while CO₂ originates. Follow-up, carbon monoxide is regenerated from carbon dioxide by adding a solid deoxidizing agent (carbon, coke, charcoal, etc.) through the Boudouard reaction. This reaction kinetics is determined by the chemical reaction rate at low temperatures, by the diffusion rate at higher temperatures.

For an effective progression of the reduction, the following properties and conditions need to be considered:

- a reducing agent ratio to side products;
- dividing of solid reducing agents;
- a proper supply of gaseous reducing agents to the reduced material;
- porosity or permeability of the reduced material, which has been specified – by a size of particles, their structure, surface area, formation of clusters and other properties;
- a layer thickness and density;
- a motion of the reduced material;
- heat supply for endothermic reactions;
- a time and thermal course of the reaction.

The “Höganäs” process is the most significant one among iron powder manufacturing procedures. The fine Fe₃O₄ magnetite and a reducing mixture consisting of coke mixed with lime are input raw materials for this process. Both the raw materials are dried-up separately in rotary kilns and

then crushed to particles < 0.5 mm. Moreover, Fe_3O_4 is separated from undesirable adulterants by applying a magnetic field. Reduction is carried out in a tunnel gas-heated furnace and lasts for approximately 90 hours at 1200°C temperature. As soon as temperature in the retort increases, coke burning along with ensuing CO formation will occur, thus reducing Fe_3O_4 to iron metal while oxidizing to CO_2 . The generated CO_2 reacts with the coke while forming a new CO , which reduces further magnetite to iron metal. The reduced particles are bonded, thus forming the Fe-sponge which is then disintegrated to powder using special procedures. The powder obtained this way has very good compressible and sinterable properties (Fig. 2. 17).

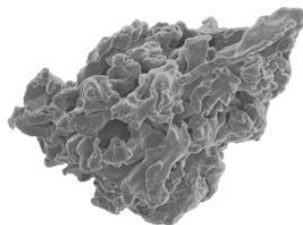
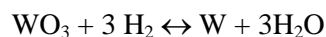


Fig. 2.17 Shape and morphology of Fe-powder made by the Höganäs process for a manufacture of self-lubricating bearings [11].

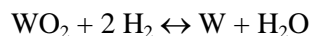
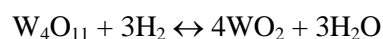
2.3.1.2 Reduction of non-ferrous metal oxides

Manufacture of W-powder

The initial material for the manufacture of tungsten powder is tungsten trioxide - WO_3 , which is most frequently reduced by hydrogen or carbon. However, the reduction by carbon is only used, if W-powder for the tungsten carbide manufacture is to be made. The WO_3 reduction by hydrogen proceeds in accordance with a heterogeneous equilibrium reaction, the summary equation of which can be defined:



Partial reactions of the WO_3 reduction by hydrogen are as follows:



The first stage of WO_3 reduction takes place at temperatures of $700 - 750^\circ\text{C}$, the second stage at temperatures of $800 - 900^\circ\text{C}$, when the reduction to tungsten metal occurs. The applied temperature and a size of oxide particles are of essential influence on the powder tungsten particle morphology and size (Fig. 2. 18), which can be affected in a broad range from 0.5 up to $500 \mu\text{m}$ by changing these parameters. WO_3 sublimation begins at temperature of 850°C , W_4O_{11} at 900°C and WO_2 at 1050°C . When these oxides sublime, the particles enlarge their size depending on temperature and the reduction state, whereas higher temperature leads to a formation of coarse-grained powder tungsten. The size of particles can be lessened by increasing the hydrogen flow rate, as the rate of reactions running at a lower temperature increases. Highly pure hydrogen, made using electrolysis of NaOH water solution, is used for the reduction. It is carried out in a tube furnace with continuous counter flow supply of hydrogen ($800 - 1000$ l/h), which has to be thoroughly dried-up and purified from oxygen and CO_2 . WO_3 is filled into nickel trays, creating an even layer several millimeters high. The reduction degree is checked by the so-called oxidation number (the gain in weight when oxidized in a contact matter), which must not differ from the theoretical value of 26.09% by more than 0.2% .

The manufactured tungsten powder is subjected to further technological procedures in order to

obtain demanded semi-products – pressing by 200 – 250 MPa pressure, pre-sintering at temperature of 1150 – 1300 °C, final sintering at temperature of 3000 °C in hydrogen. For a manufacture of wires and filaments, tungsten powder with granularity of 2 – 10 µm is used.

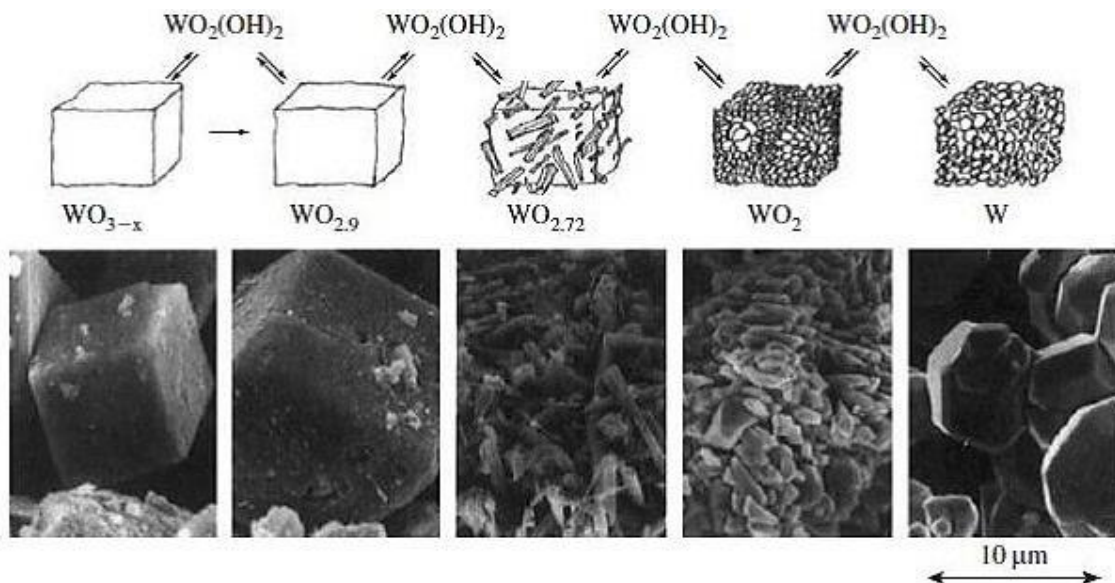
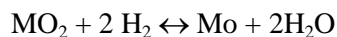
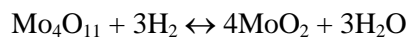
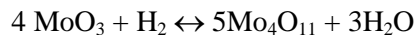


Fig. 2.18 Change of tungsten oxide morphology during the reduction at temperature of 1000 °C [12].

Manufacture of Mo-powder

Powder molybdenum can be obtained in a similar way as powder tungsten by reduction of molybdenum trioxide - MoO_3 . By a process of roasting a sulphide concentrate, MoO_3 concentrate is prepared, which is contaminated by 10 – 20 % of impurities. Prior to reduction its refining is needed, carried out most frequently by sublimation of molten MoO_3 at temperature of 1000 – 1100 °C. The reduction runs in three steps:



The reduction of molybdenum compounds by hydrogen at one temperature mostly leads to a formation of relatively coarse powder unsuitable for further applications. An insufficient control of a particle growth relates to a continuous contact of as-reduced metal with H_2O vapours and with still existing MoO_3 , which is transported with the aid of the vapour phase. Therefore, in order to achieve an optimal size of particles (2 – 12 µm), the two-stage reduction is carried out at various temperatures in a divided or continuous furnace:

I. stage: 700 °C, a formation of the violet brown MoO_{2+x}

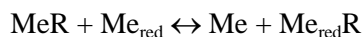
II. stage: 1000 – 1100 °C, reduction to Mo metal

Factors affecting the powder quality:

- purity of the raw material;
- H_2 flow rate;
- a layer thickness in the tray;
- time-thermal conditions of the reduction.

2.3.1.3 Reduction of metal compounds with metals (metallothermy)

Metal making through reduction of their oxides and halogenides by metal reducing agents is of a less significance in comparison with other procedures. This procedure is applicable in particular for compounds of metals of IVa – VIa groups in the periodic table, where this is enabled by thermodynamic conditions of the reaction:



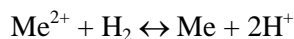
The synthesizing free enthalpy of the reaction is more positive than the free enthalpy of the reaction products. Ca, Mg, Na, Si and Al are used as metal deoxidizing agents for reduction of oxides. Reduction of halogenides is used for obtaining metals which cannot be reduced from oxides at all, or only with difficulties. Raw materials are in a form of chlorides or fluorides from which the given Me metal is displaced by the R metal, which has a higher affinity for chlorine (fluorine) than the Me metal, for instance Mg, Na, K, Ca.

Metallothermy is utilized for a manufacture of metal powders, such as Ta, Nb, Ti, Th, Zr, V etc. A product resulting from the reactions is mostly a metal sponge which is then milled to powder of a demanded granulometry.

2.3.1.4 Reduction of powders from water solutions

Metal ions can be reduced from water solutions and thus also segregated in a dispersed form with the aid of solid, liquid or gaseous reducing agents or by electric current. Of the current-free methods, only reduction from water solutions of metal salts with the aid of gaseous reducing agent (H_2 or a cracked gas, CO) has found its technical use; the procedure is used for the manufacture of Cu, Ni and Co of 99.8 % purity. Due to a small size of the obtained powder particles, being around 1 μm , these particles have a tendency to form agglomerate. This method is advantageous in a combination with hydrometallurgy which allows processing of relatively poor metal ores, or in some case side-products.

Metal ions in the solution react with the reducing gas – hydrogen, while forming metal precipitates as described in the equation:



The equilibrium constant of the reaction:

$$K_p = \frac{[\text{H}^+]^2}{[\text{Me}^{2+}]p_{\text{H}_2}}$$

where Me^{2+} and H^+ are concentrations of metal and hydrogen ions, p_{H_2} is hydrogen pressure

Free enthalpy of the reaction ΔG depends on the equilibrium constant K_p and electrochemical potentials ε_{H} and ε_{Me} . The hydrogen potential value is determined by pH of the solution and H_2 pressure:

$$\varepsilon_{\text{H}} = \varepsilon_{\text{H}}^0 - 0.058 \text{ pH} - 0.058 \log p_{\text{H}_2}$$

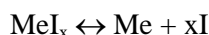
For these reduction processes applies:

- Hydrogen potential ε_{H} depends strongly on the solution pH – becomes more negative with the increasing pH value (the H^+ concentration decreases) or increasing p_{H_2} value.
- A change in the concentration of metal ions has a negligible effect on the metal potential – thus the favourable conditions for a thorough reduction and precipitation of the dissolved metals are given.
- In highly acid solutions only Ag and Cu ions can be reduced to metals; in order to reduce Sn, Ni, Co and Cd ions, the solution pH has to be ≥ 5 .

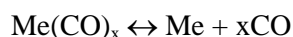
- Under constant pH and p_{H_2} conditions, metals with very close potentials can be selectively reduced ($\varepsilon_{Ni}^0 = -0.23$ V, $\varepsilon_{Co}^0 = -0.27$ V).

2.3.2 Powder making from the vapour phase

In this process, powder is obtained from metal compounds which can be transferred to the vapour phase in a suitable way (e.g. by heating). An advantage is a manufacture of very fine and active powders of relatively pure metals or metal compounds for special purposes: the decomposition process runs as described in the following equations:

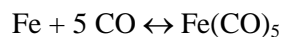


or



With an increasing temperature, in metal halogenides (e.g. ZrI_4) dissociation to metal and halogen occurs, in metal carbonyls to metal and CO.

The carbonyl process has a technical significance for the manufacture of fine Fe and Ni powder of high purity, and with a limitation also for Mo, although other metals form volatile carbonyls as well - Mn, V, Cr and W. Reactions of carbonyl formation and decomposition can be described in equations:



These are reactions the equilibrium of which depends highly on temperature and pressure (Fig. 2. 19). For carbonyl formation, CO is used at temperatures 200 – 250 °C and at an elevated pressure (7 – 30 MPa) which is applied on an appropriate metal source – ore, fine steel scrap, sponge iron, Ni-granulate, etc. Accompanying undesirable elements, such as S, Si, Cu and P, do not form these carbonyls. The gaseous product is fluidized by pressure and stored in vessels. If necessary, prior to decomposition it can be refined by filtration and distillation (the distillation temperature for $Fe(CO)_5$ is 103 °C, for $Ni(CO)_4$ – 43 °C).

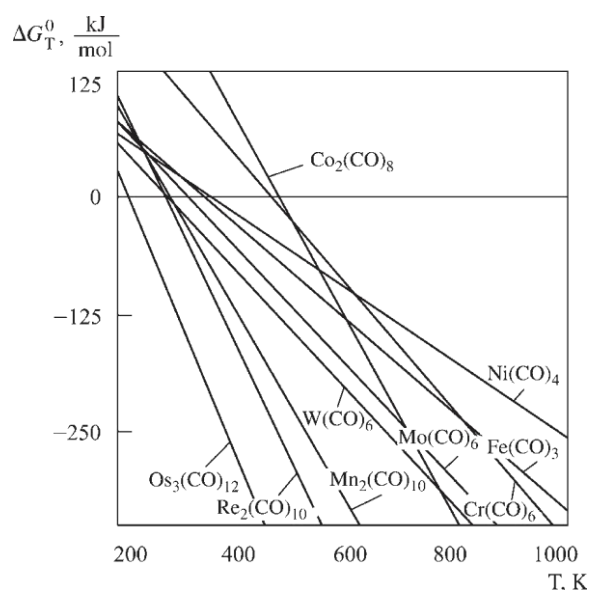
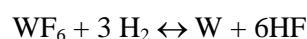


Fig. 2.19 Temperature dependence of free enthalpy ΔG for thermal decomposition reactions of metal carbonyls.

The carbonyl decomposition is an endogenous reaction running in a heated cylinder at temperature of 200 °C for Ni(CO)_4 or at 250 °C for Fe(CO)_5 . Under standard conditions, ball-shaped particles of a laminated structure and in size of 2 – 15 μm occur. Oxygen and carbon content is then reduced through a following hydrogen annealing. In Fe(CO)_5 decomposition the reduced Fe can act catalytically, while forming CO_2 , Fe_3C and FeO . Ammonia is added to minimize these undesirable reactions.

Even very fine W powder with granularity around 1.5 μm can be obtained by the method of decomposition of gaseous compounds. WF_6 is used for its manufacture, whereas the reaction runs in the presence of the reducing agent:



Reduction is carried out in a turbulent layer, leading to a formation of ball-shaped particles with excellent pressing properties.

2.3.3 Hard material powder making

Hard material making is carried out by thermomechanical reactions in a solid, liquid or vapour state. Initial materials can be both metals or their oxides and non-metals or their compounds mostly in a dispersive form. This concerns above all a manufacture of carbides, nitrides and silicides, where either coarse-grained powder or fine sintered particles are obtained. Further processing includes a mechanical disintegration of reaction products, removing side reaction products and cleaning reaction products.

2.3.3.1 Manufacture of carbides

Metal carbides are mostly manufactured by carburization of metals or their oxides – see Table 2.1.

Table 2.1 Initial material and conditions of carburization reactions for making various types of carbides.

Carbide	Preparation – input material	Temperature of carburization reaction
WC	$\text{WO}_3 + \text{carbon (soot)}$; $\text{W} + \text{carbon (soot)}$	1400 – 1600 °C
	$\text{W} + \text{carbon (soot)} + \text{CH}_4$	1200 – 1400 °C
Mo_2C	$\text{MoO}_3 + \text{carbon (soot)}$; $\text{Mo} + \text{carbon (soot)}$	1200 – 1400 °C
	$\text{Mo} + \text{carbon (soot)} + \text{CH}_4$	1100 – 1300 °C
TiC	$\text{TiO}_2 + \text{carbon (soot)}$	1700 – 1900 °C
ZrC	$\text{ZrO}_2 + \text{carbon (soot)}$	1800 – 2000 °C
VC	V_2O_5 or $\text{V}_2\text{O}_3 + \text{carbon (soot)}$	1100 – 1200 °C
NbC	Nb_2O_5 or $\text{Nb}_2\text{O}_3 + \text{carbon (soot)}$	1300 – 1400 °C
TaC	$\text{Ta}_2\text{O}_5 + \text{carbon (soot)}$; $\text{Ta} + \text{carbon (soot)}$	1300 – 1500 °C

2.3.3.2 Manufacture of mixed carbides

- Carbide powder AC + carbide powder BC; reaction temperature 1700 – 2000 °C.
- Metal powder A + metal powder B + furnace black; reaction temperature 1500 – 1700 °C.

- Metal oxide AO + metal oxide BO + furnace black; reaction temperature 1500 – 1700 °C.

2.3.3.3 Manufacture of nitrides

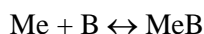
Nitrides of metals of IVa, Va and VIa groups in the periodic table are technically significant. Manufacturing processes for TiN, ZrN, HfN, NbN, TaN nitrides are as follows:

- thermochemical reaction of powder metal and N₂ at 1200 – 1400 °C temperature;
- thermochemical reaction of powder metals and NH₃ at 1200 – 1400 °C temperature.

The manufacture of nitrides from metal oxides is economically more profitable, however, the resulting products are not of such a quality as from metals.

2.3.3.4 Manufacture of borides

The manufacture of borides by mutual reaction between metals Me and B during sintering or melting can be expressed as a simple reaction:



Other manufacturing processes for borides consist in a reaction of a metal with a B compound:

- a) $\text{MeO} + \text{B}_2\text{O}_3 + \text{Al}(\text{Mg}, \text{Si}) \rightarrow \text{MeB} + \text{Al}(\text{Mg}, \text{Si})_x\text{O}_y$
- b) $\text{MeO} + \text{B}_2\text{O}_3 + \text{C} \rightarrow \text{MeB} + \text{CO}$
- c) $\text{MeC} + \text{B}_4\text{C} + \text{B}_2\text{O}_3 \rightarrow \text{MeB} + \text{CO}$
- d) electrolysis of molten salts: $\text{MeO} + \text{B molten salt} \rightarrow \text{MeB} + \text{salt melt}$
- e) $\text{Me}(\text{halogenide}) + \text{B}(\text{halogenide}) + \text{H}_2 \rightarrow \text{MeB} + \text{hydrogen halogenide}$

2.3.3.5 Manufacture of silicides

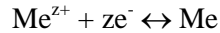
Silicides of various metals can be also prepared using several processes:

- a) $\text{Me} + \text{Si} \leftrightarrow \text{MeSi}$
- b) $\text{MeO} + \text{SiO}_2 + \text{Al}(\text{Mg}) + \text{S} \rightarrow \text{MeSi} + \text{S containing slag}$
- c) $\text{MeO} + \text{SiO}_2 + \text{C} \rightarrow \text{MeSi} + \text{CO}$
- d) $\text{CuSi} + \text{MeO} \rightarrow \text{MeSi} + (\text{Cu} + \text{CuO} - \text{SiO}_2)$
- e) Electrolysis of molten salts: $\text{MeO} + \text{K}_2\text{SiF}_6 \rightarrow \text{MeSi} + \text{KF}$
- f) $\text{Me} + \text{Si}(\text{halogenide}) + \text{H}_2 \rightarrow \text{MeSi} + \text{hydrogen halogenide}$

2.4 Electrochemical production methods

Approximately 60 metals can be successfully obtained via electrolysis, where electric current acts as a reducing agent: An electrolyte can be a solution or a molten salt conducting the current as a result of presence of ions. Electrolysis from water solutions is used to make powder metals not having too high affinity for oxygen as Cu, Fe and Ni. Highly reactive powders (e.g. Be, Ta, Nb, Th, ...), which form highly stable oxides, have to be segregated from molten salts by electrolysis. From the point of view of powder metallurgy, tantalum making from molten salts is of a great significance. While electrolysis from water solutions takes place at slightly elevated temperatures (to 60 °C), electrolysis from molten salts requires quite high temperatures depending on the melting point of an applicable (binary or ternary) salt eutecticum, which has to contain an appropriate concentration of the metal to be segregated.

The electrolysis basic equation:



Nernst equation for equilibrium potential:

where R – universal gas constant ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$); F – Faraday's constant; $\varepsilon_{\text{Me}}^0$ – normal potential of metal; z – atomicity of metal; c_{Me}^{z+} – concentration of ions in a solution.

For a metal to segregate from electrolyte, its potential has to be more negative than $\varepsilon_{\text{Me}}^0$.

Faraday's laws of electrolysis:

$$m = \frac{I \cdot t \cdot M}{z \cdot F}$$

where m – weight of an element segregated on the electrode (g); I – segregation current (A); t – acting time (s); M – molar mass of the segregated metal (g/mol); z – a number of elementary charges needed to segregate one molecule.

In a simple event, electrolysis runs on two electrodes connected to direct current, where an anode is made of metal the ions of which are in the solution. When electric current passes across, the metal on the anode (positive electrode) becomes dissolved and on the cathode (negative electrode) becomes segregated. During electrolysis a migration of positive ions (cations) to the negative electrode (cathode) and negative ions (anions) to the positive electrode occurs (Fig. 2. 20).

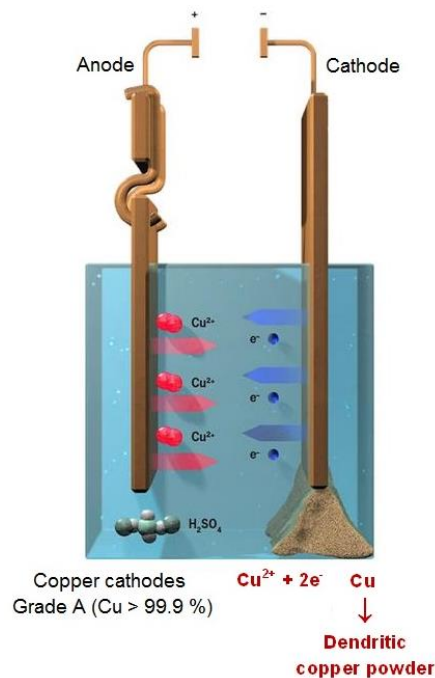


Fig. 2.20 Electrolysis principle [13].

Reduction takes place on the cathode – electropositive components are segregated (metals, hydrogen); oxidation takes place on the anode – electronegative components are segregated. The lowest voltage which has to be imposed on the electrodes, so that continuous electric current can pass across and electrolysis can run, is called the decomposition voltage.

The basic characteristics of powders made using electrolysis is their high purity and a dendritic or sponge structure, good compressibility, high strength of non-sintered compacts and high activity at sintering. However, the following disadvantages are connected with the process of the manufacture of powders using electrolysis:

- the process requires to refine the electrolyte from residual impurities, in particular from salt residues after the fusible electrolysis
- high cost of electric power
- only the manufacture of elementary powders is of a practical significance
- the resulting product has to be cleaned and disintegrated, which means extra costs.

Main parameters affecting a dimension, shape and structure of particles:

- current density;
- metal ion concentration;
- electrolyte conductivity;
- temperature;
- bath circulation;
- in special cases an addition of surface-active substances to constraint the growth of nuclei.

The resulting particle shape is given especially by the nucleation rate and a concentration of metal ions (Fig. 2. 21). The high nucleation rate and high concentration lead to a formation of smooth and dense particles. Electrolytes with low conductivity, such as for instance molten salts, tend to form coarse dendritic powders.

To ensure the direct segregation of the powder on the cathode, while utilizing electric current to the maximum, the conditions of the electrolysis must be as follows:

- low concentration of segregated ions;
- high conductivity of the electrolyte (addition of acids or salts);
- high current density at low temperature of the bath, or temperature of the cathode;
- immovable or weakly moveable electrolyte.

For the fusible electrolysis the material has to be as pure as possible, whereas the cathode may be manufactured of steel, aluminium, high-melting point metals, graphite, etc. The anode is made of a raw metal, plates, cathode plates of electrolytic refinement, etc.

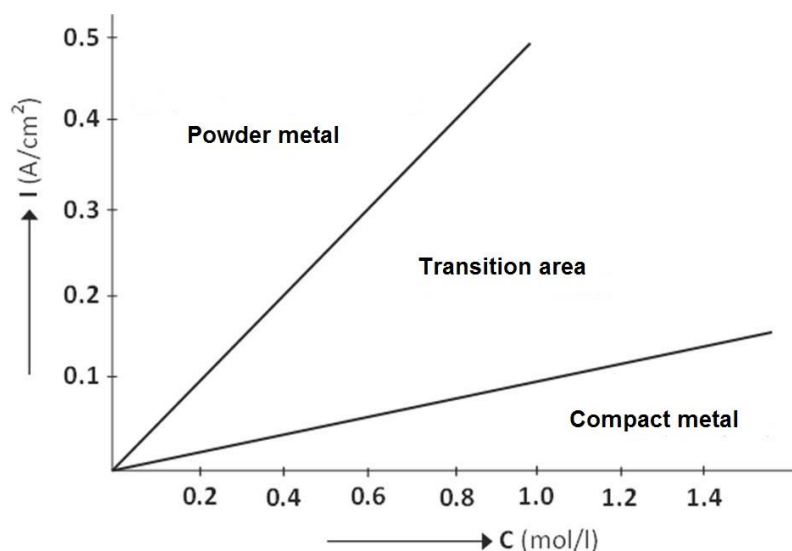


Fig. 2.21 Relation of the current density to the concentration of metal ions.

2.4.1 Preparation of powders from water solutions

2.4.1.1 Copper powder making

CuSO_4 and H_2SO_4 are used as an electrolyte for the manufacture of Cu powder. An acid addition increases the electrolyte conductivity, decreasing a voltage needed to suppress a formation of copper oxide. As hydrogen ions are segregated on the cathode with a decreasing pH value, the increasing acid content leads to a decrease of metal yield at the given current as a result of a consumption of the current for hydrogen segregation (especially for electrolyte temperatures $\geq 25^\circ\text{C}$). The copper content in the solution affects the electric current utilization and a size and density of particles (Table 2.2).

Table 2.2 Influence of the copper content on the current utilization and a size and density of particles.

Copper content in the solution	Current utilization	Particle size	Particle density
(g/l)	(%)	(μm)	(g/cm^3)
4	78	< 38	0.5
35	97	> 125	2.5

Owing to electrolyte heating during the electrolysis it is necessary to cool it down, so that the temperature does not exceed $50 - 60^\circ\text{C}$. An elevated temperature results in the electrolyte conductivity increase, a better utilization of current, a formation of fine and dense coagulates and a higher proportion of oxides. The cathode current density during the electrolysis is 600 up to $4000 \text{ A}/\text{m}^2$. The current density increase causes a formation of fine dense powders and enhanced segregation of hydrogen. The anode current density is always lower than the cathode one in order to prevent passivation. The coagulate (segregated powder particles) is removed from cathodes on a regular basis, afterwards it is washed, subjected to reduction annealing and processed to fine particles by milling. Morphology of electrolytic copper particles is shown in Fig. 2.22.

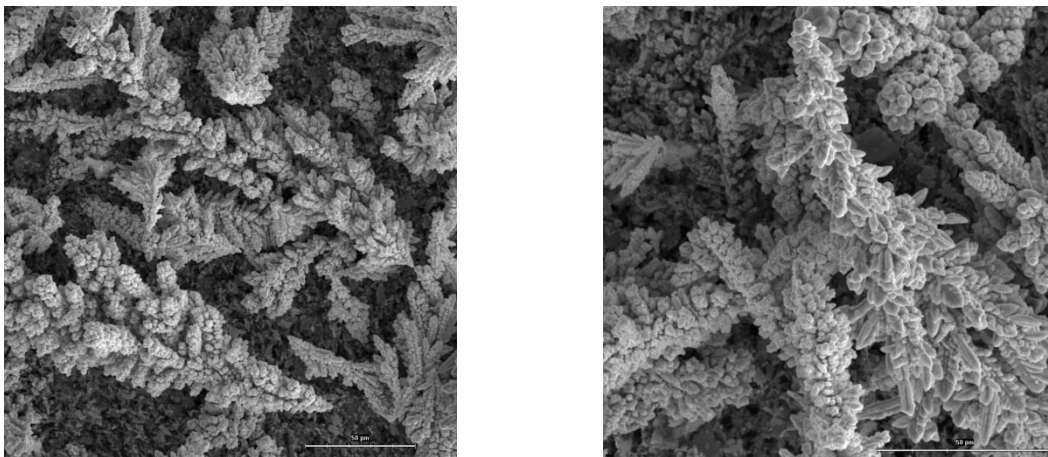


Fig. 2.22 Dendritic shape of electrolytic copper particles.

2.4.1.2 Iron powder making

Iron powder making through electrolysis was industrially significant till the 70s of the last century. Its importance was brought down considerably with the development of well compressible sponge iron and the use of carbonyl iron of even higher purity. For iron making, FeCl_3 solution with

AlCl_3 addition for the conductivity increase is used as an electrolyte, or FeSO_4 . The segregated iron is formed by a tough, brittle layer, which has to be processed by milling to a demanded granulometry. The cathode voltage and current density has to be set, so that hydrogen can originate at the same time. Atomic hydrogen easily penetrates the α – iron lattice, which leads to significant embrittlement. The resulting powder is then annealed for internal stress reduction and hydrogen content decrease.

2.4.2 Melt electrolysis

This involves obtaining metals via electrolytic procedure, wherein a metal is segregated from appropriate salt melts. For electrolysis of melts generally the same electrochemical laws apply, as for electrolysis of water solutions. An electrolyte consists of a mixture of salts, mostly chlorides or fluorides, which form binary or ternary eutectica with a low melting point into which salts of segregated metals are added and dissolved. Thanks to their high specific electrical conductivity at high temperatures, chlorides of alkaline metals or rare earth metals are often the main components of melts. Voltage is set below the decomposition voltage level of (a more negative) alkaline metal. As with electrolysis from water solutions, in electrolysis of molten salts the particles are coarser adequately with the higher metal ion concentration in the electrolyte, longer time for the formation and growth of a layer, lower cathode current density and higher temperature.

As a result of low electrical conductivity of the electrolyte, the originating particles have a shape of coarse-grained dendritic crystals. The current efficiency is only 60 % due to running side processes, such as back diffusion of as-reduced metal or metal falling-off the cathode. Particularly powder tantalum and beryllium is manufactured using this procedure.

2.4.2.1 Manufacture of tantalum powder

Electrolytes for tantalum making comprise 50 – 70 % KCl , 20 - 35 % KF , 5 – 10 % K_2TaF_7 and 4 – 5 % Ta_2O_5 for stabilization of the anodic process. Heated cast iron container serves as an electrolyzer, the anode is formed by a vertical graphite rod. The electrolysis takes place at temperatures 700 up to 900 °C, whereas the cathode current density can be up to 4000 A/m^2 . K_2TaF_7 and Ta_2O_5 are added during the electrolysis. After several hours the melt is grown-through by tantalum crystals and the electrolysis can be stopped. After cooling-down the metal and salt mixture is milled and washed with water. Fine particles ($\sim 75 \mu\text{m}$) prevail at high current density, coarse particles ($\sim 750 \mu\text{m}$) prevail at high temperature. A content of impurities is usually low.

2.4.2.2 Manufacture of beryllium powder

For the manufacture of powder beryllium, $\text{BeCl}_2 + \text{NaCl}$ melt is used (6:4 – molar ratio). The electrolyzer consists of a heated Ni-crucible inside which a graphite anode and nickel cathode is placed; the latter comprises a basket for collecting fallen-off precipitates. The electrolysis takes place at temperatures of 330 to 380 °C, at current density of 720 A/m^2 . Be – precipitate is separated daily from the cathode in a form of flakes and further washed with water, diluted HNO_3 and alcohol. The product (99.5% Be) is contaminated with Fe, C, O_2 and Cl. Be purity can be enhanced up to 99.85 % with the help of the refining analysis.



Summary of terms

Mechanical alloying

Reduction processes

Atomization

Electro-chemical processes



Questions to the topic

- 2.1. Describe qualitative changes occurring during disintegrating
- 2.2. Which are the key process parameters of the water atomization?
- 2.3. What is the main application of Ellingham–Richardson diagram?



Solved tasks

Exercise 2.1

Cast iron chippings of the initial size of 300 μm , originating when machining, are milled to powder of a size of 110 μm for a period of 8 hours. Determine an additional time needed to reduce the particle dimension to a size of 75 μm .

♦ Solution

As the powder is constant (energy for a unit of time), a calculation of energy needed to reduce the dimension from 110 μm to 75 μm allows calculating the additional time of milling.

The particle dimension change depending on the total energy is defined in the relation:

$$W = g \cdot (D_k^a - D_p^a)$$

where $a = 2$.

$$\frac{W_2}{W_1} = \frac{g (D_k^a - D_p^a)}{g (D_k^a - D_p^a)} = \frac{g (75^2 - 110^2)}{g (110^2 - 300^2)} = \frac{9.51 \cdot 10^{-5}}{7.15 \cdot 10^{-5}} \cong 1.33$$

The energy change from 110 μm to 75 μm is a 1.33 multiple of the energy needed for the reduction from 300 to 110 μm . This implies that the time needed is $8 \cdot 1.33 = 10.6$ hours.



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3. PROPERTIES AND CHARACTERIZATION OF POWDER MATERIALS



Study time: 5 hours



Objective

- Definition of physical and technological properties of powder materials
- Methods of particle size analysis
- Measurement techniques of specific surface area of powder particles
- Determination of technological properties of powder



Lecture

Observation of properties of metal powders is important above all for understanding powder metallurgy basic processes. A behavior of powders during particular processes of their transformation to a compact material depends on many parameters. The better control of properties of an initial powder material, the more precisely the final product is made, with lesser allowable deviations of its properties. Properties of metal powders, especially a particle size, shape and distribution, depend on a method of their manufacture and treatment. When characterizing powders, it is necessary to evaluate both properties of individual particles (size, shape, chemical composition, microstructure, density, microhardness) and also their common, volume properties, such as flowability, surface properties etc.). Properties of metal powders can be generally divided into basic, technological and combined properties:

1. Basic properties

- particle size;
- particle shape;
- particle size distribution;
- microstructure, microhardness and porosity of particles;
- specific surface of particles.

Basic properties belong among the most important properties of metal powders, therefore they must be defined as exactly as possible.

2. Technological properties

- apparent density;
- compressibility;
- flowability;
- bulk volume;
- tap density;
- compactibility;
- sinterability.

These are properties created by a large number of different powder particles. There are more or less obvious relations between basic and technological properties.

3. Combined properties

- electrical conductivity;
- thermal conductivity;
- magnetic properties;
- melting point.

These powder properties relate both to basic and technological properties and particularly to physical character of a metal or an alloy.

3.1 Basic properties of metal powders

A definition of the term “particle size” is quite difficult because metal powder particles are not of the same size and can be of a complicated shape which is difficult to measure. Therefore a simplified assumption is usually necessary for a shape in order to reduce a number of dimension information to a single parameter. In principle, technically prepared metal powders are mixtures of particles of different sizes. Particle size distribution in these mixtures is adhered to certain rules which are defined by a powder type, its manufacture and processing. A particle size depends both on the measurement method and the specific parameter to be measured, and on the particle shape. That’s why analyses of particle sizes on various apparatuses do not give the same results for the same particle size due to a difference in measured parameters. For a spherical particle, the dimension is specified by a single parameter – a diameter. If a particle shape is more complicated, defining a single parameter is obviously difficult. Determination of a particle size and shape is specified in ČSN 42 0890-12, 13.

3.1.1 Particle size

A particle size can be defined on the basis of geometrical characteristics of a particle projection – the so-called geometrical diameter. Considering the particles being generally irregular, it is pragmatic to define their size by a single dimension. In principle, this is a diameter of a sphere being equivalent with the particle, i.e. some of its quantifiable physical property is identical – the so-called equivalent diameter (Fig. 3.1). For example:

D_a – a diameter of a sphere which has an identical projection area A as the particle

D_V – a diameter of a sphere which has an identical volume V as the particle

D_S – a diameter of a sphere which has an identical surface S as the particle

D_{St} – a diameter of a sphere which has an identical sedimentation rate (according to Stokes) as the particle

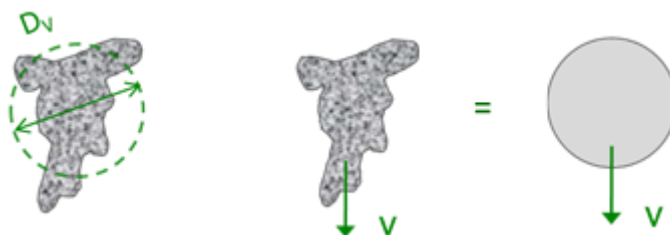


Fig. 3.1 Definition of D_V , an equivalent diameter of a sphere.

Determination of an equivalent diameter:

$$D_A = (4A/\pi)^{1/2}$$

$$D_S = (S/\pi)^{1/2}$$

$$D_V = (6V/\pi)^{1/3}$$

For example, to define completely a dimension of a leaf-shaped (flake-shaped) particle, it is necessary to know at least two parameters – a diameter and a thickness. For a rounded, though irregular, particle, a dimension can be described using a projection height h , a maximum length l or a horizontal

width w . It is very difficult to define a single dimension of a particle for an unrounded irregular particle shape (Fig. 3.2).

A range of particle sizes used in powder metallurgy (Fig. 3.3):

- Macroscopic particles* – defined as “sieveable”. The bottom boundary of their size is around 50 μm . They can be further divided to very coarse-dispersive ($> 500 \mu\text{m}$) and coarse-dispersive (500 – 50 μm).
- Microscopic particles* – the bottom boundary of their size is 1 μm .
- Submicroscopic particles* – particles of a size $< 1 \mu\text{m}$.
- Ultrafine or colloid particles* – particles of a size $< 0.1 \mu\text{m}$.

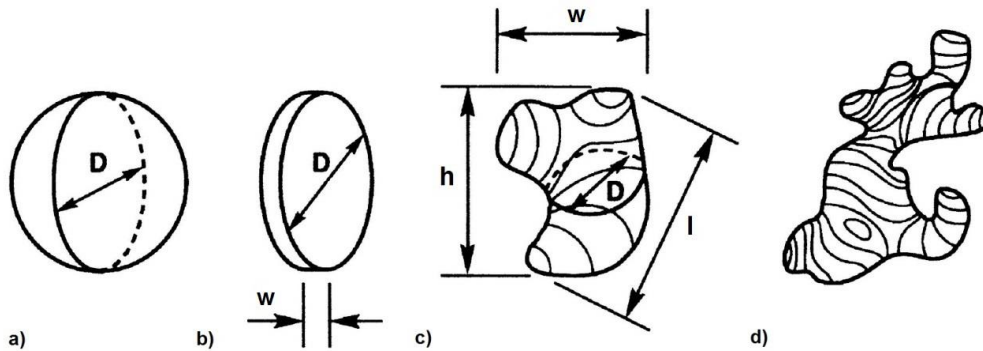


Fig. 3.2 Particle dimension description: a – spherical shape; b – flake shape; c – rounded irregular shape, d – irregular shape [1].

Fig. 3.3 Particle size range and measuring methods used in powder metallurgy.


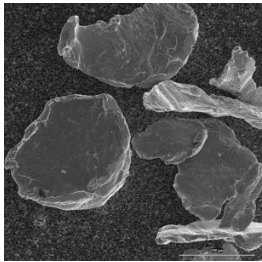

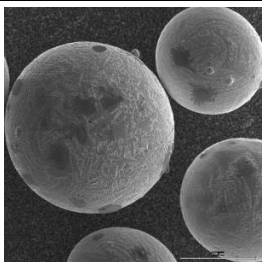



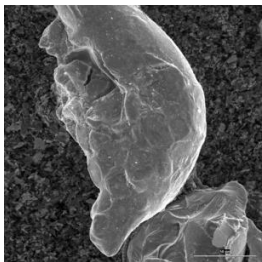

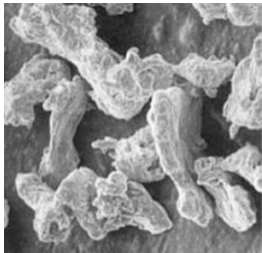

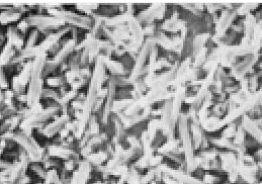
Powder marking	Very coarsely dispersive	Coarsely dispersive	Finely dispersive	Very finely dispersive	Colloid dispersive	Molecular dispersive
Particle size range	$> 500 \mu\text{m}$	500 - 50	50 - 5	5 - 0.2	0.2 - 0.02	< 0.02
Measuring method	Coarse sieve analysis	Fine sieve analysis	Optical light microscopy Sedimentation		Electron microscopy	




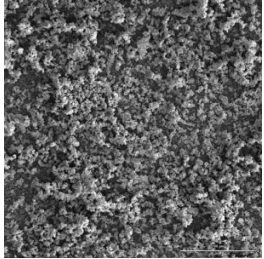

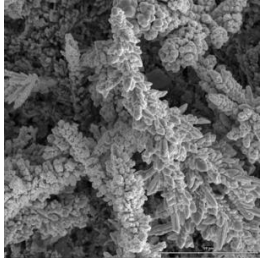
3.1.2 Particle shape

A grain shape depends on a powder type and a method of its manufacture. Various shapes of powder grains according to outer geometrical features are shown in Table 3.1. Particles do not differ only by shape but often also by surface quality. Some particles can have an almost smooth surface, e.g. particles prepared by granulation, melt atomization, condensation or carbonyl decomposition. Other powders can have somewhat rough surfaces, e.g. Fe powder manufactured by reduction or the RZ process. The most straightforward shape descriptor is the aspect ration, defined as the maximum particle dimension (l_{max}) to minimum particle dimension (l_{min}):

- spherical particle: 1;
- ligamental particle: 3 to 5;
- flake particle: > 10 .

Table 3.1 Various shapes of powder grains according to outer geometrical features.

<p>Flaky (mechanical comminution)</p>		
<p>Spherical (atomization, carbonyl (Fe), precipitation from a liquid)</p>		
<p>Rounded (atomization, chemical decomposition)</p>		
<p>Irregular shape (atomization, chemical decomposition)</p>		
<p>Irregular rod-like (chemical decomposition, mechanical comminution)</p>		
<p>Acicular (mechanical comminution)</p>		

<p>Angular (mechanical disintegration, carbonyl (Ni))</p>		
<p>Particles with internal pores (porous, spongy) (reduction of oxides)</p>		
<p>Dendritic (electrolysis)</p>		

3.1.3 Particle size distribution

Each powder material has particles of different sizes; the sizes decrease continuously from a maximal size down to a bottom boundary. From the practical point of view, this size range is divided to several classes, each of which covers particles with a specific difference in size.

Size characteristics can be presented as distribution functions defining a quantitative proportion of particles belonging to a specific size parameter. These quantitative proportions can be described either as a cumulative or a frequency distribution. The frequency distribution is displayed in a form of a histogram (Fig. 3.4) or as a continuous derivation of a cumulative distribution (Fig. 3.5). In histograms, on the x axis the size ranges of particular fractions are plotted and on the y axis the appropriate number of particles, most frequently in % or mass % (sieve analysis). Plotting a total percentual content or a weight of all particles of the specified and smaller diameter on the y axis is often more advantageous. This way an integral or cumulative curve of the particle size distribution can be obtained (Fig. 3.4). Various types of coordination systems are used, for instance linear (both axes) and linear/logarithmic.

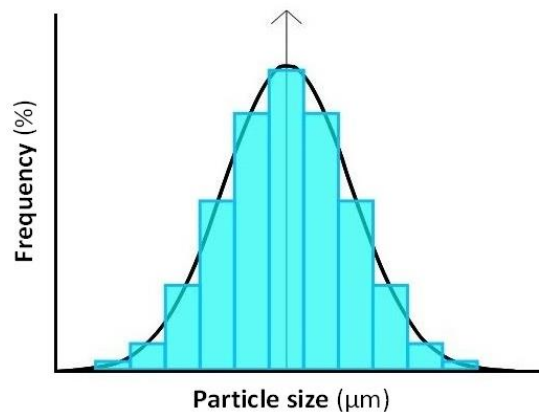


Fig. 3.4 Particle size distribution histogram [2].

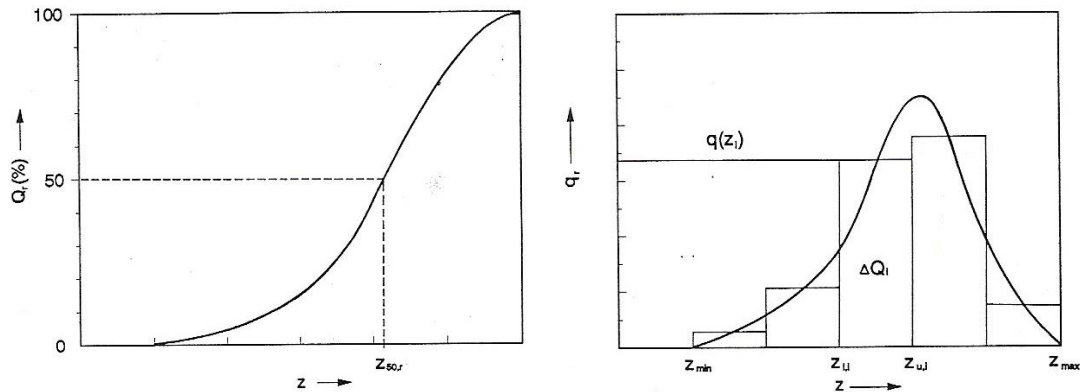


Fig. 3.5 Particle size distribution: a) cumulative distribution Q_z ; b) frequency distribution q_z (a differential shape and a discrete shape (histogram)) [3].

Particle size distribution can be determined using various methods according to the degree of dispersion. In practice, for coarse powders of a size above 50 μm the sieve analysis is used, for fine-grained powders e.g. microscope measurements, sedimentation, air separation, laser particle size analyzer, etc.

Powder distribution in individual classes and a preparation of defined mixtures of particles of a specified size is of a considerable importance in powder metallurgy. This way a mixture of coarser and finer particles can be prepared in such a ratio that after mixing and filling into a compacting press die a quite consistent compact is created, in which cavities between large particles are filled with a fine-grained proportion.

3.1.3.1 Particle distribution laws

Metal powder particle distribution is governed by specific laws which are different for mechanically disintegrated powders and for powders manufactured by a different process. Mechanically disintegrated powders abide by the Rosin – Rammler law on grain distribution of a milled material. This law is described in an empirical equation:

$$R = e^{-bo^n}$$

where R – residue on a sieve; o – inside diameter of a mesh; b – constant; n – exponent defining a powder distribution width

Aside from the Gaussian curve of the particle size distribution, the Rosin – Rammler law includes also a function describing a milling process influence.

The particle size distribution of powders not processed mechanically generally abides by the normal distribution Gaussian rule. However, there are characteristic curves different from the ideal Gaussian curve in practice, which may have a lot of reasons, such as a formation of clusters.

A distribution of non-milled, fine-dispersive powders can be individually characterized by a mean size and a grain size variance. A mean particle size d of powder substances characterized by the normal Gaussian frequency curve is described in the equation:

$$d = \frac{n_1 a + n_2 b + n_3 c + \dots + n_x x}{100}$$

where $a, b, c \dots x$ – a size of particles of particular classes; $n_1, n_2, n_3, \dots n_x$ – percentual proportions of a number of grains in the particular classes (frequency)

According to the normal frequency curve, describing the grain distribution, the particle size variance S can be calculated as follows:

$$S = \mp \sqrt{\frac{n_1(a-d)^2 + n_2(b-d)^2 + n_3(c-d)^2 + \dots + n_x(x-d)^2}{100}}$$

In powder metallurgy there are several shapes of the particle size distribution curve – see Fig. 3.6. In the powder manufacture, there are not only one-dimensional powders (monodisperse). A typical powder is polydisperse, with a broad range of particle sizes.

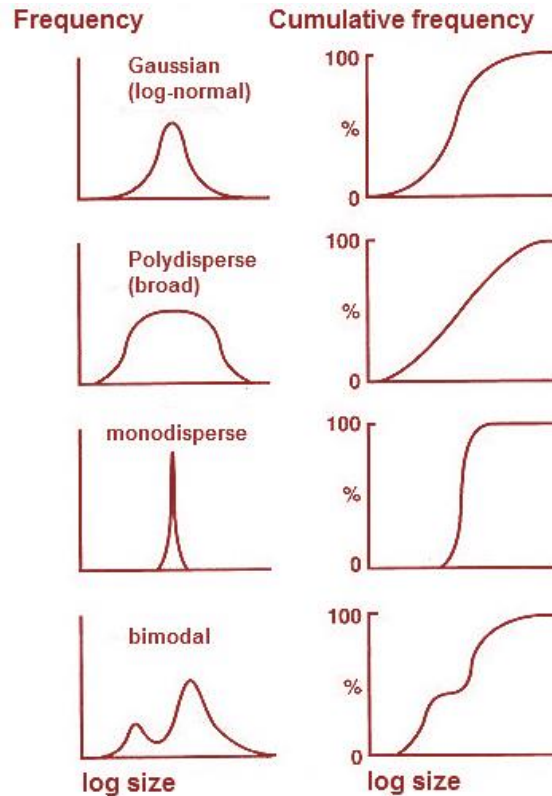


Fig. 3.6 Comparison of basic types of particle size distribution curves [1].

3.2 Determination of basic properties of metal powders

3.2.1 Particle size determination using a sieve analysis

A sieve analysis is used for determination of a distribution of particle sizes $> 50 \mu\text{m}$. It is carried out with a help of a system of sieves which are set to a vibrational motion (140 – 160 cycles/min). The detailed conditions of a sieve analysis are described in MPIF Standard 05 (ČSN ISO 4497 standard “Metallic powders. Determination of particle size by dry sieving”). Using special sieves, the scope of the sieve analysis can be extended up to $5 \mu\text{m}$.

A sieving machine consists of a system of sieves with various mesh sizes (Fig. 3.7). These sieves comprise a wire netting with an exactly defined wire thickness and spacing between particular wires. Micro-sieves made of metal foils, manufactured using the electrochemical method, can be used for the sieve analysis of very fine particles. With the help of sieving the particular fractions of particles, which have fallen through all the upper sieves, but have not fallen through the bottom sieve, can be obtained on each sieve (Fig. 3.8). The number of the used sieves depends on various diameters of the measured particles. Dry sieving is applicable for relatively large, non-cohesive powders. Fine and cohesive powders need to be analysed through wet sieving (Fig. 3.9). Particles of a size $< 40 \mu\text{m}$ are designated as undersize powders.



Fig. 3.7 Sieve analyzer and various types of sieves [4].

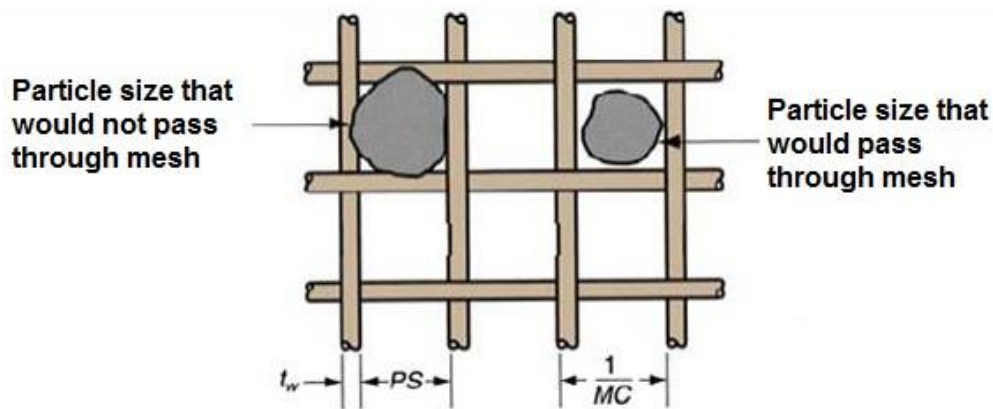


Fig. 3.8 Sieve analysis principle [3].

A content of particular fractions X_n (%) can be calculated according to the equation:

$$X_n = \frac{m_n}{n} \cdot 100$$

where m – tested sample weight (g); m_n – given fraction weight (g)

Fractioning the powder substances on sieves is based on meeting three basic conditions:

- High probability that each particle can get to the immediate vicinity of meshes in sieves during sieving \Rightarrow an adequate mutual motion of individual particles.
- Particles of sizes smaller than sieve mesh sizes fall through these meshes \Rightarrow forces connecting particles into an agglomerate are not as high to prevent gravitational transport of a particle through a mesh.
- Particles of sizes near to the sieve mesh sizes do not block the meshes permanently \Rightarrow these particles occur around the meshes with the same probability as other particles.

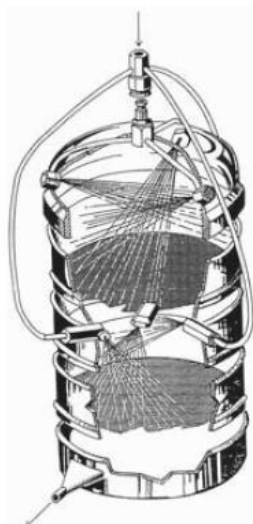


Fig. 3.9 Wet sieve analysis kit [5].

3.2.2 Particle size determination using a sedimentation method

In sedimentation procedures, a particle size is determined on the basis of their rate of fall in a quiet environment, mostly in a liquid or air. At the beginning of the measurement, the concentration of the measured particles in a suspension is uniform and corresponds to a value C_0 . In the course of time its change in the liquid volume occurs. After a defined time t , in a specific sedimentation height h a concentration C is determined (Fig. 3.10). This concentration can be determined by a gravimetric or photometric method or using X-rays.

On condition of spherical particles and within the Stokes' law scope, i.e. at Reynolds number $Re \leq 0.25$, the particle size D_{st} can be determined from the fall rate:

$$D_{st}^2 = \frac{18}{g} \frac{\eta}{(\rho_s - \rho_L)} \frac{h}{t}$$

where g – gravitational acceleration (m/s^2); η - viscosity of the liquid (or air) ($m^2 \cdot s^{-1}$); h – sedimentation height (m); t – sedimentation time (s); ρ_s – specific weight of particles (kg/m^3); ρ_L – specific weight of the liquid (or air) (kg/m^3).

For irregular particles, D_{st} is a diameter of an equivalent sphere which has the same rate of fall as particles. The sedimentation procedures are only applicable for particles of size ranging between 1 – 60 μm . Accuracy of the sedimentation analysis depends on the used sedimentation environment which must not react with particles and has to prevent an agglomerate formation. Depending on the material type, the most widely used liquids are water, ethylene glycol, cyclohexane, oils, butanol, etc. The concentration must not be higher than 0.2 vol.%, so that the falling particles cannot influence one another.

The sedimentation analysis is usually performed with the aid of the Andreasen pipette consisting of a calibrated measuring cylinder with a height of 0 – 200 mm and a volume of 500 – 600 ml and a pipette for sampling with a volume of 10 ml. Suspension samples are taken-off within time intervals t by a pipette connected through a three-way cock to an aspirating arm immersed down to a depth h . Taking-off a higher number of samples in the time intervals is performed in order to find out changes in the powder concentration down in the defined depth of the original suspension depending on time. In order to make accurate measurements, instruments are inserted into a thermometer. The taken-off samples are desiccated thoroughly dry and the resulting dry weight is determined with 0.1 mg accuracy.

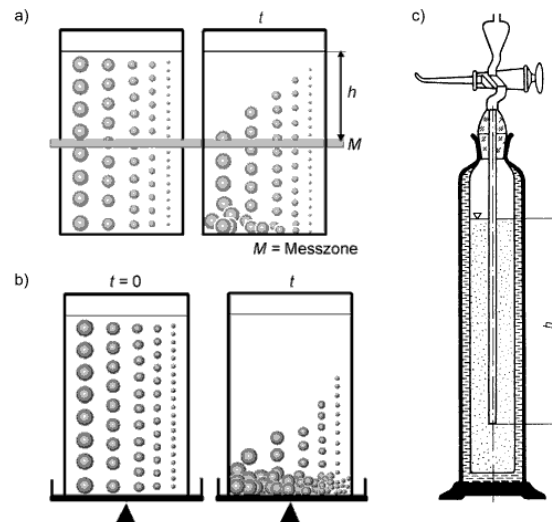


Fig. 3.10 Principle of the sedimentation analysis using the Andreasen pipette [6].

If the sedimentation rate in the gravitational field is too low, centrifugal acceleration with the help of an ultracentrifuge can be applied instead of gravitational acceleration. When centrifuging, a particle moving away from the axis of rotation is moving by a variable, more and more increasing speed. In the equation below a variable quantity x defines a fact that the centrifugal acceleration depends on the distance from the axis of rotation. The centrifugal force provides a constant speed for particles, while an air flow attains the size separation according to the Stokes' law. Lighter or smaller particles are diverted away by an air stream and thus separated from larger particles. A position of the interface x is read in various instants of time. The particle size separation can be varied through regulation of the disc rotational speed and air flow velocity:

$$v(x) = \frac{dx}{dt} = \frac{D_{St}^2 \cdot (\rho_S - \rho_L) \cdot \omega^2 \cdot x}{18 \cdot \eta}$$

This method is applicable for the powder size range from 1 up to 150 μm .

3.2.3 Determination of particle size and shape by microscopic method

If powder particles are smaller than the smallest sieved fraction, the grain size is measured with the use of a microscope. The lower limit is given by the resolving power of the microscope and for the optical light microscope it is typically 0.3 – 0.5 μm . When using an electron microscope, particles ranging between 10 – 0.003 μm can be measured.

The microscopic measurement is rather time consuming, however, this is the most accurate method in spite of all subjective errors. Next to the powder size determination, another advantage lies in a possibility to assess also a particle shape and structure. A detailed description of the test is described in BS 3406-4:1993 (ČSN 42 0890-13 standard "Testing of metallic powders. Determination of particle size by microscopic method").

For faultless measuring a perfect preparation of samples is necessary, which will prevent clustering of particles or their segregation. The simplest method is to spread the measured powder onto the microscope slide. To prevent clustering of particles, a drop of technical gasoline with alcohol should be spread on the slide, in which the particles are distributed evenly. While spreading the powder, vaporization of the technical gasoline with alcohol occurs. The particles are fixed onto the slide using the suitable oil.

Another method is to measure powder particle size on scratch patterns after being imbedded to an applicable material. This way the particle structure can be observed as well. A disadvantage is that maximal dimensions of particles cannot be measured because individual particles are placed randomly

in the basic material.

3.2.4 Specific surface determination

The specific surface affects the so-called surface activities of powder compacts during sintering and provides an important driving force for transport of the material during the sintering process. The specific surface of powder materials usually refers to 1 g of the material. The specific surface calculation from a particle size determined by the sieve analysis, the sedimentation analysis or the microscopic method comes out from an assumption that all particles have a spherical shape and a smooth surface. However, these assumptions are not met in most of the cases.

Current methods of the particle specific surface analysis do not measure the surface directly, but they are based on a determination of properties (adsorption, gas permeability) relating to the surface.

3.2.4.1 Adsorption method

This method was developed by S. Brammer, P. H. Emmet and E. Teller (BET method) and this is the most significant method for particle surface measuring. It is based on the adsorption of a noble or other gas on a powder particle surface. Generalized BET equation:

$$\frac{P}{X(P_o - P)} = B + A P/P_o$$

$$X_m = (A+B)^{-1}$$

where P – partial pressure of the adsorbate; P_o – saturation pressure of the adsorbate depending on the gas type and temperature; X – amount of the adsorbed gas under pressure P ; A , B – constants;

The method principle lies in covering the surface of powder particles of G_p weight with a mononuclear layer of gas molecules (Fig. 3. 11). The specific surface S_o of powder can be determined from the gas amount consumed in order to create the mononuclear layer X_m and the surface area of the adsorbed molecule A_o :

$$S_o = \frac{X_m N_o A_o}{G_p M}$$

where M – adsorbent molecular mass; N_o – Avogadro's number.

As the surface being available for the gas adsorption includes also pores and surface roughness, reliable data on the powder particle surface can be obtained. A basic assumption for the measurement accuracy is creation of only a mononuclear layer of the adsorbed gas. This is not met on edges, in corners and active points on a surface where layers with a higher number of molecules are formed as a result of bonding forces.

Nitrogen, argon and crypton are the most widely used adsorption gases. For the adsorption to run according to the BET equation, the adsorption measurement has to be carried out above the evaporation temperature of a gas at standard pressure. This is 77.4 K for nitrogen. Prior to the start of the measurement, a thorough degassing of the instrument and the sample to be measured is necessary, which is carried out by heating to 200 – 300 °C under high vacuum (10^{-4} Pa). Then a free space in an adsorption container is determined using helium which is only slightly adsorbed to the surface of particles and the container walls. Afterwards the helium is drained off the measured space, the adsorption gas is lead to a burette (e.g. nitrogen) and its volume is measured (with regard to temperature and pressure). A part of the gas is adsorbed on the powder surface and the gas volume is determined again. Regarding the fact that the measuring space volume is known, a gas volume decrease corresponding to the volume of adsorbed molecules can be determined. Further points for the BET straight line can be obtained by intaking gas again and changing the pressure (Fig. 3.11).

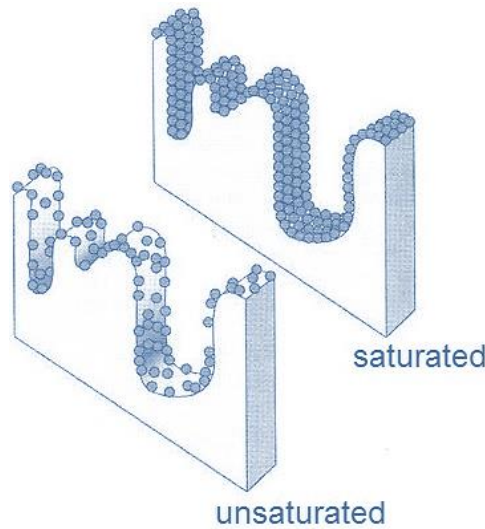


Fig. 3.11 Particle surface saturated (formation of a mononuclear layer) and unsaturated with an adsorption gas [1].

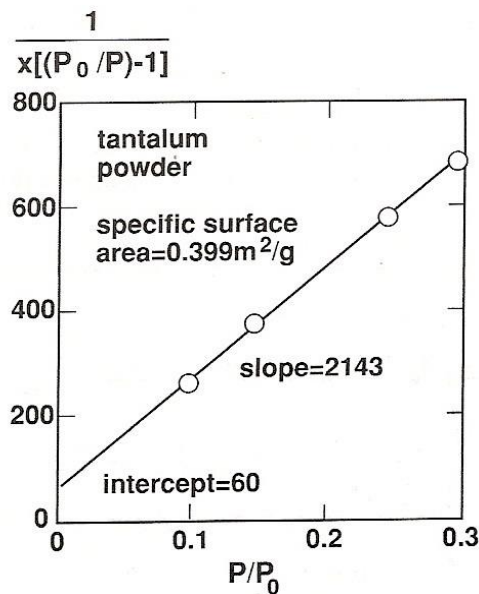


Fig. 3.12 BET straight line for tantalum powder [1].

3.2.4.2 Permeability method

The “Fischer Subsieve Sizer” method belongs among simple methods for determining required values in a short time. It uses air which is pumped into an apparatus under 10^5 Pa pressure (Fig. 3.13).

A powder sample is put into a measuring cell which is created by a calibrated tube. There the sample is fixed with the help of two porous plugs and compacted to porosity 40 – 70 %. When gas is passing through the sample, a drop in pressure Δp occurs which is determined using a manometer. Depending on the sample porosity, this data is corrected and converted to specific surface values with the aid of tables. This method can be used to measure powder sizes ranging between 0.15 – 50 μm . The result of the permeability method is the powder specific surface which is not usually consistent with the specific surface determined using sorption methods. The sorption methods measure the total surface area including pores and cracks, while the permeability methods are only able to measure the surface available to flowing gas.

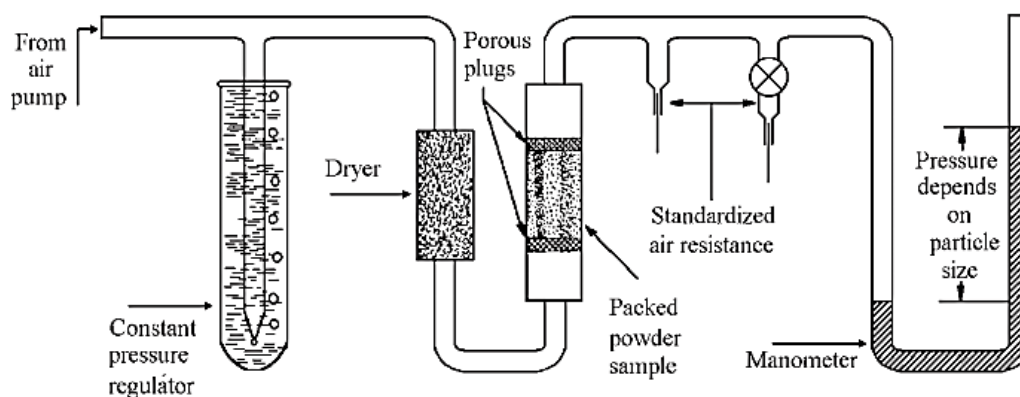


Fig. 3.13 “Fischer Subsieve Sizer” permeability method principle [7].

3.3 Technological properties

Knowledge on powder particle size, size distribution and shape is not sufficient for the complex characterization. Static and dynamic behaviour of material during technological processes needs to be known for the complete description. Technological tests modelling partially some processes during technological operations are carried out on this purpose.

3.3.1 Determination of flowability

Powder flowability is a property similar to viscosity of a liquid. It is an ability of powder to flow through pipelines, feed hoppers and inside cavities of pressing tools. It is described as a time period for which a given amount of powder (50, 100 g) flows through a funnel with 60° apex angle and a defined hole (ϕ 2.5 mm). The scheme and dimensions of the Hall flowmeter funnel are shown in Fig. 3.14. A detailed description of the test is given in MPIF Standard 03 (ČSN EN ISO 4490 standard “Determination of flow rate of free-flowing metal powders using the hall apparatus”).

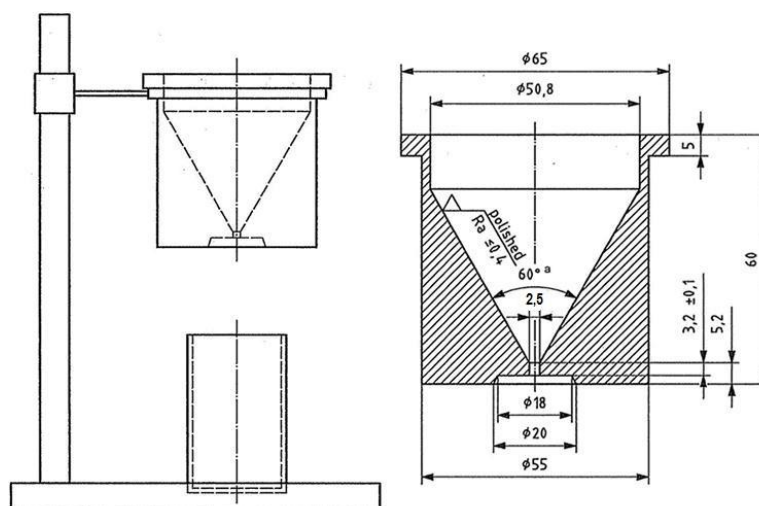


Fig. 3.14 Scheme of an apparatus for powder flowability determination – Hall funnel [8].

The resistance to powder flowing from the funnel is given by friction of powder particles among each other and friction between particles and the funnel walls. The funnel geometry plays an important role. Friction conditions depend on the particle specific surface. For particles with a large specific surface the friction is higher and the flowing ability worse than for particles with a small specific surface. Moreover, for small particles a formation of “bridges” impeding the continuity of the

material flow occurs as a result of an increase of surface forces. Flowability becomes also worse with high porosity and roughness of particle surfaces. Another factor affecting this property significantly is a particle shape. Angular or dendritic particles exhibit the worst flowability because individual particles cling to one another mechanically (jamming occurs), which impedes powder flowing through the outlet hole. Powder with optimal flowability can be made by extending a particle size spectrum and changing their proportional content.

For pneumatic conveyance, a powder adhesion to a base plate is also important. A principle of its determination consists in spreading a layer of the assessed powder on a base plate which is being raised as long as the powder gets to motion. In this moment the friction force and the gravitational force are in a balance (Fig. 3.15):

$$m \cdot g \cdot \sin \alpha = \mu \cdot m \cdot g \cdot \cos \alpha$$

where α – angle of the base plate; g – gravitational acceleration (m/s^2); μ – friction coefficient.

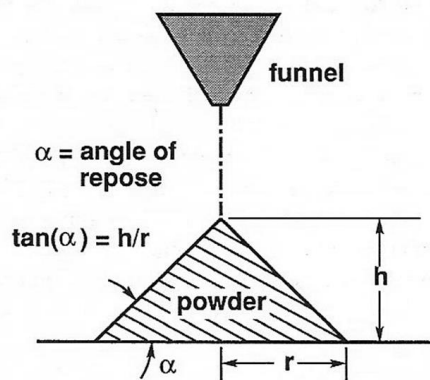


Fig. 3.15 Determination of the powder adhesion to a base plate [1].

The equilibrium is set at the angle of repose α , which characterizes powder adhesion to the given type of the base plate material. Other parameters affecting adhesion of particles are their shape and size, material and a method of processing of the powder and a design of the base plate. The following methods have also found a use for measuring the angle of repose (Fig. 3.16):

- titling table;
- rotating cylinder;
- ledge method;
- crater method (discharge method);
- dynamic angle of repose.

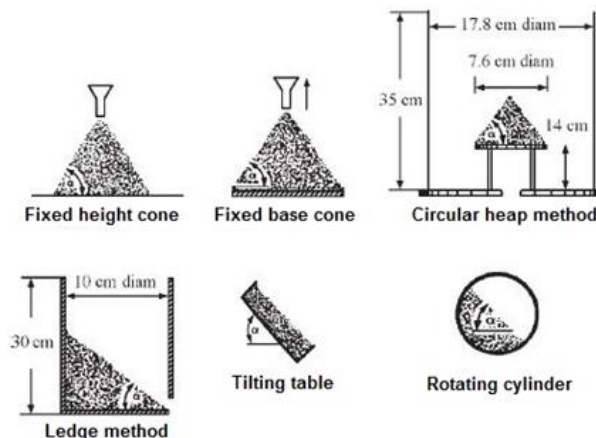


Fig. 3.16 Methods used for measuring the angle of repose [8].

3.3.2 Determination of apparent density and tap density

Apparent density is defined as a loose powder weight to volume ratio (g/cm^3). A principle of the test, which is carried out in the same apparatus as when determining powder flowability, consists in pouring powder through a defined funnel or funnel system into a container of a constant volume (Fig. 3.17). After determining a weight of the powder in the container, the apparent density can be calculated. A detailed description of the test is given in MPIF Standard 04 (ČSN EN ISO 3923-1 standard “Determination of apparent density of free-flowing metal powders using the hall apparatus”). Apparent density is of a great technical importance for determination of weighed amounts in order to compress components of demanded shapes and dimensions, above all when pressing on mechanical presses with automated filling of pressing dies or when pressing complicated components.

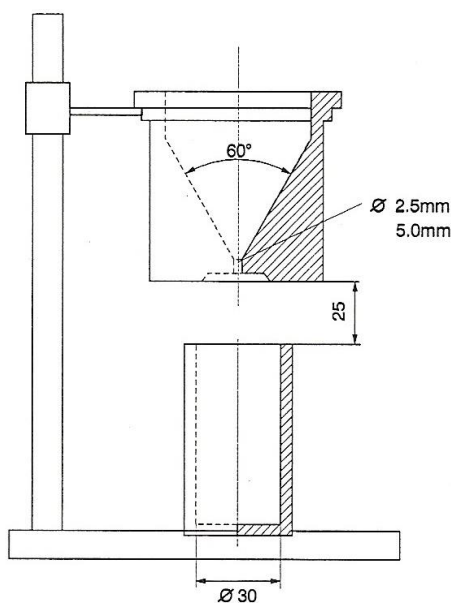


Fig. 3.17 Determination of apparent density of powder [8].

Considering the fact that powders being filled freely are not distributed evenly and cavities, which distort measurements, may occur between particles, the so-called tap density (g/cm^3) is very often determined, too. This is density of powder manually or mechanically tapped-down to a constant volume in a measuring cylinder. The volume is usually determined after 3 – 5 minutes at vibration frequency of c. 120 s^{-1} . A detailed description of the test is described in MPIF Standard 46 (ČSN EN ISO 3953 standard “Determination of Tap Density of Metal Powders”).

3.3.3 Compressibility of metal powders

Conditions for a determination of compressibility of metal powders in uniaxial compression are defined in MPIF Standard 45 (ČSN EN ISO 3927 standard). A cohesion test consists in barrel rumbling of compacts and observing a drop in their weight.

Basic terms:

Compressibility of powder – an ability of powder to reach a determined shape, volume weight and mechanical strength by pressing.

Compactibility of powder – an ability of powder to achieve a determined volume weight at a given compacting pressure.

Cohesion of powder after pressing – an ability of powder to maintain a shape against external mechanical forces.

Values of the mentioned characteristics are influenced by powder material substantially. The

more formable the material, the higher relative density of a compact can be achieved. All factors deteriorating formability of compact materials (addition agents, dislocations) deteriorate also powder compressibility. This effect is usually overlaid by an influence of a particle shape. While a particle shape has an importance especially at low pressing pressures and with sponge particles, plastic properties of powder are of the main significance at high pressures. By reason of friction between particles, larger particles can be compressed (compacted) better than fine particles. Powders with a broad spectrum of particle sizes exhibit the best compressibility as a result of high filling density (Fig. 3.18). Pressing additives for friction reduction improve compacting, however, on the other side, they may reduce the powder cohesion after pressing.

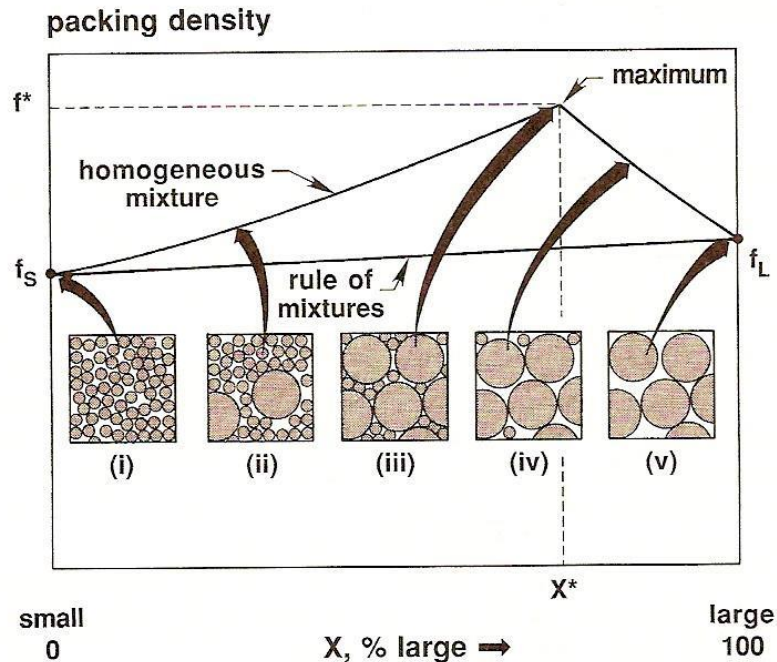


Fig. 3.18 Packing density as a function of a composition of a mixture containing spherical-shaped powder with different particle sizes [1].



Summary of terms

Particle size

Particle shape

Particle size distribution

Specific surface area

Flow rate

Apparent density

Compressibility



Questions to the topic

3.1. How is varied the particle shape and morphology with manufacturing techniques?

3.2. What are the methods of particle size analysis?

3.3. How is measured the flow rate and apparent density of powder materials?

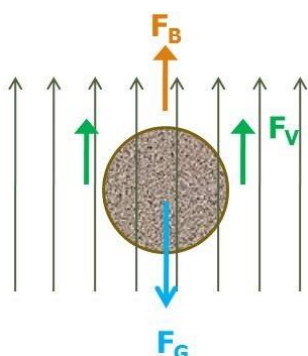
3.4. What is application and principle of BET analysis?



Solved tasks

Exercise 3.1

The sedimentation analysis was used to determine particle size of the spherical-shaped Ni-powder. The particle size is estimated to be around 8 mm. If the powder is dispersed in water on top of the sedimentation column of a height $H = 100$ mm, what the estimated sedimentation time will be?



$$g = 9.8 \text{ m/s}^2$$

$$\rho_{\text{Ni}} = 8.9 \text{ kg/m}^3$$

$$\rho_{\text{H}_2\text{O}} = 1 \cdot 10^3 \text{ kg/m}^3$$

$$\eta = 1 \cdot 10^{-3} \text{ kg/m/s}$$

♦ Solution

$$F_G = \frac{g \cdot \rho_S \cdot \pi \cdot D^3}{6} ; F_B = \frac{g \cdot \rho_L \cdot \pi \cdot D^3}{6} ; F_v = 3\pi \cdot D \cdot v \cdot \eta$$

g – gravitational acceleration; F_B – buoyant force; F_G – gravitational force; F_v – viscous drag force; η – liquid viscosity; v – limiting (constant) velocity

For a particle to fall down in a liquid at the constant velocity, the condition must be met:

$$F_B + F_v = F_G$$

$$\frac{g \cdot \rho_S \cdot \pi \cdot D^3}{6} = \frac{g \cdot \rho_L \cdot \pi \cdot D^3}{6} + 3 \cdot \pi \cdot D \cdot v \cdot \eta$$

$$v = \frac{g \cdot D^2 \cdot (\rho_S - \rho_L)}{18 \cdot \eta} \quad \dots \text{Stokes' law}$$

$v = H / t$ (H – a height of a column of a dispersion settling over a time t)

$$v = \frac{9.8 \cdot (8 \cdot 10^{-6})^2 (8.9 \cdot 10^3 - 1 \cdot 10^3)}{18 \cdot 1 \cdot 10^{-3}} = 2.75 \cdot 10^{-4} \text{ m/s} ;$$

$$t = H / v = 0.1 / 2.75 \cdot 10^{-4} = 363,64 \text{ s} \approx 6 \text{ min.}$$



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4. POWDER CONDITIONING AND HEAT TREATMENT



Study time: 2 hours



Objective

- Methods of powder sorting
- Influence of additives on the technological properties of powders
- Characterization of a mixture quality
- Mixing of homogenous and heterogenous powders



Lecture

In most cases a manufactured powder is not just usable for powder metallurgy applications. Therefore it must be processed, in particular by the following reasons:

- sorting according to particle size;
- increasing purity or hardening elimination by annealing;
- addition of a lubricant (sliding agent) and a binding material;
- mixing of various fractions;
- mixing of various materials;
- granulation.

4.1 Sorting of powders

Particles in a green powder usually occur within a broad size range. In order to reach the optimal density and compressibility of the used powder, a specific composition in term of particle size needs to be ensured. Therefore the powder is sorted to various fractions from which a demanded composition can be obtained through mixing. Sorting is carried out using the following methods:

Sieving – sorting loose materials to various size classes with the help of vibration sieves. It is used for powders of a grain size > 0.04 mm.

Air sorting – sorting powder to size classes by a properly controlled air stream. Lighter particles are wafted farther than large and heavy particles. Particles ranging between $0.02 - 0.1$ mm can be sorted this way.

Floating – sorting powder to size classes by a properly controlled stream of water or other liquid.

4.2 Annealing of powders

Powder reduction is needed in case their surface oxidation occurred as a result of surrounding conditions. The reduced powder needs to be processed as soon as possible by reason of its high reactivity which increases, while a grain size decreases. Reduction is carried out in sintering furnaces in an atmosphere of hydrogen or cracked NH_3 . The reduction temperatures of technically significant metals are shown in Table 4. 1.

Al, Cr, Mn and Ti metals cannot be reduced efficiently in a technical scope. They have to be manufactured by a process preventing oxygen contamination. Reduction is carried out at as low temperatures as possible by several reasons:

- economical viewpoint;

- avoiding agglomeration of particles;
- less forces for disintegration, by which a risk of re-oxidation and hardening is reduced.

Table 4.1 Temperatures of hydrogen reduction of oxides of technically most significant metals.

Metal	Reduction temperature
	(°C)
Co	600 - 700
Cu	≥ 250
Fe	~ 700
Ni	600 – 700
W	750 – 800
Mo	900 – 1000

4.3 Additions and admixtures

Various additional pressing additives (plastificators, lubricants, etc.), which are used in order to reduce friction between pressing tool walls and between individual particles, are added to powders very often, in particular to those with poor compressibility. They also reduce wear of pressing dies and their “sticking”. In Table 4.2, commonly used additional pressing additives are shown, which are added to pressing mixtures in an amount ranging between 0.2 to 1 wt.% (most frequently zinc or lithium octadecanoate). Higher contents can lead to the product degradation during evaporation. In general, the use of pressing additives leads to a decrease of flowability and bulk density of powders (Fig. 4.1).

Table 4.2 Commonly used pressing additives.

Additive	Melting temperature	Dissociation or vapour temperature
	(°C)	(°C)
$\text{Zn}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	140	335
$\text{Ca}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	180	350
$\text{Al}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	120	360
$\text{Mg}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	132	360
$\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$	116	360
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ (Stearic acid)	69.4	360
$\text{C}_{22}\text{H}_{46} - \text{C}_{27}\text{H}_{56}$ (paraffin)	40 – 60	320 – 390
MoS_2	1185	-
WS_2	1200	-
WO_3	795	-
graphite	3500	-

Lubricants have to be removed before sintering not to prevent formation and growth of metallic bonds. Sintering additives or binders are metal additives which are added to initial mixtures to improve the sintering process. They are usually partly or completely dissolved during sintering, thus sintering occurs in the presence of a liquid phase. Fillers are other additional agents which are mixed to metal powder in a specified amount. They evaporate during sintering, thus a demanded porosity degree occurs in the final product.

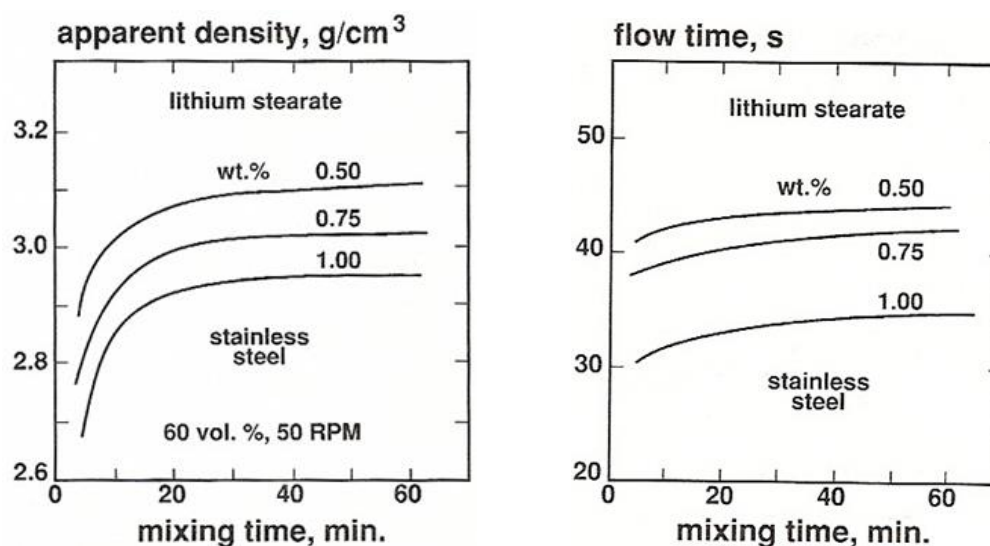


Fig. 4.1 Influence of lithium stearate addition on apparent density and flowability of stainless steel powder [1].

4.4 Mixing of homogenous and heterogenous powders

Mixing of powders and their homogenization is carried out both in order to achieve a uniform quality of an initial raw material and thus also a good reproducibility of production and to reach proper technological properties of the processed powder. It is necessary to reach a specific granulometric composition of powder with regard to the following:

- Filling density – smaller tool dimensions, higher performance.
- Compressibility – lower compacting pressure and thus higher density.

The very mixing is carried out in various types of devices – see Fig. 4.2. Drum mixers are advisable for easily mixable components. For intensive mixing, fixed casing mixers or rotating casing mixers are used in which spiral, screw or blade stirrers are placed. Three mixing mechanisms are dominant during powder homogenization – diffusion, convection (flow), shear (Fig. 4.3).

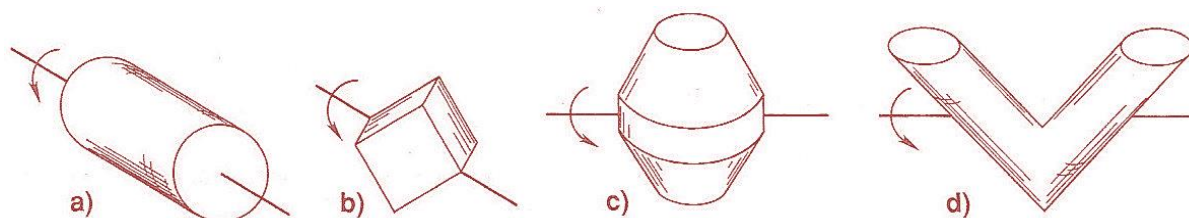


Fig. 4.2 Various types of mixing machines [1].

Proper mixing additives may be used to ensure good mixing and avoid a formation of agglomerates (clusters). These are e.g. alcohol-based fluids which do not affect behaviour during

sintering and decrease interparticle mutual forces. As a result of a longer time of mixing the so-called “overmixing” may occur, leading to particle distribution homogeneity deterioration. Therefore in a certain instant, when an optimal mixing has been achieved, the so-called stabilization additive is sometimes added (for instance oleic acid in benzole), which increases interparticle forces again.

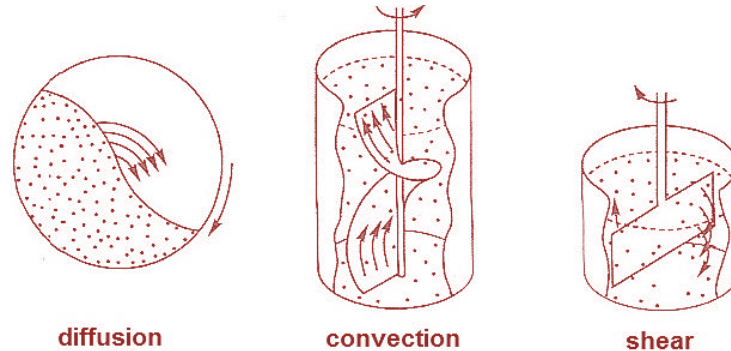


Fig. 4.3 Schematic illustration of mixing modes [1].

4.5 Evaluation of powder mixtures

An important role for a manufacture and properties of “composites” using powder metallurgy procedures plays distribution of components in the powder mixture, and thus in the final product. The higher the mixture quality, the larger the contact surface between components. Examples of various distributions are shown in Fig. 4.4. A tendency to segregation of powder particles depends on differences in particle sizes and shapes and particularly on their density. These differences may be adjusted, if fine particles are heavier than coarse particles. However, a problem occurs in the case of coarse particles with higher density, when fine particles float on the powder mass surface. The highest quality mixture is achieved as shown in Fig. 4.4-b), featuring a statistically distributed admixture and not containing agglomerates. Powder mixtures which tend to segregation have to be processed adequately, e.g. with a stabilizer.

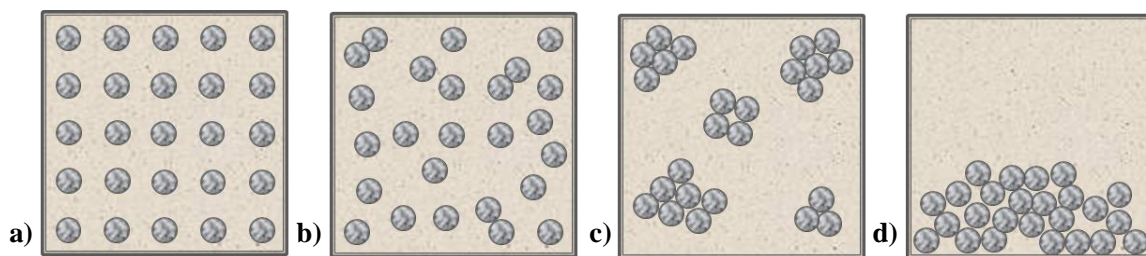


Fig. 4.4 Possible ways of particle distribution during mixing: a) arranged distribution; b) random (statistical distribution); c) formation of clusters (agglomerates); d) segregation of particles.

4.5.1 Characterization of a mixture quality in macro-volumes

To determine a mixture quality in macro-volumes, a deviation s needs to be defined, which characterizes composition variances in an observed material. The so-called variation coefficient V is used to describe these relations:

$$V = \frac{s}{q} = \frac{\sqrt{\frac{1}{n} \sum_{i=1}^n (q_i - q)^2}}{q}$$

where s – standard deviation of a composition; q – required concentration of an observed component;

q_i – concentration of a component in the i -th sample; n – number of samples.

The lower the V value, the higher the mixture quality. For its determination it is necessary to determine a content of admixtures in a series of weight- or volume-stable samples analytically.

4.5.2 Characterization of a mixture quality in micro-volumes

Characterization of a mixture in micro-volumes is carried out either in a mixture or in a compact. In the case of admixture content $\geq 5\%$, its distribution corresponds with the statistical (normal) distribution. With this admixture content $\leq 5\%$, the distribution is characterized by the Poisson distribution.

In this case the admixture distribution does not occur according to the variation coefficient, but pursuant to the homogeneity coefficient H :

$$H = \frac{s^2}{\bar{X}}$$

where \bar{X} – mean value of a number of particles on an observed area. If $H > 1$, the distribution is not statistical.

4.6 Granulation of powders

Granulation can be performed in several ways:

- Using granulation additives (e.g. glycol, glycerin, paraffin, etc.)** - carried out on balling discs. Very fine powders ($< 1\ \mu\text{m}$) are pelletized without organic additives, whereas pelletizing has a higher effect at specific humidity - H_2O addition.
- Mechanical granulation** – powder is ground to a proper size of granules after pre-pressing at lower pressures.
- Thermal granulation** – powder, usually in bulk, is pre-sintered and subsequently disintegrated to a required size.



Summary of terms

Sieving

Annealing

Homogenization

Segregation

Variation coefficient

Granulation



Questions to the topic

- 4.1. What are the sorting methods of power materials?
- 4.2. What are the pressing additives and why are they used?
- 4.3. How can the mixture quality be evaluated in micro- and macro-volume?



Solved tasks

Exercise 4.1

Determine a critical rotational speed N_c (rpm) of a cylindrical mixing device (mixer). N_K represents equilibrium between the centrifugal and gravitational force.

♦ Solution

The centrifugal force acting on a particle of a weight m at the mixing device wall is described:

$$F_c = m \cdot v^2 / r$$

The gravitational force acting on a particle is described:

$$F_g = m \cdot g$$

The outer velocity v of the mixer depends on the rotational speed N (RPM) and the rotation diameter d :

$$v = \pi \cdot d \cdot N$$

$$F_c = F_g$$

$$m \cdot v^2 / r = m \cdot g$$

$$2 m \cdot \pi^2 \cdot d^2 \cdot N^2 / d = m \cdot g$$

$$2 \pi^2 \cdot d \cdot N^2 = g$$

$$N_K = \sqrt{\frac{g}{2 \cdot \pi^2 \cdot d}} = \sqrt{\frac{g}{2 \cdot \pi^2}} \cdot \sqrt{\frac{1}{d}} = \frac{0.71}{\sqrt{d}} \text{ RPS} = \frac{42.3}{\sqrt{d}} \text{ RPM}$$

**References**

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5. ALLOYING METHODS AND MICROSTRUCTURE OF POWDERS



Study time: 2 hours



Objective

- Alloying methods of metal powders
- Rapid solidification, temperature gradient, undercooling
- Powder microstructure in dependence on solidification conditions



Lecture

5.1 Alloying of powders

Alloying of powder influences its technological properties, sintering process and in the final stage also final properties of a sintered product. Several alloying processes are applied in practice (Fig. 5. 1):

1. **Mechanical mixing of individual components of an alloy (“mixed alloying”)** – a mixture is well compressible, sometimes even better than the metal itself and chemical composition can be varied easily. Higher segregation and dustiness is an advantage. It is used for a manufacture of parts without high requirements for strength.
2. **Pre-alloyed powders** - due to alloying elements have high hardness which deteriorates compressibility. These powders are commonly prepared by the melt atomization, where segregation phenomena are suppressed as a result of high cooling speeds. From these powders, highly homogenous semi-products can be made, such as high-speed steels, heterogenous alloys of copper, nickel etc. Mechanical alloying is another way to make these powders.
3. **Partially (diffusion) alloyed powders** – made by mixing elementary or pre-alloyed powders followed by diffusion annealing. These powders feature good compressibility and low segregation of admixtures.
4. **Hybrid powders** – obtained by mixing pre-alloyed or partially alloyed powders with elementary (pure) powders or powder ferroalloys to achieve a required chemical composition.

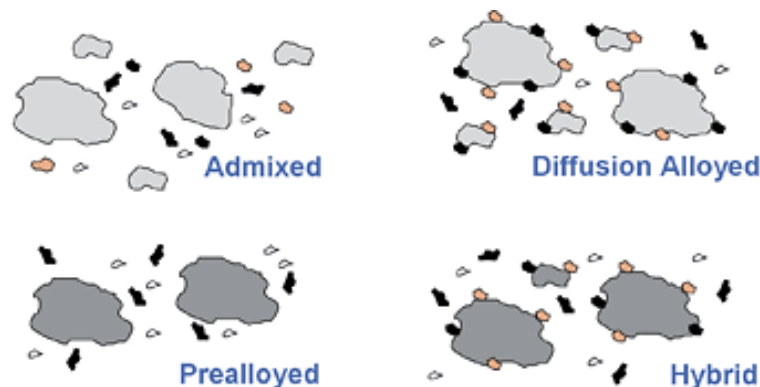


Fig. 5.1 Methods of alloying of metal powders [1].

5.2 Powder microstructure

Powders prepared by rapid solidification (e.g. melt atomization) have a different structure than materials prepared under equilibrium conditions of crystallization. Rapidly solidified powders can contain also new phases including the amorphous structure with much smaller dimensions of the microstructure, non-equilibrium composition and substantially decreased segregation.

In contrast to the classic casting technology, where cooling speeds are typically below $100\text{ }^{\circ}\text{C/s}$, the cooling speed ranging between $10^3 - 10^4\text{ }^{\circ}\text{C/s}$ can be achieved for atomized powders with a large surface per a volume unit. If particles are very small, considerably high thermal extraction can be achieved by cooling speeds from 10^6 up to extremely $10^8\text{ }^{\circ}\text{C/s}$. Cooling speed change induces a decrease in segregation rate in an alloy. In Fig. 5.2, a microstructure change in 40 % Pd – 30 % Cu – 30 % Ag alloy depending on the cooling speed is documented. There is fivefold difference in magnification of the microstructure images in order to show dramatic differences in the microstructure. In the cast alloy (Fig. 5.2a), there is an evident segregation in the coarse dendritic structure, while the atomized powder (5.2b) exhibits much more homogenous microstructure with a decreased segregation. Increasing initial microstructure homogeneity considerably reduces the number of manufacturing steps needed for a formation of electrical contact from this alloy.

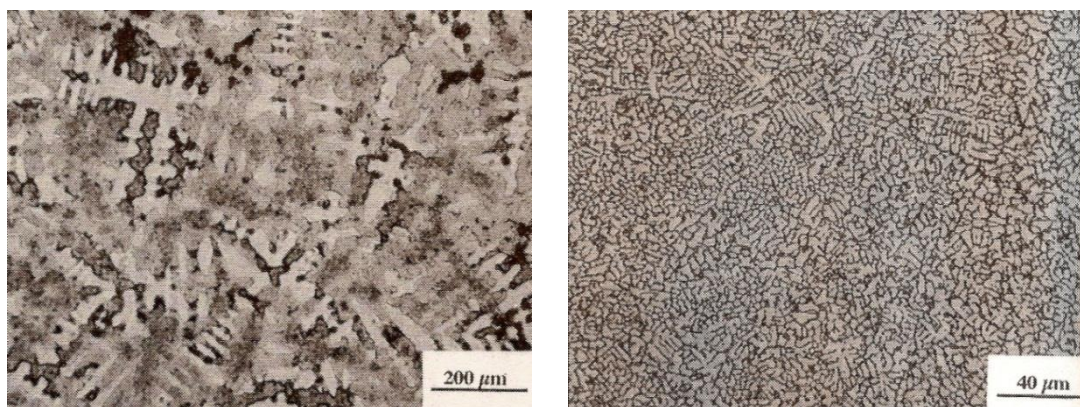


Fig. 5.2 Example of refinement of the rapidly solidified 40 % Pd – 30 % Cu – 30 % Ag alloy and segregation decrease [2].

In Fig. 5.3, particles with the dendritic microstructure on the surface are shown. In this case a molten drop of a melt fell down to a just solidified small particle and radial dendrites have grown outwards from the nucleation point on the surface – an example of the heterogenous nucleation. Segregation relates to the dendritic structure, too. Dendrites have higher melting temperature as a result of a different composition in comparison with interdendritic areas. The rate of segregation or homogenization in atomized powders can be roughly assessed from a grain size and a spacing between secondary dendrite arms λ .

A more homogenous microstructure with a shorter spacing between dendrite arms corresponds with a greater degree of undercooling which is characteristic for rapid solidification (cooling) and a smaller particle size. The interrelationship between the cooling speed and the secondary arm spacing for various types of materials is shown as an example in Fig. 5.4.

Key parameters affecting a resulting powder microstructure are undercooling and a temperature gradient in powder (Fig 5.5). Both the parameters grow, while the particle size decreases. If the particle is subjected to undercooling of a great degree, conditions for heat transfer and segregation of elements cannot be promoted anymore. This leads to a change to an equiaxed microstructure, which changes to a microcrystalline structure gradually along with increasing undercooling (Fig. 5.6).

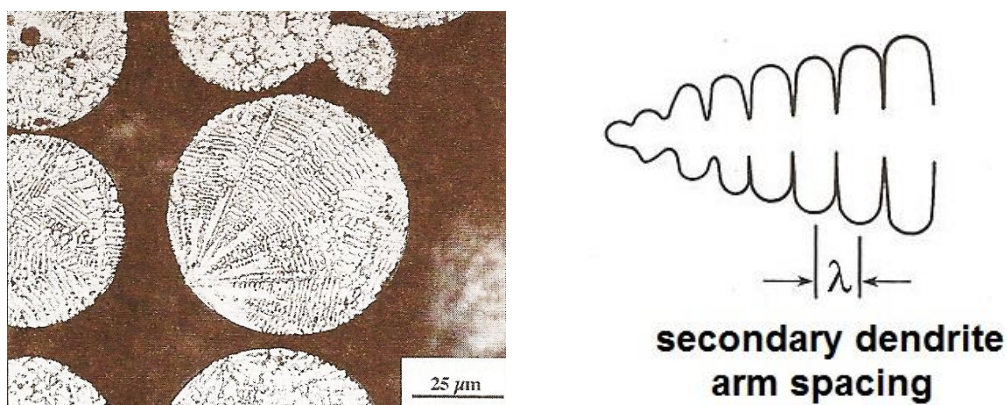


Fig. 5.3 Particles with the dendritic microstructure on the surface and the spacing between secondary dendrite arms [2].

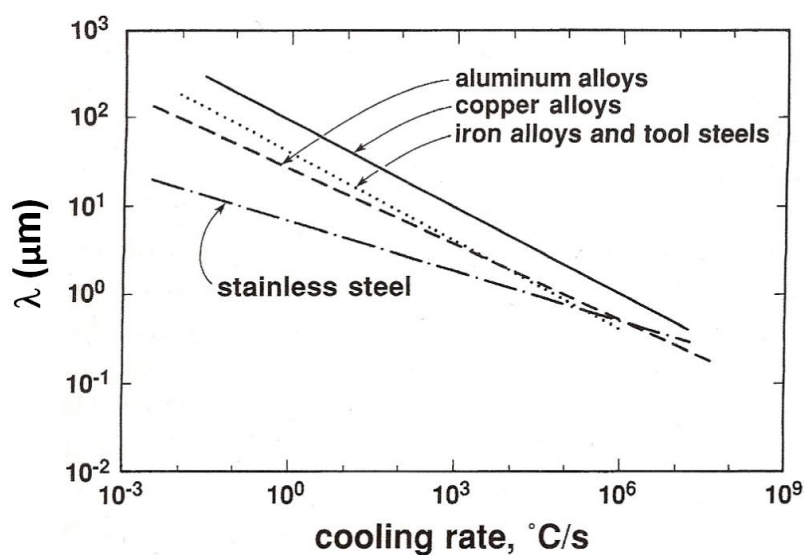


Fig. 5.4 Interrelationship between the cooling speed and the secondary arm spacing for various types of materials [2].

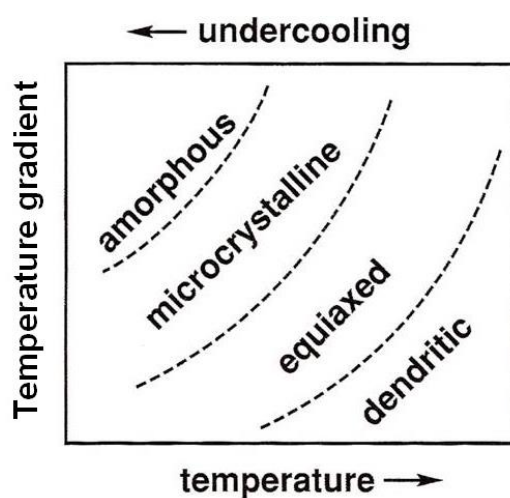


Fig. 5.5 Influence of undercooling and a temperature gradient on a formation of various morphologies of particle structures [2].

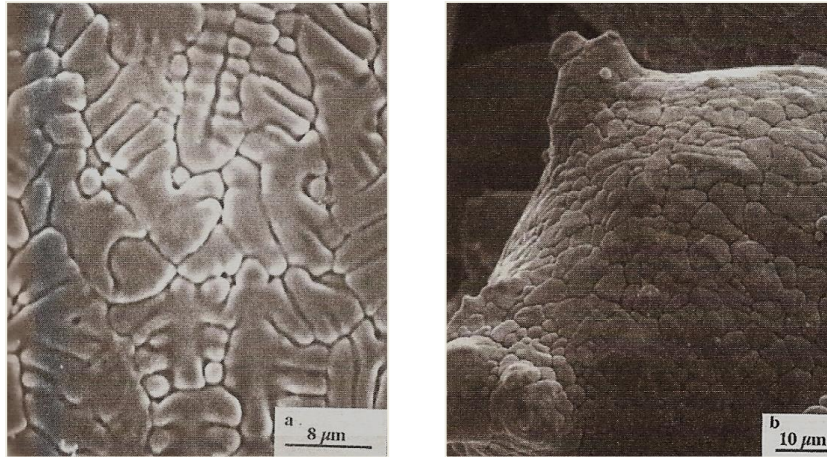


Fig. 5.6 Comparison of surfaces of powder particles with the dendritic and equiaxed structure [2].



Summary of terms

Alloying methods

Rapid solidification

Undercooling

Amorphous microstructure

Dendritic microstructure



Questions to the topic

5.1. What are the alloying methods of metal powders?

5.2. What are the key factors in respect to the type of microstructure expected by rapid solidification?



Solved tasks

Exercise 5.1

Internal energy of materials is temperature dependent, but in principle independent from the surface area. However, interphase energy is proportional to a particle size. Consider such a size of a particle, where the interphase (volume) energy is equal to the surface energy. At room temperature the internal energy of gold ξ is around 600 MJ/m^3 and the interphase energy (voltage) γ is 1.4 J/m^2 . What is the radius of this spherical particle of gold?

♦ Solution

Total energy is equal to:

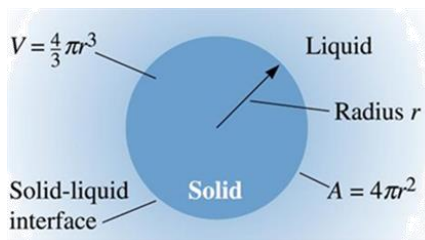
$$E_T = \gamma \cdot S + \xi \cdot V$$

$$\gamma \cdot S = \xi \cdot V$$

$$\gamma \cdot 4\pi r^2 = \xi \cdot \frac{4}{3}\pi r^3$$

$$\gamma = \xi \cdot r/3$$

$$r = 7 \cdot 10^9 \text{ m} = 7 \text{ nm}$$



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6. SHAPING AND COMPACTION OF POWDER MATERIALS



Study time: 6 hours



Objective

- Processes occurring during compaction of powder materials
- Classification of compaction methods of powder materials
- Principle and application of pressure-assisted compaction methods of powder materials
- Principle and application of pressureless compaction methods of powder materials



Lecture

Methods for compacting of powder materials can be divided to two basic groups:

1. *Compaction with the aid of static or dynamic compacting pressure at room or elevated temperature* – compacting by single-action or multi-action static compacting pressure in a die with an upper and bottom punch for high-volume manufacturing of parts of various types: forging, isostatic pressing, extrusion pressing, rolling, hot pressing e.g. for draw tools from cemented carbides.
2. *Pressureless compaction* – free pouring (e.g. a manufacture of filters), jolting, vibration compacting e.g. for fuel elements for nuclear technology and the ceramic casting method.

In Table 6.1, basic differences in behaviour of powder particles during their pressure forming and pressureless forming are shown.

Table 6.1 Basic differences in behaviour of powder particles during pressure compacting and pressureless compaction.

Pressureless compaction (loose poured particles)	Pressure-assisted compaction (deformed particles)
Particles are freely placed by gravitational forces	Particles are placed more closely by applying pressure to overcome interparticle adhesion and friction
Particles maintain their shape	Surface contact of particles, whereas a size depends particularly on compacting pressure – metal contacts
Temperature distribution between particles is equilibrium	Even during cold pressing a local temperature increase occurs on places of particle contacts (as a result of interparticle friction). Some diffusion processes may occur as well.
A crystal lattice of particles includes original imperfections.	Due to the plastic deformation an increase of dislocation density occurs inside particles.
Density is low	Density increases and depends on a deformation ability of the material, particle morphology and

	compacting pressure.
A shape of pores depends on the particle morphology	A shape of pores depends on the pressing method and the applied pressure
Pores are open (interconnected) – open porosity	Most of the pores are open, closed pores are existing already, too.

Cold forming involves all methods by which compacts can be made which have a demanded geometrical shape with such dimensions, so that after sintering they have final dimensions and such a consistency (green strength), that it is possible to handle them (e.g. to take-off from a pressing tool, to place into a sintering furnace etc.). The necessary “green” strength can be achieved by compacting, i.e. reducing porosity and increasing particular interparticle adhesion. Pressing is used most frequently for this purpose.

6.1 Fundamentals of pressing processes

When pouring powder, particles become arranged by acting of gravitational forces. Poured powders include bridges and cavities which can be reduced by jolting and vibrations.

By using slurry, a tighter arrangement can be reached due to reduction of interparticle friction. After drying-up of “cast” shape compacts, they can be handled freely. When pressing in tools, which is prevailing in the industrial scale, a shape body is subjected to a complicated mechanical loading. The applied compacting pressure leads to the compaction of powder. However, the pressure distribution in a compact is not uniform, which is given by the fact that a part of the incoming energy is consumed to overcome the friction between particles and mould walls and among particles themselves.

6.1.1 Processes occurring during compaction of powder materials by compacting pressure

If stress and density gradients caused by friction on the die walls are not taken into account, the achieved compact density is only a compacting pressure function. The following processes run in a compact with an increasing pressure (Fig. 6.1): 1. Arrangement of particles occurs, formed clusters (bridges) are removed and cavities are filled. 2. A contact between particles increases as a result of the plastic deformation and a particle surface is levelled. An oxidation layer is torn and a formation of the agglomerate occurs by mechanical interlocking of particles. Particles are strengthened. 3. Further on, when pressure increases, an increase of a contact surface between particles and further strengthening of particles occur, adhesion between particles increases and particles, which have run out of their plasticity, disintegrate.

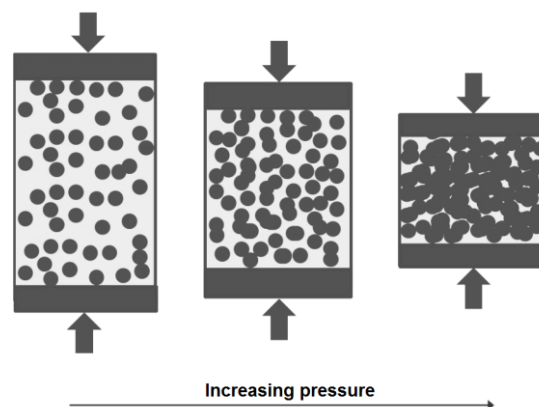


Fig. 6.1 Processes running in a compact with increasing pressure.

According to the quality of the powder, which can consist of particles of different sizes or various chemical composition, these processes can run simultaneously and they occur more or less depending on the powder properties. A density and porosity change influences other measurable values which can be used for a description of properties of compacts, in particular for formable materials. For example, this is hardness which depends on a degree of strengthening, a powder size, a degree of oxidation etc., or electrical conductivity which increases with decreasing porosity at first, but an increasing hardness slows down this rise.

During die pressing the conditions are strongly affected by friction on the die walls, which causes uneven distribution of material density in a compact. During single-action pressing, the highest compacting pressure is on edges of a pressing tool, the lowest on the bottom edge of a compact. During double-action pressing, i.e. when using a movable upper and bottom punch, compacts of a double height can be pressed. The pressure distribution is better than during the single-action pressing, but it is also influenced by friction on the pressing mould walls.

Inhomogeneous pressure distribution in the vertical and horizontal direction causes a disintegration of a compact to horizontal layers of a “plate” shape while pushed-off from the die. According to some authors, during pressing parabolic areas are formed in a compact, which do not contain a tangential component of stress. On these areas, there is no shear motion of particles, and not even occurrence of cold welded joints.

Consider a cylindrical compact of a diameter D and height l , where its element dl is analysed (Fig. 6.2). The pressure in the upper part of the element p and the pressure passing through an element p_b differs by a normal (perpendicular) force acting against friction. Force equilibrium along the compression axis can be expressed mathematically as:

$$\sum F = 0 = A \cdot (p_b - p) + \mu \cdot F_n$$

$$\text{where } F_f = \mu \cdot F_n; A = \pi D^2/4$$

The normal force can be expressed with the aid of an applied press and a constant of proportionality z , which changes with a compact density:

$$F_n = \pi \cdot z \cdot p \cdot D \cdot dl$$

The friction force F_f can be calculated directly from the normal force and the friction coefficient μ as:

$$F_f = \pi \cdot \mu \cdot z \cdot p \cdot D \cdot dl$$

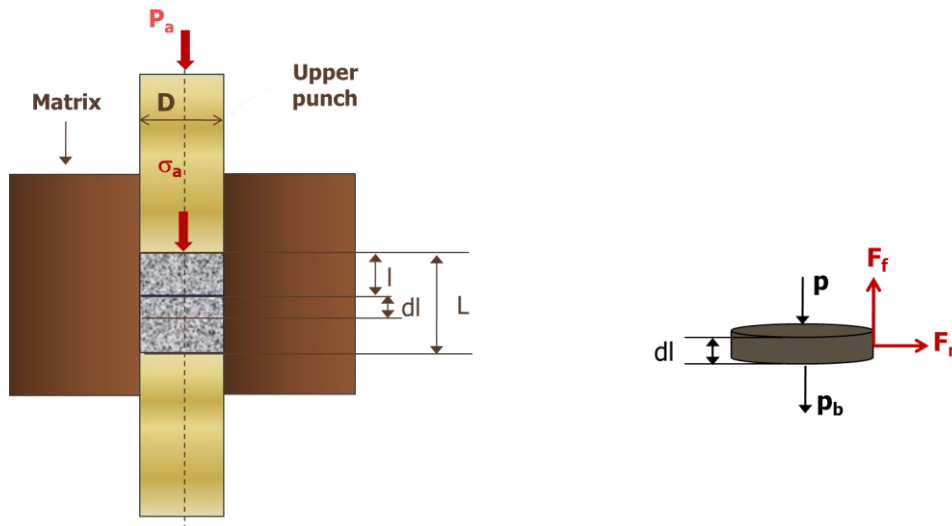


Fig. 6.2 Relation of the applied compacting pressure to its distribution in the compact volume.

Combining the above mentioned relations, the difference in pressures dp of the upper and

bottom part of the element can be expressed as:

$$dp = p - p_b = -F_f / A = -4 \mu \cdot z \cdot p \cdot dl / D$$

Through integration of the above mentioned relation regarding the height of the compact, the following relation of the pressure p_x in a point x under the punch can be obtained:

$$p_x = p \cdot \exp(-4 \mu \cdot z \cdot x / D)$$

This equation is applicable for the single-action pressing. The relation implies that the pressure decreases with an increasing distance from the punch in the depth under the punch.

The double-action pressing has a profile of the simultaneous compacting pressure profile both from the upper and from the bottom punch. For this type of compression the obtained relation p_x is valid, however, the distance x expresses the distance to the nearest punch. The result is a more homogenous pressure distribution in the compact. In such a case the pressure distribution depends on the compact height to diameter ratio, which should be as low as possible. The single-action compression is usually limited to a simple geometry of a compact.

6.1.2 Activation effect of pressing

When shapes and sizes of particles and their contact areas are changing during pressing, lattice and structure imperfections occur (e.g. dislocations the number of which is proportional to the increasing compacting pressure and pressing speed). These increase the activity structure of powder, which has been formed during its manufacture, and thus also free energy of the dispersive substance and during the follow-up sintering lead to an increase of compaction intensity. Phenomena contributing to the sintering process activation are influenced by pressing conditions. These are in particular as follows:

- a change in a particle specific area by further disintegration;
- an enlargement of a particle contacting area as a result of a failure of surface oxidation layers;
- an increase of the number of lattice imperfections.

These phenomena belong among the main ones, which have a crucial influence on a sintering process and thus on the final product properties.

6.2 Pressure forming

Die pressing finds the best practical use of the mentioned powder material forming processes.

6.2.1 Die pressing

Properties of compacts depend on the pressing process to a great extent. In Fig. 6.3, basic principles of the most widely used processes of die pressing are shown. The double-action pressing is preferred, as it ensures more favourable density distribution and complex density of a compact. Further, it enables to eject a compact off a die faster.

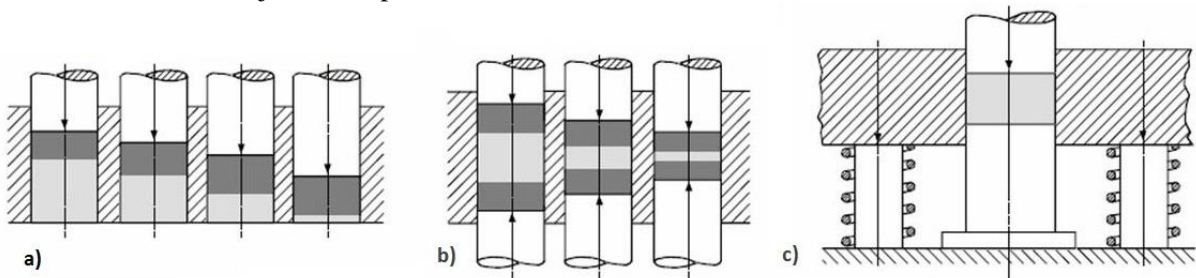


Fig. 6.3 Methods of die pressing: a) single-action pressing; b) double-action pressing; c) floating die pressing [1].

During this pressing method the powder poured into a die occupies a height H (loose powder height) and at the upper and bottom punch acting simultaneously it is compressed to a height h . In Fig. 6.4, the particular cycles of the pressing process are shown – 1. Filling a die with powder; 2. Pressing of the powder; 3. Ejection and take-off of a compact.

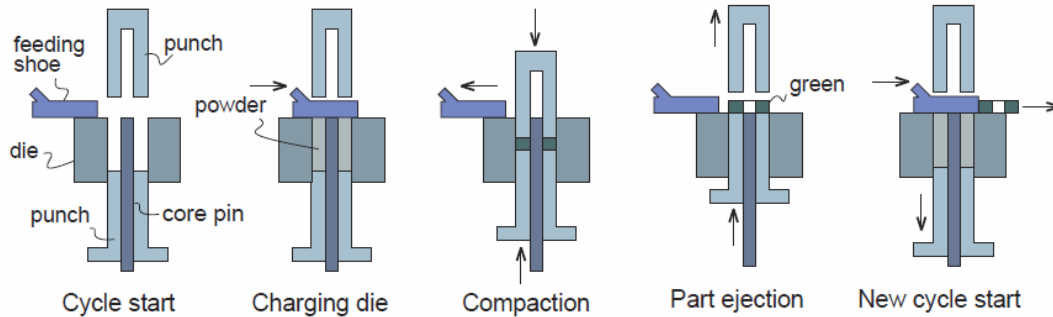


Fig. 6.4 Particular cycles of the process of die pressing [2].

6.2.1.1 Powder behaviour during pressing

Powder behaviour when compressed can be evaluated from various points of view. To determine dimensions of pressing tools, a ratio of a loose powder height H to a compact height h is important. In order not to extend a pressing path, the height H has to be as short as possible, which assumes an adequate powder apparent density. The $H:h$ ratio should not exceed a value of 3.

A degree of compaction at pressing is usually characterized by relative density which is defined as a ratio of a density of a porous compact to an adequate compact material density. The relation of relative density to compacting pressure for selected metal powders is given in Fig. 6. 5.

In principle, high density of compacts is required. It ensures a satisfactory strength and manipulability of a compact and its low shrinkage during the subsequent sintering, so that demanded dimensions of a product can be achieved more easily. However, the enhancement of density of a compact is limited by economical and constructional factors. The density enhancement requires higher compacting pressures, resulting in faster wear of pressing tools and an increase of dimensions of pressing machines. Therefore in a case of an unsatisfactory density, other enhancement methods are to be used, e.g. coining. This means a re-pressing of a compact in order to achieve accurate dimensions and to improve properties, while enhancing the relative density substantially at the same time.

Regarding to pressing and sintering, contending demands are often posed on powders. For good sintering, fine powders with a large specific surface are demanded. However, these materials have the high loose powder height H and thus the pressing process is made more difficult. A similar situation is for mechanically “activated” powders which are often strengthened as much that their deformation is not possible at room temperature. Then, these compacts exhibit low relative density after pressing. To enhance the density, such powders must be processed in a different way.

In principle, the very pressing can be performed in two ways:

- **Pressing by a stable compacting pressure** – performed on hydraulic presses which have to be set to a required maximum compacting pressure. Compacts may show certain differences in height as a result of different properties of the initial powder material. Pressing force calculation:

$$F = S \cdot p$$

where F – pressing force (N), S – total compressed area (m^2), p - compacting pressure ($\text{N} \cdot \text{m}^{-2}$).

- **Pressing to a constant height** – performed on mechanical presses with a constantly set stroke of a punch. Differences in the initial powder quality result in density changes of obtained compacts. Determination of the loose powder height:

$$H_v = H_s \cdot q$$

where H_v – loose powder height (mm), H_s – height of a compressed part (mm), q – filling coefficient ($q = k/s$); k – density of a compact (kg.m^{-3}), s – apparent density of powder material (kg.m^{-3}).

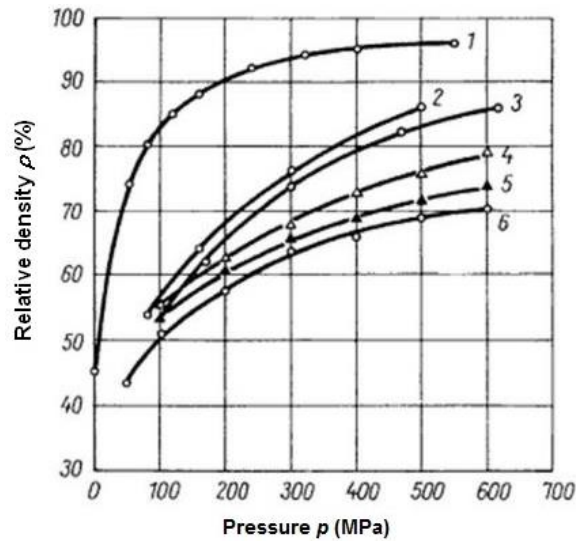


Fig. 6.5 Relation of the relative density to the compacting pressure for selected metal powders: 1 – Al, 2 – electrolytic Cu, 3 – sponge Fe, 4 – electrolytic Fe, 5 – carbonyl Fe, 6 – H_2 -reduced W [3].

6.2.1.2 Manufacture of complicated compacts

Certain limitations need to be respected in manufacture with regard to forming of compacts. These include above all high sensitivity to notches. When die pressing, a compact height to diameter ratio should not exceed a value of 2, max. 3. Further, thin walls and sharp transitions of a surface are to be reduced – see Fig. 6.6.

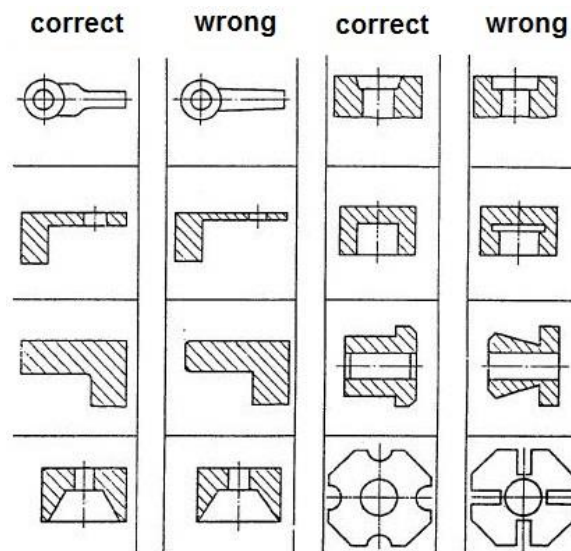


Fig. 6.6 Structural design of shaped parts of sintered Fe [4].

A proper design and specifications of pressing tools ensure their long-time service life and proper functioning. For a low-volume manufacture, pressing tools of tool steels are usually used, for a high-volume manufacture - cemented carbides. When designing a pressing tool dimension, one has to consider shrinkage, or swelling, of a compact as a result of sintering and “relaxation” (elastic

recovery) after ejection of a compact from the die. Pressures applied during pressing are limited by a tool shape and a type of material. Moreover, a pressing tool design is influenced by the pressure intensity, a movement, a shape complexity and a demanded surface finishing. Compressed powder shapes are usually complicated and consisting of several levels or thicknesses in a pressing direction, therefore the successful pressing of complicated shapes demands an independent control of tool movements – Fig. 6.7.

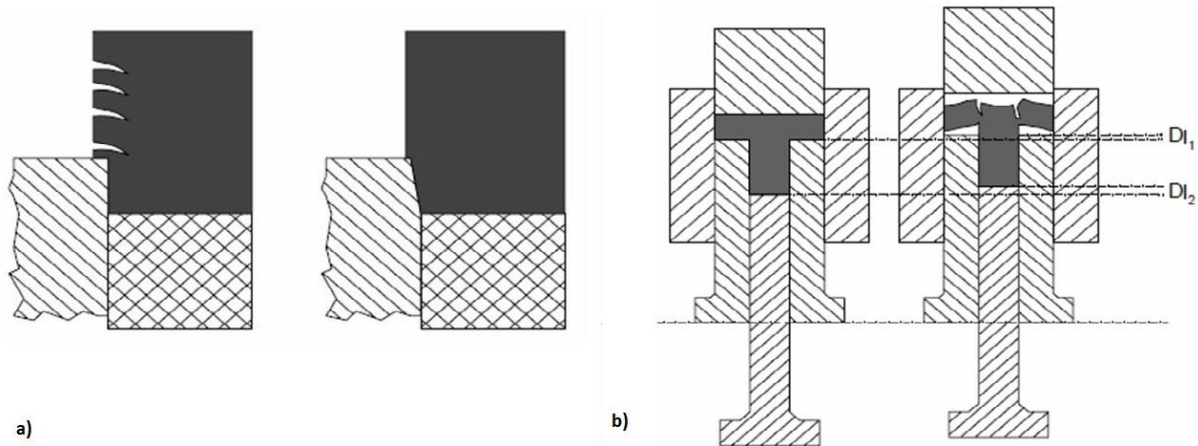


Fig. 6.7 Ways of crack origination during pressing as a result of an improperly designed pressing tool: a) different dilatations of two bottom punches; b) ejection of a compact in a sharp corner of a die [1].

When forming parts with an unequal height, it is necessary to use several different punches which are connected. Their movement is controlled, so that particles can only move along the direction of the pressing. Separation of as-compressed sections from the rest of the compact by shear must be avoided. This leads to an origination of cracks which do not reach up to the surface and cannot be eliminated during sintering (Fig. 6.8).

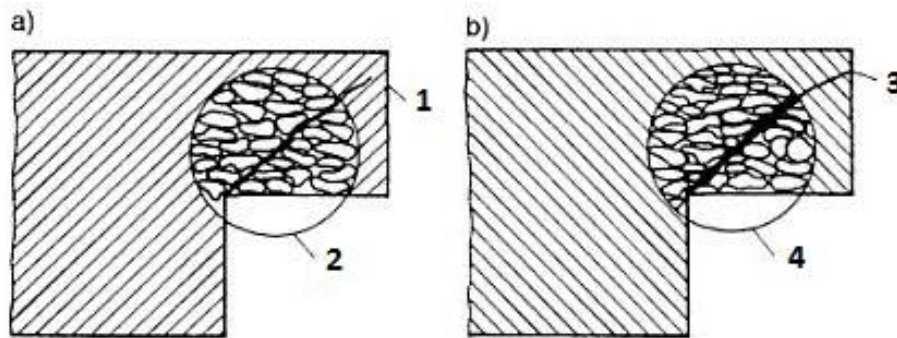


Fig. 6.8 Typical errors during the pressing: a) crack origination during the pressing as a result of improper filling (1 – the crack does not reach to the surface, 2 – the area of failure is smooth); b) crack origination during the ejection (3 – the crack protruding and visible, 4 – the fracture area is rough) [3].

6.2.1.3 Presses

Productivity of pressing procedures depends particularly on efficiency of used presses. In modern aggregates, the entire pressing process is software-controlled (die filling, pressing, ejection of a compact, etc.) In principle, two types of presses are used:

- **Mechanical presses** – up to a pressing force of 1000 kN; they allow a manufacture of a high number of compacts per unit of time. A number of strokes ranges between 20 – 100 per minute (Fig. 6.9a).

- **Hydraulic presses** – above a pressing force of 1000 kN; the pressing force is well-controllable. However, the pressing speed is low and they allow 10 – 15 strokes per minute (Fig. 6.9b).



Fig. 6.9 Hydraulic (a) and mechanical (b) press made by DORST company.

6.2.1.4 Hot pressing

This is pressing while heating the powder, the precompressed piece or the pressing tool. In this pressing arrangement, forming and sintering processes take place at the same time. Therefore this procedure is sometimes called the pressure sintering.

Hot pressing is applicable for powder materials in bulk, compacts or pre-sintered compacts. Tools for pressing up to temperatures of 600 °C are made of heat-resistant steels. Above this temperature, ceramics and graphite are used (up to temperatures of 3000 °C). Examples of various arrangements of hot pressing are shown in Fig. 6.10.

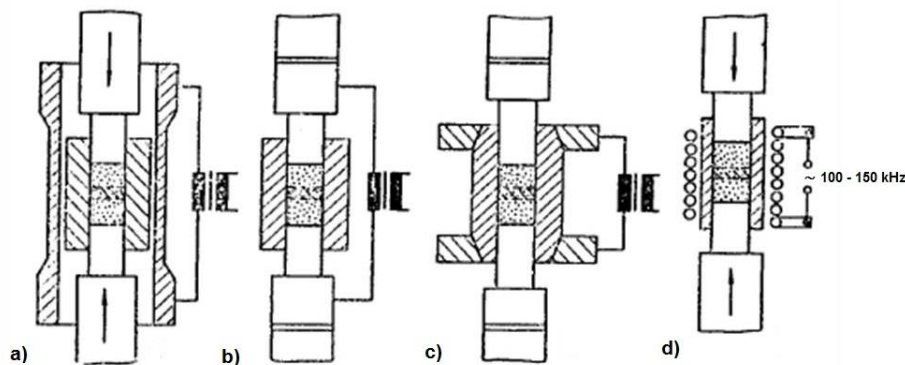


Fig. 6.10 Schematic depiction of the hot pressing equipment: a) indirect heating through a heating tube or a heating spiral; b) direct heating by passing current through punches; c) direct heating of a die; d) induction heating of a die or a compact [4].

Temperatures above 800 °C are achieved by direct heating of a tool or a compact. In order to avoid powder oxidation, the pressing equipment is placed into a casing with a protective atmosphere inside. The hot pressing technology is used for difficult to press powders and difficult to sinter powders - e.g. dispersion-hardened powders, cermets etc. Another application is a manufacture of compacts of cemented carbides with low porosity.

A low productivity and high wear of pressing dies resulted in seeking possibilities for

achieving demanded effects. For cemented carbides, isostatic additional compacting at high temperatures is applied.

6.2.2 Extrusion

This is a procedure of metal powder compaction or semi-products, manufactured by pre-pressing, or possibly by pre-sintering, in a continuous strand. The process can be carried out at a normal or elevated temperature (sintering temperature). In the case of extrusion pressing at room temperature, a mixture of powder and a plastificator is pressed through a nozzle into rods or tubular forms. A plastificator is an additive, usually an organic substance (e.g. wax, methylcellulose, synthetic resin, etc.), which is added to metal powders in order to form a plastic pasty material suitable for forming. A principle scheme of the direct and indirect way of extrusion is shown in Fig. 6.11.

The extrusion technology is used for all materials which can be processed using powder metallurgy procedures. These are cemented carbides, high-temperature materials with high hardness and especially technical ceramics. A pressing mixture contains 20 – 30 % of a plastificator which has to be removed prior to the actual sintering. The compacting pressure is performed using e.g. a piston or a screw. Fine powders require higher pressures than for coarse powders extrusion, because more joints occur, which are fractured and welded repeatedly during the process. A schematic depiction of a powder material extrusion machine is shown in Fig. 6.12.

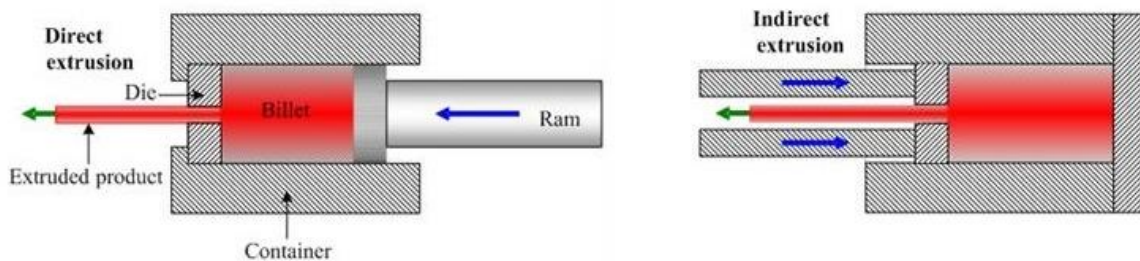


Fig. 6.11 Extrusion methods: a) indirect extrusion; b) direct extrusion [5].

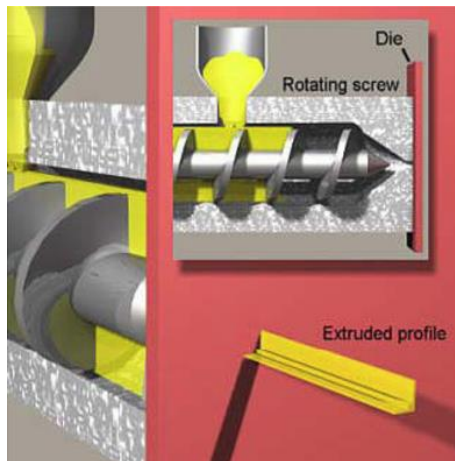


Fig. 6.12 Schematic depiction of the powder material extrusion machine [6].

Powder extrusion at higher temperatures is similar to compact material processing. An initial material is in a form of pre-compacted or pre-sintered material. To avoid oxidation and contamination from extrusion process lubricants, the material can be canned to a container of a mild steel plate. This method allows reaching high density for such materials, which have oxide coatings by reason of high affinity for oxygen, therefore they are difficult to sinter - for instance Al, Mg, Ti, high-speed steels, etc. Extrusion pressing of sintered materials, such as high-speed steels or superalloys, where almost

porousless structure can be achieved, or of sintered materials dispersion-hardened by oxides, is very effective. The used cans oxidize during the process, so they are removed from the compact by stripping, or possibly by chemical etching.

6.2.3 Powder rolling

Rolling processes can be basically divided according to the direction of rolling and material feeding – see Fig. 6. 13.

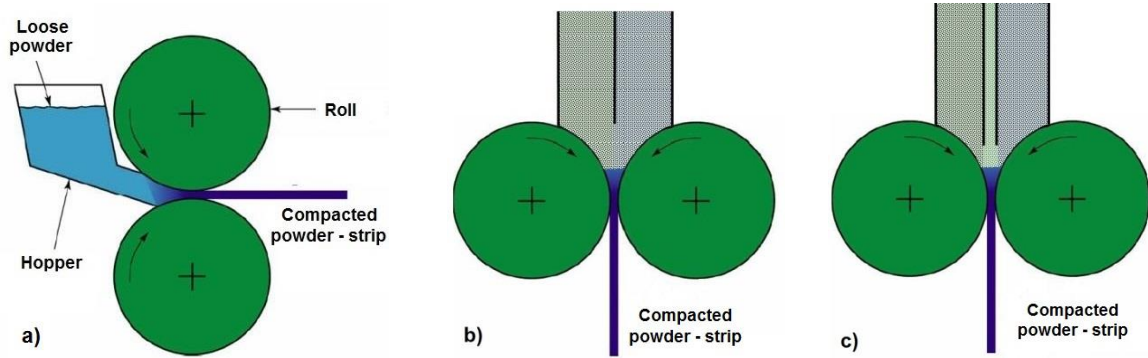


Fig. 6.13 Powder rolling arrangement: a) horizontal arrangement with a screw powder feed, b) vertical powder feed (bimetal), c) vertical powder feed (trimetal preparation) [7].

Processes occurring during powder rolling are shown in Fig. 6.14. In a region 1, there is a non-compacted loose powder material. When passing into the second zone, characterized by an angle α , the compacting process induced by friction between contra-rotating rolls and powder particles starts to be performed. The applied forces reach the maximum values in the narrowest point between the rolls. In contrast to rolling of compact materials, the acting pressure increases slowly at first.

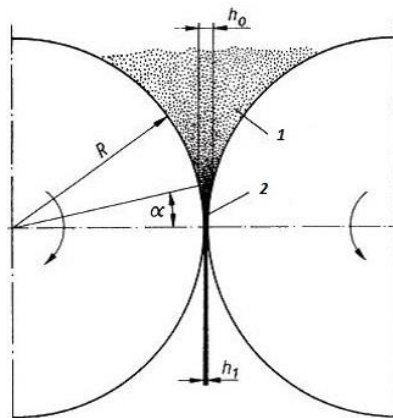


Fig. 6.14 Powder in the rolling gap: region 1 – non-compacted powder, region 2 – zone of powder compaction [3].

Only at the end of the compaction zone the pressure increases as much that the running-out strip has a satisfactory strength. A relation between a thickness h_o and h_l can be expressed as follows:

$$\frac{h_o}{h_l} = \frac{2 R (1 - \cos \alpha)}{h_l} + 1$$

If neglecting a difference in a speed of powder inlet and strip running-out, a relation applies for the powder density in the zone 1 (ρ_o – bulk density) and the rolled strip density ρ_l :

$$\frac{\rho_1}{\rho_0} = \frac{2 R (1 - \cos \alpha)}{h_1} + 1$$

The value h_1 represents the strip thickness, which must not be exceeded at the demanded density ratio ρ_1 / ρ_0 . It can only be varied by a change of a radius of rolls. The bulk density ρ_0 is given by powder properties. The same applies for the angle of repose α , moreover, it can be changed within a narrow limits by roughing the rolls.

When planning a technical arrangement of powder rolling, there is often a tendency to implement subsequent sintering of a green strip, further cold forming, annealing with a possible further cold rolling into one technological line. However, owing to various speeds of individual operations, it is sometimes more effective to perform these operations separately.

For powder materials which can be processed by casting and rolling into strips, rolling is preferred because thin strips can be made with only low number of passes through the rolling stand. However, a disadvantage is a higher price of the initial powder material and low rolling speeds, therefore this process is always considered for individual respective cases.

The powder rolling technology is often the only possible way of processing for a manufacture of porous strips or strips of special materials or those difficult to form. For example, this is the manufacture of strips with special magnetic or electrical properties made of Al-Ni-Co or Cu-Ti alloys. Further, this method is applied for the manufacture of coated strips for friction and sliding materials (Fig. 6.13a) and bimetallic (Fig. 6.13b) or trimetallic strips (Fig. 6.13c).

6.2.4 Isostatic pressing

At isostatic pressing the powder is encased in a sheath on which pressure transferred by gas, rubber, plastic material or liquid is applied. In this case, hydrostatic pressing is used.

The main advantage of this method lies in a fact, that friction between powder and die walls, which resulted in uneven distribution of pressure, tension and compact density, is removed. The sheath, in which the powder is encased, has to have special properties. At high pressure, it has to behave as a liquid medium in order to transfer the pressure to the powder isostatically. At standard pressure, it has to behave as a solid material to maintain its shape, on which accuracy of the compact depends, even after filling with heavy powder.

Isostatic pressing enables to reach higher densities of pressed materials (Fig. 6.15), to manufacture components of larger dimensions and to process powders difficult to compress - e.g. a manufacture of molybdenum rods.

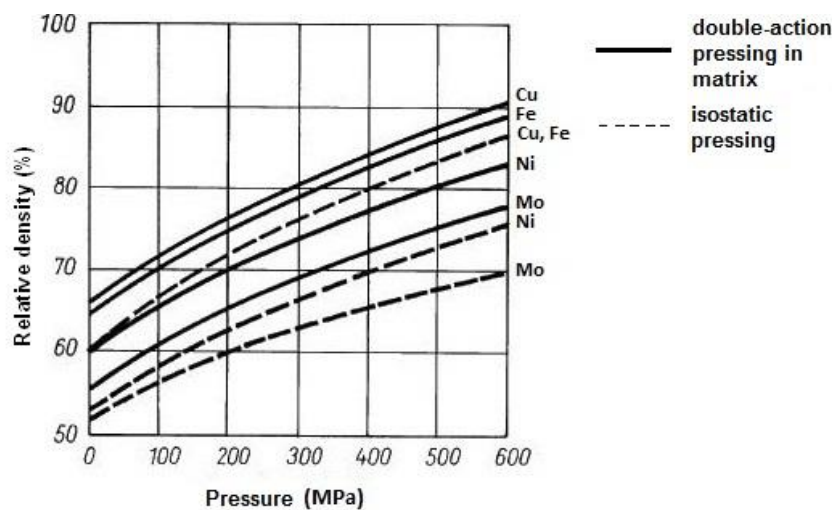


Fig. 6.15 Density increase by isostatic pressing [3].

6.2.4.1 Cold isostatic pressing (CIP)

This isostatic pressing procedure is carried out in a steel pressure vessel. After closing, the required pressure ranging from 200 MPa (for ceramics and graphite) up to 400 MPa for metal powders is developed through appropriate equipment. For compaction, a delay on the maximum pressure for only several seconds is sufficient, but its decrease has to be performed slowly (especially in lower pressure regions), so that cracks cannot occur.

In term of a structural design, there are two basic concepts of the pressure vessel. The ASEA system - closing the pressure vessel with a cover hold down by a specially adapted frame ("wet bag" method – Fig. 6.16).

When pressing smaller parts, substantially higher pressing outputs can be achieved in a device called as a "system with a bolt closure with a dry sheath" ("dry bag" method – Fig. 6. 17). Powder is filled into a flexible tube an upper and bottom opening of which is connected to a pressing chamber. Then the openings are closed and pressure is transferred through a liquid which encloses a flexible sheath. After finishing the pressing and evacuating the chamber, the flexible sheath is moved to the pressure housing walls and thus the compact is freed to be taken-out.

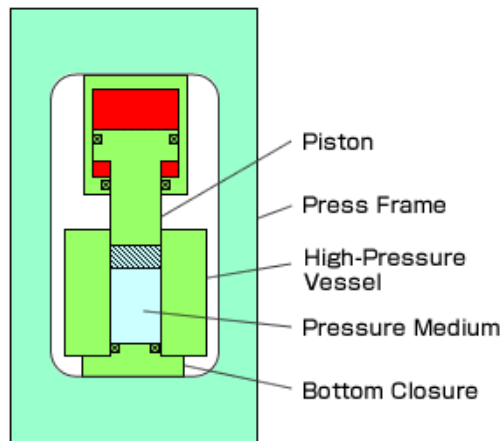


Fig. 6.16 Principle diagram of the cold isostatic pressing – the ASEA system (isostatic press made by KOBELCO, LTD) [8].

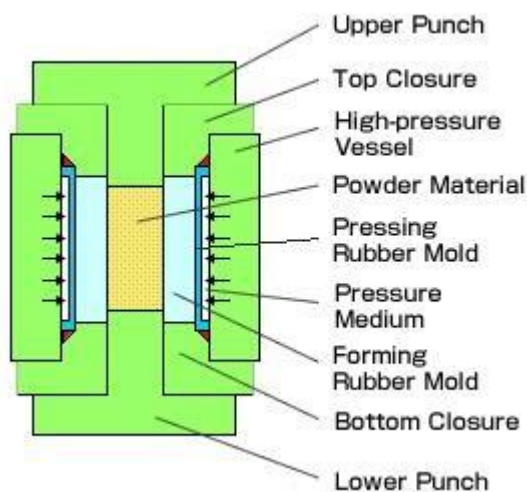


Fig. 6.17 Principle diagram of the cold isostatic pressing – the dry bag method with a bolt closure (isostatic press made by KOBELCO, LTD) [9].

The isostatic pressing is used mainly for compacts of larger dimensions and rotating shapes from materials difficult to form. Products of SiN, ceramics and graphite, cemented carbides (rolls, dies), molybdenum, tungsten, etc. can be obtained this way. Molybdenum and tungsten powders are processed by this technology to consumable electrodes for arc remelting, which have a weight of 1 – 2 tons. A principle diagram of individual process steps of the dry bag cold isostatic pressing is depicted in Fig. 6.18.

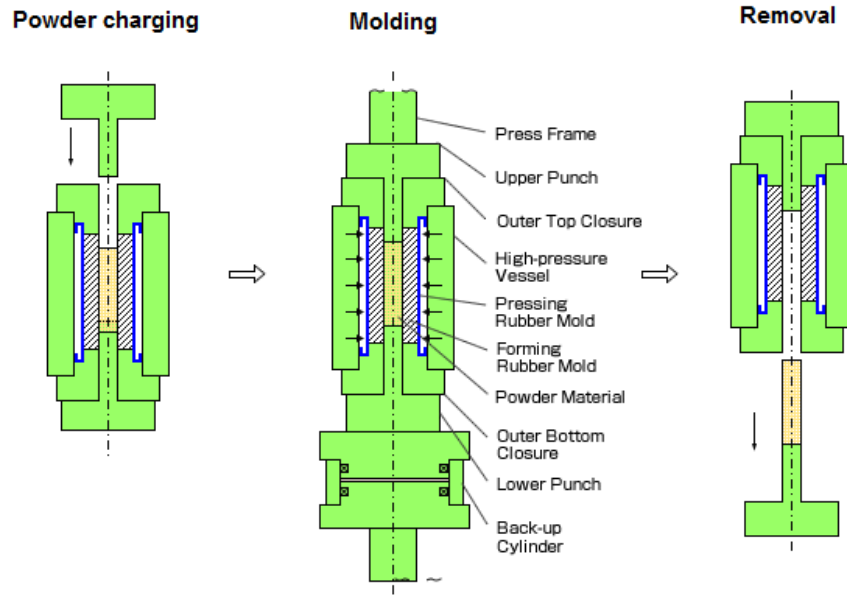


Fig. 6.18 Principle diagram of individual process steps of the dry bag cold isostatic pressing [9].

6.2.4.2 Hot isostatic pressing (HIP)

For hot isostatic pressing, which is nowadays performed at temperatures up to 2000 °C, a heating device is installed inside a pressure vessel. An important part is a thermal insulation cylinder separating a working area (high temperature application) from the steel pressure vessel a temperature of which must not exceed c. 150 °C, so that tensile properties of the steel housing cannot drop (Fig. 6.19).

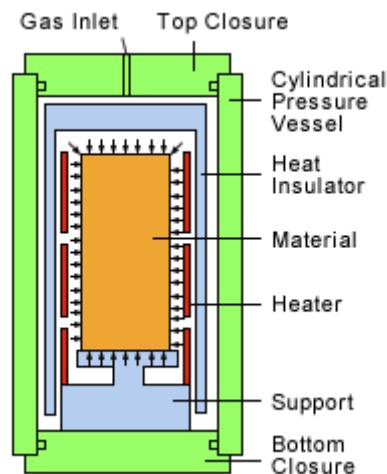


Fig. 6.19 Principle diagram of the hot isostatic pressing [10].

Argon is used as a medium for pressure transfer, while working with pressures up to 200 MPa.

Non-porous sintered materials can be hot isostatically pressed without any further actions. Porous compacts and powders have to be placed into a sheath of plate (commonly steel or titanium) or glass and they are evacuated.

Hot isostatic pressing makes use of a combination of elevated temperature and isostatic pressing by gas. A principle diagram is depicted in Fig. 6. 20. Powder is placed into a flexible sheath and vacuum degassed. The sheath is closed hermetically and inserted into the working area of a press. Pressure is transferred through an inert gas or an auxiliary medium. While heating the container, pressure is increasing. The sheath can be removed by machining (simple shapes) or acid leaching (complex shapes) – Fig. 6.21.

The HIP technology is used e.g. for high-speed steels, Ti-alloys and superalloys. Its advantage is a possibility of processing large sintered parts with very low (residual) porosity. For example, in cemented carbides the content of pores after pressing and sintering is 1 – 2 %. The powder compaction to close-to-finished (near-net) dimensions allows reaching a high material utilization.

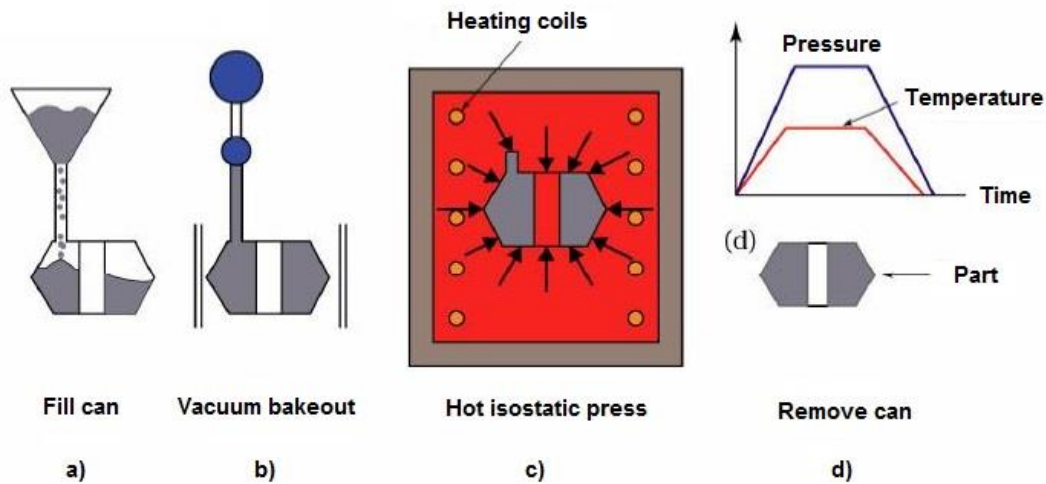


Fig. 6.20 Particular steps during the hot isostatic pressing [7].

Another application of the hot isostatic pressing is an additional compaction of castings by which a homogenous structure without pores and shrinkage holes can be obtained (Fig. 6. 22). An advantage of this process, i.e. a combination of casting and HIP, is reaching higher static and particularly dynamic strength, better ductility, better machinability with higher quality of a work-piece surface, higher corrosion resistance as well as longer operating life of parts.

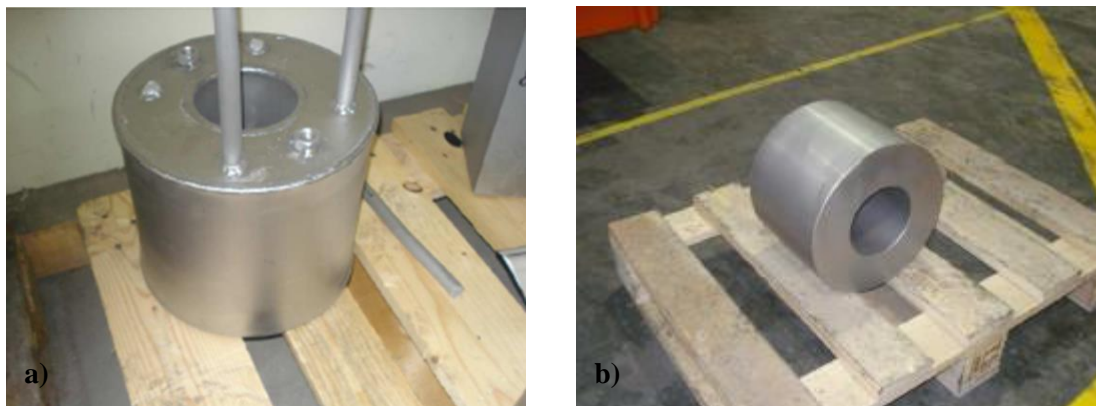


Fig. 6.21 Encasing of powder material (a) and the finished product after annealing and machining (b) [11].

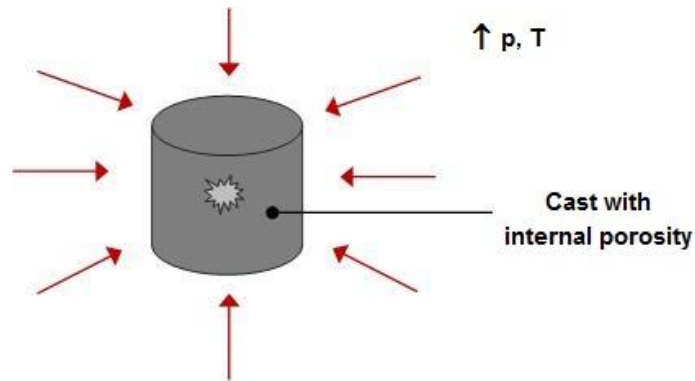


Fig. 6.22 Additional compaction of castings.

6.2.5 Powder forging

This technology combines powder metallurgy advantages with die forging processes. This way quite complicated shapes with high density (up to 99.5 %) and product accuracy can be produced (Fig. 6. 23). In general, either forging of a non-sintered compact (i.e. powder forging) or of a sintered compact, mostly in a hot protective atmosphere, can be performed. Technological operations of forging:

- preparation of a powder mixture – mixing of powder metal with pressing additives (lubricants, graphite, etc.);
- pressing of preforms;
- heating in order to remove lubricant under a protective atmosphere;
- sintering (in the case of a sintered compact forging);
- forging;
- finishing operations (heat treatment, smoothing etc.).



Fig. 6.23 Connecting rods manufactured by powder forging [12].

6.2.6 Explosive compaction

When powder compacting by explosive detonation, methods using explosion either on a free area (Fig. 6. 24) or in closed pressure vessels can be used.

Technical solutions for explosive compaction on a free area can be as follows:

- Powder materials are directly compacted (the so-called contact system)** – a container with powder is in a direct contact with a charge, resulting in rod shaped or tubular compacts.
- Explosive pressing with a flat charge** – a manufacture of plate shaped semi-products.

Forming powders by detonation in closed pressure vessels is in principle very similar to

conventional pressing of metal powders. Usual systems cylinder – piston can be used, whereas an impulse is imposed on a punch either through a pressure wave or a shock wave of a steel cylinder set to motion by detonation of an appropriate explosive charge.

This dynamic and high-energy process of forming enables enhancement of mechanical properties of powder products.

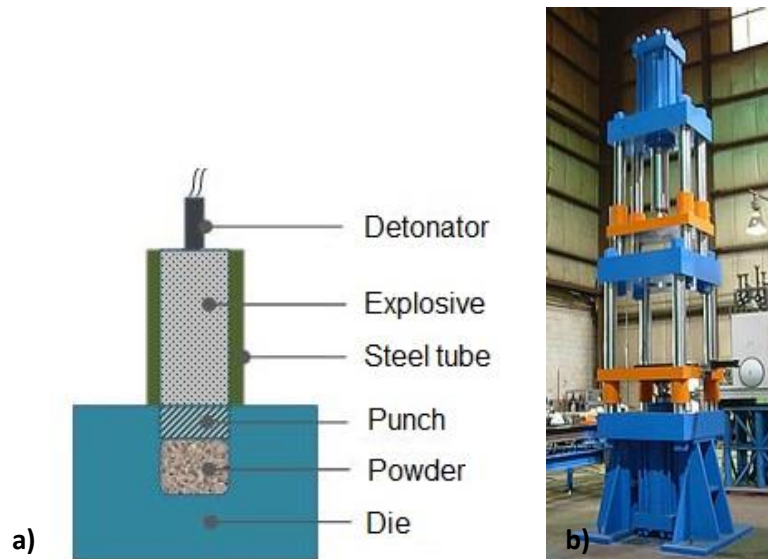


Fig. 6.24 Principle diagram of the explosive compaction of powder materials (a) and the industrial equipment for the explosive compaction (b) [13].

6.2.7 Metal injection moulding

Powder injection moulding (PIM) is based on a technically developed plastic injection moulding technology which is combined with a classical powder metallurgy. Depending on a type of the used injected powder, PIM includes two modifications: 1) Ceramic powders (CIM – Ceramic Injection Moulding) and 2) metal powders (MIM – Metal Injection Moulding)

This technology allows obtaining products with precise dimensional tolerances which cannot be obtained by conventional pressing and sintering (± 0.08 to 12 mm). This accuracy usually enables to leave out further processing. In principle, very fine powders are used, so that sintering times are as short as possible. The procedure of the manufacture of parts using MIM technology is shown in Fig. 6.25.

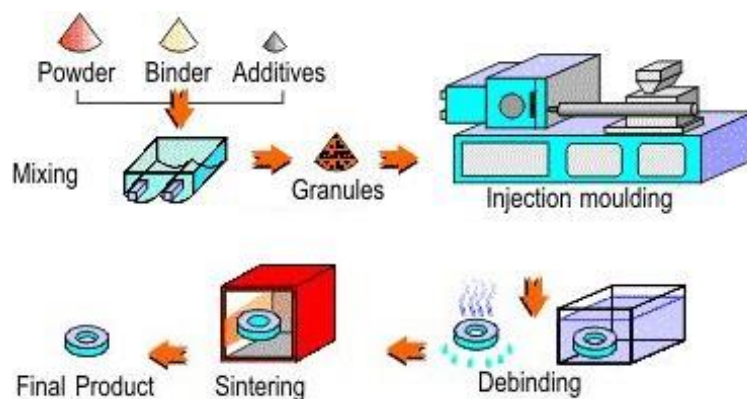


Fig. 6.25 Particular phases of the metal injection moulding technology [14].

It consists of the following phases:

- a) **Mixing powder with a binder (wax, polymer)** – powder with particle size $< 25\ \mu\text{m}$ and a spherical shape is mixed with a proper bonding agent, which determines rheological properties of the mixture. A particle surface has to be clean and smooth to enable a formation of a binder thin film. Metal powders are prepared by gas or water atomization, or possibly by carbonyl decomposition.
- b) **Granulation** – forming powder material to a specific shape to be handled more easily.
- c) **Injection moulding** – includes heating a mixture above a binder melting point ($150 - 180\ ^\circ\text{C}$) (binder plastification), injecting the melt into a mould under pressure of $15 - 30\ \text{MPa}$ and cooling the mould down to solidify the powder and binder mixture (Fig. 6. 26). The compact is called a “green body”.

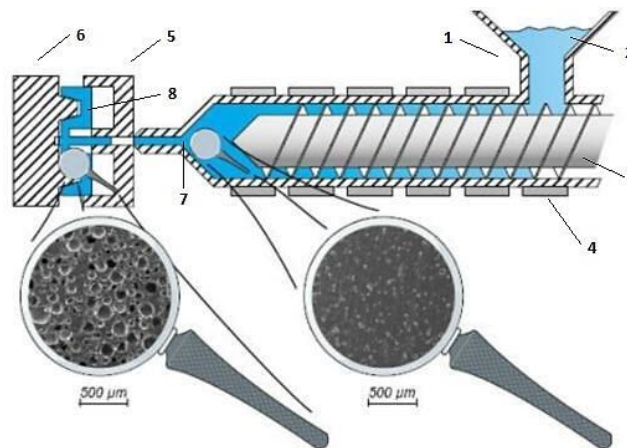


Fig. 6.26 Schematic depiction of the injection press and its main components: 1 – feed hopper, 2 – granulate, 3 – reciprocal screw, 4 – heating, 5 – a stationary half of a mould, 6 – a moving half of a mould, 7 – melt, 8 – compact [15].

- d) **Binder removal** – this is a key process, critical for product properties, therefore it requires very careful control. In this phase, “extraction” of the binder out of the compact occurs, after which a porous structure is formed, the so-called “brown body”. Time needed for the binder removal depends on the used method, a maximum thickness of a compact wall and a bonding system and can last up to several days. Basic methods of the binder removal involve the following: 1) thermal decomposition – heating a compact, so that the polymer binder can melt, decompose and ultimately evaporate; 2) catalytic decomposition of the mixture; 3) dissolving the binder by appropriate solvents; 4) gelatinization and evaporation of the binder. A change in colour of the compact after the particular processes is shown in Fig. 6.27.



Fig. 6.27 Change in colour of the compact after the particular processes: a) the compact after injecting, b) the compact after the binder removal, c) the sintered finished product [16].

- e) **Sintering of a compact** – a thermal process in which individual separate particles are agglomerated and form final demanded strength of the product. This phase is related to considerable shrinking, which may reach as much as 30 % as a result of high porosity of the part after the binder removal. Relative density typically ranges around 95 % and higher. Mechanical properties roughly correspond to properties of forged metal of the same composition.

MIM technology products are used mainly in applications for high-volume manufacturing, where it leads to as much as 70 % production cost reduction. For example, these are applications for military industry (triggers, hammers, cartridge ejectors), in electronics for a manufacture of complicated and precision parts for telecommunication, printers, copying machines, video recorders, cameras, etc., in health service for scissors, parts of medical and dental instruments, in automotive industry for safety elements for airbag systems, fuel injection, turbochargers, etc. (see – Fig. 6. 28).



Fig. 6.28 Examples of MIM technology applications.

6.3 Forming without external pressure

All methods of forming without applying external pressure have a common principle, that an appropriate amount of a proper nonmetallic material is added to metal powder, so that an originated suspension is either liquid to be cast or formable. This matter has to be utterly removable from a product, namely under such conditions not to deteriorate a product's shape before achieving a satisfactory strength through sintering. Main advantages are as follows:

- no need for costly presses and pressing tools, that means low purchasing cost for equipment
- even smaller batches can be produced at low cost
- size of manufactured parts can be enlarged.

6.3.1 Ceramic casting method

Into a plaster mould either a full casting is cast or a hollow one onto a metal core. A hollow casting can be also obtained in a way that after settling a layer of solid particles in a specific thickness on a mould walls, the remaining slurry is poured out. This method is wide-spread in ceramics. It is called a slurry casting method; slurry is a common name for a suspension of fine clay in a carrier liquid, most frequently in water.

For preparation of the slurry for metal powders the same principles as for ceramics are applied. Slurry is the more stable, the finer the powder is and the higher the viscosity of the liquid carrier is (metal powder to liquid ratio 3:2). As metal powders are often coarser than ceramic ones and viscosity cannot be increased with regard to casting, stabilizers play a decisive role for the slurry preparation (e.g. sodium and ammonium salts of alginic acid). The stabilizers allow the slurry to be processed prior to separation of the solid state suspension from the liquid and settling onto the bottom of the mould. On the contrary, liquid separation from the suspended phase is necessary in a mould a front side of which has to be permeated by a continuous capillary system which takes the liquid carrier away.

6.3.2 Freeze casting of suspensions

Draining the liquid phase away from the suspension through a porous wall is not always advantageous. For thicker suspensions with a smaller amount of the liquid, a technology of suspension injection into a metal mould with a following freezing is used. Water with addition of starch or latex is used as the liquid phase. Water is then removed from frozen castings by vacuum sublimation or slow drying. Porosity is quite high (30 to 33 %) and in some cases can be reduced by infiltrating metal. For example, turbine blades of TiC are fed with Cr-Ni-Co based alloy after sintering.



Summary of terms

Die pressing

Isostatic pressing

Metal injection molding

Rolling

Extrusion

Ceramic casting method



Questions to the topic

- 6.1. Which are the pressure-assisted methods of powder compaction?
- 6.2. Characterize the processes running in a compact with an increasing pressure.
- 6.3. What is a reason of inhomogeneous pressure distribution during die pressing?
- 6.4. What is the difference between hot and cold isostatic pressing?
- 6.5. Which technology can be prepared the bi-metal or tri-metal strips?
- 6.6. Which methods are used for the binder removal from MIM compact?
- 6.7. What is the application of ceramic casting method?



Solved tasks

Exercise 6.1

Final fraction density in powder compaction determines a maximum amount of lubricant to be added. Determine the weight fraction (percentage) of a lubricant in a form of zinc stearate which is added to copper powder compressed to 85 % of the theoretical density.

♦ **Solution**

$$\rho_{\text{Cu}} = 8.9 \text{ g/cm}^3$$

$$\rho_{\text{L}} = 1.09 \text{ g/cm}^3$$

$$f = 85 \%$$

$$w_L = \frac{(1-f) \cdot \rho_L}{\rho_L(1-f) + \rho_{Cu} \cdot f} ; \quad w_L = \frac{(1-0.85) \cdot 1.09}{1.09(1-0.85) + 8.9 \cdot 0.85} ; \quad w_L = 2.11 \text{ wt.}\%$$



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7. SINTERING



Study time: 6 hours



Objective

- Sintering fundamentals
- Stages of sintering (Two-particle model)
- Mechanism of material transport
- Pore structure in sintering
- Single component sintering
- Multicomponent sintering
- Activated sintering



Lecture

Sintering is a process during which material is transformed from a dispersive (powder) state with a large specific surface to a compact state without achieving a melting point. Essential phenomenological displays of sintering are the strength increase and porosity decrease. For one-component systems, sintering is carried out at temperature of 0.6 to 0.75 of the melting point of a sintered material. Multi-component systems (powder mixtures) are generally sintered at temperatures near to or slightly higher than the melting point of a component with the lowest melting point.

Depending on required properties of the sintered material the sintering process can be single-step or multistep. For example, for a manufacture of porous filters or for minimal requirements for tensile properties (self-lubricating bearings) one sintering without any further compacting operations is enough. For higher demands, an additional material compaction and additional sintering in order to enhance density, strength and ductility can come after. If needed, a technology with a combined thermo-mechanical processing is used, such as hot pressing, isostatic hot pressing and forging. Final compaction can be ensured by filling (infiltrating) a compact or a presintered skeleton with an element with a lower melting point, as e.g. for Fe-Cu products or W-Cu contacts. Strength and hardness can be enhanced by an additional surface or bulk heat treatment.

Sintering can run without simultaneous application of an external pressure, which is a much more frequent way than sintering under pressure called as hot pressing. In the case of sintering without an external pressure the only driving force of the sintering is a reduction of the total surface energy.

In Fig. 7.1 an overview of sintering processes is schematically depicted. Types of sintering processes in a binary system with a eutectic transformation are shown in Fig. 7.2. At T_1 temperature, sintering runs only in a solid state (one-component system – solid solution). If the temperature was increased to T_2 , a transient liquid phase occurs in the system during sintering as a result of the eutectic transformation. At T_3 temperature, sintering runs in the presence of a stable liquid phase (multi-component system – solid solution+melt) Structure differences in a material sintered in a solid state and in the presence of a liquid phase are evident in Fig. 7.3.

7.1 Fundamentals of processes occurring during sintering

There is not any complex theory of sintering, thereby any physical law which could describe the sintering process in its complexity, enabling a prediction of properties of powder metallurgy

products.

In general, a phenomenological theory of sintering has to express changes in any of the basic properties caused by sintering depending on variables, such as time t , temperature T , etc. Shrinkage in volume or linear shrinkage is what is considered the basic property:

$$\frac{\Delta V}{V_0} \approx \frac{3\Delta l}{l_0} = f(t, T, p, \mu, \gamma_s)$$

where p – pressure; μ - chemical potential; γ_s – surface and interface stress.

Owing to the fact that a cause of shrinkage and also of an increase of strength is mass transfer, the sintering theory is based on a study of physical laws for mass transfer.

A driving force of sintering in a solid state is a decrease of free energy in a system, which is a result of:

- reduction of a specific surface area as a result of growth of interparticle contacting areas;
- decrease in a volume of pores and/or spheroidization of pores;
- elimination of disequilibrium concentration of lattice defects (spot defects, dislocations) in powder;
- in multi-component systems: Elimination of disequilibrium states thanks to mutual solubility (homogenization of concentration gradients) or chemical reactivity characterized by free energy in a solution or possibly by a formation of compounds.

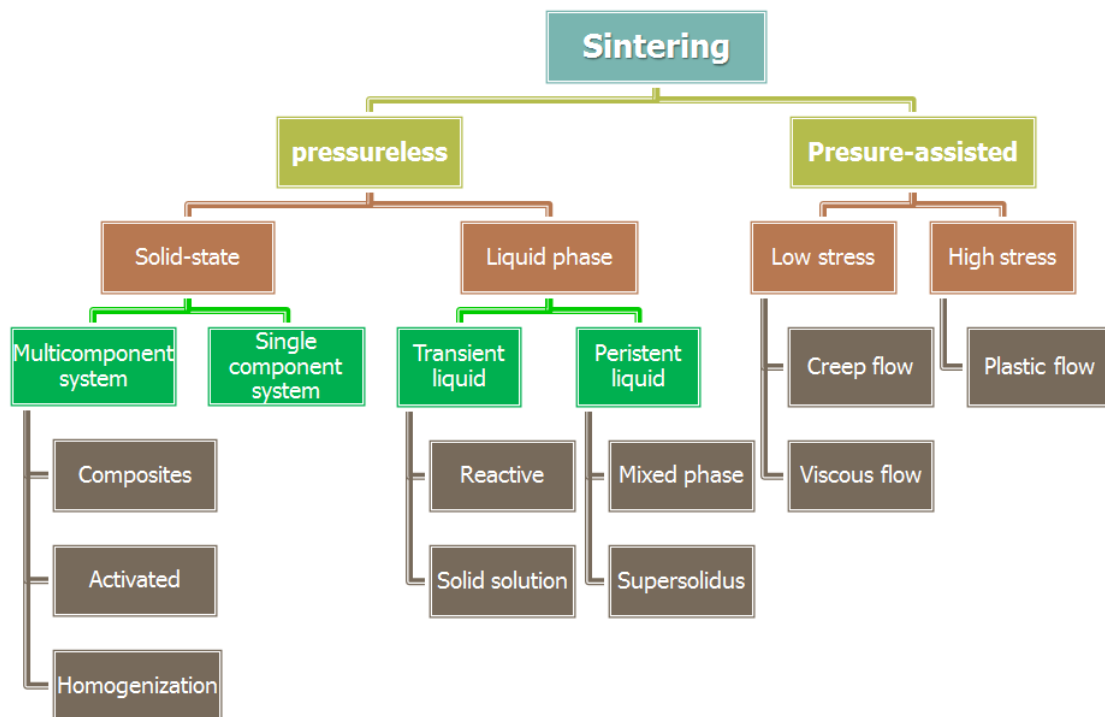


Fig. 7.1 Overview of sintering processes.

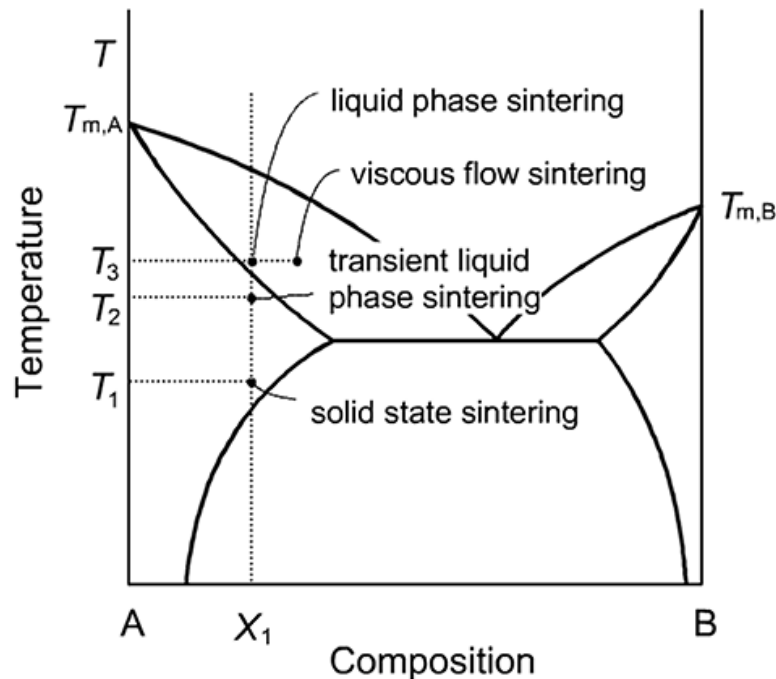


Fig. 7.2 Types of sintering processes in a binary system with a eutectic transformation [1].

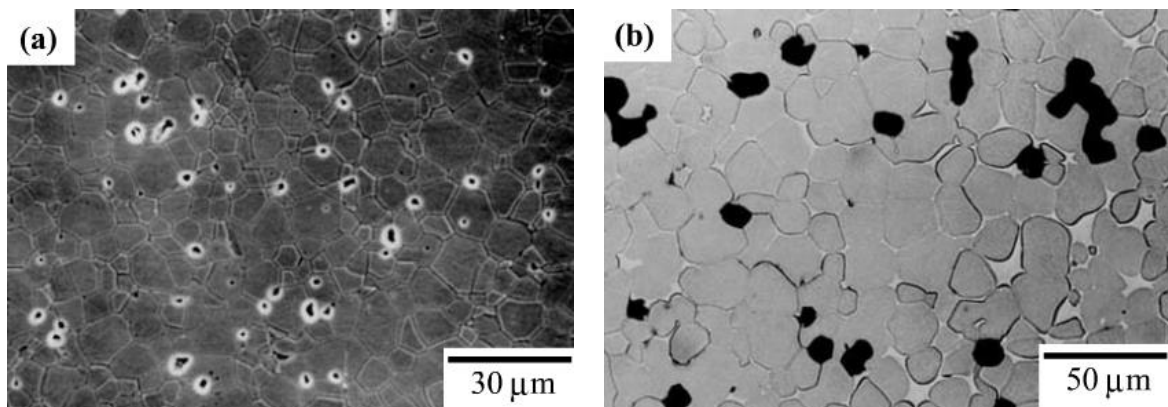


Fig. 7.3 Structure differences in a material sintered in a solid state (a – Al_2O_3 , polyhedral grains) and in the presence of a liquid phase (b - 98W-1Ni-1Fe, rounded grain boundaries as a result of re-precipitation) [1].

7.2 Mass transport in single component system

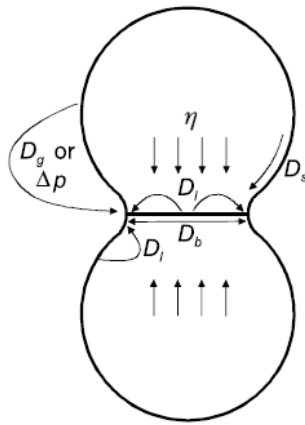
For one-component systems only solid state sintering comes into question. In the case of sintering without application of pressure and $\gamma_x = \emptyset(T)$ applies, a relation for shrinkage in volume can be simplified to:

$$\Delta V/V_0 = f(t, T)$$

Observations of processes of pure metal sintering have shown that there is a certain minimum sintering temperature T_{Smin} and that in the last stage of sintering the shrinkage changes only very slowly, that means it is very difficult to remove all pores from a sintered product.

In general, more mechanisms of mass transfer are applied by which material connections (necks) between particular particles are formed and porosity is reduced – Fig. 7.4 and . Above all,

there are mechanisms in which the mass transfer is realized by motion of atoms to a distance order-of-magnitude longer than their spacing in a lattice is. These can be motions of individual atoms – various types of diffusion or motions of entire lattice regions – plastic flow.



Material transport mechanism	Material source	Material sink	Related parameter
1. Lattice diffusion	Grain boundary	Neck	Lattice diffusivity (D_l)
2. Grain boundary diffusion	Grain boundary	Neck	Grain boundary diffusivity (D_b)
3. Viscous flow	Bulk grain	Neck	Viscosity, η
4. Surface diffusion	Grain boundary	Neck	Surface diffusivity (D_s)
5. Lattice diffusion	Grain boundary	Neck	Lattice diffusivity (D_l)
6. Gas phase transport			
6.1 Gas diffusion	Grain boundary	Neck	Vapor pressure difference (Δp)
6.2 Evaporation/condensation	Grain boundary	Neck	Gas diffusivity (D_g)

Fig. 7.4 Mass transfer mechanisms [1].

Factors influencing sintering of one-component systems are divided to:

A. Primary factors

1. Total actual contacting area.
2. Free surface energy of all surfaces including pores.
3. Mutual orientation of contacting areas.
4. Diffusion coefficients (lattices, boundaries of grains and surfaces).
5. Critical shear stress (at participation of plastic flow).
6. Vapour pressure and evaporation velocity (at participation of evaporation and condensation).
7. Crystalline structure and a type of bonding.

B. Secondary factors

1. Surface activity (actual surface structure).
2. Lattice activity (cold forming, internal stress, lattice imperfections induced by a manufacturing operation).
3. Allotropic modification.
4. Foreign materials:
 - a) soluble
 - b) insoluble
 - c) surface layers (e.g. oxide layers)
 - d) gas (adsorbed by effect of a sintering atmosphere etc.)

In term of occurring actions, the sintering process can be divided to three stages (Fig. 7.5):

1. **Initial stage** – formation of contacting areas (necks) and their growth.

2. **Intermediate stage** – a phase of rapid shrinking. After reaching a specific size of a neck, the initial particles lose their identity. A coherent net of pores is formed and grain growth with a formation of a new microstructure occurs. Grain boundaries are extended from a pore to a pore. With this stage the highest shrinkage is connected.
3. **Final stage** – a slow proximation to the theoretical density. In a region of 90-95 % of the theoretical density a proportion of closed pores increases rapidly and spheroidization of particular pores occurs. If gas was incaved in pores, further compaction is not possible as the gas pressure in pores is in equilibrium with the surface stress.

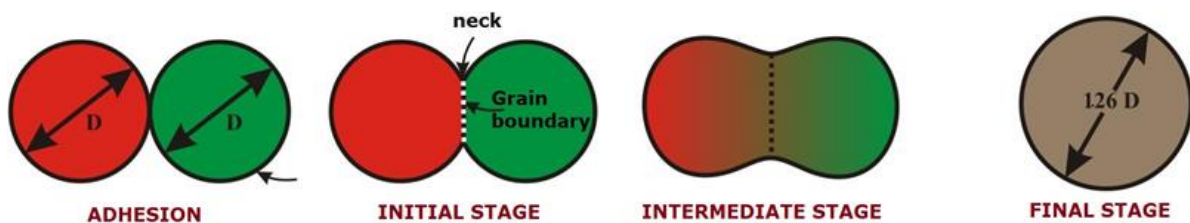


Fig. 7.5 Sintering process stages – a model of two spherical particles.

Vacancies and atoms move along particle surfaces (surface diffusion), along grain boundaries (grain boundary diffusion) and through the lattice (viscous flow or volume diffusion). Also, couples (vacancy-atom) with a dislocation structure can climb via plastic flow and dislocation. Further, vacancies can migrate among pores, thus leading to a growth of large pores, while small pores decrease (shrink).

Surface transport processes (Fig. 7.6a) give neck growth without a change in particle spacing (no densification or shrinkage) since the mass flow originates and terminates at the particle surface. Surface diffusion (SD) and evaporation-condensation (E-C) processes two most important contributors to surface transport controlled sintering. Surface diffusion dominates the low-temperature sintering of many metals (including Fe). Evaporation and condensation is not so wide-spread, but it is applied for sintering low-stable materials, such as lead or alloys. While the surface as well as bulk mass transfer contributes to the neck growth, a crucial difference is in the shrinkage during sintering. For densification to occur, the mass must originate from a particle interior with a follow-up deposition at the neck.

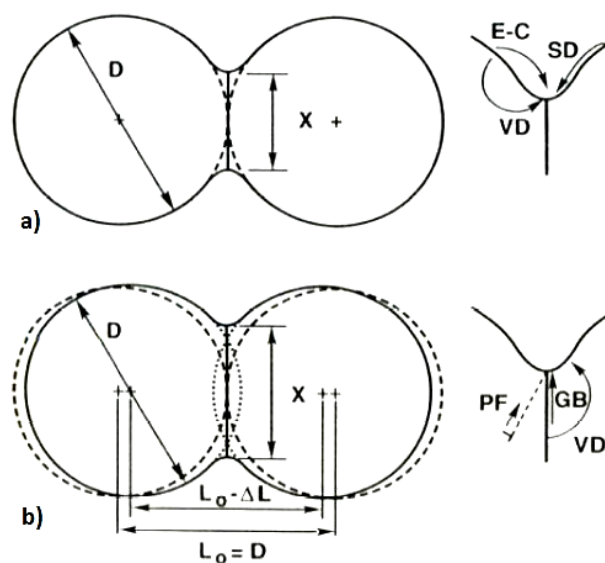


Fig. 7.6 Schematic depiction of transport mechanisms: a) surface transport; b) bulk transport [2].

Bulk transport (Fig. 7.6b) includes volume diffusion (VD), grain boundary diffusion (GB), plastic flow and viscous flow. Plastic flow (PF) is usually important only during the heating period, especially for compacted powders where the initial density is high. Surface tension stress is generally sufficient to generate new dislocations. Amorphous materials, such as glass and polymers, densify by viscous flow; particle sintering occurs in a rate which depends on particle size and material viscosity. A viscous flow mechanism is also possible for metals with a liquid phase on grain boundaries. Grain boundary diffusion belongs to dominant mechanisms of material transport for most of crystalline materials and has an essential influence on densification. In general, the bulk transport is most active at higher temperatures.

7.2.1 Origination of a contacting area between particles and its growth

An amount of mass transported per a unit of time depends at constant conditions on which mass transfer mechanism is applied. For each of them equations can be found on the basis of theoretical assumptions, which describe a change in a geometrical shape depending on the sintering time at the defined constant temperature. Boundary conditions must be simplified in order to enable the mathematical expression. This concerns above all a particle shape and size, where a basic condition is a spherical shape of particles of the same size. Though, this assumption is the most distant from real conditions, but from the mathematical point of view it has been mastered best.

When sintering two spherical particles of a diameter D , which are so small that their own weight can be neglected, their bonding occurs. The actual bonding occurs on the basis of reduction of a mutual surface through several stages (Fig. 7. 5) and a result is a sphere of a final diameter $D_f = 1.26 D$.

A solid contact formation and its growth into a neck connecting both particles (Fig. 7.7) is performed on the basis of capillary pressure (Laplace pressure) which can be generally expressed as:

$$\sigma = \gamma(1/r_1 + 1/r_2)$$

where σ - surface stress, possibly specific surface energy; r_1, r_2 – the largest and smallest radius of a surface curvature (Fig. 7. 8).

For convex surfaces of a sphere (or for bonding pressure of spherical pores), where $r_1 = r_2 = D/2$ (or r) applies, the capillary pressure is equal to:

$$\sigma = 2\gamma/r = 4\gamma/D$$

Using a circular approximation to a neck shape with a radius P , which is approximately equal to X^2/D , the stress corresponding to a concave curvature in the neck is given by a relation:

$$\sigma = \gamma(1/X - D/X^2)$$

The equations imply that the stress applied on the sphere surface is a compressive stress and the stress acting in the neck is a tension stress.

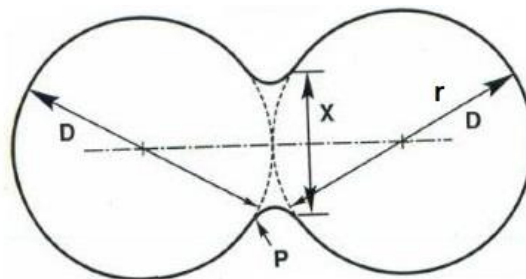


Fig. 77. Solid contact formation and its growth to a neck between two particles: X – neck diameter; D – initial diameter of a particle; P – neck curvature radius [2].

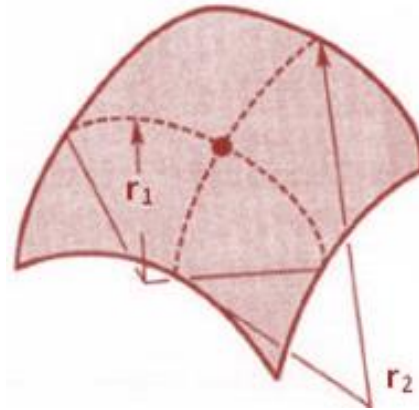


Fig. 7.8 The largest (r_1) and the smallest (r_2) radii of a surface curvature [2].

A model of a sintering initial stage expresses a neck size ratio X/D as a function of the sintering time t under isothermal conditions of growth:

$$(X/D)^n = (B \cdot t)/(D)^m$$

where X – neck diameter; D – particle diameter; t – isothermal sintering time; B – a set of material and geometrical constants; n , m and B – constants depending on a mass transfer mechanism.

This model applies generally for the neck size ratio below 0.3. A diffusion coefficient is included in a parameter B . The equation explains some key factors of the sintering process in the initial stage. A high sensitivity to the reverse value of particle size means that smaller particles sinter more rapidly. Surface diffusion and grain boundary diffusion increases along with a decreasing particle size in comparison with other processes, while lattice (volume diffusion) also contributes to metal powder sintering. In all the cases temperature appears in an exponential member (the Arrhenius equation), which means that little temperature changes can be of a high influence. Time has a relatively little influence compared to temperature and a particle size. In Table 7.1, constants n , m and B for mass transfer particular mechanisms are shown.

Table 7.1 Constants n , m and B for mass transfer particular mechanisms.

Material transport mechanism	n	m	B
Viscous flow	2	1	$3 \gamma / (2 \cdot \eta)$
Plastic flow	2	1	$9 \pi \cdot \gamma \cdot b \cdot D_v / (k \cdot T)$
Evaporation/condensation	3	1	$(3 P \cdot \gamma / \rho)^2 (\pi/2)^{1/2} (M/(k \cdot T))^{3/2}$
Lattice (volume) diffusion	5	3	$80 D_v \cdot \gamma \cdot \Omega / (k \cdot T)$
Grain boundary diffusion	6	4	$20 \delta D_b \cdot \gamma \cdot \Omega / (k \cdot T)$
Surface diffusion	7	4	$56 D_s \cdot \gamma \cdot \Omega^{4/3} / (k \cdot T)$

Bulk transport processes change spacing between particles, since a neck growth occurs. The powder compact shrinkage is a result, then. Particle centers approaching one another can be related approximately to a neck size as follows:

$$\Delta L/L_0 = X/2 D$$

The shrinkage during the sintering initial stage can be expressed by the kinetic law:

$$(\Delta L/L_0)^{n/2} = B \cdot t / (2^n \cdot D^n)$$

where $n/2$ ranges between 2.5 to 3.

7.2.2 Viscous flow

For amorphous organic and inorganic polymers and glasses, these capillary forces are sufficient for the material to flow to a contacting zone and for centers of individual particles to get nearer to one another at the same time. Material flow occurs by viscous flow of molecules. At the beginning of sintering this assumption corresponds to the time-dependent viscous flow determined by Frenkel:

$$(X/D)^2 = (3 \cdot \gamma \cdot t) / (D \cdot \eta)$$

where η – viscosity; t – sintering time

Above the limited temperature region the material viscosity changes with the temperature dependence (approximation):

$$\eta = \eta_0 \cdot \exp(Q/k \cdot T)$$

Flow rate is influenced by the viscosity η .

7.2.3 Evaporation - condensation

A phenomenon which is defined by the Kelvin-Thomson equation has the same effects for evocation of capillary forces as the surface curvature (Fig. 7.9):

$$p_a = p_o \left(1 + \frac{2 \cdot \gamma \cdot V_o}{a \cdot k \cdot T_a} \right)$$

where V_o – volume of an atom; a – curvature radius; k – Boltzman constant.

Pressure of vapours on a curved surface p_a is different from the equilibrium pressure above a flat surface p_o . Then, a pressure change is given by the relation:

$$\Delta p = p_o \left(\frac{2 \cdot \gamma \cdot V_o}{a \cdot k \cdot T_a} \right)$$

If this relation is applied to a sintering model for two spherical particles, then evaporation occurs on convex areas and re-condensation occurs on concave areas. Thus the material transport and a contacting area growth are enabled.

A vapour equilibrium pressure depends on the absolute temperature in accordance with the Arrhenius equation:

$$p = p_o \cdot \exp(Q/k \cdot T)$$

where p - vapour pressure; p_o – material constant; Q – evaporation activation energy; k - Boltzman constant

Materials in which the mass transfer mechanism occurs by evaporation-condensation process include e.g. NaCl, PbO, TiO₂, H₂O, Si₃N₄, BN, ZrO₂. In many other materials this transfer runs at typical sintering temperatures very slowly, so it is usually ignored. Or in the contrary, when sintering small particles with a large surface area, this transfer may be dominant.

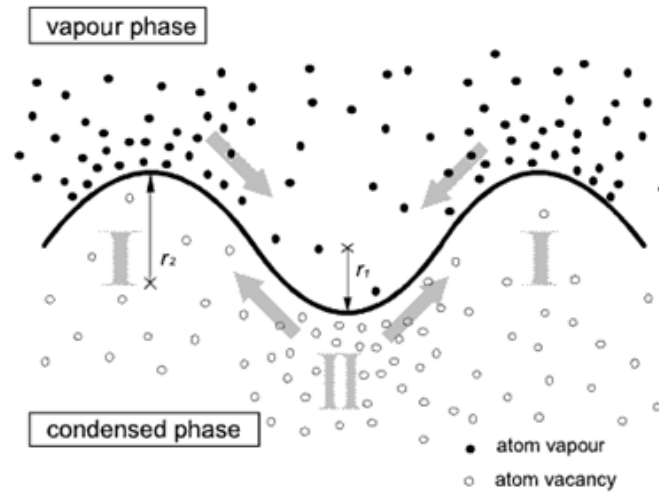


Fig. 7.9 Flow of vacancies and atoms of a vapour phase in a curved interface region [1].

7.2.4 Surface and volume diffusion

The Kelvin-Thomson equation is applicable also for vacancies. Instead of the vapour pressure, a concentration of vacancies near a curved area (c_a) and a concentration of vacancies near a flat area (c_o) are substituted into the equation:

$$c_a = c_o \left(1 + \frac{2 \cdot \gamma \cdot V_o}{a \cdot k \cdot T} \right)$$

A change in the concentration of vacancies near a curvature of a crystal surface compared to the equilibrium concentration c_o on a flat area is given by this equation:

$$\Delta c = c_o \left(\frac{2 \cdot \gamma \cdot V_o}{a \cdot k \cdot T} \right)$$

The concentration of vacancies is higher on the concave area and lower on the convex area. The concave areas, which are subjected to tension stresses, are a source of vacancies as a result of their increased concentration. The convex areas (grain boundaries), which are subjected to compressive stresses, act as a place of origination of vacancies. There is an equivalent flow of atoms in the reverse direction; atoms are displaced by volume or surface diffusion, and thus the particle contacting area increases. A time change of the ratio of the contact x and the spherical particle radius is expressed by the relation $x^n/a^m \sim t$ in which a value of n and m exponents depends on a mass transport process. In the case of the bulk mass transport (volume diffusion) the relation is as follows:

$$\frac{x^5}{r^2} = K \frac{\gamma \cdot D_s \cdot \Omega}{k \cdot T} \cdot t$$

where K – a constant depending on a type of diffusion; D_s – a volume diffusion coefficient; $D_s = D_L c_o$ (D_L – a coefficient of auto-diffusion of vacancies); Ω – a volume of one atom.

The volume diffusion occurs in metals and high-melting point oxides in the first stage of sintering. This process is connected with particle centers approaching one another – shrinkage occurs. Transport of atoms to the neck surface occurs along grain boundaries which are in a contact (Fig. 7.10).

Surfaces of crystalline solids are usually not smooth, but consist of defects that include ledges, kinks, vacancies and adatoms – see Fig. 7.11. Surface diffusion involves the motion of atoms between the surface defects. The population of these sites and the motion of atoms are thermally activated processes, meaning temperature has a significant influence on surface diffusion. Further we have to

consider also a crystallographic orientation, because certain orientations are more favourable for diffusion.

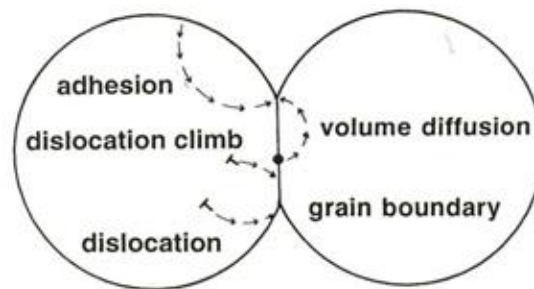


Fig. 7.10 Possible diffusion vacancy pathways [3].

A typical surface diffusion event involves three steps that might be slow and diffusion rate controlling:

1. Breaking an atom away from existing bonds (typical for ledges). The population of ledges depends on both the surface orientation and temperature.
2. A random motion of atoms across the surface, usually as a fast step.
3. The atom must reattach (place itself) at an available surface site.

The populations of sites and the ease of motion of atoms determine the surface diffusion rate. Highly curved surfaces and high temperatures increase the defective site population, leading to more surface diffusion.

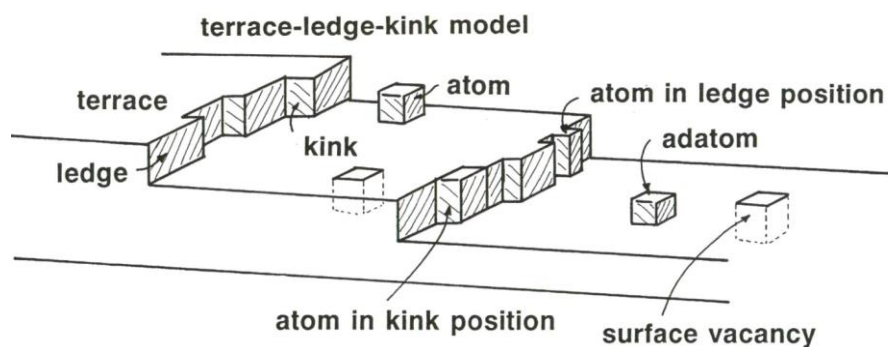


Fig. 7.11 Schematic depiction of crystalline material surface [3].

Surface diffusion is an active process during heating to the sintering temperature. In comparison with other transport mechanisms, it usually applies that the activation energy for surface diffusion is less than that for other mass transport mechanisms and initiates at lower temperatures. The surface diffusion slows as the surface defect structure is consumed or as the available surface area is lost to sintering bonds.

As the sintering proceeds, the significance of the surface diffusion diminishes, however, it may affect a motion of pores during grain growth. Migration of atoms on a pore surface occurs from a low curvature region to a high curvature region, while a pore is “dragged” by a moving grain boundary. Further on the surface diffusion acts in correlation with other processes, where densification is controlled by the material transport along grain boundaries and its redistribution.

The surface diffusion mechanism applies as a result of the different vacancy concentration on concave and convex curved areas, leading to the material redistribution, but only on a surface. It is characteristic for surface auto-diffusion that it does not produce any shrinkage.

Volume diffusion, or lattice diffusion, involves the motion of vacancies through a crystalline structure. The rate of volume diffusion is dominated by three factors: temperature, composition and curvature (or pressure). The volume diffusion share in the sintering process in metals is given by the equilibrium number of vacancies, increasing with temperature. In compounds, temperature and stoichiometric composition are the controlling parameters.

7.2.5 Grain boundary diffusion

Grain boundaries are sites with high density of imperfections. The diffusion coefficient in this area is higher and the diffusion activation energy is lower than in the crystal volume.

Grain boundary diffusion is relatively important to the sintering densification of most metals and many compounds. Grain boundaries form in the sinter bond between individual particles due to misaligned crystals. In principle, this is a collection of repeated misorientation steps – see Fig. 7.12. The defective character of the grain boundary allows mass flow with an activation energy that is usually intermediate between surface diffusion and volume diffusion. Even if the grain boundary is rather narrow, this is still an active mass transfer way. Grain boundary diffusion depends on grain size or the amount of grain boundary area per unit volume.

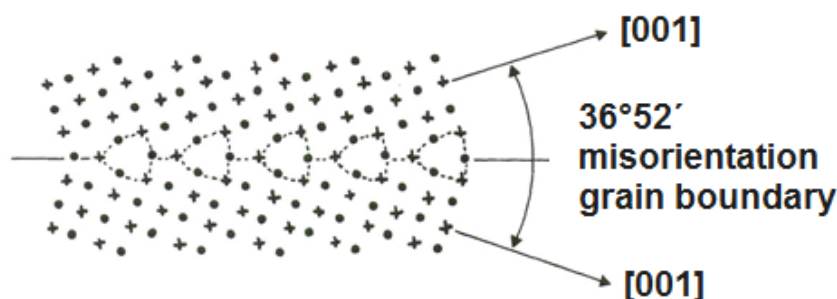


Fig. 7.12 Grain boundary misorientation [3].

As the sintering proceeds, mass transport occurs between pores via the grain boundaries, leading to pore coarsening. This is most active late in sintering when the grain boundary is an inefficient vacancy sink and a tough structure becomes so strong that it resists further densification: vacancy accumulation on a grain boundary requires motion of the boundary.

7.2.6 Plastic flow

Dislocations play a role as a vacancy sink place, improving mass transport during sintering. Atoms flowing against vacancies would enlarge a neck and a particle diameter would lessen. Dislocations form half-planes, which absorb vacancies and emit atoms, leading to a directed auto-diffusion due to capillary forces.

Plastic flow, i.e. dislocation motion due to the sintering stress, is one of the most discutible aspects of the sintering theory. Two possible paths of the dislocation motion are usually mentioned:

1. Dislocation climb due to vacancy absorption.
2. Dislocation glide (slip) due to the surface stress exceeding the deformation stress at the sintering temperature.

It is most probable that dislocation is involved in sintering during heating, particularly if powders were subjected to plastic deformation during compression. Dislocations interact with vacancies during sintering and improve mass transport. The dislocations climb by the absorption of vacancies emitted from the pores, leading to annihilation of the vacancies and dislocation motion to new slip planes.

The effective diffusion coefficient is higher than the volume diffusion coefficient, in particular during the initial heating to the sintering temperature, as long as the active dislocation density is at

least $2 \cdot 10^8 \text{ cm}^{-2}$. This can contribute to 10 – 100 fold increase of sintering rate during the initial stage. Shear stress is of a maximum value near the neck surface, where its growth is most active. As the neck enlarges, the shear stress declines below the deformation stress for the given material and the process becomes inactive. Therefore the plastic flow is important in the early stage of sintering. Dislocation flow can also be induced by a phase transformation during heating, but this is restricted to polymorphic materials.

7.2.7 Pore structure during the sintering process

A product prepared from a powder material represents a “combined” material, in which there are voids and powder particles are in a contact (an ideal model). As a result of a decrease of free surface energy, widening and rounding of contacts between particles originated in the first stage of sintering occur. Particle size, shape and structure state affect particle deformation rate and growth of strength of a compact. These changes are typical for the early stages of sintering. Further decrease in mostly continuous “phase of voids” with a mean diameter r_{mean} occurs. This intermediate sintering stage is characterized by the mean distance between vacancy sources and annihilations being shorter in comparison with r_{mean} . In the final stage pores interconnect and particles lose appearance of individual grains. Vacancy sources and annihilations continuously move away from one another due to defect recovery and recrystallization. While spheroidization occurs, the increasing pore shrinkage leads to a declining pore population (to a complete recovery of a part of pores). The pore structure change in the particular sintering stages is schematically depicted in Fig. 7.13. Point-to-point interparticle contact grows to a neck shape (7.13a). After the initial stage the sintering rate depends on grain boundaries and pore shapes (7.13b). At the beginning of the intermediate stage pores are positioned on grain boundaries (7.13c). As the sintering process proceeds, pores begin to adopt a cylindrical shape, leading to densification and decreasing of pore radii (7.13d). In Fig. 7.14, a pore network structure during the intermediate sintering stage is shown, characterized by interconnecting of pores placed on grain boundaries.

These procedures may also include local processes not connected with a decrease in volume, such as void formation and growth of individual pores and growth of individual pores due to vacancy dissolution and their coalescence. Owing to these processes, the rate of sintering of a compact decreases with a duration of sintering.

For spheroidization and shrinkage of pores the same basic processes apply as for formation of contacts and particle growth.

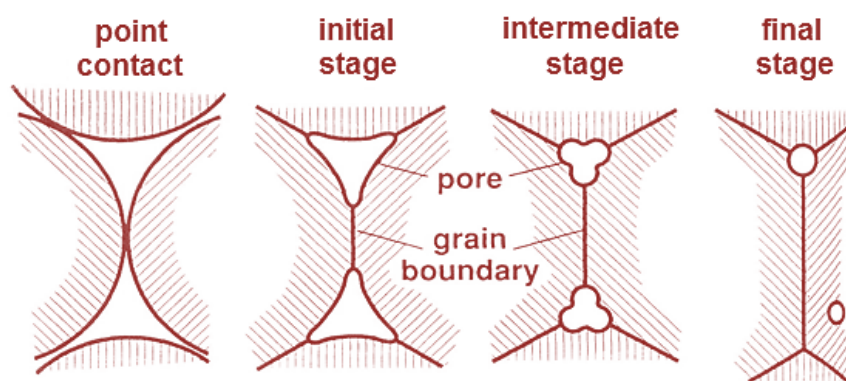


Fig. 7.13 Pore structure change during particular sintering stages [3].

In crystalline materials pores shrink during sintering by means of viscous diffusion flow and volume diffusion. Pores represent a “vacancy reserve” from which vacancies under an applied pressure diffuse into a metallic matrix and sink on a surface. Outer surfaces of sintered products, pore surfaces, dislocations and grain boundaries and subgrain boundaries are usually dislocation sink places.

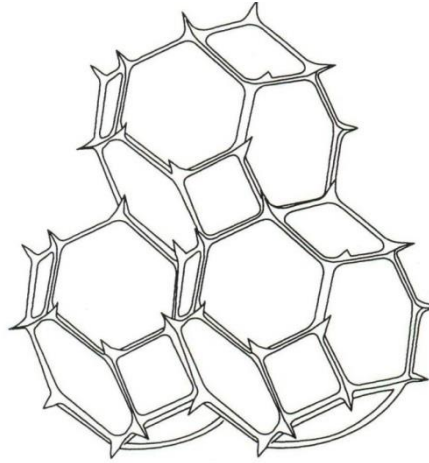


Fig. 7.14 Pore network structure in intermediate stage of sintering – interconnection of pores situated on grain boundaries [3].

Basic tendencies at sintering can be, with regard to a ratio of a pore mean diameter r_{mean} and a mean diameter of a structure element (grain or subgrain) l_{mean} , divided to two limit cases.

If $r_{\text{mean}} \gg l_{\text{mean}}$ (Fig. 7. 14a), then pores extend across a wide range of a matrix deteriorated by boundaries. Then this matrix can be considered an isotropic viscous material with the viscosity coefficient:

$$\eta_{\text{KG}} \approx \frac{k \cdot T}{D_s V_o} l_{\text{stred}}^2$$

In this case the pores vanish with the viscous flow, i.e. vacancy flow to grain boundaries that are near the pore, or possibly connected to it. This process can be important for the intermediate stage in which a fine boundary net occurs. For practice, this implies that the shrinkage can be affected by increasing the effective diffusion coefficient and defect density.

If $r_{\text{mean}} \ll l_{\text{mean}}$ (Fig. 7. 15b), there is a rich flow of dislocations for greater distances. Vacancies dissolve in crystalline surroundings of defects and further diffuse to more distant sink places. In this vacancy dissolution process the volume diffusion plays an important role. This may be significant for a later sintering stage, when a structure coarsening occurs due to recrystallization and grain growth. Zones with a low, or possibly none, concentration of pores can originate near boundaries of large grains.

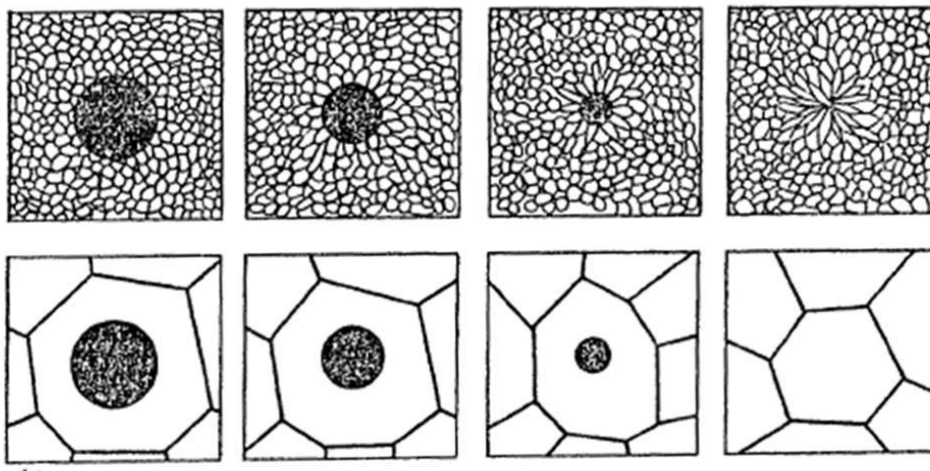


Fig. 7.15 Schematic depiction of pore recovery: a) $r_{\text{mean}} \gg l_{\text{mean}}$; b) $r_{\text{mean}} \ll l_{\text{mean}}$. [4].

Diffusion and coalescence change pore distribution, but neither the total volume of pores, nor the material density, changes. Due to a decrease of the total area of pores and an increase of the pore mean diameter, an excess of vacancies decreases gradually and together with a decrease of porosity the grain growth is enabled again.

During the later sintering stage the interaction between pores and grain boundaries can have three forms (Fig. 7.16):

1. Pores inhibit grain growth.
2. Pores are dragged by moving boundaries.
3. Boundaries are separated from pores which are subsequently isolated inside grains (pores move more slowly than grain boundaries).

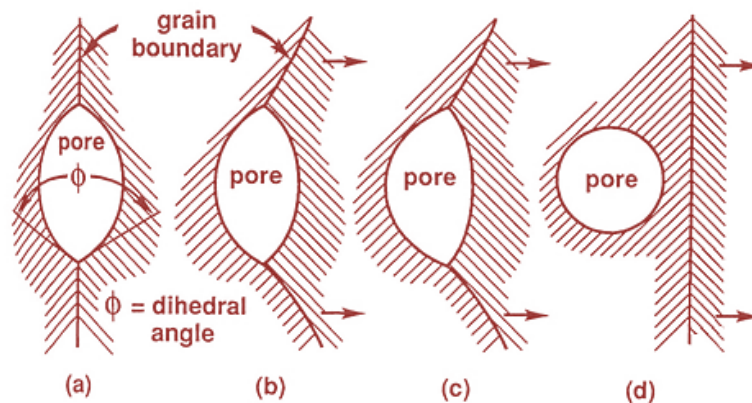


Fig. 7.16 Sequence of actions leading to isolation and spheroidization of pores in the final sintering stage: a) a pore on grain boundaries featuring an equilibrium dihedral angle between a solid and vapour phase; b)-c) grain growth – a pore is dragged by moving boundaries; d) isolation of a pore as a result of its detachment from grain boundaries [3].

In Fig. 7.17, two possible “pore – grain boundary” configurations during sintering are shown. Pores are placed either on corners of grains or inside grains. The system energy is lower when pores are placed in corners of grains, because pores reduce the total boundary area. If a boundary was separated from a pore, the system energy is increased proportionally to an amount of newly originated interphase regions. Therefore at the beginning of the intermediate sintering stage a negligible separation of pores from boundaries is expected. While densification continues, pore mobility decreases, which enables its separation in a combination with a decreasing pinning force (attachment on grain boundaries). The pore separation from grain boundaries limits the final density. Therefore it is very important to minimize this phenomenon through a careful temperature control.

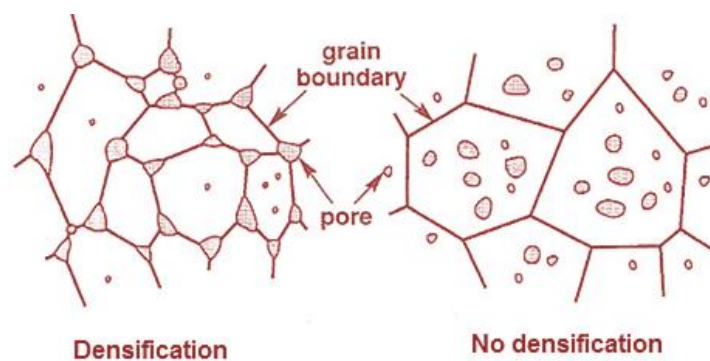


Fig. 7.17 Two possible “pore - grain boundary” configurations during sintering: pores are placed in grain corners (a) or inside grains (b) [3].

A combination of large pores and large grains leads to separation of pores from boundaries (Fig. 7.18). At the beginning of sintering, large pores are immovable and boundaries of small grains are blocked. In a later sintering phase, there are several small pores as a result of shrinkage and grains are relatively large. To avoid separation, pores must be movable enough to be able to move along with grain boundaries at the same time. This implies that sintering requires a meticulous control of an initial powder microstructure and temperature mode to achieve full densification.

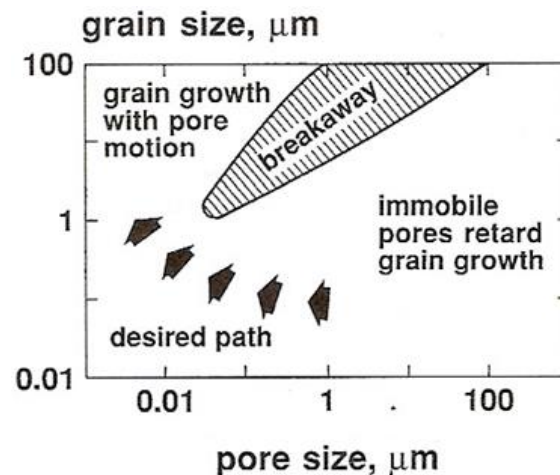


Fig. 7.18 Conditions on which grain growth can cause separation of pores and prevent full densification by origination of isolated pores [3].

7.2.8 Sintering diagrams

Sintering diagrams, the so-called Ashby's diagrams, are based on an assumption of no grain coarsening during sintering. These diagrams identify the dominant sintering mechanism and the rate of sintering as a result of all the mechanisms acting together. In Fig. 7.19 an example of Ashby's diagram is shown for W-powder of grain size of 4 μm containing 4 regions – a region of adhesion, grain boundary diffusion, surface diffusion and volume diffusion. Adhesion between particles occurs at the very beginning of the sintering process. For the initial stage of sintering the surface diffusion is dominant and grain boundary diffusion in the later stage.

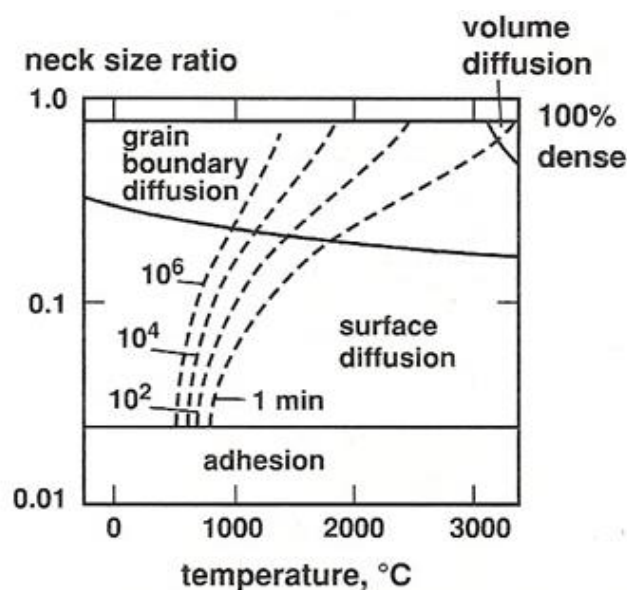


Fig. 7.19. Sintering diagram for W-powder of grain size of 4 μm [3].

Boundary lines between the particular sintering mechanisms indicate the same sintering rate of two neighbouring mechanisms. For metal materials, grain boundary diffusion and surface diffusion are dominant. Both these mechanisms are strongly particle size dependent.

7.3 Sintering in a multicomponent system

The above mentioned thoughts considered sintering powder of one metal. However, powder metallurgy can be applied also for a manufacture of products which are made from a mixture of various metals in a random ratio, namely those forming solid solutions only to a limited extent or being totally insoluble, and it is even possible to sinter powder metals with nonmetals. Both initial materials and products of their mutual reactions – solid solutions and compounds – can occur in a structure of sintered multicomponent alloys.

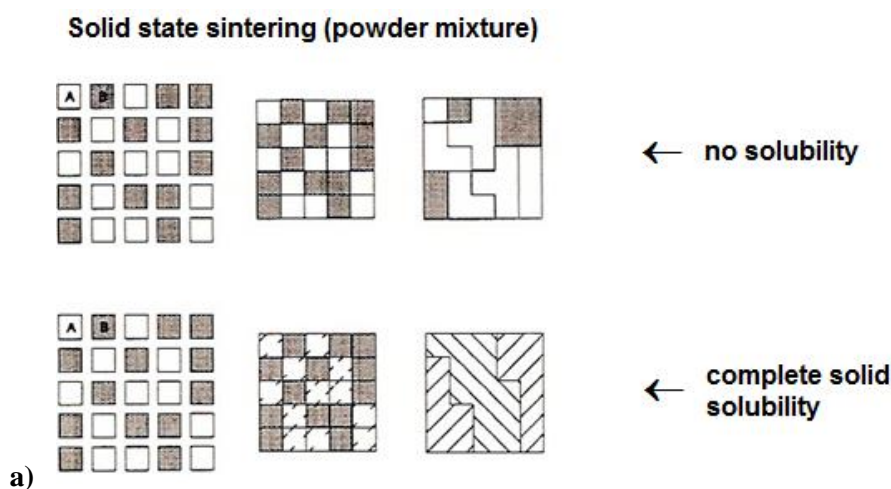
In multicomponent (heterogenous) systems, sintering proceeds in a different way according to a type of the given system. If phases in a powder mixture were not in equilibrium at sintering temperature, then sintering occurs not only through reducing free surface energy and defect density, but depends also on heterodiffusion processes, leading to the system equilibrium. Generally, it can be stated that free energy of the system decreases through balancing concentration gradients.

From the point of view of various properties of such components their interaction can result in a positive or negative influence on finished product properties. Induced stresses can occur during cooling as a result of different phase thermal expansion coefficients. For mutually soluble structures, these stresses are removed by plastic deformation, provided at least one phase had a lower limit of elasticity than the strength of a phase boundary. Under inverse conditions, tensile stresses occur on phase boundaries, which are eliminated by plastic deformation or cracks.

The following three types of sintered structures can originate from mixed powders:

1. A powder mixture of like composition with different particle size – high filling density.
2. Solid solutions – homogenization of a powder mixture occurs through diffusion.
3. Composites – sintering of two different phases.

Sintering processes in heterogenous systems can be divided to sintering without the presence of a liquid phase (in the solid state) and in the presence of a liquid phase. In Fig. 7.20, possibilities of behavior of components in a binary system during sintering are schematically depicted. For sintering in the solid state, the particular components can be mutually completely soluble (e.g. formation of solid solutions) or insoluble. If one of the components had a melting point lower than the sintering temperature, a liquid phase originates during sintering. Then the particular components can also be either completely mutually soluble or insoluble.



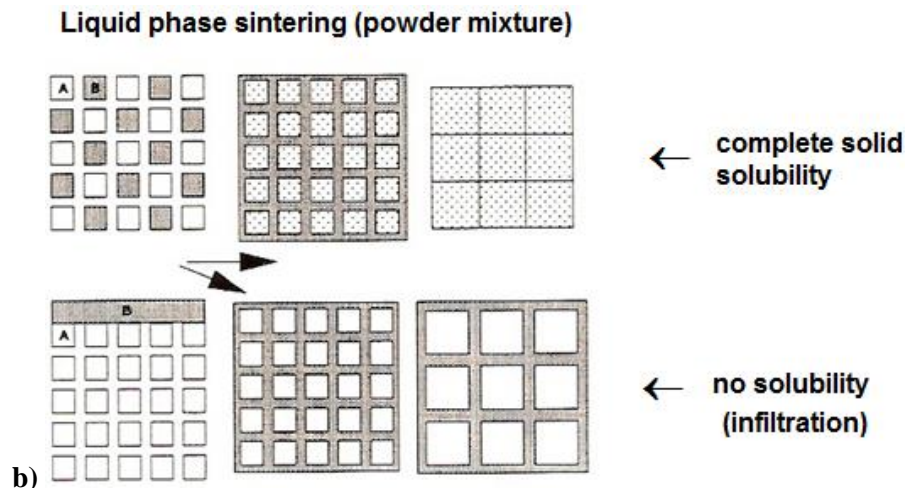


Fig. 7.20. Behavioral possibilities of components in a binary system during sintering [5].

7.3.1 Sintering in a solid state

From the thermodynamic point of view, mutual sintering of particles of powder A and B is possible, only if the following applies:

$$\gamma_{AB} < \gamma_A + \gamma_B$$

where γ_A , γ_B – surface stress of A and B materials; γ_{AB} – surface stress on a boundary of an area of AB particles

The driving force acting to extend the contacting area increases, as long as γ_{AB} decreases. If $\gamma_{AB} > \gamma_A + \gamma_B$ applies, the contacting area does not growth, because extending of the AB contacting area leads to an increase of surface energy. Sintering of identical particles to each other occurs.

If inequality $\gamma_{AB} < \gamma_A + \gamma_B$ applies, then further separation is possible:

$$\gamma_{AB} > \gamma_A + \gamma_B$$

when the contacts build up with an approach of the mid-points up to a „critical distance“ only. On the contrary, if:

$$\gamma_{AB} < \gamma_A + \gamma_B$$

then a phase with a larger surface energy is covered with a phase with a lower surface energy, namely through the surface diffusion or evaporation and condensation.

As soon as the A particle is completely covered by the B particle, further compaction takes place the same way as in the one-component system between particles B-B. Atoms on the interphase boundary are disarranged, so that a phase connection on the interphase boundary can be ensured and γ_{AB} can be as low as possible. For contacting phases with the same crystal bonding the bond strength is defined by valence forces.

For a different structure of atoms in a lattice, such as an ionic and metallic bonding in cermets (metal-oxide), the boundary strength is defined by van der Waals or adhesion forces. The arrangement of atoms on the phase boundary can be accelerated by dissolving procedures occurring simultaneously, which makes sintering easier.

If powder mixture components are mutually soluble, the actual sintering process is overlaid by a homogenization process and a formation of new phases (Fig.7.21). The diffusion coefficient characteristic values can exceed values determined in a nonporous material and a reverse of the prevailing diffusion direction can occur. Changes in the sintered system, which is characterized by the binary diagram, sintering temperature and composition, depend on the sintering time (Fig.7.22).

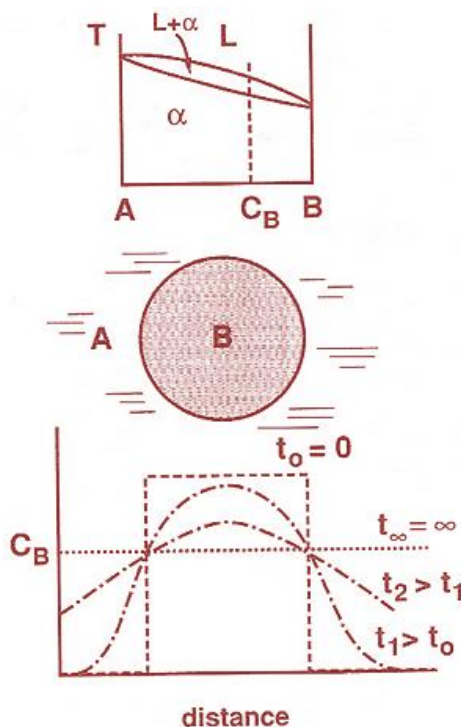


Fig. 7.21 Homogenization in the one-phase binary system of a powder mixture with an average composition c_B [3].

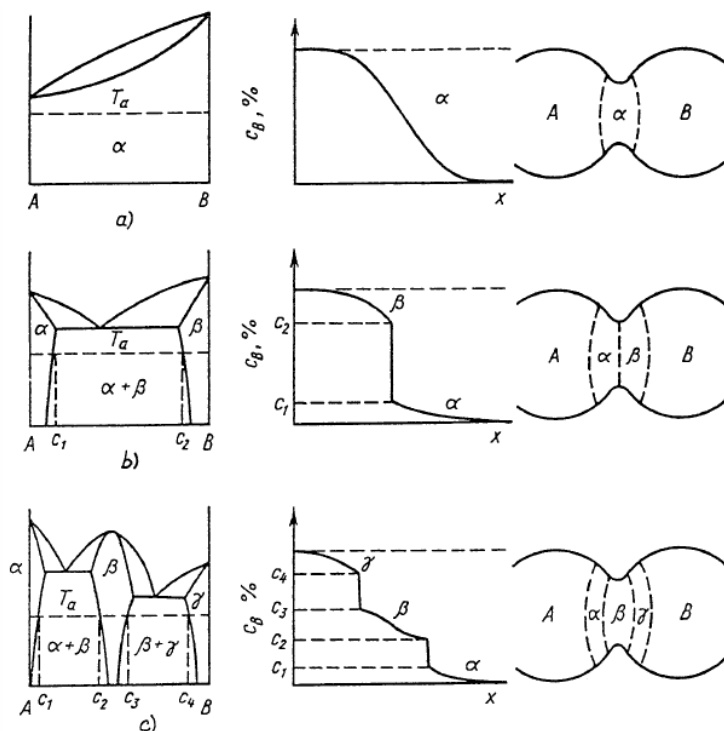


Fig. 7.22 Schematic depiction of relations in the binary diagram and origination of phases in a place of contact of various particles (T_a – sintering temperature) [4, 6].

Formation of an alloy in a place of contact of AB particles occurs, that first of all phases corresponding with the equilibrium binary diagram originate. Their distribution depending on the previous contacting area is controlled by diffusion coefficients and is usually asymmetrical.

The actual compaction can occur through partial, rather complicated processes. At a noticeable difference in partial diffusion coefficients, such as in Cu-Ni system, it may be possible, that diffusion pores sometimes originate in a phase with a higher diffusion coefficient (Cu) (Kirkendall phenomenon) and particles in a phase with a lower diffusion coefficient (Ni) exhibit an increase in volume. Aside from the volume diffusion, the flow of the material which is needed for the material homogenization can occur through the surface diffusion. In Fig. 7.23, origination of a pore in Cu-Zn system as a result of the Kirkendall phenomenon is shown, where Zn to Cu diffusion rate is higher than the diffusion rate of Cu to a newly originating phase (brass).

Other complications for the sintering process can emerge in components having substantially different heterogeneous diffusion coefficients ($A \leftrightarrow B$) in comparison with autodiffusion coefficients ($A \rightarrow A$, $B \rightarrow B$), leading also to a different growth rate of a contact (neck) AB than in a case of AA or BB. As a result, stresses inducing plastic deformation or leading to a separation of individual particles can occur.

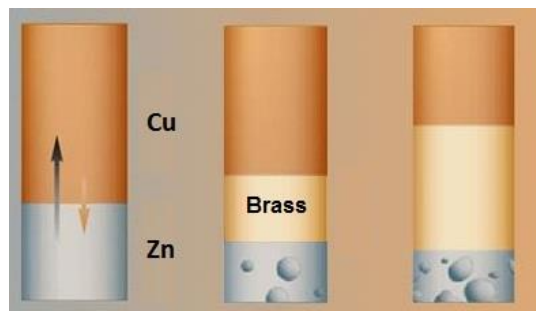


Fig. 7.23 Kirkendall phenomenon in Cu-Zn system [7].

7.3.2 Liquid phase sintering

The sintering process is affected by a liquid phase in a way and extent which depends on an amount and time of origination of the melt. If no mean equilibrium concentration of a sintered alloy occurred during the isothermal sintering, in which a solid and liquid phase was in equilibrium, an occurrence of a melt is a transient phenomenon (a tendency to achieve the equilibrium state).

Wettability of a solid phase by a liquid phase has a crucial significance for the sintered alloy quality (Fig.7.24). For a liquid to wet a solid, the following relation applies for a change in the specific surface energy (according to Dupré):

$$\Delta\gamma = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

where γ_{SV} – surface stress between a solid and vapour phase; γ_{LV} – surface stress between a liquid and vapour phase; γ_{SL} – surface stress between a solid and liquid phase.

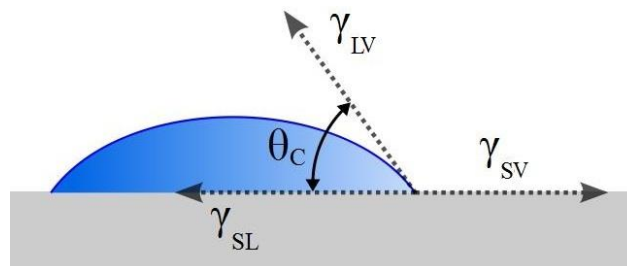


Fig. 7.24. Wetting angle definition[8].

For a contact between S-L to originate, $\Delta\gamma$ must be positive, that means $\gamma_{SL} < \gamma_S + \gamma_L$. According to Young-Dupré, wettability can be expressed by a value of a wetting angle α :

$$\cos \omega = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Through a combination of the above mentioned equations, we obtain a relation enabling to assess the effect of a wetting angle on a change in the sintered material resulting structure:

$$\Delta\gamma = \gamma_{LV} (1 + \cos \omega)$$

The lower the ω magnitude and surface stress on the interfacial area, the higher the energy increase. Wettability can be positively influenced by alloying elements without affecting other properties of the sintered material. It is important for sintering in the presence of a liquid phase, that wettability of a solid phase by a liquid is as high as possible, i.e. $\omega \Rightarrow 0^\circ$ (Fig.7.25)

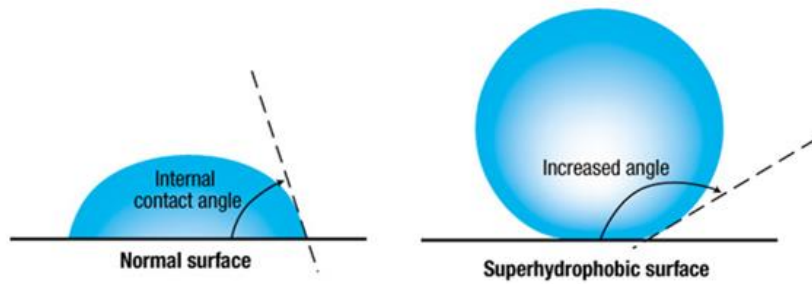


Fig. 7.25 The melt well wetting a solid (a) and not wetting a solid surface (b) [9].

In other events, such as for cemented carbides, good conditions for wettability are set spontaneously, while accompanying elements of a solid phase are dissolved in a melt (Fig.7.26).

If the wettability angle ω exceeds a defined value (Fig.7.25), a melt cannot penetrate between powder particles and becomes isolated. Solid particles form a solid skeleton in which the melt is roughly distributed. This reduces the melt effect on compaction and in the end leads to sintered products not meeting demanded requirements.

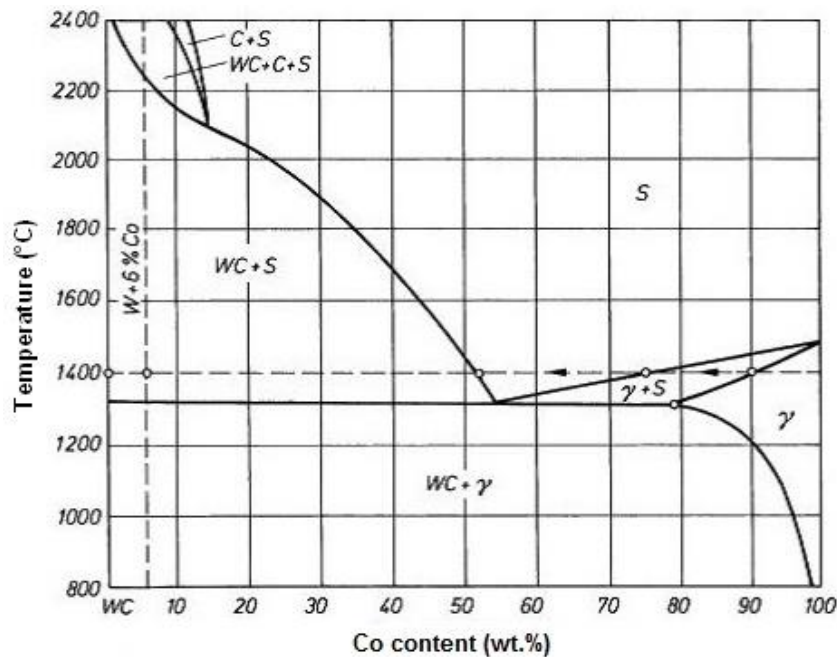


Fig. 7.26 Pseudobinary phase diagram WC-Co [6].

If a particle surface is completely wettable ($\omega \approx 0^\circ$) and surface energy between particles equals:

$$\gamma_{SS} > 2 \gamma_{SL}$$

then the melt is under pressure and has a tendency to reduce the surface energy. It penetrates among particles and envelopes each of them in a melt film (Fig.7.27). Then a sintered product compaction begins along with an arrangement change. In the initial sintering phase, a grain boundary “collapses” as a result of melt wetting and a polycrystalline particle splits up to individual crystals due to “reprecipitation”. These new crystals (grains) spheroidize and coarsen afterwards (Fig. 7.28).

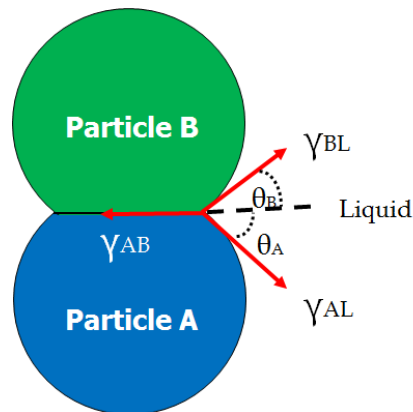


Fig. 7.27 Wetting of grain boundaries occur, if ω_A and ω_B get close to 0.

Cemented carbides WC-Co behave in a similar way. WC+Co mixtures (usually < 20 wt.% Co) are sintered up to temperature T_T by means of Co. During sintering Co absorbs so much WC, that the melt is in equilibrium with WC (Fig.7. 26). The melt readily wets WC and penetrates into pores among WC particles. For coarse-grained WC alloys, possibly with a low content of Co, shrinkage is at first determined by a dislocation process and after its impoverishment by WC dissolution and reprecipitation.



Fig. 7.28 Schematic depiction of the reprecipitation process.

7.4 Activated sintering

This is sintering under simultaneous application of special factors speeding-up the sintering process. Activation is performed by applying gaseous substances in a sintered environment, applying liquid substances (e.g. a liquid phase originating during heating), applying solid substances (e.g. sinterability enhancing additives) and applying external mechanical factors (e.g. pressure in sintering under pressure called hot pressing).

A compact (body) of powder material is in a nonequilibrium state and tends to get to an

equilibrium state during sintering. In comparison with compact materials, powder compacts exhibit a certain “activity” which is influenced by its previous history (powder manufacturing and processing). The “activity” of a single-phase system can be divided to a structural and geometrical part. A geometrical “activity” is determined by a specific surface and shape of particles, pores and contacts (that means capillary forces). On the contrary, the structural “activity” is determined by a degree of failure of powder particles, that means a surface relief condition, a density of spot defects, dislocations and grain boundaries. This implies that compaction of an amorphous porous material is determined by its geometrical activity, as far as its viscosity during isothermal sintering is the contact viscosity. For crystalline materials both types of the activities are applied.

The sintering process activation methods are shown in Fig.7.29. In general, the structural activity enhancement occurs, leading also to enhancement of kinetics of the sintering basic processes. Time to achieve the density and strength, equalization of the inhomogeneity in the sintered material volume and also equalization of the concentration in a multicomponent system is shortened. Properties are improved as well, or the sintering temperature, needed for obtaining required properties, decreases.

A sintering process activation can be performed both in the sintering process (e.g. with the aid of gas additives to the sintering atmosphere and the ultrasonic sintering) and by powder pre-processing (addition of alloying elements or forming in order to increase density of structure defects).

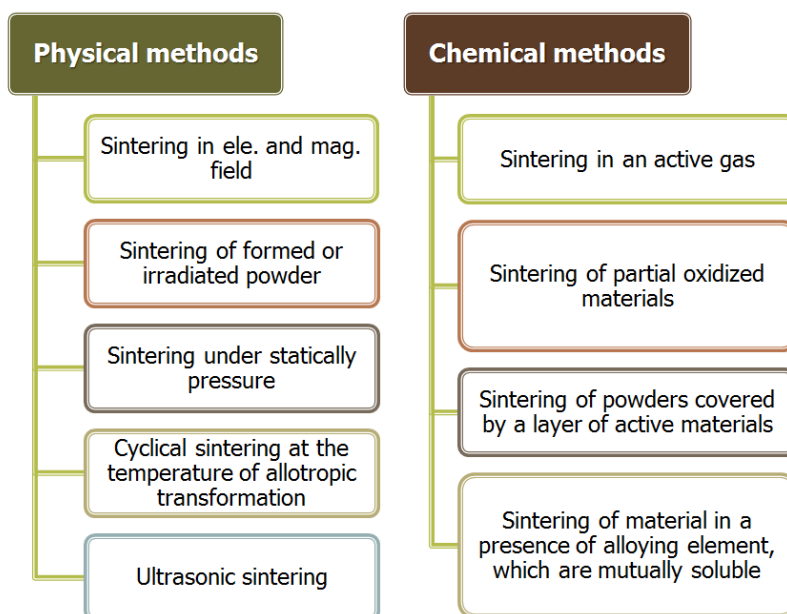


Fig. 7.29 Sintering process activation methods.

7.4.1 Activation of the material surface transport

The activation of material transport on a surface of powder or pores is enabled by intensification of the surface diffusion or by evaporation and condensation, when the effective surface diffusion coefficient or the vapour pressure is increased. The surface diffusion coefficient is higher and not so depending on temperature as for the volume diffusion. Therefore a relatively higher contribution of the surface diffusion can be expected, as long as the surface of pores is still large and temperature is quite low, that means in a stage of a formation of a contact and its growth. This procedure is very often applied for Fe, Ni, W, Mo, Cu and powder pre-oxidation or cyclic oxidation and reduction during sintering is used.

The activation of material transport with the help of vapour phase, i.e. through an increase of the metal vapour effective pressure, can be performed using a gas additive to the sintering atmosphere (HCl, NH₄Cl, NH₄F) which forms volatile compounds with metal. On places of the surface of

particles and voids with high surface energy (corners, edges), MeX_n – type halogenides originate rapidly (Me – metal, X – halogen) which are volatile at the sintering temperature and decompose again. Free metal is then segregated on places with low surface energy. Under advantageous conditions a continuous material transport can be ensured, when the surface becomes smoother and rounder and a contact stronger.

7.4.2 Activation of the material bulk transport

In principle, for the material bulk transport to intensify, two ways are possible:

1. Increase of a concentration of vacancies and their diffusion.
2. Increase of density of dislocations and grain boundaries.

Here the additional deformation of powder (mechanical activation) by milling, high-speed compaction or electrolytic segregation at higher density of current is applied.

However, an excess of vacancies originating during the mentioned processing processes recover in a very short time of 10^{-2} s. For this reason the above mentioned possibilities to influence the sintering process can be only used, if such a source of vacancies is available, which is active during sintering for a specific time. Such an event occurs, when the additional metal is soluble in a basic metal in an amount around 15 %. Powder particles are either pre-coated electrolytically or only during heating of a compact to the sintering temperature are coated with a metal, which originates by decomposition of the given metal compound.

Then it depends on a magnitude of partial diffusion coefficients, linear dimensions of layers and particles, whether the activation of the entire volume of a particle connected with diffusion is reached, and thus speeding up of shrinkage, or whether only a surface zone is influenced and thus mainly a contacting area growth is advanced.

7.4.3 Activation through a liquid phase

There are many systems which can be compacted by sintering in a solid phase, when a part of melt originates, which is highly advantageous for the entire process. The hardenable Cu-Ti alloy (Fig. 7.30) shows how diverse changes can be in a sintered system which tends to reach the equilibrium state through a partly melted phase.

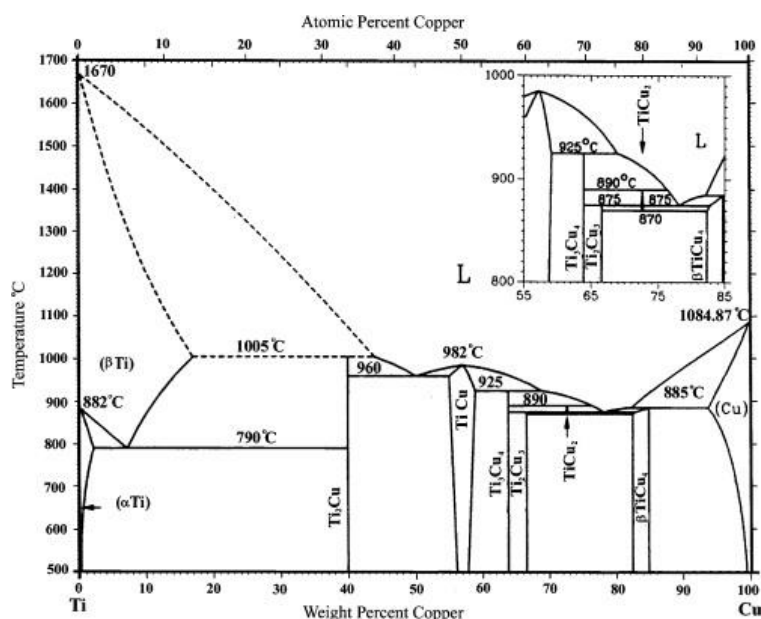


Fig. 7.30 Binary diagram of Ti-Cu system [10].

The processes occurring during sintering a compact of Cu – Ti alloy at temperature of 910 – 920 °C, manufactured of mixed powder metals (Ti 2-5%), are as follows:

Cu – has a higher diffusion coefficient than Ti \Rightarrow Cu diffuses preferentially into Ti and changes its composition (all intermetallic phases according to the binary diagram are formed in several minutes)

A liquid phase occurs between Ti_2Cu_3 - $TiCu_3$ for a short time The melt wets Cu, which has contained a little Ti so far, and penetrates its voids \Rightarrow the diffusion area enlarges (the area Cu – melt).

Rapid equalization of a concentration in a direction of crystals \Rightarrow the melt becomes enriched with Cu and solidifies. Pores originate on places of Ti particles, α -crystals are hardenable.

7.5 Technical devices and procedures

Properties of sintered products are determined by a number of factors, which occur in the sintering process and have to be ensured to be reproducible. The following are among the important characteristics:

- A selection and control of a working temperature.
- A use of a proper working atmosphere.
- A method to ensure a proper temperature.
- A size, shape and number of processed compacts etc.

7.5.1 Protective atmosphere

By reason of a porous structure the compacts have a higher tendency to react with an ambient atmosphere. Therefore, the sintering atmosphere has a great influence on the sintering process. A protective gas selection is performed in order to prevent oxidation of compacts during sintering, or possibly to reduce the existing oxides and thus increase the interparticle contact and ensure the material transport during sintering (Fig. 7.31). The most widely used protective gases for sintering are given in Table 7.2.

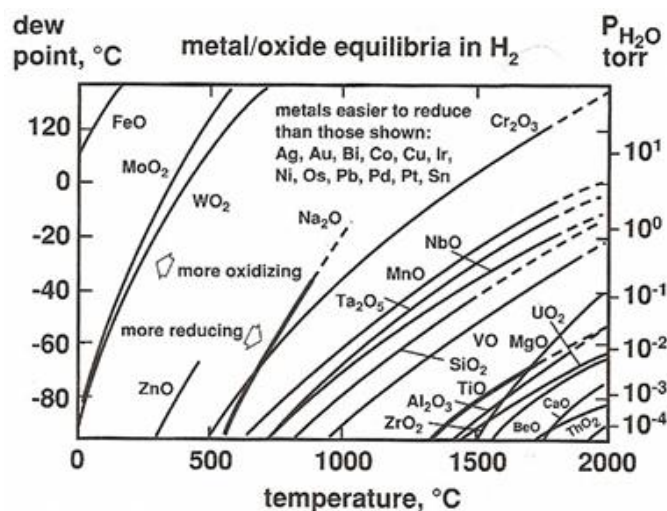


Fig. 7.31 Relation of reduction of metal oxides to the hydrogen dew point and temperature [2].

7.5.2 Sintering furnaces

The main function of sintering furnaces is to ensure conditions for reaching a required compaction of material – sintering processes. In Table 7.3, the used materials are divided according to sintering temperatures.

Table 7.2 Protective gases used for sintering.

Gas	Material
H ₂	Fe, steel + Cu, stainless steel Cu, bronze, brass, SK, Mo, W
Dissociated NH ₃	Fe, steel + Cu, Cr, Mn, Ni, Si, Cu, bronze, brass, W, Cemented carbides
Endogas	Fe, Fe – Cu alloys, Fe – Ni, Fe – C, Cu, Ni, Ag,
Exogas	Fe, Fe – Cu, Cu alloys, Ni alloys, Ag
Vacuum	SK, Cr – Ni alloys, reactive metals, Ti, Ta, Al, soft magnets, carbonyl Fe, hard magnets

Table 7.3 Sintering temperatures for selected metal and non-metal materials.

Material	Sintering temperature (°C)
Al	to 600
bronze	600 – 850
Cu	600 – 900
Ni	1000 - 1150
Fe - structural parts	1000 – 1300
Stainless steel	1100 – 1350
Soft and hard magnetic mat.	1200 – 1300
Cemented carbides	1400 – 1500
nitrides	1400 – 2000
MoSi ₂	1700
Al ₂ O ₃	1800 – 1900
Refractory metals W, Mo, Ta	2000 – 2900

Sintering furnaces can be classified as follows (Fig. 7. 32) according to:

- a) the protective gas;
- b) the heating;
- c) the operation.

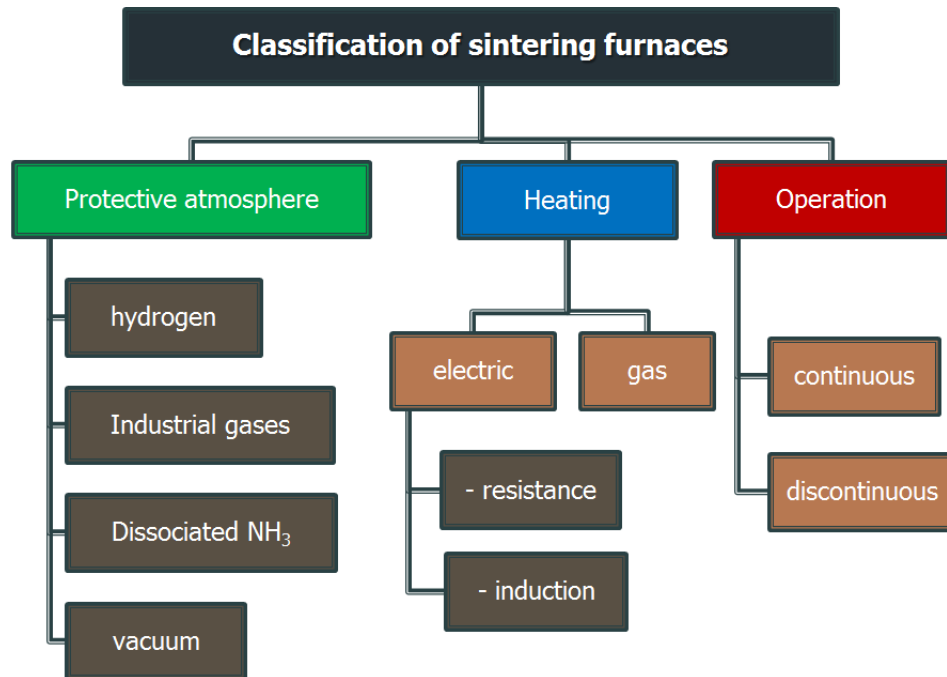


Fig. 7.32 Classification of sintering furnaces.

7.5.3 Infiltration with metal

Filling (infiltration) with metal – filling the compacts, semi-sintered or sintered metal skeletons with a melted metal. It is carried out either through a complete immersion into a molten metal or a partial immersion, whereas the molten metal is soaked into the porous metal compact by capillary forces. Or another method is to place a low-melting metal on a porous compact to which the low-melting metal leaks-in after exceeding the melting point and fills-in pores and voids. The above mentioned infiltration methods are shown in Fig. 7.33.

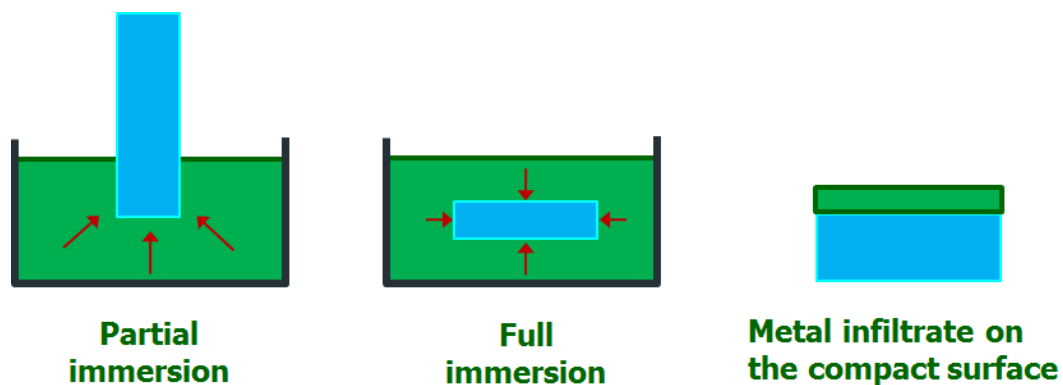


Fig. 7.33 Methods of infiltration of a porous compact with a molten metal.

The infiltration is used to prepare composite materials which cannot be made by the classical metallurgy and they are difficult to be manufactured by powder metallurgy. Examples of these materials are given in Table 7.4.

Table 7. 4 Examples of infiltrated materials.

Basic material	Infiltrate	Application
W, Mo	Cu	Ele. constacts
W, Mo, Ni	Ag	Ele. constacts
Fe, ocel	Cu, Cu alloys	Structural parts
Fe, Cu, Cu – Ni	Pb, Pb alloys	Sliding materials
Ni – Cr – slit	Fluorides	Sliding materials
Fe, bronz	Olej	Sliding materials
Grafit	Fe	Sliding materials
W	Ag, Cu	Rocket technology
W	Cu, Ni	Nuclear technology
Ni Fe	Hg	Radar components



Summary of terms

Solid phase sintering

Two-particle model

Diffusion paths

Evaporation-condensation

Viscous flow

Pore structure

Infiltration

Liquid phase sintering

Sintering furnaces and atmospheres



Questions to the topic

- 7.1. Which factors can influence the sintering proces in single component system?
- 7.2. Which mass transport mechanisms can be employed during sintering?
- 7.3. Characterize the stages of sintering proces.
- 7.4. When does the sintering take place with a transient and permanent liquid phase?
- 7.5. What is the principle and application of infiltration?
- 7.6. Jaký je princip infiltrace roztaveným kovem?
- 7.7. Why must the protective atmosphere be used during sintering?



Solved tasks

Exercise 7.1

Gas incaved in a pore can hamper densification in the final sintering stage. In the critical point, when the densification gets stopped, the surface energy of spherical pores is in equilibrium with the gas pressure:

$$2\gamma_{sv}/r = p_g$$

If the compact was sintered in argon at p_1 pressure, then the pore radius when closing the pores, which occurs at 8 % porosity, is r_1 . What will be the final pore size, if $r_1 = 10 \mu\text{m}$, $p_1 = 101\,325 \text{ Pa}$ and $\gamma_{sv} = 2 \text{ J/m}^2$?

♦ **Solution**

If a number of pores and temperature is constant, then:

$$p_1 \cdot V_1 = p_2 \cdot V_2$$

The final sizes of pores r_2 can be estimated from the following relation:

$$r_2 = [r_1^3 \cdot p_1 / (2\gamma_{sv})]^{1/2}$$

$$r_2 = [(1 \cdot 10^{-6})^3 \cdot 101325 / (2 \cdot 2)]^{1/2}$$

$$r_2 = 5.03 \cdot 10^{-6} \text{ m} = 5 \mu\text{m}$$

The pore size, no matter the sintering time, will stabilize on the final size 5 μm .

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8. POWDER METALLURGY PRODUCTS



Study time: 10 hours



Objective

- Products of powder metallurgy
- Fe-based PM products
- Non-ferrous metal PM products
- Sliding materials and sintered bearings
- Friction composite
- Magnetic materials
- Hard materials
- Contact materials
- Porous material



Lecture

Powder metallurgy technology is applied above all in the following fields:

1. **A manufacture of powder metals, alloys and compounds as a material for a direct use** – utilization in various technological fields (protective and decorative coatings, pyrotechnics, welding and surfacing, catalyzers in chemical industry, cementing materials for hydrometallurgy etc.).
2. **A manufacture of materials and products with special properties which cannot be achieved by classical metallurgy and metal processing** – cemented carbides, dispersion hardened materials, porous metal materials, friction and sliding materials, contact materials of W-Cu, W-Ag type, composition of metal with nonmetal, such as Cu-C, Fe-C, Ag-CdO, superhard materials, etc.
3. **A manufacture and processing of materials and products of common materials with typical or high technical parameters, but with advantageous technical-economic indicators** – lower production cost, lower consumption of metals and energy, suitable conditions for process automatization, wage cost saving, etc.

Main limitations of powder metallurgy technology include high costs of initial powder materials, high costs of pressing tools, limitations in shape and size of products and necessity for the optimal series production, which is usually considered 50000 product pieces.

Powder metallurgy products find their highest usage in the automotive industry, in industrial engines and generators, as various components in household appliances and hobby tools, electronics, etc. (see Fig. 8.1).

In Fig. 8.2, components in various parts of a passenger vehicle manufactured by powder metallurgy are shown.

The main group of products is represented by materials based on iron and non-ferrous metals. Powder metallurgy enables to manufacture components which, with a proper material selection regarding to functional properties and reliability, are adequate to components manufactured by chip machining. Product properties are determined particularly by porosity, composition of used alloys and a manufacturing process.

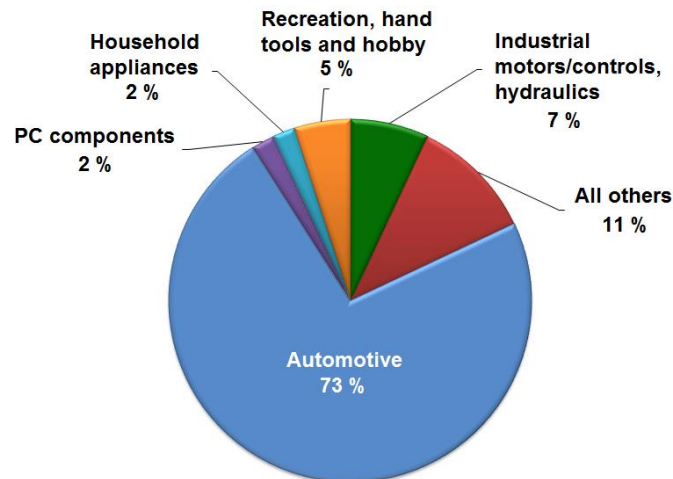


Fig. 8.1 Application of powder metallurgy products in various industrial branches.



Fig. 8.2 Application of powder metallurgy products in various parts of a passenger vehicle [1].

8.1 Fe-based PM products

8.1.1 PM products based on iron with low or medium strength

PM product strength values can be improved through two basic methods:

1. Decrease in porosity.
2. Alloying with appropriate additives.

Powder compressibility has a critical influence on a decrease in porosity of a sintered product. Fig. 8.3 shows that even unalloyed Fe powders differ considerably in density achievable after

pressing. When using all technological possibilities for compaction (pressing, sintering, forging after sintering, HIP) and having 5 % residual porosity, iron unalloyed powders enable to obtain a value of tensile strength around 300 MPa and ductility up to 25 %. A comparison of strength characteristics of the sintered iron and carbon steel, which are strongly dependent on density, powder properties and sintering conditions, is shown in Fig. 8.4. Main applications of the unalloyed iron powder are in a manufacture of machine parts for low loads and a manufacture of soft magnets working in direct current electrical fields.

Iron-based alloys can be prepared by various methods:

- a) Mixing of powders of elementary metals or pre-alloys.
- b) Diffusion alloying of powders.
- c) Using pre-alloys prepared e.g. by melt atomization.
- d) Mixing of powders of elementary metals and pre-alloys, the so-called hybriide alloys.

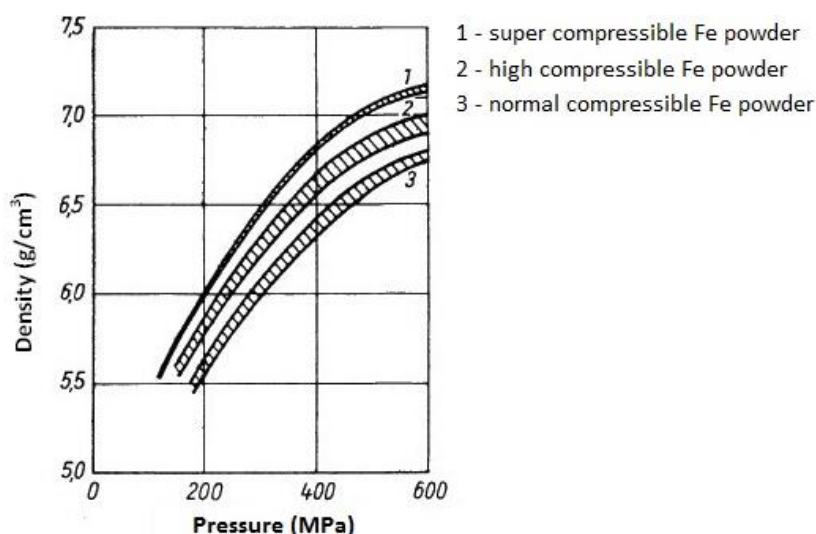


Fig. 8.3 Comparison of compressibility of various types of Fe-powders [2].

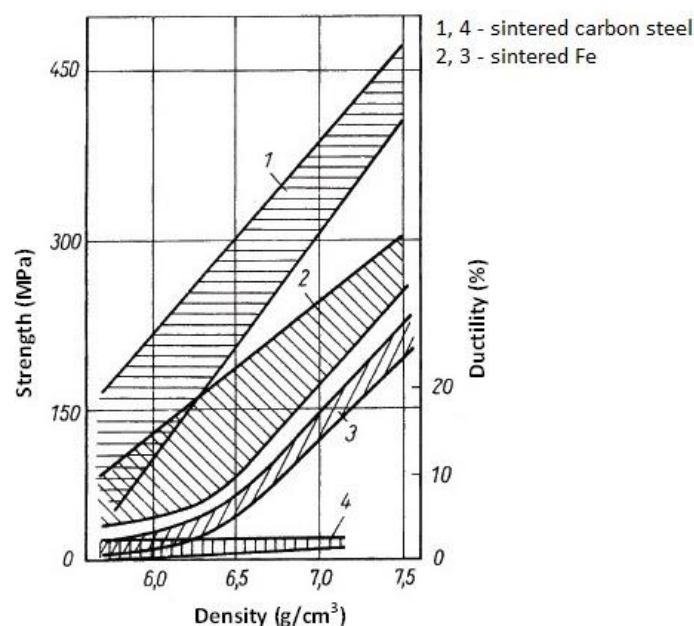


Fig. 8.4 Comparison of strength characteristics of the sintered iron and carbon steel [2].

Carbon steels exhibit a ferritic-pearlitic structure after sintering (Fig. 8.5a). At density c. 7.2 g/cm^3 ($\rho_{\text{rel}} = 90 \%$) and with hypoeutectoid content of C, their strength can be increased by hardening from 400 MPa to 700 MPa, leading to origination of a martensitic structure (Fig. 8.5b).

Aside from iron and steel powders, mixtures of powders of Fe and graphite or white cast iron containing around 3 % C and mixtures with partially decarburized cast iron powder are used. More wide-spread applications of Fe-C based sintered materials are limited by the following factors:

- A necessity of sintering in a non-decarburizing atmosphere which makes the technology more costly.
- Achieving a low ductility limiting their use for a narrow field, such as a manufacture of components for dampers.

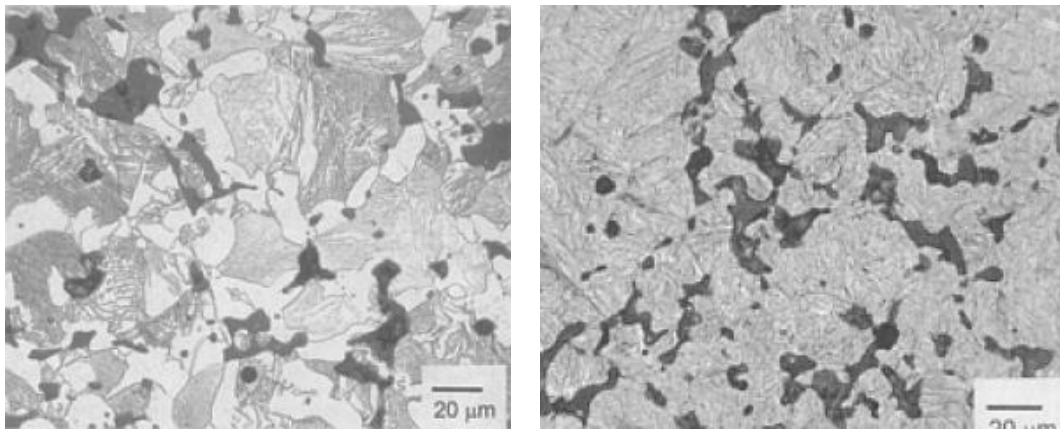


Fig. 8.5 Microstructure of low-carbon steel in a sintered condition (a – ferritic-pearlitic structure) and after heat treatment (b – martensitic structure) [3].

Other applications are iron-based alloys with Cu, Ni and Mo additives in a combination with C, possibly even P, which exhibit increased strength characteristics. For these alloys, strength of 400 to 600 MPa at ductility 2 – 20 % can be obtained by simple pressing and subsequent sintering. The above mentioned alloying elements have a very positive influence on powder metallurgy processes. Copper has a mild reducing effect to oxides, nickel and molybdenum facilitate the sintering process which, as a result of origination of bonds with alloying elements, can take place at lower temperatures below 1150°C . Precision of products can be also influenced by copper. The so-called infiltration (filling) with copper allows obtaining products with limited porosity and ensuing increased strength. The infiltration principle of filling-in interconnected pores in structural parts with an alloy of a lower melting point than the basic material is shown in Fig. 8. 6. Sintered products based on Fe-Ni, possibly Fe-Ni-Cu, which have also enhanced ductility and good weldability, exhibit similar or better strength characteristics than Fe-Cu alloys.

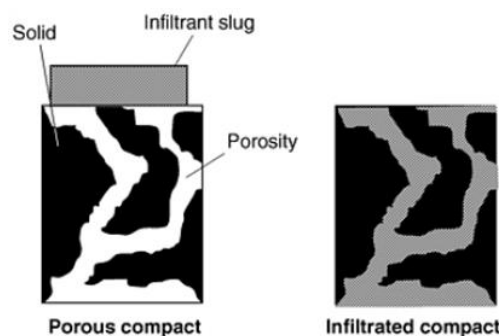


Fig. 8.6 Principle of infiltration of a product with copper [3].

8.1.2 High-strength iron-based PM products

Strength of 600 to 700 MPa, which can be obtained while maintaining optimal sintering conditions for Fe-Cu-Ni systems, can be further increased by alloying with carbon. However, higher carbon content deteriorates the powder compressibility and sintering has to be performed in a carefully controlled atmosphere or in vacuum. Products with density of 7.2 g/cm^3 , containing 7 % Ni, 2.5 % Cu and 0.7 % C, exhibit strength of 640 MPa, 3.5 % ductility and hardness 90 HRB in the sintered condition. In the hardened condition, strength increases up to 1060 MPa and hardness above 44 HRC, while ductility decreases down to 1 to 2 %.

For precision products, carbon in a combination with $\text{Ni} \leq 5 \%$ and $\text{Mo} \leq 2 \%$ allows for alloy treated steel. The developed high-strength steels containing c. 7 % Ni and 0.8 % C exhibit strength up to 900 MPa. Shrinkage exceeding 2% is a disadvantage, so this type of steel is not advisable for precision products. However, this drawback can be removed by a subsequent calibration of a product with follow-up alloying with shrinkage-limiting elements. An influence of various alloying elements on tensile strength and hardness is evident from Fig. 8. 7.

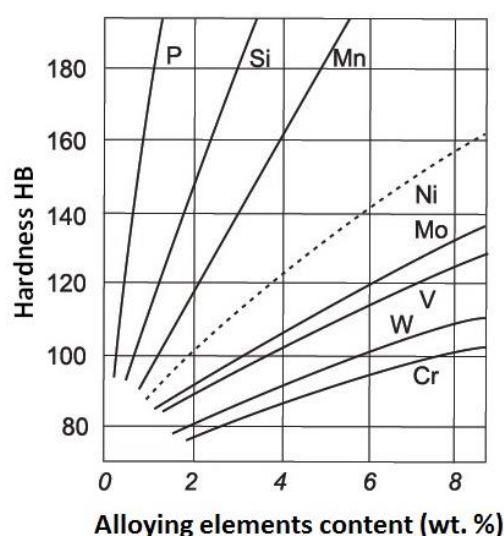


Fig. 8.7 Influence of alloying elements on iron tensile strength [2].

For PM, diffusion alloyed Fe powders are advisable, maintaining advantages of good compressibility of an unalloyed Fe powder and limiting disadvantages of multicomponent mixtures relating to their tendency to segregate. For example, Högenäs company manufactures Distaloy type powders (Fig. 8. 8) alloyed with Ni, Cu and Mo, which have pressing properties comparable to Fe powder. The demanded chemical composition of the steel is achieved by graphite addition, so the material is applicable even for hardening and heat treatment.

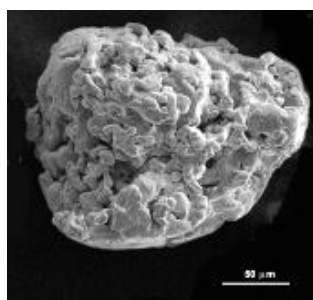


Fig. 8.8 Fine particles of copper, nickel and molybdenum diffusion bonded to the surface of Fe particles (Distaloy process) – SEM image [4].

The manufacture of PM products of powder steels alloyed with all component elements has to cope with problems ensuing from a low formability of particles (unsatisfactory pressing properties), a need for sintering at higher temperatures ($\geq 1250^\circ\text{C}$) and maintaining an exact composition of the protective atmosphere.

Carbides, e.g. Cr_2O_3 , being relatively oxidation-resistant and well-diffusible to iron, have a favourable effect on sintering pre-alloyed components of a powder mixture.

Steels alloyed with manganese for the manufacture of precision products are preferred due to their good hardenability and low costs for alloying elements. However, a diffusion-dependent formation of alloys in order to reach the demanded properties requires sintering temperature around 1280°C , a dry protective atmosphere (cracked ammonia) with an additional purification on getters (an active material which chemically bonds or adsorbs gas atoms or molecules and at the specified conditions does not release them anymore). The sintering process is speeded-up by a formation of a transition liquid phase which originates on the basis of the origination of compounds (eutectica) based on Fe-Me-C (Me - alloying element) with the melting point ranging between 1080 to 1210°C . Shrinkage, which these steels tend to, can be compensated by Cu addition by 2 %. As steel hardenability is strongly density-dependent, a technology of their manufacture is based on double sintering, possibly forging of powders. The hardenability-density relation for steel is shown in Fig. 8.9.

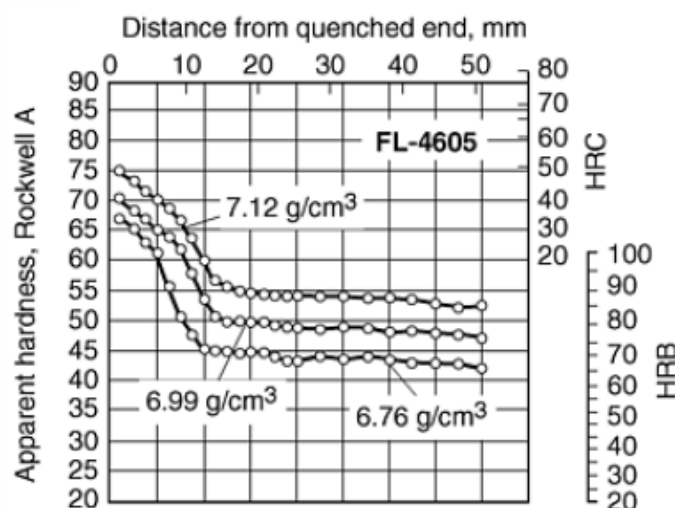


Fig. 8.9 Relation of hardenability to the sintered steel density (1.8 % Ni, 0.65 % Mo) [3].

Shaped products with density of 7.3 g/cm^3 and strength of 700 MPa can be obtained by double pressing and sintering. Strength can be increased up to 1000 MPa and density to 7.7 g/cm^3 by subsequent forging. A further increase in strength ranging from 1190 to 1950 MPa is performed by steel ageing.

8.1.3 Stainless steel PM products

For metastable austenitic Fe-Ni and Fe-Cr-Ni alloys, strength $\geq 1500\text{ MPa}$ can be achieved by thermomechanical processing even at maintaining an excellent ductility. Similar properties of these alloys can be achieved also by powder metallurgy. The Maraging-type steel with a high content of alloying elements can have a following composition: 15 % Ni, 7 % Co, 5 % Mo and $\leq 3\%$ Ti or Al. These austenitic steels, which are vacuum-sintered, after martensitic hardening reach strength ranging between 800 up to 1800 MPa and ductility to 4%. However, the manufacture of precision products is made difficult due to high shrinkage (to 3 %) Ti or Al presence in hardenable steels affects a formation of segregated intermetallic compounds (e.g. Ni_3Al), however, a high affinity of these metals for oxygen hinder sintering processes in a protective atmosphere. Generally, the mentioned obstacles

can be overcome by increasing alloying elements to 18 % Ni, 8 % Co and 7 % Mo without Ti and Al. In the cases, when a requirement for high corrosion resistance is imposed on steels, ferritic and austenitic steels are used. By reason of guaranteed homogeneity, both these types of steels can be made using powder metallurgy technology from a mixture of components or steel powders of a demanded composition. In spite of a high affinity of chromium for oxygen, in particular chromium-nickel steels have found their usage in powder metallurgy. For sintering a highly pure and dry gas is used, such as cracked ammonia, hydrogen or vacuum. Mechanical properties and corrosion resistance of compacts strongly depend, next to powder properties, also on sintering conditions, in some case on possibilities of oxide coating reduction and preventing re-(further) oxidation. The sintering temperature usually ranges between 1120 to 1320 °C, whereas the sintering time is around 120 min. A relation of a length change (shrinkage) and strength characteristics on sintering conditions is evident in Fig. 8. 10. Dimensions of stainless steel products vary from the smallest ones for electronics and fine mechanics to medium dimensions for machines, transport technology and household appliances.

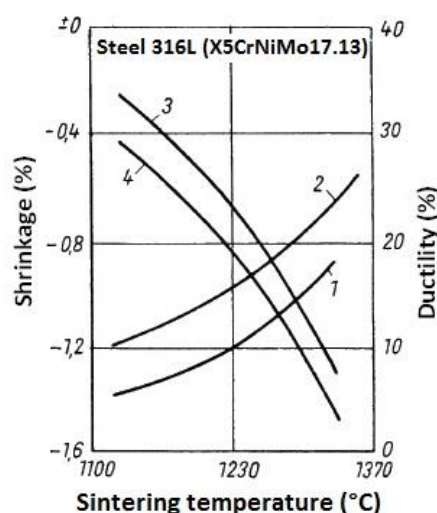


Fig. 8.10 Relation of a length change (shrinkage) and strength characteristics on sintering conditions
1,3 – ductility, or more precisely shrinkage, after sintering in cracked NH₃; 2,4 - ductility, or more precisely shrinkage, after sintering in hydrogen [3].

If high requirements for precision were specified, the technology of double sintering is used, which reduces shrinkage and improves ductility, however, its influence on an achieved strength is only negligible. Admixtures which form a liquid phase during sintering, such as alloys alloyed with boron or Cu₃P and Ni₃P, represent an alternative to the double sintering. A highly densifying effect allows decreasing a sintering temperature below 1250 °C. Strength of these steels reaches a value of 500 MPa at ductility 12 to 20 %. An achieved density ranges between 7.3 to 7.75 g/cm³, however, it is accompanied by a high shrinkage (above 3 %). A residual porosity decreases the steel corrosion resistance, when an uneven corrosion promoted in pores can occur at unfavourable conditions.

8.1.4 Sintered high-speed steels

High-speed steels belong to a group of ledeburitic steels. When these types of steels solidify, an inhomogenous structure originates as a result of macro- and micro-segregation of primary carbide crystals (Fig. 8.11). Elimination of chemical composition inhomogeneities is reached through casting ingots of smaller dimensions and accelerated cooling of a melt. Obtaining the demanded hardness, cutting properties, wear resistance and a shape stability of the tool is ensured by high degree hot forming, the result of which is a change in the material structure.

Powder metallurgy allows avoiding macro-segregation through the melt atomization and reducing substantially also micro-segregation by rapid cooling and solidification of the obtained

powder particles. Refinement of high-speed steel powder particles, which would result in improved compressibility, is not applicable due to a non-permissible oxygen content increase. The increased oxygen content hampers maintaining the accurately specified C content, which determines the final steel hardness.

A satisfactory solution for achieving high density (porosity $\leq 1\%$) consists in the application of sintering by forging and for a manufacture of semi-products hot isostatic pressing. Another economically profitable alternative is a manufacture of shaped tools by powder die pressing and by sintering, whereas the used powder is obtained by a melt atomization with a follow-up heat treatment for improvement of compressibility. After die pressing or cold isostatic pressing, compacts are sintered in vacuum at temperature $\leq 1200\text{ }^{\circ}\text{C}$ for a period of 30 to 240 min.

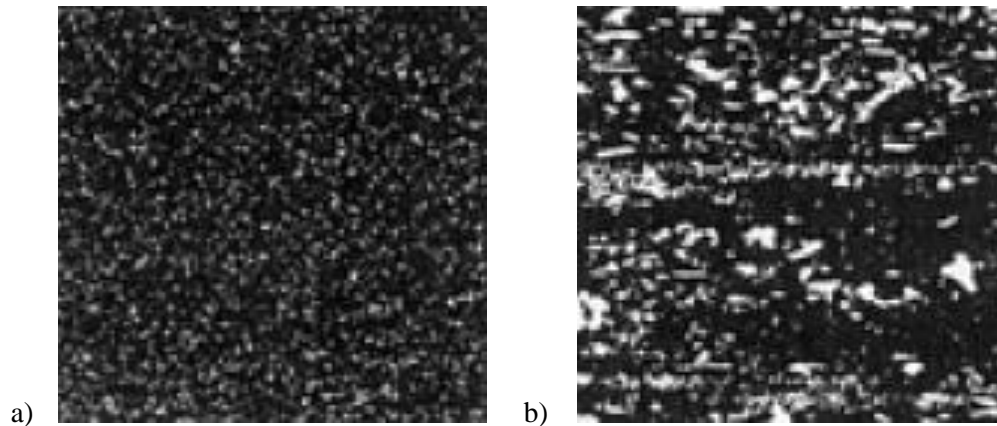


Fig. 8.11 Comparison of a tool steel microstructure manufactured by powder metallurgy (a) and casting (b) [3].

The first state-of-the-art manufacturing procedure for products from high-speed steel powders consists in the steel atomization by an inert gas with an origination of spherical particles with a size around $100\text{ }\mu\text{m}$ and oxygen content $< 100\text{ ppm}$, in cold isostatic pressing and hot pressing into blocks (Fig. 8.12). Forging or rolling follows. The residual material of a capsule is removed in the final manufacturing phase e.g. by lathe-turning, milling, etc.

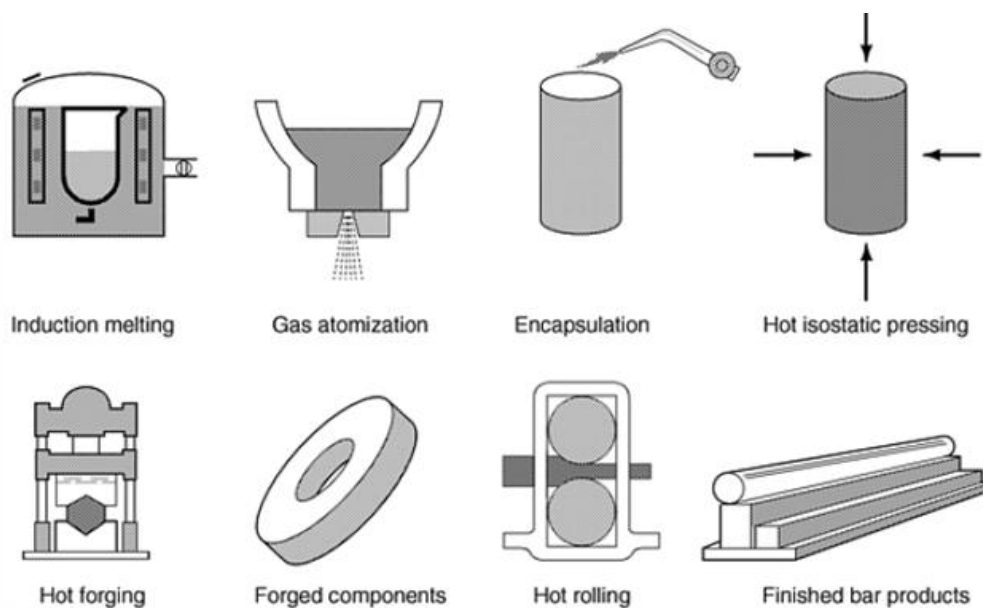


Fig. 8.12 Schematic depiction of particular steps of the manufacture of high-speed steels [3].

8.2 Non-ferrous metal PM products

Regarding to their price and lower strength values, the amount of sintered products of non-ferrous metals is lower in comparison with steel products. These materials do not offer any advantages in term of strength to weight ratio. They are preferred in cases, when a sintered material features higher electrical and thermal conductivity and higher corrosion resistance. Chemical stability in copper-based products is comparable to austenitic chromium-nickel steels and in 65 % Ni + 35 % Cu alloys reaches still higher values of resistance under specific conditions. In contrast to stainless steels, for these types of materials there are no problems with a preparation by powder metallurgy technologies. These facts and functional possibilities offered by non-ferrous metal sintered products are used e.g. for a manufacture of filters, friction bearings, friction materials and contacts in electro-technical applications.

8.2.1 Copper-based sintered products

Copper powders allow achieving high density after pressing. The sintering takes place at relatively low temperature using protective atmospheres of various compositions (cracked NH_3 , N_2 , H_2 ...). To avoid hydrogen disease, well dried-up protective gases and above all pre-reduced Cu powders need to be used. A special attention needs to be paid to brass sintering, where evaporation of zinc needs to be avoided. In this case, sintering is carried out either in closed retorts, where a demanded partial pressure of Zn is set or in the presence of CO, which prevents zinc oxidation during sintering.

The sintering temperature of Cu and alloys ranges between 600 to 1000 °C, for Cu-Ni alloys can reach up to 1300 °C. The sintering time ranges from 30 minutes up to several hours - for example for Cu-Ni powder mixture the sintering time is up to 8 hours in order to ensure high homogeneity of the alloy. The material can be prepared from pre-alloyed powders with some % of alloying elements or by mixing elementary elements resulting in origination of a powder mixture.

In comparison with iron powders, lower compacting pressures are used. To ensure density of 7 g/cm³ (20 % porosity), a pressure of 350 MPa is needed, for density of 8 g/cm³ (9 % porosity), a pressure of 650 MPa is needed. Aside from the compacting pressure variation, higher density can be reached by using a proper combination of % proportion of powder size fractions. An increasing content of alloying elements such as Zn or Sn deteriorates powder pressing properties. In Fig. 8. 13, strength characteristics of sintered products based on non-ferrous metals, which are dependent on their final density, are evident.

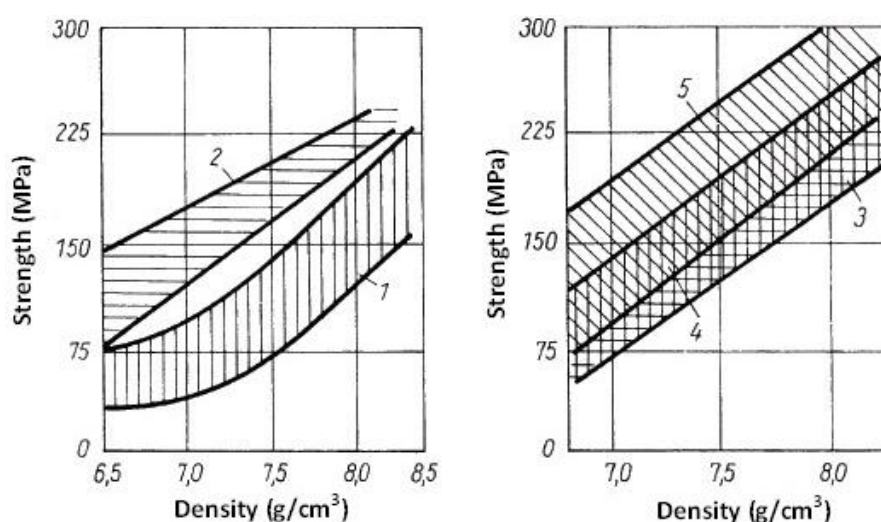


Fig. 8.13 Strength characteristics of sintered products based on non-ferrous metals depending on density: 1 – copper, 2 – CuSn10, 3 – CuZn10, 4 – CuZn20, 5 – Ni-Ag [2].

Generally low strength of copper, achieved particularly at low density, and relatively high shrinkage, which relates to the high sintering temperature, can be prevented by double sintering. From the point of view of electrical conductivity, not even highly pure copper materials with very high relative density achieve values of OFHC copper (oxygen free, high conductivity).

For bronzes, the application of double sintering is necessary in cases they are made from a powder mixture of elementary elements and high homogeneity of the alloy is demanded. Compacts tend to increase their volume, which is caused by a formation of mixed crystals (they have a larger specific volume) with smelted Sn which dissolves in Cu. Products from alloyed bronze powders feature a negligible shrinkage only when powder is subjected to homogenous annealing prior to pressing, i.e. δ -phase is removed. Brasses and Cu-Ni alloys also tend to shrink in the mentioned field of achieved densities.

Beryllium bronzes and Cu-Ti alloys take up a special position among copper-based sintered materials. For a preparation of Be-bronzes with 2 % Be, electrolytic Cu powder and a pre-alloy Cu-Be with 26 % Be is used. At density 8 g/cm³, after solution annealing and hardening for a period of 3 hours at temperature of 310 °C, they reach hardness 195 HB. A homogenous structure can be obtained by sintering a heterogenous powder mixture at temperature of 840 to 920 °C for a period of 3 to 8 hours.

Regarding Be toxicity, Cu-Be alloys require special precautions and their preparation, requiring homogenous chemical composition before solution annealing, is time-consuming. On the contrary, sintering of Cu-Ti alloys with 1.5 to 5 % Ti is quite simple. These alloys are prepared from mixtures of powder metals (powder of an alloy of a demanded composition is not advisable due to a formation of Ti oxides on particle surfaces) with a particle size $\leq 40 \mu\text{m}$, hydrogen pre-reduced at temperature $\leq 500 \text{ }^\circ\text{C}$. The powder mixture compressibility corresponds to the copper powder. Sintering takes place at temperature 900 to 1000 °C for a period of 2 to 30 minutes in an inert gas protective atmosphere which eliminates hydridation of Ti. Above 900 °C, a eutectic, possibly over/above-eutectic, melt originates, which accelerates homogenization and densification of the heterogenous mixture during sintering significantly. A formation of compounds can be controlled by a choice of sintering conditions, so that high electrical conductivity with lower hardness can be obtained after hardening at only partial solution of Ti in Cu in the sintered material or high hardness at lower electrical conductivity can be obtained at an extensive solution of Ti. For alloys containing around 3 % of Ti, a reachable hardness is observed preferably. For alloys containing around 1.4 % of Ti, very favourable electrical conductivity is achieved a value of which depends on the temperature of sintering and dissolving of Ti in Cu.

8.2.2 Aluminium-based sintered products

In term of the use, aluminium-based sintered materials offer a favourable strength to mass ratio in a range up to 450 MPa, a favourable corrosion resistance and applicability to electrochemical surface finishing (eloxing) in comparison to iron-based materials. Problems occurring during sintering relate to oxides on particle surfaces and originate usually during the manufacture of the powder. Oxygen content in powders is usually $\leq 2 \%$, whereas oxides are not reducible during the sintering process. A preparation of Al powders using a melt atomization by an inert gas allows the oxygen content decrease below 0.3 %.

Powders of unalloyed Al (with a content of c. 0.15 % Fe, 0.1 % Si, 0.3 % Al₂O₃), Cu, Mg, Mn, Zn or Si are used for the manufacture of shape products. Powders of the mentioned admixture elements exhibit a thermally dependent solubility of Al, which allows hardening of sintered products. During the sintering process new phases originate, including low-melting ones, which homogenize the powder mixture in the course of the sintering process. To promote sintering, all alloys contain Mg which assists in breaking an oxide layer on the Al-particle surfaces before sintering by forming AlMg eutectics at 450 °C, with a subsequent formation of MgAl₂O₃ spinel.

Powder mixtures are compressed at 140 to 550 MPa. Regarding high ductility of aluminium, higher density can be achieved than for Fe or Cu powders. Sintering usually takes place in nitrogen,

less in vacuum or cracked ammonia. Other reducing or inert atmospheres lead to impaired properties of the sintered material. Unalloyed powder can be fully densified without undesirable dimensional changes by cyclic sintering at temperature of 600 to 660 °C for a period of 1 hour in vacuum. Powder mixtures require a careful control of the sintering process because of a formation of new phases (compounds).

Basic aluminium-based alloys made by powder metallurgy include:

- 1. Al-Si - based alloys** – PM methods allow preparing materials with a fine and homogenous microstructure which cannot be obtained by conventional methods (casting), such as hypereutectic alloys of Al-Si type (Si content higher) than 20 % - Al26Si8Ni). Silicon has very low solubility in aluminium therefore it precipitates as pure silicon, enhancing wear resistance of the material by its hardness. An increase in mechanical properties and thermal stability of a structure can be achieved by alloying with Ni, Fe, Mn, etc. Ni with Al create an important intermetallic phase Al₃Ni, which is temperature stable as a result of low Ni diffusivity and very low solubility in Al. Al₃Ni particles strengthen grain boundaries and prevent their growth at elevated temperatures.
- 2. Al-Fe - based alloys** – are prepared by a rapid solidification method (e.g. the melt atomization). Alloying with iron increases aluminium strength at high temperatures thanks to dispersion of secondary phase particles. Intermetallic phases Al₃Fe₂, Al₃Fe exhibit very high melting temperature. Al-Fe-X – type alloys (X = Ce, Mo, Cr, V) feature very good mechanical properties at elevated temperatures. Strength and high temperature stability is determined by finely dispersed particles of incoherent intermetallic phases which hamper grain boundary motion. Mechanical alloying enables to obtain alloys with extremely fine grains which are stabilized by fine dispersion particles of aluminium oxide and carbide. Due to an ultrafine microstructure, these alloys exhibit high strength characteristics. Mechanical alloying technology enables to obtain alloys with extremely fine grains which are stabilized by fine dispersion particles of aluminium oxide and carbide.
- 3. Al-Mg - based alloys** – are prepared by mechanical alloying and feature increased strength, while not decreasing toughness and corrosion resistance. For example, Al4Mg0.8O1.1C and Al4Cu1.5Mg0.8O1.1C alloys feature an attractive combination of tensile strength, fracture strength, toughness and corrosion resistance. An advantage of these alloys is a decrease in specific weight by 5 % in comparison with other high-strength alloys (applications in the aircraft industry).
- 4. Al-Ti – based alloys** – are prepared by mechanical alloying. Ti has very low solubility in Al. A noticeable refinement of titanium particles occurs during the milling process and TiAl₃ particles originate through a subsequent in situ reaction in the heating process during the powder compaction. These alloys exhibit an ultrafine temperature stable structure with fine and homogeneously distributed TiAl₃ particles (20 up to 250 nm).
- 5. Al-Al₄C₃ - based alloys** – these dispersely hardened alloys (e.g. DISPAL and TEDAL) are prepared by the reaction milling method. The alloy structure depends on an amount of Al₄C₃ dispersoid ⇒ the DISPAL material structure with 1 vol.% of dispersoid is characterized by non-equiaxed grains elongated in the direction of extrusion pressing with a size of 1.4 to 1.6 mm in the direction perpendicular to the pressing direction; the material structure with 10 vol.% of Al₄C₃ is formed by equiaxed grains with a size of 0.6 to 0.8 mm ⇒ significant structural changes influence the strength characteristics.
- 6. Al-Al₂O₃ - based alloys** – are prepared above all by a powder mixture extrusion pressing. Hardening of these alloys is based on a superposition of the dispersion strengthening by oxide particles and subgrain strengthening.

In Fig. 8.14, the strength and hardness temperature dependences of various aluminium-based sintered products are depicted.

Al-alloys obtained by the rapid solidification method can be divided into three basic groups in term of their properties and applicability:

- **High-strength wear-resistant and corrosion-resistant alloys** - Al-Si, Al-Si-Fe, Al-Zn, Al-Zn-Mg-Cu-Ni-Zr. Applications: in the automotive industry for a manufacture of pistons, weight levers, connecting rods, synchronizing rings, brake hubs and discs, parts for compressors (blades, rotors, bushings) and for electronic components.
- **Alloys for the use at elevated temperatures (480 °C)** - Al-Fe-Mo, Al-Fe-Ce, Al-Fe-C-Si, Al-Cr-Zr. Applications: in the aircraft industry as a substitution for titanium alloys for airplane structural parts; their advantage is a decrease in weight by 10 to 12 % for supersonic and combat airplanes and by 5 to 10 % for transport airplanes.
- **Alloys with a low specific weight and an enhanced elasticity modulus** - Al-Li, Al-Li-Zr, Al-Li-Mg, Al-Li-Cu, Al-Li-Cu-Mg, Al-Li-Cu-Mg-Zr. The main alloying element is lithium in a range of 1.5 to 3.5 %, which allows a decrease in a product specific weight by 7 to 12 %; each percent of lithium in the alloy decreases the specific weight by 3 %, while increasing the modulus of elasticity by around 6 %.

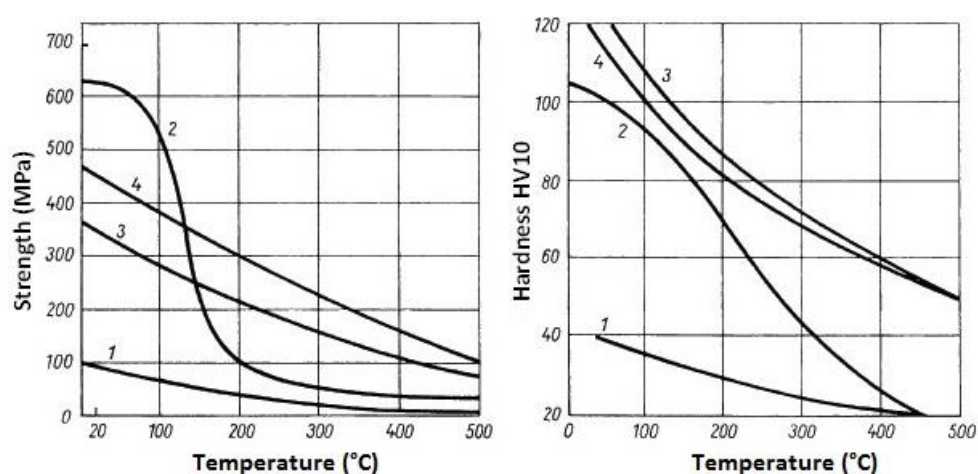


Fig. 8.14 Strength and hardness temperature dependences of various aluminium-based sintered products: 1 – 99 % Al; 2 – AlZnMgCu; 3 – SAP with 10 % Al_2O_3 ; 4 – Al with 4 % C as Al_4C_3 [2].

8.2.3 Titanium-based sintered products

Around 65 % of titanium-based sintered products find their usage in the aircraft technology. Compared to the conventional production, components manufactured by powder metallurgy bring 50 up to 80 % of savings in the machining and 70 to 80 % savings in material.

Titanium-based sintered products are prepared from a pure titanium powder mixture and alloying elements or a pre-alloyed titanium powder and alloying elements, in some case powder of an alloy of an appropriate composition can be used. Powders are well cold compressible in a die or using the isostatic pressing. Sintering takes place in high vacuum between 1100 to 1300 °C. Alloyed powders compressible with difficulties are formed at temperatures of 900 to 950 °C by die pressing, possibly by isostatic pressing or are forged from pre-sintered semi-products.

Static strength of sintered parts (tensile strength, yield strength, fracture strength) is comparable or better than for rolled or forged materials, however, formability is a bit lower. Enhanced demands for dynamic strength can be met through achieving high density using the HIP method, which virtually corresponds to the compact material density. The most widely used alloy is TiAl6V4.

8.3 Sliding materials and sintered bearings

Porous, oil saturated bearings are the most widely used bearings not requiring any maintenance. Their proportion among sintered bearings is 70 % at minimum. They exhibit 15 to 30 % porosity, whereas 98 to 99 % of pores are interconnected. In accordance with a selection of the initial

powder, the pore size can be 1 to 20 μm . 500 up to 2000 open pores fall on 1 mm^2 . A length of porous channels ranges between 1000 to 2000 m/cm^3 of the bearing material. Pores are saturated with age-resistant oil, which does not require an increased care for a long-term lubrication.

A formation of a lubricating film on a compact bearing with an external oil supply is different from a formation of a lubricating film on a porous bearing. On a compact bearing the carrier liquid layer is formed by hydrodynamic pressure which originates in a gap between a surface of a shaft and a bearing as a result of a relative motion of the surfaces. A required thickness of the carrier layer is formed, when a specified sliding speed has been achieved.

On porous, oil-saturated materials an equilibrium state occurs in a gap in a rest state; the equilibrium state has occurred between a shaft and a bearing under acting of capillary forces. This implies that just from the beginning of the motion, there is an oil film between a shaft and a bearing which creates favourable starting-up conditions. While increasing a load of the shaft, the gap between a shaft and a bearing surface grows less in the direction of loading. Advantages and special features of the use of sintered bearings include:

- excellent properties in still and emergency conditions;
- applications in installations, when pollution with dropped-down lubricant is not permissible;
- applications for oscillating movements and low speeds of gliding surfaces, where a continuous oil film cannot be created on compact bearings;
- applications for vertical or inclined positions, where a lubricating oil could drain-off from compact bearings;

Nevertheless, porous bearings have also drawbacks, such as:

- oil-saturated porous bearings have limited circumferential speeds of supported shafts owing to a thin thickness of the created film;
- due to a considerably high proportion of pores, sintered bearings have low strength and they are sensitive to impacts and bruising by edges in comparison with a compact material.

For sintered bearings, tin bronzes 90/10 and Fe-Cu alloys are preferred, which can contain admixtures of graphite, lead or MoS_2 . The initial materials for the manufacture of sintered, oil-saturated bearings are powder alloys prepared by gas and water atomization, particles of which show rugged shapes. In order to reach a demanded porosity, pressures of 200 to 300 MPa are used. Porosity and a volume of pores can be controlled by a choice of a proper form of particles, their size distribution and technological parameters. Under standard conditions, a service life of bearings is 3000 – 4000 hours, under optimal conditions up to 10000 hours.

8.3.1 Composite materials metal – lubricant

For higher demands on sliding properties and for elevated temperatures, metal-based materials with solid lubricants implemented-in are applied. Cu-Sn, Cu-Pb, Cu-Zn, Cu-Ni, Cu-Al, Cu-Sn-P, Fe-Ni and Fe-Mo alloys, possibly Ni, Co and Al - based alloys, are used as matrices. The commonly used lubricants are graphite, MoS_2 , less often Bi, Pb, ZnS, Cu_2S , CdS, CaF_2 , BaF_2 , WSe_2 , NbSe_2 , etc. A graphite proportion ranges from 10 to 30 %. However, while the graphite content increases, the composite material strength drops sharply, therefore the maximal proportion is controlled by the lower permissible strength limit.

Iron and alloys prevail as a metal matrix. In the case of higher demands for corrosion resistance, Cu-based, or Ni-, Co-, W- and Mo-based materials are used, or Cr-Ni steels. Except from a composition, properties of sliding materials with a solid lubricant depend also on a structure of implemented-in particles. For example, for iron-based materials the sliding properties depend on a proportion of ferrite, pearlite and free cementite, on a kind of the lubricant and a method of implementing-in, and porosity is very important as well.

At present days the use of self-lubricating porous bearings is wide-spread and they are applied

e.g. in difficult-to-access places with a troublesome service, in locations, where lubrication would depreciate products, in equipment, where a silent run is demanded, etc. They are sintered from powder materials, so that a product contains 15 – 30 % of uniformly distributed pores, around two thirds of which should be open. Prior to use, the pores get saturated with oil (grease), which penetrates between the friction surfaces and prevents dry friction, while the equipment is running. The basic material for the manufacture of self-lubricating bearings is a leaded bronze (10 % Pb), then there are bearings based on iron powder, iron and copper powder, possibly aluminium powder. Pressing the powder mixture at lower pressures (200 to 300 MPa) and lower sintering temperatures (750-900 °C for Cu, 950-1150 °C for Fe) ensures the appropriate porosity. Examples of self-lubricating bearings are shown in Fig. 8.15.



Fig. 8.15 Examples of commercially manufactured self-lubricating bearings [5].

Very high requirements for sliding properties can be ensured by using materials alloyed with sulphur. Sulphur and compounds decrease the friction coefficient in iron-based materials, increase the wear resistance and promote the fine lamellar pearlite origination. Sulphur is applied in an elementary form or as FeS, Cu₂S, ZnS, PbS, but particularly Mo₂S in an amount to 2 %, graphite content is usually 1 to 3 %. Good friction conditions are based on a formation of oxide and sulphide surface layers.

8.3.2 Carbon and graphite materials

Materials based on carbon and graphite can be largely modified owing to their tribological properties. Carbon and graphite thermal conductivity has the same order of magnitude as for the plain steel, thermal expansivity is around $\frac{1}{2}$ to $\frac{1}{4}$ of steel expansivity, modulus of elasticity is 10 – 20fold lower than for the plain steel. Compressive strength is around tenfold higher than tensile strength.

Mechanical properties of these materials depend only slightly on temperature. The use of these materials in the air is limited to temperatures 350 to 500 °C due to their tendency to oxidation. Carbon-based materials are resistant almost to all chemicals, with the exception of highly concentrated oxidizing acids and molten alkalis.

Low lattice cohesion on the graphite surface is strengthened by an adsorbed water vapour. For a critical value of partial water vapour pressure (400 Pa), the friction coefficient grows and wear increases. Graphite and carbon bearings can be applied in water vapour environment to temperatures of 650 °C and in CO environment to 750 °C.

Carbon materials are prepared from mixtures of various types of carbon products and bonding agents (resin, pitch), compacted and annealed subsequently. The carbonization (pyrolysis) of binders occurs and carbon bridges originate, ensuring cohesion between carbon particles. Amorphous carbon adopts a graphitic structure above 2000 °C. The product properties depend strongly on the initial form of carbon and conditions of the preparation. After a heat treatment, porous carbon materials can be saturated by high-molecular polymers, low-melting metals (Pb, Sn, Sb) or a solid lubricant (MoS₂). Another technology of preparation uses a mixture of graphitized carbon, resin, metal powder and solid

lubricant. The mixture is hot-compressed into a demanded bearing shape. Depending on conditions of the preparation the material can contain 5 – 7 % of high-molecular polymers (a phenolic resin) or up to 30 % of metal in a carbon matrix.

In practice, carbon bearings can be used under similar conditions as self-lubricating metal-graphite composite materials (Fig. 8.16).



Fig. 8.16 Examples of commercially manufactured graphite bearings [6].

8.3.3 Composite materials metal – PTFE (polytetrafluorethylene)

They find their use when requirements for self-lubricating properties arise, which cannot be met by oil-saturated materials. Low mechanical strength of PTFE causes their creep just at the room temperature, which together with high wear limits their use in a form of composite materials. Wear can be reduced by several orders of magnitude using the proper filler. Minimum wear is commonly reached for materials with the filler content around 40 %.

A preparation of the material involves mixing additional components with PTFE powder, the mixture compacting and sintering at temperature of 360 °C in an inert gas or vacuum. For mechanical and tribological properties to increase, multiple sintering and pressing is applied. Examples of various types of bearings based on metal-PTFE are shown in Fig. 8.17.



Fig. 8.17 Examples of various types of bearings based on metal-PTFE [7].

8.3.4 Sintered materials for demanding conditions

Bearings, which are to resist high specific pressures and enable operation at high temperatures with demands for self-lubricating properties, are manufactured by powder metallurgy technology from alloys based on Mo, W and Co or based on Cr-Ni steels. After sintering, porous materials are saturated by molten inorganic fluoride. Bearings based on Cr-Ni steels can either perform their function in

oxidation atmosphere to 700 °C or in non-oxidation atmosphere to 900 °C. Bearing materials of the mentioned types have been developed for rocket engines and other high-temperature applications, such as molten salt pumps, nuclear technology equipment etc. The bearings are applicable for circumferential speeds ranging between 6 up to 60 m/s.

If extremely long operating life is required for bearings, materials based on WC-Co (10 – 15 % Co) and TiC-NiMo hardmetals are used. Lubrication is ensured by oil, water or water solutions. Bearings for hot water pumps and chemical equipment for high-temperature synthesis are examples of the use. Hardmetal bearings are applicable also for dry operating conditions at elevated temperature (WC-Co to 500 °C, TiC-NiMo to 700 °C).

Sintered materials with a steel matrix and TiC addition are advisable for liquid-lubricated bearings. TiC content can reach up to 50 %. The steel matrix is adapted to operating conditions. Cr, Mo, Co, W etc. are used as alloying elements. The materials can be hardened.

8.4 Friction materials

A friction material manufactured by powder metallurgy technology is a material prepared from a mixture of metal, possibly even nonmetal, powders, exhibiting a high friction coefficient stable in a broad temperature range and having high abrasive resistance. These friction materials, sometimes designated as metal-ceramic or composite friction materials, must combine two properties in a balanced way – an ability to transfer high torque by friction and to ensure a defined glide of the frictional couple. These materials are used in brake (brake pads) and clutch systems (e.g. linings) to convert kinetic energy to thermal energy, while motion mechanisms are accelerated or slowed-down, eventually stopped. They can work dry or in oil.

High requirements are imposed on friction materials which must ensure not only high performance, but also a space-saving solution and a low weight of the used material. They exhibit enhanced stability of properties at high service temperatures and high thermal conductivity which can be improved by thermal balance of the frictional couple significantly. Powder metallurgy technology allows manufacturing of composite materials based on a basic metal, for friction materials this is iron and bronze, and a non-metal - SiO₂, graphite, Al₂O₃, mullite, MoS₂, BaSO₄ etc. The friction coefficient is enhanced by SiO₂, Al₂O₃, mullite etc. Graphite, MoS₂, possibly lead, act as solid lubricants which prevent seizure. The friction coefficient for these materials ranges from 0.2 to 0.6. With higher friction coefficients seizing occurs, with values lower than 0.2 the friction areas would be extremely large. For medium to high performances the main additive to the metallic matrix is graphite. For high performance machines, over-loaded transport means and mining equipment, or for airplanes, ceramic materials are applied as well.

Requirements for friction materials:

- the friction coefficient has to be independent of operating conditions;
- elimination of seizing;
- ability to resist high thermal loading;
- adequate thermal conductivity;
- satisfactory strength.

Other material requirements include fine engagement, rapid vapour dispersion, corrosion resistance and possible independency of friction characteristics on ambient conditions (temperature and humidity of air, pressure etc.).

8.4.1 Manufacture of friction materials

A manufacture of friction materials consists in mixing powder raw materials in a demanded ratio and granulometric composition, pressing this mixture into required shapes onto copper plated

sheets, sintering the obtained semi-products in a protective atmosphere (N_2 , H_2 , cracked NH_3) under applied pressure and subsequent finishing operations (coining, smoothing, calibration etc.).

A high proportion of non-metal dust particles requires for metal powders to create a solid matrix. A high sintering activity of powders is important, therefore sponge and dendritic powders with a high surface activity and particle size $> 150 \mu m$ are used preferably. The powder activity may be increased e.g. by milling. Sintering in the presence of a liquid phase is used, too. Forming of powder is carried out mainly by pressing under pressures of 200 to 400 MPa. For Cu-based products sintering takes place at temperatures of 600 to 950 °C, for Fe-based products at temperatures of 950 to 1150 °C for a period of 1 to 3 hours. In most events the friction materials are sintered with steel carriers under pressure 0.1 to 4 MPa. Cohesion can be enhanced significantly using fluxing and soldering agents. Cu-based friction materials for operation in oil are often sintered in the loose condition in heated containers or sintered on plates on which a work layer is created. Rolling of powder mixtures is used, too, or rolling-on to plate carriers.

8.4.2 Cu-based friction materials for dry operation

These materials are applied in the manufacture of high-performance clutches and brake systems. As a matrix, Cu-Sn bronzes are prevailing; Cu with Mn, Ni, Cr, Co etc. alloys are used as well. Cu-Ti system is very interesting; its favourable course of sintering and hardenability predestinates its use in friction mechanisms for high performances. Mechanical properties can be influenced by compacting pressure and sintering temperature. For example, for Cu-Sn bronzes with graphite, yield strength can be improved by 20 to 30 % through an increase of sintering temperature from 750 °C to 850 °C. In Fig. 8.18, a relation of friction and abrasion properties of a friction composite (70 % CuSn10) to a varied Pb, SiO_2 and graphite content is depicted. Full lines refer to regions of the friction coefficient constant values, the dashed line refers to a region of wear. It is evident from this figure that the high content of lead and graphite is needed for good wear resistance, while SiO_2 content must be $\leq 10 \%$. Higher contents of SiO_2 cause an intensified formation of layers of oxide silicates on a contacting area, which have only a negligible cohesion with a basic material and increase abrasion wear.

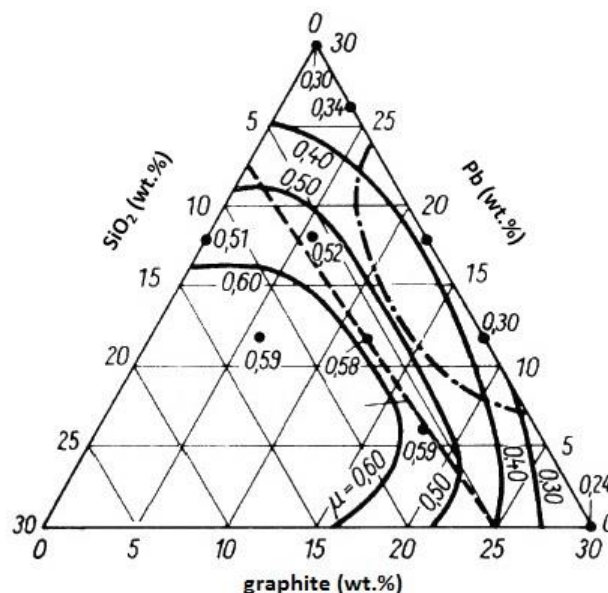


Fig. 8.18 Relation of tribological properties to the composition (Pb, SiO_2 and graphite) of a friction composite (70 % CuSn) [2].

As a counterpart in the frictional couple, gray cast iron, carbon steel, treated low-alloyed, non-hardenable as well as hardenable steels are applicable. The mentioned frictional couples are used for

tractors, ground and road construction equipment, cranes, airplanes, presses, cableways, hoisting devices, braking engines and equipment for chipless machining. In Fig. 8.19, an example of copper-based brake lining is shown.

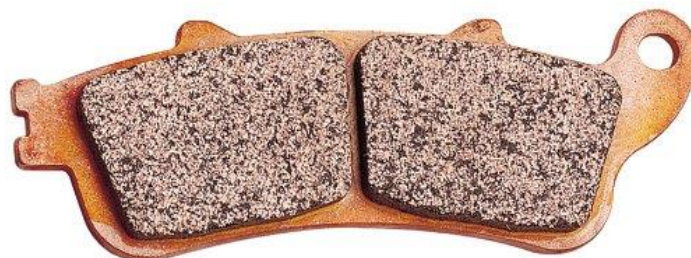


Fig. 8.19 Copper-based brake lining [8].

8.4.3 Cu-based friction materials for the operation in oil

With regard to the equilibrium which occurs between hydrodynamic pressure in an oil filter and capillary forces in pores it is evident, that a population and sizes of pores influence a formation of an oil film between the friction couples. Among others, pores also affect an oil circulation which is related to cooling of materials. Exceptionally favourable conditions occur in the event of interconnection of a system of large pores by small pores. For the oil film to be drained-off and circulation to be accelerated, grooves and a system of contacting points are formed on the friction surface of functional parts, leading to an origination of centrifugal forces with the oil flowing through a lamellae system and to an increase of heat dissipation from 50 to 70 %.

8.4.4 Fe-based friction materials for dry operation

Main advantages of iron-based friction materials are saving of non-ferrous metals, favourable price, a high friction coefficient and satisfactory abrasive resistance. A dominant component is graphite, the content of which ranges between 10 to 30 %. The graphite content above 15 % substantially reduces wear at higher friction speeds. Contents reaching above 25 % reduce strength of composites very significantly, which limits their applicability. The graphite content influence on the friction coefficient and wear is depicted in Fig. 8.20.

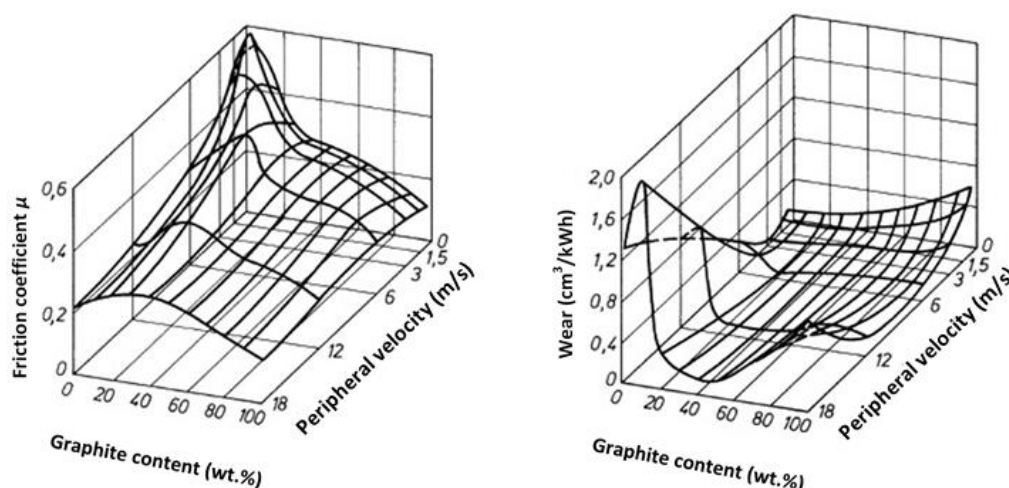


Fig. 8.20 Graphite content influence on tribological properties of iron-based sintered materials under uniform loading [2].

In almost all friction composites optimal properties of admixtures of low-melting metals (Pb,

Bi, Sn, Cd) are reached, which are not dissolved in the metallic matrix. For example, by 5 % Pb addition the wear is reduced down to around a half. The friction coefficient rises at low tribological loads, while at higher loads drops by c. 25 % after reaching the melting point of lead.

For friction effects to stabilize and for wear to reduce, other nonmetallic admixtures aside from graphite are used including mineral substances, such as asbestos, mullite, silica, sillimanite, aluminium silicates etc., or carbides of metals, nitrides, phosphides and sulphides (FeS , PbS , MoS_2 , Sb_2S_3 , BaSO_4). The above mentioned additives promote a formation and stabilization of reaction layers, leading to a friction material loadability increase.



Fig. 8.21 Iron-based brake pads for Toyota cars [9].

In order to observe relations of friction conditions to wear of a material based on Fe with a graphite addition, it is necessary to observe a friction couple temperature on contacting surfaces and to consider a fact that 70 to 80 % of mechanical energy is converted to thermal energy. Aside from thermal conductivity of the material friction layer, the total balance of heat dissipation from a clutch or brake depends on geometrical dimensions and a constructional design.

8.4.5 Friction materials with metallic bonding and high percentage of nonmetallic admixtures

For heavy-duty service conditions, materials with a high content of thermally stable ceramic components come into question. As bonding phases with good thermal conductivity copper alloys are used in particular, in special events also Fe and its alloys or Ni and Mo. Metal oxides (Al_2O_3 , SiO_2 , MgO , TiO_2) and other mineral materials (mullite, sillimanite, silicates) are used as nonmetallic additives. Additives are often added in order to modify tribological properties, such as graphite, low-melting metals, sulphides, carbides, phosphides or intermetallic phases (Laves' phases of Co-Mo-Si or Co-Mo-Cr-Si systems) which are very hard and wear-resistant. A content of additives implemented-in to a metallic matrix is commonly higher than 50 vol.%.

In addition to friction materials with a metallic matrix, composites carbon – carbon fibers with implemented-in ceramic additives are used as well. A high proportion of nonmetallic additives ensures thermal stability of friction materials. Maximum work temperatures range around 600 to 1000 °C. In Fig. 8.22, a comparison of tribological properties of a composite Fe-graphite with/without an additive of ceramic phases is plotted. However, this type of friction materials also imposes high requirements on counter-materials, so grey cast iron and low-alloyed steels have only a limited usage in a contacting couple with a high content of a ceramic phase. For counter-materials, high alloyed and thermally stable steels are usually chosen or the contacting surfaces are covered with wear-resistant layers. The above mentioned materials are applied in heavy duty clutches and brakes, e.g. for airplane landing brakes which must sustain not only multiple use, but enable also a space and weight saving design solution.

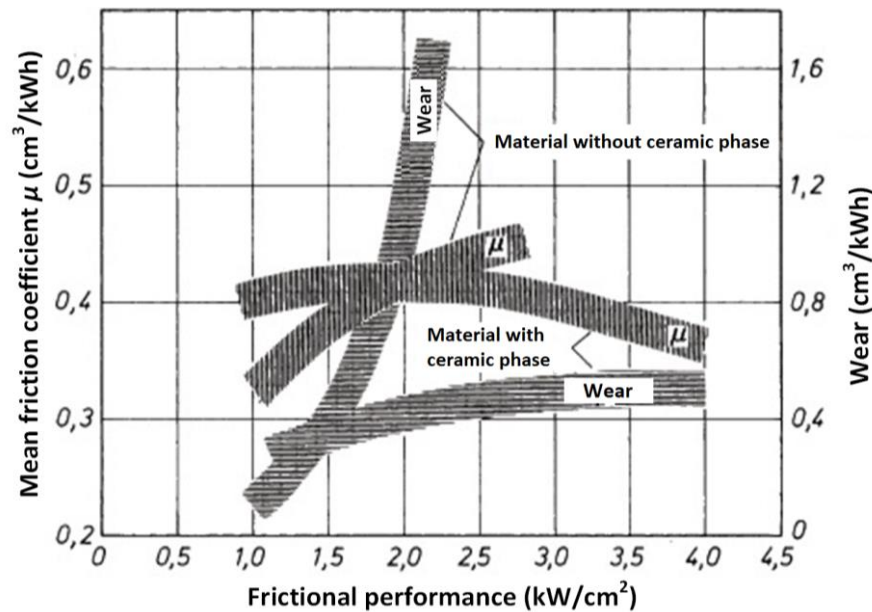


Fig. 8.22 Comparison of tribological properties of a composite Fe-graphite with/without an additive of ceramic phases [2].

8.5 Porous materials and filters

Generally, materials manufactured by powder metallurgy technology show a specific porosity. Many times, this porosity deteriorates material properties. For some of them the manufacturing technology is intentionally chosen, so that a product reaches a defined required porosity. These materials include above all sliding materials and the so-called metal filters. Porosity of sliding materials is to 30 %, porosity of metal filters of powder materials reaches up to 60 % and of metal fiber filters up to 90 %. A determining factor is permeability of highly porous materials, i.e. many-sided openness of pores.

For the manufacture of metal filters, bronze and stainless steels are used most frequently as an initial material, and further, in some special events, nickel and titanium based materials. In term of morphology, these are spherical-shaped particles of a size of 0.040 to 1 mm or, for stainless steel materials, thin fibers. The manufacture consists in forming powder materials by pressing in tools and subsequent sintering. For complicated shapes, which cannot be directly compressed, the metal powder is poured into an appropriate, commonly steel, container which gives the demanded shape to the powder. In this container, sintering is carried out. For large-dimension parts (1000 mm in length, 320 mm in diameter and a wall thickness of 3 mm), the processing is carried out through isostatic pressing. The basic functional properties of sintered metal filters include porosity, flow capacity and filtration ability. In comparison with typical filtration materials (ceramics, paper) the metal filtration materials feature the following advantages:

- uniform porosity and filtration ability;
- mechanical strength (tensile strength 30 MPa, bending strength 60 MPa);
- resistance to higher temperatures and their changes (200 to 400 °C according to the material type);
- corrosion resistance to an aggressive environment;
- possibility to connect the filters together;
- possibility of a universal application.

Fields of the use of sintered metal filters are shown in Fig. 8.23. These are particularly the following applications:

- filtration material for gases, air, combustion gases;
- safety fuses of tinary gases in the welding technology;
- filtration of cooling media in cooling aggregates;
- sound muffling, pressure impact absorption, gas dispersion in liquids, filtration of highly viscous materials, such as plastic materials etc.

A selection of an appropriate material for the manufacture of a metal filter depends particularly on the following factors:

- a type of the filtered substance;
- required porosity, and thus also permeability;
- required mean size of pores, and thus also filtration ability;
- filtration conditions (temperature, pressure);
- required shape and size of the filter.



Fig. 8.23 Various types of metal filters [10].

A shape and dimensions of a filter are determined in accordance with operation conditions for which the filter is intended. When designing a filter shape, one needs to consider above all the following: a filtration area, a way of fitting of the filter in a device and the filter strength. A size of metal filters is defined by the technological equipment. When using the classical pressing, it is necessary to respect principles for the design of parts manufactured by powder metallurgy technology (length to diameter ratio, wall thickness etc.). Isostatic pressing is advisable for long parts. The following belong among the most commonly manufactured filter shapes: tubular, circular flat, flat square and rectangular filter, conical filter with/without a bottom, plate filter, conical flanged filter, pan filter.

8.5.1 Filters made of spherical particles

Filters of spherical particles (Fig. 8.24) ensure a uniform size of pores and max. 50 % porosity. They find their use above all for cleaning of pressure gases. For a high proportion of spherical particles to be achieved, surface stress increasing additives are added to sprayed metals, e.g. 0.05 % P for Sn-bronzes. Uniform porosity can be achieved, providing that a deviation of a particle size from the mean diameter is not higher than 10 %. Bridges, diameters of which are around 15 % of particle diameters, originate during the sintering process. Bridges are carriers of the filter strength and their other physical properties. Sintering takes place in a loose state after the vibration tapping.

According to a particle size of the used material, filters with a pore size from 3 up to 200 μm can be made. Bronze filters are applicable to 200 $^{\circ}\text{C}$ in a standard atmosphere and to 450 $^{\circ}\text{C}$ in a protective gas atmosphere.

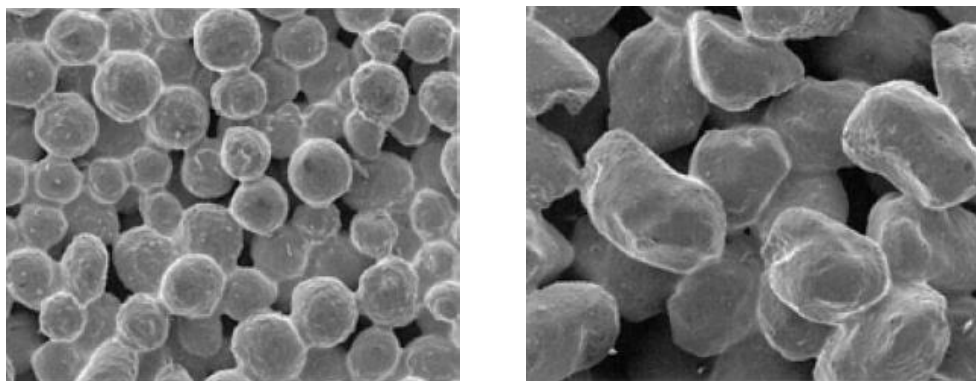


Fig. 8.24 Morphology and a shape of particles for a manufacture of metal filters [3].

8.5.2 Filters made of irregular particles

They are made from powders consisting of rugged (Fig. 8.25) or dendritic particles, whereas maximum porosity of 70 % can be achieved. Permeability is lower in comparison with filters from spherical particles, pressure losses are higher. A proportion of impermeable pores is larger and roughness of channels is higher. For the manufacture, powders of high-alloyed steels, Ni and alloys are used, but also Cr-, Mo-, Ta-, Pb-, Al-, Ti-based materials and for high thermal stressing even powders based on Ni-Mo alloys. A pore size ranges from 1 to 200 μm . Die pressing is the most widely used forming method. Volatile admixtures of powder allow affecting the final porosity and reaching the required permeability of a filter. Large-dimension filters are pressed isostatically. The technology of application of powder with a liquid and plastificator additive can be used for a manufacture of shape products and even strips, which are sintered periodically or continuously.

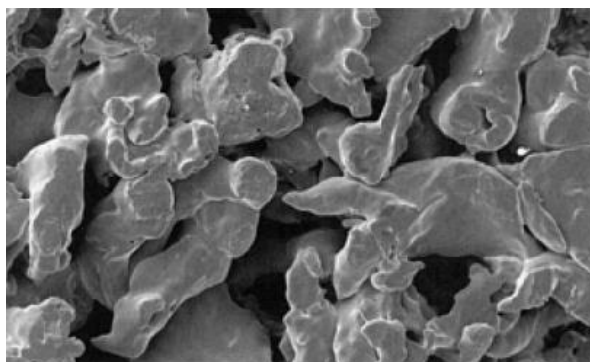


Fig. 8.25 Morphology and a shape of irregular particles for a manufacture of metal filters [3].

One of other variants is a preparation of a material with pores of the same size, parallel arranged, which can be achieved e.g. by parallel arrangement of copper fibers to Fe powder. Sintering takes place above the copper melting temperature, whereas the molten copper is transported into the surrounding Fe skeleton, thus increasing its strength. On the place of the original Cu fibers the parallel-arranged pores remain, the diameters of which correspond with the diameters of the original fibers. This type filters achieve maximum porosity of 45 %, whereas their strength is 4 to 8 fold higher than for loose powder filters.

8.5.3 Filters made of metal fibers

When using metal fibers or wires (Fig. 8. 26), 90 % porosity can be achieved, sometimes even up to 98 %. Wires of a diameter up to 250 μm or fibers of 4 up to 65 μm diameter are used for the manufacture of filters. A fiber diameter to length ratio can range between several hundred to a

thousand fold. Fibers can be vibration felted with/without using pressure and sintered. More frequently, fibers are stirred-up in a liquid of high viscosity and processed to a homogenous structure after draining-off the liquid.

A procedure of fiber sintering differs from the procedure of powder sintering due to a “softened” contact and different diffusion conditions. The prevailing mass transport depends on diameters of fibers. Very fine fibers with diameters below 10 μm are mainly sintered under the acting of surface diffusion, while volume diffusion is prevailing for fibers with diameters above 10 μm . As the material volume shrinkage during sintering is not related to the surface diffusion and at elevated temperatures a release of fibers deformed during felting occurs, a porous material volume increase can be observed. On the contrary, felted fibers of larger diameters condition the volume diffusion, leading to the shrinkage and compensating a release of deformed fibers, so only negligible dimensional changes of a product occur.

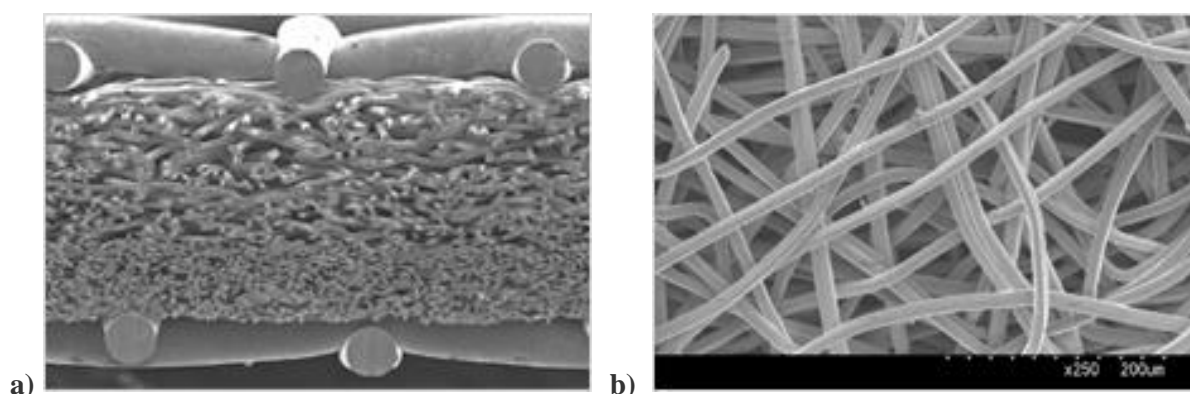


Fig. 8.26 Cross-section of a filter made of metal fibers (a) and metal fibers for a manufacture of filters of stainless steel (b) [11].

8.6 Dispersion hardened materials

A dispersion hardened material is defined as a sintered material hardened by insoluble finely dispersed metallic or nonmetallic phases. A principle of the dispersion hardening consists in introducing the second-phase particles into a mono- or poly-component matrix in a defined stage of the preparation. Particles can be introduced into the system in an external way (alloying) or they originate in the preparation process (internal oxidation, reaction milling etc.). Moreover, the system can include also precipitates next to a matrix and dispersoid. Affecting the basic metal properties by these phases consists particularly in their interaction with dislocations. On the basis of these interactions, the material strength, yield strength, stress-rupture strength and other properties increase.

8.6.1 Dispersion hardened aluminium materials

This type of material is known particularly under the designation SAP. In general, this is an aluminium sprayed powder which is subsequently milled in ball mills. During milling surface oxidation occurs, Al_2O_3 originates and its content increases, while the particle size decreases. The temperature dependence of an aluminium-based material strength and hardness is evident from Fig. 8.27. Another type of dispersion hardened aluminium, namely $\text{Al}-\text{Al}_4\text{C}_3$, is also prepared by the reaction milling technology. Aluminium powder sprayed by nitrogen is homogenized with a corresponding amount of carbon (to 5 mass %) in a form of graphite or furnace black in an attritor. The powder obtained by milling is then heat processed, so that during the processing a reaction occurs between aluminium and carbon, leading to Al_4C_3 origination which acts as a dispersoid. This type of material has been developed for structural components in the automotive industry, mainly for pistons,

cylinder heads and other thermally stressed parts. It exhibits long-term load resistance at temperature of 773 K and short-term above 873 K.

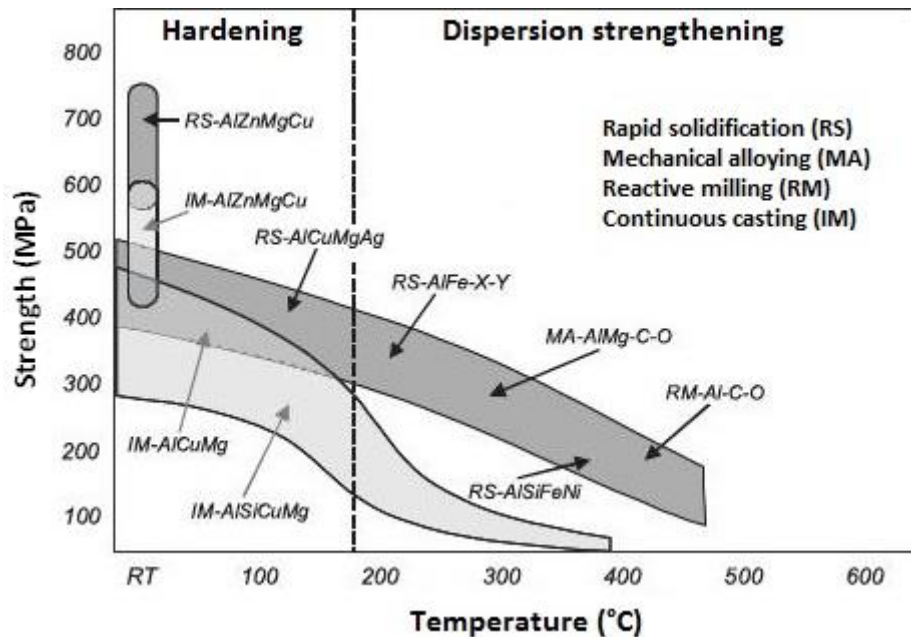


Fig. 8.27 Schematic depiction of strength of various aluminium-based materials depending on the operation temperature and hardening mechanism [2].

8.6.2 Dispersion hardened nickel-based materials

These are particularly composite materials with a metallic matrix hardened by nonmetallic particles. The first types of these nickel-based materials include nickel with 2 % of ThO_2 , possibly with an addition of chromium to improve heat resistance (Ni-20Cr-2ThO_2). Due to its radioactivity, thorium dioxide was in newer materials replaced by yttrium oxide Y_2O_3 . These composites are prepared by mechanical alloying of powders in ball mills, whereas La_2O_3 , CeO_2 , Al_2O_3 , ZrO_2 can be other dispersive phases. Alloys dispersion hardened by oxides must meet the following requirements:

- oxide must be stable;
- oxide particle size 10 to 50 nm;
- oxide amount 0.4 to 4 vol.%;
- mean interparticle spacing 50 to 300 nm;
- melting temperature above 1300 °C.

Inconel MA 754 and Inconel MA 6000 feature excellent heat resistance at 1000 °C in comparison with superalloys manufactured by the classical process, thermal fatigue resistance and dimensional stability. Inconel MA 758 with the higher chromium content can be used also at temperature of 1150 °C. The manufacture of superalloys via powder metallurgy is displayed in Fig. 8.28:

1. Preparation of spherical pre-alloyed powder, particle size modification, homogenization (particle size distribution).
2. Forming of the powder mixture in order to achieve full density using a technology of extrusion with subsequent hot forging (improvement of mechanical properties, especially high-temperature strength and ductility) or HIP.
3. Heat treatment for stabilization of carbides and precipitates and γ' phase (Ni_3Al).

Other dispersion hardened materials may include dispersion hardened lead into which additives are added, such as PbO or Ni. Silver-based materials are hardened by appropriate oxides (CdO) or nickel.

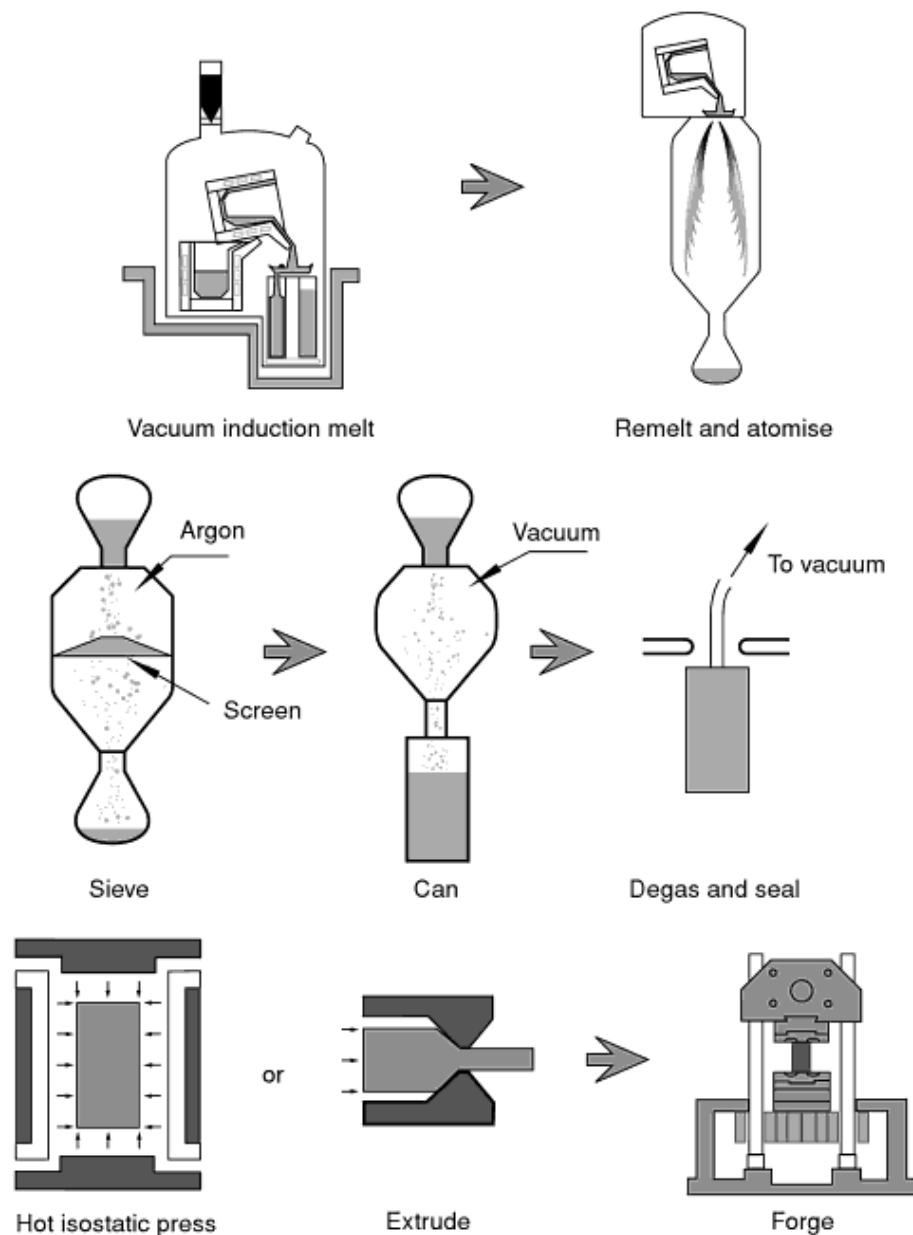


Fig. 8.28 Manufacturing technology for a gas turbine disc from Ni-superalloy [12].

8.7 Contact materials

Electrical contacts close electrical circuits, serve for electric current transmission and for disconnection of a closed electrical circuit. These, many times contradictory, requirements cannot be often provided by pure metals or their alloys. However, powder metallurgy technology enables to combine different properties into one material. Materials for a manufacture of contacts can be divided to:

1. Materials based on high-melting point metals.

2. Dispersion hardened silver-based materials.
3. Composite materials based on metal-graphite.

Fields of use of various types of contact materials depending on voltage and electrical current are depicted in Fig. 8.29.

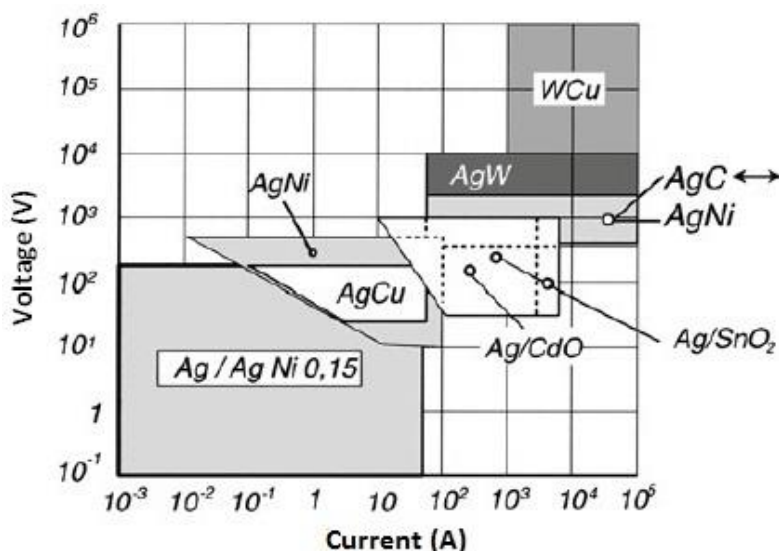


Fig. 8.29 Fields of use of various types of contact materials depending on voltage and electrical current [2].

8.7.1 Materials based on high-melting point metals

These metals find their application in a pure form or in a combination with metals featuring high electrical conductivity. Tungsten in a pure form, and in special cases molybdenum and rhenium, finds the most frequent use as a contact material. Tungsten has very high resistance to contact erosion, high thaw point and high hardness. However, it has only 1/3 of electrical conductivity of copper and it is difficult to process and to form.

It has relatively low resistance to the oxidation atmosphere at temperatures above 400 °C. On its surface an origination of oxide layers occurs, increasing the transition resistance. For the contact to be satisfactory, thrust forces higher than 1 N are needed. Tungsten is applied preferentially as a material for contacts in car electrical systems, such as disconnecting contacts, ignition electrodes and in voltage regulators. As with tungsten, molybdenum-based materials are used for the manufacture of high-voltage contacts. Compared to tungsten, molybdenum is more resistant against gases, has lower density and is better machinable. Rhenium has excellent properties for the manufacture of contact materials, however, the mass production is out of question by reason of its expensiveness. Other interesting tungsten-based materials for contacts are the so-called composite materials W-Cu and W-Ag. These materials are made by powder metallurgy technology, either by mixing powder metals or infiltrating a tungsten skeleton with an appropriate metal with high electrical conductivity (Ag, Cu) and excellent high contact erosion resistance.

8.7.2 Dispersion hardened silver-based materials

Basic types of these contact materials include Ag-MeO materials, in which CdO is mainly used as MeO, in some case other oxides (ZnO, etc.). Materials as Ag-Ni and Ag-graphite have a less technical significance. Ag-CdO materials feature high density, relatively high hardness and good electrical conductivity. In comparison with silver contacts, Ag-Ni type materials with a content of 10 – 40 wt. % of Ni exhibit better mechanical properties and good electrical conductivity, which is better than in hardenable alloys of silver with Au and Cd.

8.7.3 Composite materials based on metal-graphite

Principally, these materials have to transmit electrical energy, while having good sliding properties. The graphite content in these materials ranges between 5 - 70 %. Next to graphite, the material contains a defined amount (c. 10 %) of low-melting metals (Sn, Pb, Zn). Cu is usually selected as a metal component.

Copper and carbon are mutually insoluble components, so that powder metallurgy is the only possible technology for the preparation of these composite materials. While Cu content increases, electrical resistance decreases. Despite of additional densification, the Cu-graphite based materials for contacts show high porosity, which allows infiltration of the material with organic substances to improve sliding properties. They are used mainly in collector motors in the transportation technology (railways, trams, trolley-cars, electromobiles etc.). Larger products are made from sintered plates, smaller ones are compressed to the final shape and sintered.

8.8 Hard materials

A basis for hardness is in strong bonding forces between atoms of a lattice. Generally, the high thaw point, low thermal expansion coefficient and high modulus of elasticity are characteristic for this material group. Thanks to this combination of properties, hard materials are used also as wear-resistant and heat-resistant. Hardmetals can be divided into two basic groups:

1. Compounds of metals of IV – VIII transition group in the periodic table with elements B, N, C, Si, possibly P and S. Monooxides of metals can be also designated as hard materials.
2. Mutual B, C, N, Si compounds with a possible integration of some oxides, such as Al_2O_3 , ZrO_2 or ThO_2 , which are designated as nonmetallic hard materials. This group covers also superhard materials, such as boron nitride and diamond.

8.8.1 Cermets

These are heterogenous combinations of a metal or an alloy with one or more ceramic phases in an amount of 15 – 85 vol. %, whereas the metal and ceramic phase must not be (or only to a very limited extent) mutually soluble at the preparation temperature. Cermets are classified according to a hard refractory component – carbides, carbonitrides, nitrides, oxides, borides (TiC , TiN , TiCN , WC , Mo_2C). As a metal binder, various metals and alloys are used: Ni, Co, Fe, Cr, Mo, W, stainless steel, superalloys, titanium, zirconium, Cu- and Al-based low-melting alloys. A volume proportion of a binder depends on required properties and the use of the given material and it is usually 15 to 85 % (for cutting tools 10 to 15 wt. %). Important properties of cermets are low specific weight, which is around a half in comparison with cemented carbides, high hardness even at higher temperatures, excellent chemical stability, resistance to diffusion and oxidation wear, etc. Cermets, above all TiC - and TiCN -based ones, find their use mainly in a manufacture of cutting tools, which are used for heavy-duty cutting at high speeds characterized by removing larger amount of a material (a work-piece).

Basic types of cermets:

1. **Carbide-based cermets** – TiC carbides, or SiC , B_4C , Cr_3C_2 , are a primary hard and high-melting (refractory) component; low-melting tough metals or alloys are used as a binder (as with cemented carbides). Applications: a manufacture of cutting tools, wear-resistant materials, selected high-voltage and high-temperature systems, nuclear technology (SiC , B_4C).
2. **Carbonitride-based cermets** – manufactured with/without an addition of various carbides (e.g. Mo_2C) with the use of common binders. Applications: a manufacture of high-speed cutting tools with enhanced strength due to a better bonding between carbides and a binder – different mixability in TiC , TiN , Mo_2C and MoN quaternary system which results in the so-called spinodal decomposition to two isostructural phases with a significantly higher wettability by a binder. A schematic depiction of a cermet structure is in Fig. 8. 30. A base is a core of carbide or titanium

nitride which is not transformed during sintering. Around the core, there is an inner and outer rim, which originate during sintering of cermets and their size and structure depend on an amount and type of additive elements and sintering temperature. Individual cores are bonded with the aid of a nickel or cobalt binder.

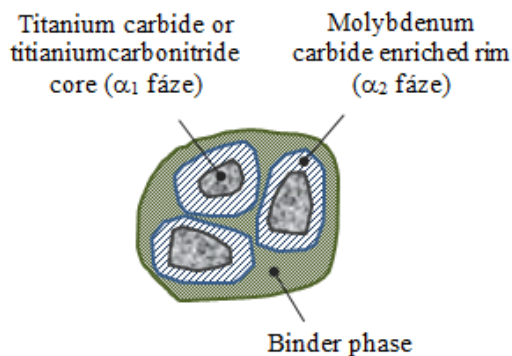


Fig. 8.30 Schematic depiction of a cermet structure.

3. **Nitride-based cermets** – represent special types of tool materials based on TiN (possibly ZrN) and particularly cubic boron nitride (CBN). They also exhibit excellent thermal and corrosion resistance.
4. **Oxide-based cermets** – cermets based on UO_2 or ThO_2 oxides are used in nuclear reactor fuel elements (Fig. 8.31); cermets based on Al_2O_3 or other high-melting point oxides are applied in a manufacture of components in a field of molten metal handling (e.g. tap holes and structural parts of furnaces).
5. **Boride-based cermets** – the main phase is formed by transition-metal borides. They provide excellent high-temperature corrosion resistance in comparison with active metals in a molten or vapour state; a combination of ZrB_2 and SiC exhibit erosive wear resistance.

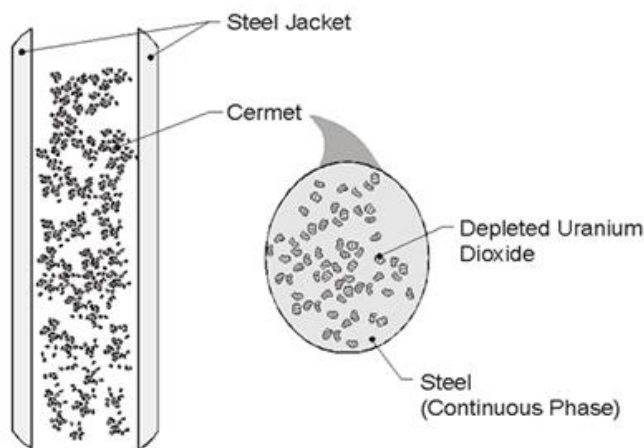


Fig. 8.31 Example of the use of UO_2 -based cermets in fuel elements [13].

Cermet manufacturing technology involves:

- a) **Preparation of powders** – a powder mixture (hard phase + pure metal) is milled in a ball mill, whereas the hard phase is disintegrated and enveloped with a binder metal.
- b) **Powder mixture compaction** – double-action pressing with a binder in special dies of hardmetal under pressure 35 to 100 MPa. Other forming processes include cold isostatic pressing, extrusion,

rolling, hydrostatic pressing, PIM etc.

- c) **Sintering** – sintering with a liquid phase prevails, whereas the sintering temperature depends on the metal-ceramics system: 850 – 1050 °C for Cu, bronze, Ag matrices; 1300 – 1500 °C for carbides and borides; 1700 – 2200 °C for oxide-based cermets; volume shrinkage 45 – 60 %. Hot static pressing, HIP, hot extrusion or pressure sintering is applied, too.

d) **Surface finishing.**

8.8.2 Syntetic diamond

These materials are classified according to a particle size, morphology, individual strength, colour, etc. In term of a particle size, they are divided to grinding ones with a particle size 40 – 100 µm and micron ones with a size to 40 µm. The main applications are as follows:

- diamond pastes – polishing in tool shops, finish grinding operations in a preparation of hardmetal and steel tools;
- grinding tools – grinding of cemented carbides, titanium and tungsten alloys with/without cooling;
- tools for engineering – diamond discs to Ø 500 mm, honing bars, grinding dressers, needle files and grinding spindles;
- tools for glass-making and optical industry – tubular drills of 6 - 50 mm for drilling holes in glass etc.;

8.8.3 Cubic boron nitride (CBN)

It is manufactured by a synthesis from hexagonal boron nitride under high temperatures and pressures (Fig. 8.32). In contrast to diamond, it has higher thermal stability and heat resistance to 1200 °C. CBN grinding discs are used mainly for grinding of tools and high-speed steels. Other applications include:

1. Tools for stone-industry – diamond segment saw blades to Ø 300 mm, frame-saws, grinding discs for flat ground and diamond low-grain crowns.
2. Tools for building and geological industry – diamond segment saw blades, diamond crowns, stabilizers and chisels.
3. Tools with an electro-deposited abrasive layer – possibilities for various shape applications without demands for large series (Fig. 8.33).



Fig. 8.32 Morphology of cubic boron nitride[14].

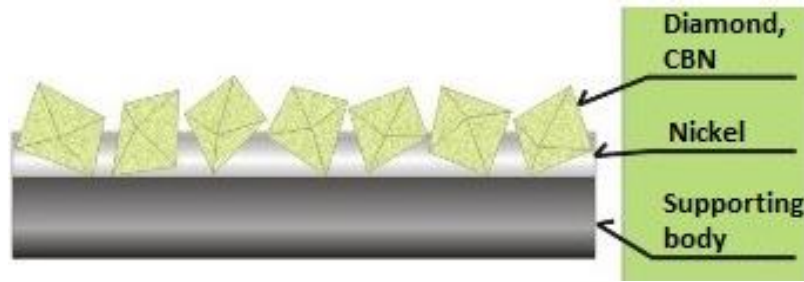


Fig. 8.33 Profile of a tool with an electro-deposited abrasive layer – the individual crystals of diamond or CBN are interconnected by a nickel layer, their thickness corresponds to around a half of the grain diameter [15].

8.9 Cemented carbides

Cemented carbides represent the oldest type of material produced by powder metallurgy technology. They rank predominantly among tool materials and partly among structural materials which feature high hardness, abrasive resistance, high compressive strength at satisfactory toughness, high elasticity modulus and favourable corrosion resistance. In term of materials, the cemented carbide consists of one or more high-melting point metal carbides, which are bonded with the aid of binding phase, usually cobalt. A basic component of almost all cemented carbides is the tungsten carbide which features high compressive strength, good thermal conductivity, high elasticity modulus and very good tolerance to the binding cobalt phase. The titanium carbide is the other technically important carbide, which is added to WC in a manufacture of cutting materials for machining of steel. TiC increases strength at higher temperature and oxidation resistance and decreases tendency to a cutting tool welding with a chip. Small amounts of NbC and TaC, which modify a structure and influence the sintering process favourably, are used in order to modify properties of WC-Co- and WC-TiC-Co-based carbides. Designation of carbidic hard cutting materials pursuant to ISO 513:2012 is given in Table 8.1. Cemented carbides are classified according to application into six groups distinguished in colour and by a letter (Tab. 8.2). Subgroups are designated with a two-digit number expressing their basic mechanical properties – with an increasing subgroup number, toughness and bending strength decreases and wear resistance and hardness increases. Types of non-coated cemented carbides with a higher number designation are used for medium to heavy machining and roughing.

Table 8.1 Designation of carbidic hard cutting materials pursuant to ISO 513:2012.

Identification letter	Material groups
HW	Uncoated cemented carbide, predominantly made from tungsten-carbide (WC) with a grain size $\geq 1 \mu\text{m}$
HF	Uncoated cemented carbide, predominantly made from tungsten-carbide (WC) with a grain size $< 1 \mu\text{m}$
HT¹	Uncoated cemented carbide, predominant titan-carbide (TiC) or titan-nitride (TiN) or both
HC	Cemented carbide like above, but coated
¹ These cemented carbides are also called "Cermet"	

The manufacture of cemented carbides employs the following steps:

1. W-ore processing and the preparation of WC powder by carburization;
2. preparation of the other carbide powders;
3. compaction (densification) of powders;
4. sintering;
5. post-sinter forming.

According to the composition, cemented carbides are classified into the following groups:

- a) WC-Co-based cemented carbides – most of the materials with S and H designation.
- b) WC-TiC-Co or WC-TiC-TaC(NbC)-Co TiC-Co cemented carbides – predominantly S designated materials.
- c) Tungsten-free TiC-based cemented carbides.
- d) Coated cemented carbides – carbides with wear-resistant coatings based on TiN, TiC, TiC+TiN, Al_2O_3 and possible combinations prepared by chemical segregation from the vapour phase.

Fields of application of cemented carbides depending on WC grain size and a cobalt content are depicted in Fig. 8.34.

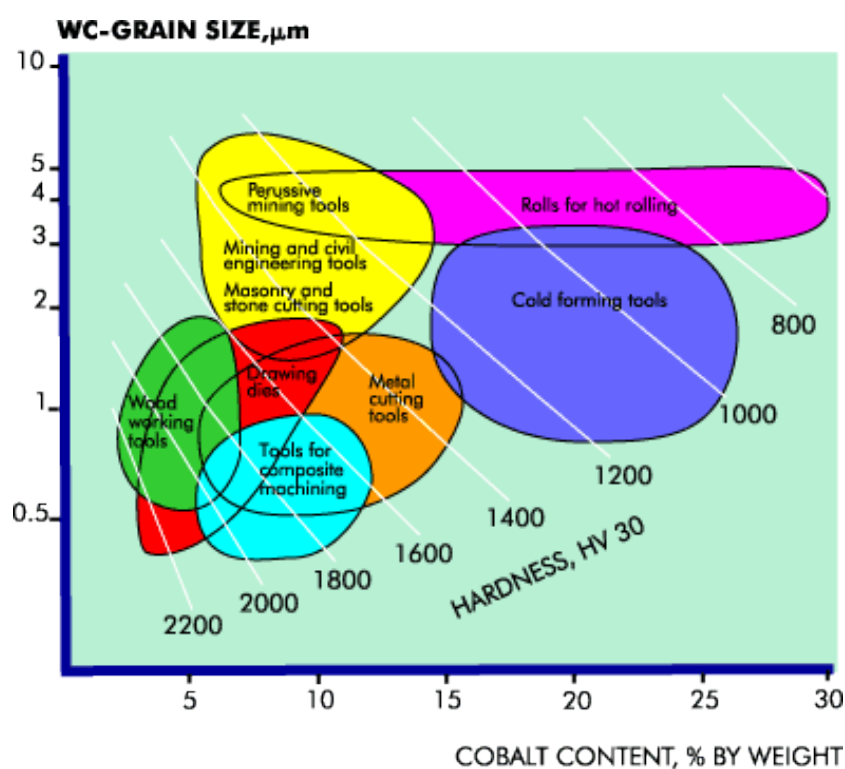


Fig. 8.34 Fields of application of cemented carbides depending on WC grain size and a cobalt content [16].

WC-Co-based cemented carbides are used mainly in the manufacture of tools for bulk and surface forming and for rock shooting and blasting. These are dies for wire drawing and bells for tube and pipe drawing, self-fluxing pins, pressing tools for powder metallurgy and ceramics technology, steel wire rolling rolls, tools for a manufacture of synthetic diamonds and cubic nitride, boron, shearing tools, tools for rock shooting and blasting and for other technology fields with high demands for material strength and abrasive wear resistance.

Table 8.2 Application and classification of hard cutting materials.

Group/ colour	Application group				Basic chemical composition	Workpiece-material
P	P01 P10 P20 P30 P40 P50	P05 P15 P25 P35 P45	↑	↓	WC (30÷82 %) + TiC (8÷64 %) + Co (5÷17 %) + (TaC.NbC)	Steel: All kinds of steel and cast-steel, except stainless steel with austenitic structure.
M	M01 M10 M20 M30 M40	M05 M15 M25 M35	↑	↓	WC (79÷84 %) + TiC (5÷10 %) + TaC.NbC (4÷7 %) + Co (6÷15 %)	Stainless steel: Stainless austenitic and austenitic-ferritic steel and cast-steel
K	K01 K10 K20 K30 K40	K05 K15 K25 K35	↑	↓	WC (87÷92 %) + Co (4÷12 %) + (TaC.NbC)	Cast-iron: Cast-iron with flake-graphite, cast-iron with ductile graphite, annealed cast-iron.
N	N01 N10 N20 N30	N05 N15 N25	↑	↓		Nonferrous metals: Aluminium and other nonferrous metals, nonmetal materials.
S	S01 S10 S20 S30	S05 S15 S25	↑	↓		Specializations and titanium: Highly heat resisting special-alloys based on iron, nickel and cobalt, titanium and titanium based alloys.
H	H01 H10 H20 H30	H05 H15 H25	↑	↓		Hard materials: Hardened steel, hardened cast-iron-materials, cast iron for chill-casting.
↑ Increasing cutting speed, increasing wear-resistance of the cutting tool materials						
↓ Increasing feed, increasing durability of the cutting tool materials						

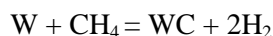
8.9.1 WC powder preparation

8.9.1.1 Preparation of WC powder by carburization

This method consists in adding an exact amount of carbon in a form of furnace black to the tungsten powder which enables a control of WC powder particle size and distribution, which together with the binder content determines the resulting final properties of cemented carbides. First, the so-called “black mixture” of tungsten powder of a required particle size and distribution together with high-quality furnace black is prepared. A homogenous carbon distribution needs to be ensured with regard to the different density of tungsten and carbon. Mixing is carried out in ball mills, attritors or

special stirring devices. The aim of the carburizing process is to make the stoichiometric tungsten carbide with 6.13 wt. % C (Fig. 8. 35) or with a small excess of free carbon (0. 01 to 0. 03 wt. %) – carbon insufficiency results in a formation of a brittle η phase.

Carburizing occurs in the presence of hydrogen at temperatures of 1400 to 2650 °C (Fig. 8. 36). Hydrogen reacts with the furnace black, leading to hydrocarbon origination (primarily CH_4), which then reacts with W, leading to WC origination:



Then, the originated carbidic particles undergo milling and screening in order to achieve a fine powder with an applicable size distribution 0.5 – 30 μm . An addition of a small amount of V, Ta or Cr carbides prevents the grain growth during sintering (0.5 – 2 %).

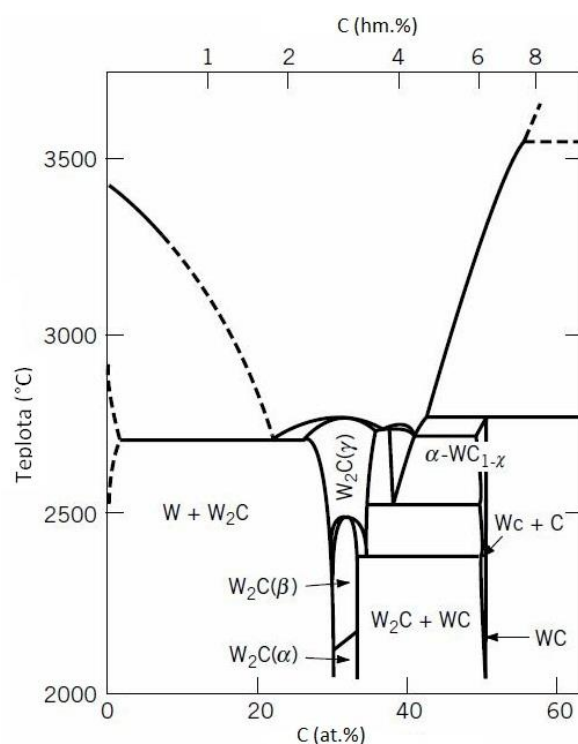


Fig. 8.35 W-C system binary diagram.

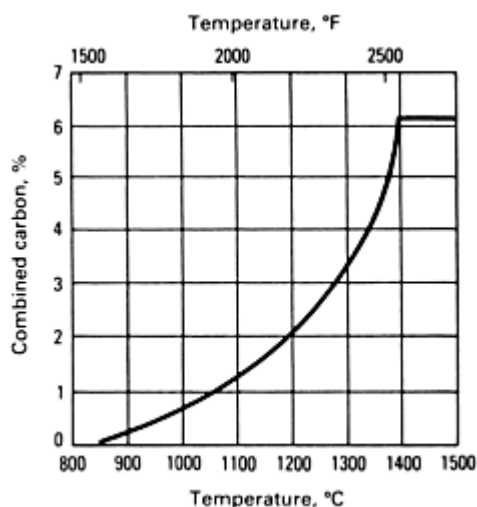


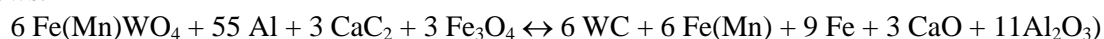
Fig. 8.36 Minimum temperature (1400 °C) for achieving the WC stoichiometric composition [2].

8.9.1.2 Menstruum process

this involves the formation of WC within a melt of auxiliary metal, such as Ni or Co. W or tungsten ore and carbon are added to the melt and react to form the carbides at temperature around 2000 °C. With a ratio of auxiliary metal to tungsten of approximately 2:1 and slow cooling of the melt, relatively coarse carbide particles (up to 1 mm) are precipitated. Finer sizes can be obtained by additional dilution and faster cooling.

8.9.1.3 Direct reduction from W-ore

The method of production of WC in a single crystal form also employs auxiliary metals, in exothermic reactions. This process involves the reduction of a mixture of W concentrate and Fe-oxide by aluminium metal, and simultaneous carburization through the addition of calcium carbide and carbon. The reactants are added in proportions that sustain an exothermic reaction above 2500 °C as follows:



The resulting product, after cooling-down, consists of WC crystals dispersed in Fe(Mn) and an admixture-containing slag. Crystalline WC is then separated from Fe(Mn) matrix in a chemical way.

8.9.2 Preparation of mixed carbides

WC-TiC, WC-TiC-TaC or WC-TiC-(Ta, Nb)C carbides are used for cutting tools to resist cratering or chemical wear. Oxides of these metals are mixed with metallic W-powder and carbon, the mixture is heated under a hydrogen atmosphere or in vacuum to reduce the oxides and form solid-solution carbides, such as WC-TiC, WC-TiC-TaC or WC-TiC-(Ta, Nb)C.

8.9.3 Preparation of powder mixtures for a manufacture of cemented carbides

A base for a powder mixture for cemented carbide production is WC mixed with a fine metallic binder (Co, Ni, Co) or with additions of other cubic carbides, such as TiC, TaC or NbC depending on the required properties and application. The mixture undergoes intensive milling (ball mills or vibratory mills, attritors), which is necessary to break up the initial carbides and to blend the various components such that every carbide particle is coated with binder metal. Milling is performed under an organic liquid (heptane, acetone) to minimize heating of the powder and to prevent oxidation of the mixture. Solid lubricants are added to the powder mixture in the final stages of the milling process. The organic liquid is removed by drying.

8.9.4 Forming of the carbide powders

Depending on the application of the specified product, a wide variety of techniques are used, e.g.:

- tools for mining and construction applications – one-direction pressing;
- high wear-resistant tools and metal forming tools – cold isostatic pressing;
- rods and wires – extrusion process.

Carbide powders do not deform during the compacting process, whereas maximum relative density of 65 % is achieved.

8.9.5 Sintering

Sintering of compacts involves removal of lubricants, densification and microstructure development and it can use a protective hydrogen atmosphere or vacuum.

8.9.5.1 Hydrogen sintering

The hydrogen atmosphere provides a reducing environment ensuring the correct carburizing and oxidizing potentials to maintain thermodynamic equilibrium. The used lubricant must be removed prior to the actual sintering at temperatures 500 to 800 °C in order to prevent material contamination by its evaporation.

8.9.5.2 Vacuum sintering

Vacuum sintering of cemented carbides enjoys wider usage than hydrogen sintering. Major advantages of the vacuum sintering:

- superior control of chemical composition;
- at pressures of 1.3 to 133 Pa, the rate of carbon and oxygen exchange between the atmosphere and the carbides is very low – the main factor controlling composition is the oxygen content of the carbide powder, not the rate of reactions with the atmosphere;
- batch process.

Because of low oxidizing potential of the vacuum sintering atmosphere, this process is more advisable for the sintering of Ti, Ta or Nb carbides that are sensitive to oxidation. Vacuum sintering also offers greater flexibility and control of the thermal cycle, particularly the heating cycle. Slow heating rates are essential, usually followed by an intermediate temperature hold to obtain optimum product quality when TaC, TiC or NbC additives are used in the initial carbide powder. Slow heating rates allow sufficient time for the C-O reactions to occur. Carbon content can vary during the sintering substantially as a result of reactions with oxygen from the powder and reactions of carbon exchange with the furnace atmosphere. Conventional vacuum sintering offers low operating cost. Examples of sintering modes are shown in Fig. 8.37.

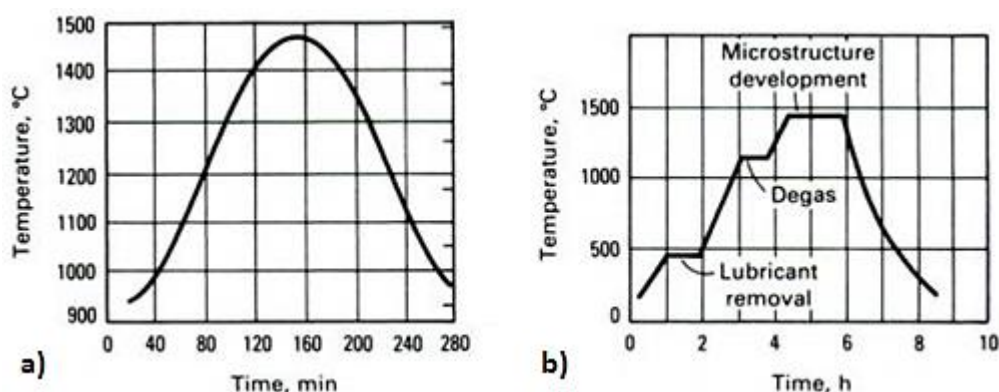


Fig. 8.37 Examples of sintering modes: a) hydrogen sintering; b) vacuum sintering [3].

8.9.6 Coating of cemented carbides

Covering the cutting tools (e.g. cutting tips) with a very thin coat of a hard material (coating) is performed for this purpose:

- to increase cutting speeds for higher heat resistance;
- to increase service life of tips;
- to increase wear resistance.

The following are the most important materials for coating:

- titanium carbide (TiC);
- titanium nitride (TiN);

- aluminium oxide (Al_2O_3);
- titanium carbonitride (TiCN).

Coatings are commonly prepared through PVD (Physical Vapour Deposition), CVD (Chemical Vapour Deposition), possibly PACVD (Plasma Assisted Chemical Vapour Deposition) technology. Tool tips with various types of coatings are shown in Fig. 8.38.

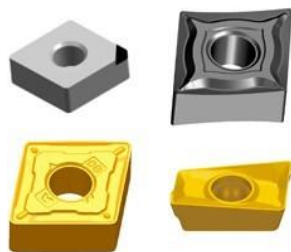


Fig. 8.38 Tool tips with various types of coatings [17].

8.9.7 Types of cemented carbides and their microstructure

The performance of a cemented carbide cutting tool is strongly composition and microstructure dependent, and the properties depend not only on the type and amount of carbides but also on the carbide grain size and the amount of the binder metal.

Tungsten and molybdenum carbides have hexagonal crystal structures, whereas Ti, Ta, Nb, V, Hf and Zr carbides are cubic. Cobalt is the most frequently preferred binder in cemented carbides due to its outstanding wetting and adhesion characteristics. Nickel is used in less than 10 % of the total production of cemented carbides because of its poor wettability, lower hardness and toughness, nevertheless, offers slightly improved corrosion and oxidation resistance.

8.9.7.1 WC-Co type cemented carbides

They consist of WC particles bonded with cobalt. For their excellent resistance to simple abrasive wear they have many applications in metal cutting. The commercially significant cemented carbides contain Co in the range of 3 to 25 wt. %; for machining purposes, cemented carbides with 3 to 12 wt. % Co and WC particle sizes from 0.5 to 5 μm are commonly used. The ideal microstructure of WC-Co type cemented carbides exhibits two phases: angular WC grains and Co-binder (Fig. 8.39). During manufacturing, the carbon content must be controlled within narrow limits – too high C content results in the presence of free and finely divided graphite, while deficiency in carbon results in the formation of a series of double carbides ($\text{Co}_3\text{W}_3\text{C}$ or $\text{Co}_6\text{W}_6\text{C}$), commonly known as η -phase, which causes severe embrittlement.

8.9.7.2 WC-TiC-Co type cemented carbides

These types of cemented carbides exhibit higher resistance to chemical attack and diffusion wear when machining steels. Tungsten carbides diffuse readily into the steel chip surface, but the solid solution of WC-TiC resists this type of chemical attack. Unfortunately, WC-TiC is more brittle and less abrasive wear resistant than WC. The content of TiC is typically no greater than 15 wt.%.

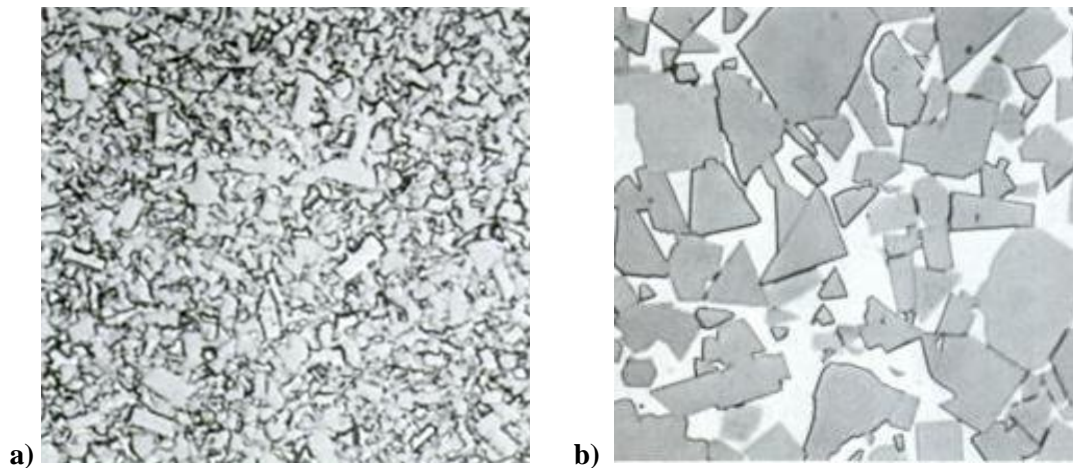


Fig. 8.39 Microstructure of the WC-Co type cemented carbide: a) 97WC-3Co (medium grain size); b) 85WC-15Co; (coarse grains) [3].

8.9.7.3 WC-TiC-(Ta, Nb)C-Co type cemented carbides

Adding TaC to WC-TiC-Co alloys partially overcomes the deleterious effect of TiC on the strength of WC-Co alloys. TaC resists cratering and improves thermal shock resistance. They are used mainly in applications involving interrupted cutting. The structure shows three phases: angular carbides, rounded WC-TiC-(Ta,Nb)C-Co solid-solution particles and Co-binder (see Fig. 8.40).

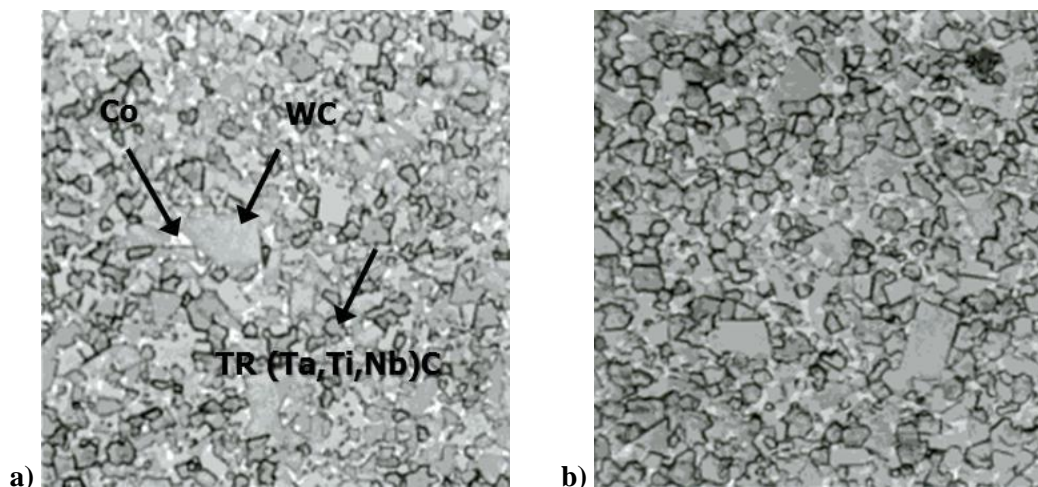


Fig. 8.40 Microstructure of the WC-TiC-(Ta, Nb)C-Co type cemented carbide: a) 85WC-9(Ta,Ti,Nb)C-6Co; b) 78WC-15(Ta,Ti,Nb)C-7Co [3].

8.9.8 Properties of cemented carbides

8.9.8.1 Hardness

- Hardness determines the resistance of a material to abrasive wear.
- It is affected by chemical composition and the level of the microstructure porosity.
- For WC-Co type cemented carbides with a comparable WC particle size, hardness and abrasion resistance decreases with an increasing cobalt content.
- Hardness decreases monotonically with increasing temperatures (Fig. 8.41).

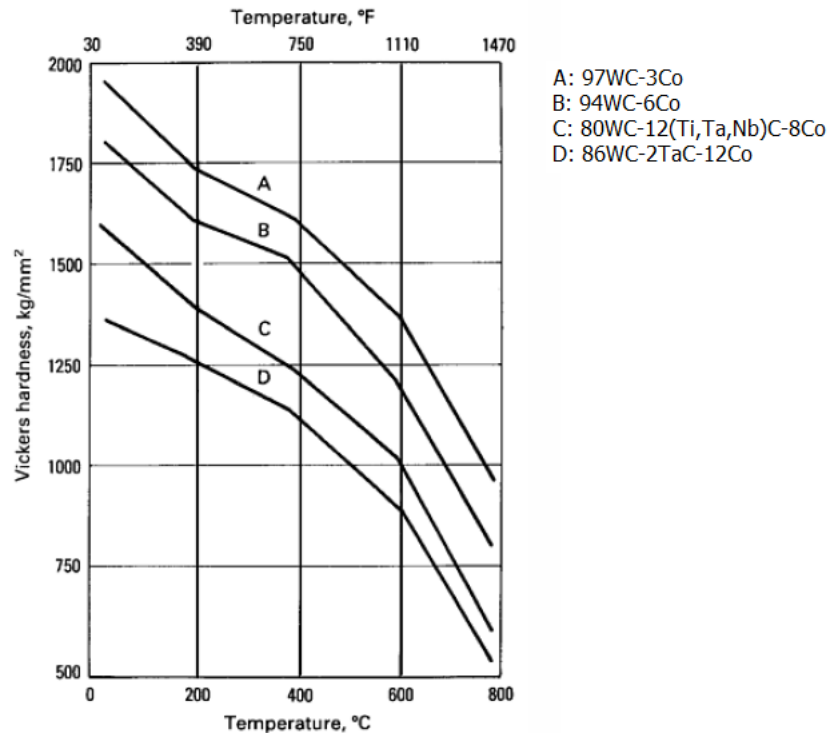


Fig. 8.41 Variation in hardness with temperature for various types of carbides [3].

8.9.8.2 Compressive strength limit

- One of the unique properties of cemented carbides is their high compressive strength, which is greater than that of most other materials - 3.5 to 7 GPa (Fig. 8.42).
- The ductility of cemented carbides is generally low at room temperature – little difference between the yield strength and fracture strength.
- The yield strength decreases with increasing temperature, whereas the rate of decrease depends on the temperature and microstructure - fine-grain alloys tend to lose their yield strengths more rapidly with increasing temperature than coarse-grain ones (Fig. 8.43).

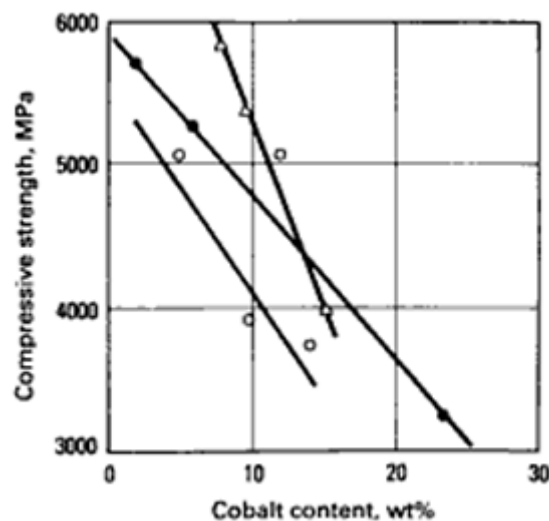


Fig. 8.42 Variation in compressive strength with the cobalt content for WC-Co type cemented carbides [3].

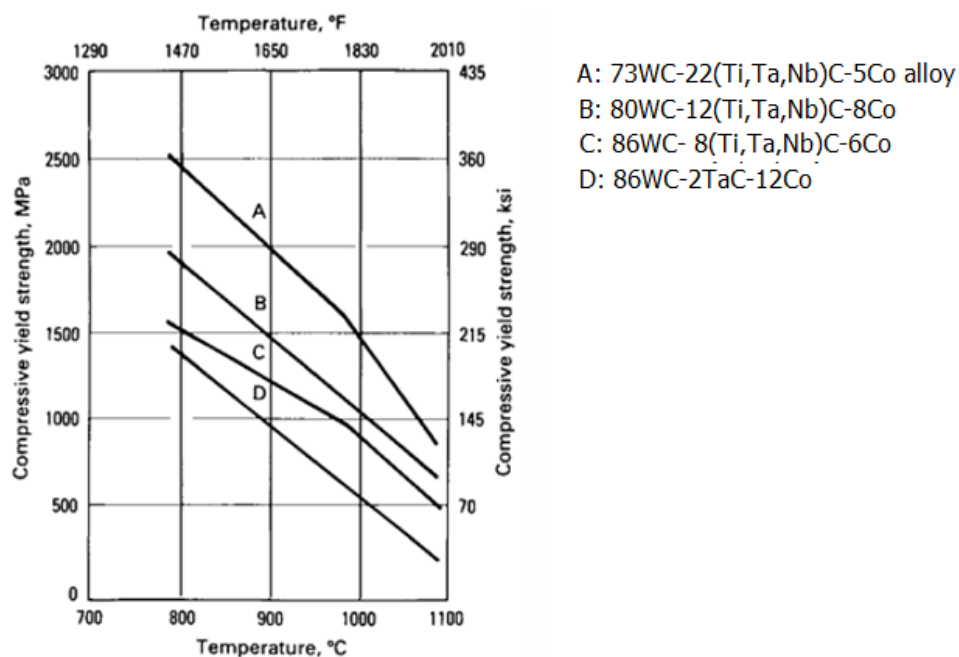


Fig. 8.43 Variation in yield strength with temperature for various types of cemented carbides [3].

8.9.8.3 Density

Density is very sensitive to chemical composition and porosity of cemented carbides and is widely used as a quality control test – 10 to 12 g/cm³ for high alloyed cemented carbides and c. 15 g/cm³ for low Co contents.

8.9.8.4 Porosity

The properties of cemented carbides are dependent on their density, which is dependent on chemical composition and porosity. Porosity is evaluated on the as-polished specimens pursuant to current standards. Three types of porosity are rated (Fig. 8.44):

- **type A** – covering pore diameters less than 10 μm (at a magnification of 200x);
- **type B** – covering pore diameters between 10 and 25 μm (at a magnification of 100x);
- **type C** – covering porosity developed by the presence (precipitation) of free carbon (at a magnification of 100x).

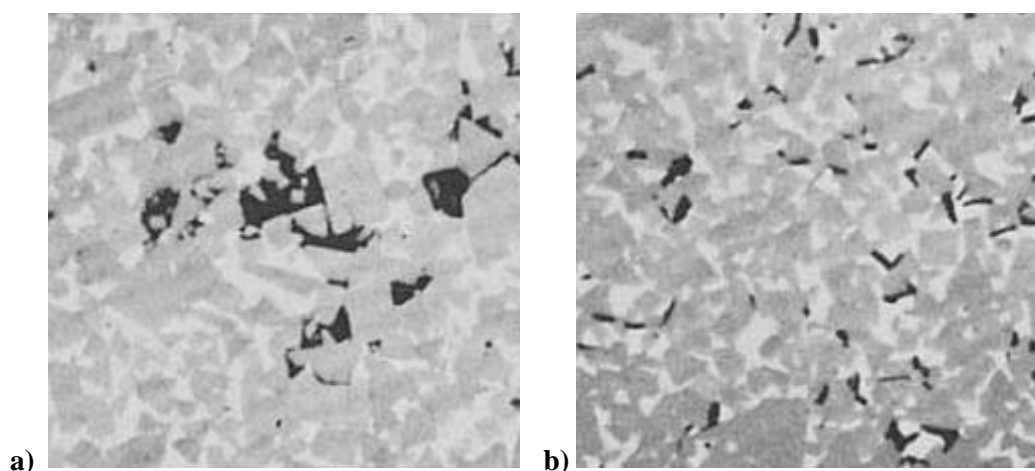


Fig. 8.44 Porosity in WC-Co cemented carbides: a) type A; b) type C [3].

8.9.8.5 Abrasive wear resistance

- It is determined by a wet-sand abrasion test (Al_2O_3 particles) or the abrasive wear resistance index.
- The abrasion resistance and hardness of the final product increases as the binder content and WC particle size decreases (Fig. 8. 45).
- A little amount of TaC (less than 1 %) has no influence on resistance to abrasion due to lower hardness compared to WC.

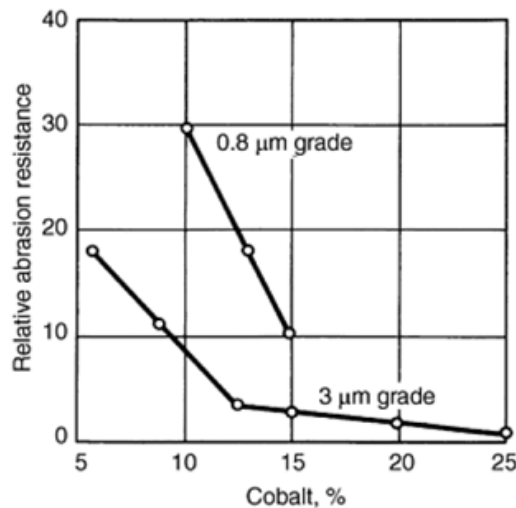


Fig. 8.45 Effect of WC grain size and Co content on relative abrasion resistance [3].

8.9.8.6 Thermal shock resistance

- This is an important property of cemented carbides that determines tool performance.
- Empirical parameters are used to evaluate tool materials for their resistance to thermal shock:

$$\sigma k / E \cdot \alpha$$

where σ – rupture strength; k – thermal conductivity; E – Young’s modulus; α – coefficient of thermal expansion.

- As the cobalt content increases, the Young’s modulus and thermal conductivity decreases, while the thermal expansivity coefficient increases (Fig. 8. 46).
- The higher the value of $\sigma k / E \alpha$ parameter, the better the thermal shock resistance.

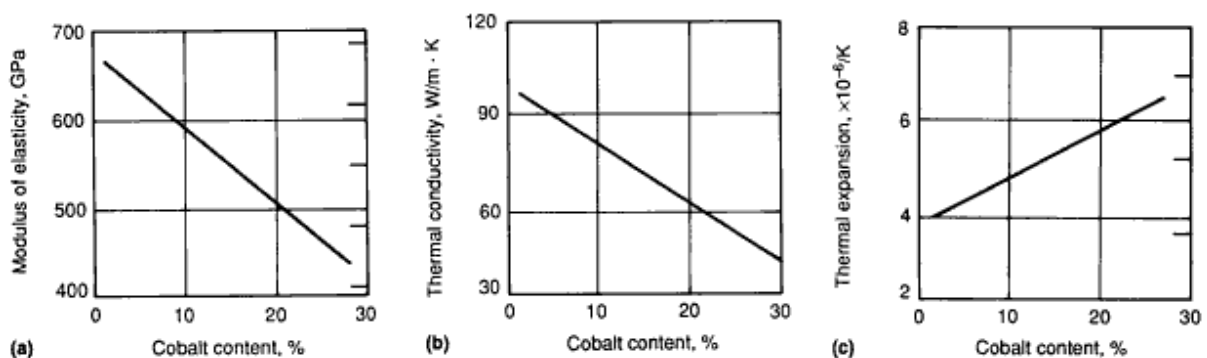


Fig. 8.46 Relation of Young’s modulus, thermal expansion coefficient and thermal conductivity to the cobalt content in WC-Co-based cemented carbides [3].

8.9.9 Cemented carbides for material forming

Cemented carbides for material forming exhibit high abrasion resistance, impact strength and corrosion resistance. In term of requirements for physical properties, the most applicable are materials based on WC-Co, possibly with TaC addition to increase wear and corrosion resistance.

Wear-resistant applications are divided as follows:

- a) **Low impact strength, high abrasion resistance** – nozzles, reamers, drills, pressing dies, glass grinders, dies for extrusion of plastic materials, shears.
- b) **Medium impact strength, medium abrasion resistance** – Al-dies for extrusion, shear edges, wire drawing dies, guide rollers, snow plow cutting edges.
- c) **High impact strength, low abrasion resistance** – pressing dies, milling rods.

8.10 Products from refractory metals

Metals, the melting point of which is higher than for iron (1536 °C), belong to the group of refractory metals. These are particularly Ti, Zr, Hf, V, Nb, Ta, Mo, W and Re. Powder metallurgy technology is used for processing these metals, in particular Nb, Ta, Mo and W, both due to their high melting point and due to high dependence of mechanical characteristics of these metals on their purity. The manufacture of powder tungsten and powder molybdenum was described in Chapter 2.3.

Powder metallurgy technology allows fabricating these metals in the required purity and with properties, which enable their further processing by common forming processes into demanded forms, such as rod, wire, sheet, foil, etc. semi-products. These metals and their alloys find wide use in many technological fields, especially in electronics and vacuum technology. The processing technology consists in the manufacture of a metal powder, its pressing and subsequent sintering, which usually takes place in two stages. For example, for tungsten, pre-sintering at temperature of 1000 to 1400 °C is usually used and final sintering at temperature 2800 to 3100 °C, for molybdenum at 2200 °C. Formability of tungsten and molybdenum strongly depends on their purity. The content of interstitial elements, such as H, O, N and C, has a very unfavourable effect. The transition temperature for W and Mo of 99.95 purity ranges between 150 and 350 °C. Niobium and tantalum are well formable up to the content of impurities (O+N+C) to 0.2 %. To tungsten, which is intended for work at high temperatures (light-bulb filaments etc.), high-melting point oxides (ThO₂, Al₂O₃, Y₂O₃, La₂O₃, CaO, K₂O) in the amount of 0.03 to 1.5 wt.% are added during its manufacture. These additives prevent the tungsten structure coarsening, which would lead to undesirable changes in mechanical properties. Modulus of elasticity and tensile strength of the selected high-melting point metals are shown in Fig. 8.47.

Tungsten, and also molybdenum in a less extent, exhibit very good tensile properties at room temperature and outstanding tensile properties at elevated temperatures. Strength of highly pure, formed and subsequently annealed tungsten reaches a value of 200 MPa at 1800 °C and a value of 100 MPa at 2200 °C. Strength of molybdenum reaches a value of 200 MPa at temperature of 1400 °C. However, when using these metals at higher temperatures, it is necessary to prevent their oxidation which they tend to. Molybdenum begins to oxidate in an oxidation atmosphere from 400 °C; above 600 °C, the oxidation is very intensive. Tungsten begins to oxidate at 500 °C and oxidation is intensive at 800 °C. For this reason, parts from W and Mo, which are intended for work in the oxidation atmosphere, must be covered with protective coatings. Especially tantalum is one of high-melting point metals, which is very advisable for the manufacture of parts intended for corrosion-aggressive atmospheres. For example, it is resistant to salts and nitric acid within a broad range of concentrations and temperatures and also to other aggressive environments. It is therefore used in the chemical industry for building of reaction vessels, equipment for the manufacture of acids, heat exchangers, pumps etc.

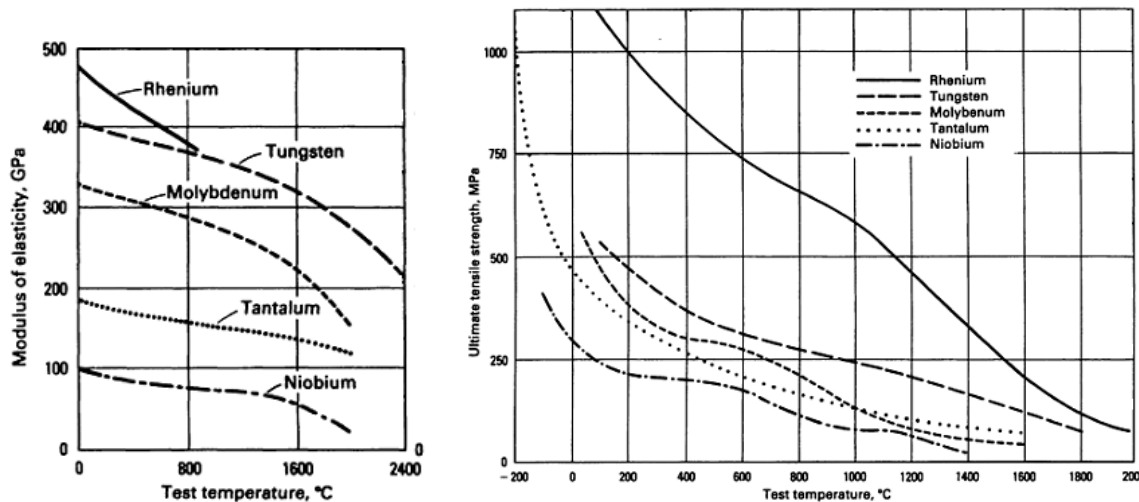


Fig. 8.47 Relation of Young's modulus and tensile strength of the selected refractory metals to temperature [3].

8.11 Magnetic materials

Powder metallurgy technology is used for preparation of AlNiCo type magnetic materials and magnetic materials based on rare earth metals (Nd-Fe-B, Sm-Co). The so-called ferrites belong into a special group. These materials rank among the so-called hard magnetic materials, or permanent magnets. A special group covers the so-called ferrites, which, in term of their design, can be hard or soft. Magnetic properties of a permanent magnet can be determined based on its magnetization curve. The basic values of the magnetization curve B_r (remanence) and H_c (coercivity) characterize the most important magnetic properties of a permanent magnet. When measured, the ferromagnetic materials are subjected to an external magnetic field, which causes a change of (induced) magnetic momentum. The maximum possible value of the energy product reachable by this material is indicated by $(BH)_{\max}$ (Fig. 8. 48).

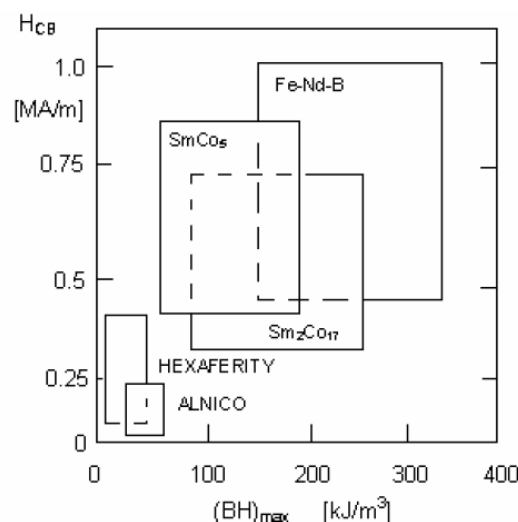


Fig. 8.48 Comparison of the maximum energy product $(BH)_{\max}$ of different types of magnetic materials.

Different magnetic materials, metallic (Nd-Fe-B, Sm-Co, AlNiCo etc.), ceramic (ferrites) and magnets bonded by a plastic material, represent different magnetic fields and can be prepared as anisotropic and isotropic.

8.11.1 AlNiCo magnetic materials

These hard magnetic materials are used for high performances and they are characterized by high brittleness and hardness. Magnetic product of these magnets reaches values of 40 to 72 kJ/m³, remanence of 0.7 to 1.35 T and coercivity of 40 to 160 kA/m. Compared to the conventional manufacturing technology by casting (formation of shrinkage cavities, segregation), powder metallurgy technology is a method of choice for obtaining a more homogenous structure, better mechanical properties and an option for possible machining by cemented carbides to desired dimensions. Various types of AlNiCo magnets are shown in Fig. 8. 49. Manufacturing technology for magnets involves the following processes:

- Mixing and homogenization of metal powders (Ni, Co, Fe); Al is used, regarding its low melting point and high affinity for oxygen, in the form of a powder pre-alloy with iron, possibly Ni.
- Pressing in dies under pressure of 500 to 1000 MPa on hydraulic or mechanical presses.
- Sintering with a liquid phase at temperatures of 1200 to 1350 °C in vacuum or a hydrogen atmosphere. The total shrinkage is usually 8-10 %.
- Improvement of magnetic properties of sintered products requires a further heat treatment.



Fig. 8.49 Examples of applications of AlNiCo magnets[18].

8.11.2 Magnetic materials based on rare earth metals

8.11.2.1 Nd-Fe-B-based magnetic materials

At present, Nd-Fe-B-based permanent magnets represent the strongest types of magnets, which allow minimization of product dimensions and cost reduction (Fig. 8.50). These magnets are used above all for applications in the automotive, power and electrotechnic industry or in medical devices, e.g. in engines of electric and hybrid vehicles, generators for water and wind power stations, computer hard discs, separators, MRI etc. Coercivity of sintered Nd-Fe-B magnets is very high, whereas BH_{\max} is about tenfold higher than for ferrite-based magnets (up to 450 kJ/m³), which allows for their weight reduction and dimension minimization. The work temperature for these magnets can be up to 230 °C, however, lower corrosion resistance is a drawback, so the magnet surface must be treated with Zn, Ni, Ag plating or epoxy resin coating. The ideal structure of the Nd-Fe-B magnet should contain small regular grains of the Nd(R)₂Fe₁₄B hard magnetic phase, which are surrounded on grain boundaries by a thin layer of Nd-rich phase, and Nd(Dy)_{1+ε}Fe₄B₄ phase. Depending on an alloying element type, which can substitute for either Fe (T) or Nd (R), further nonmagnetic or soft magnetic phases can originate in this multicomponent system.

The manufacturing technology for these magnetic materials employs induction melting of an alloy of a required composition with subsequent casting into plate moulds or onto a copper water-cooled wheel rotating at a speed of 2-5 m/s (Strip casting method - SC). The SC method is preferred

because of preventing a formation of long dendrites of the α -Fe soft magnetic phase (causing difficulties when milling) and the Nd-rich phase is finely and homogeneously distributed within the whole material volume. All the process parameters must be controlled within narrow limits – the molten alloy temperature, melt flow velocity, melt strand shape, cooling medium temperature etc. Material in a form of crushed plate castings or strips of a thickness of 0.3 to 0.5 mm, obtained via the SC method, is then subjected to hydrogen decrepitation, which, in principle, substitutes for mechanical grinding and milling. As a result of a formation of hydrides, a number of microcracks originate due to expansion stress and the material disintegration to particles (lumps) of a size of 10 – 1000 μm (Fig. 8.51). The processed material is then milled in a jet mill in a protective nitrogen atmosphere to a desired particle size of 3 to 5 μm . The powder mixture is compressed in dies with a simultaneous magnetic field application, for the particles to be aligned in the direction of its application. Sintering of compacts is then performed at temperature of 1060 to 1090 $^{\circ}\text{C}$ for a period of 2 hours with a consecutive heat treatment.



Fig. 8.50 Examples of shapes of Nd-Fe-B-based permanent magnets [19].

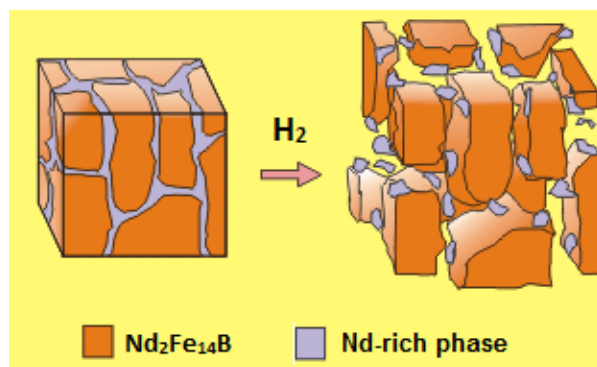


Fig. 8.51 Principle of hydrogen decrepitation in the Nd-Fe-B-based material [20].

8.11.2.2 Sm-Co-based magnetic materials

Samarium-cobalt magnets represent the second strongest type of permanent magnets next to Nd-Fe-B-based magnets. They are based on the appropriate intermetallic phases SmCo_5 and $\text{Sm}_2\text{Co}_{17}$.

The manufacture consists in induction melting of an alloy of a required composition, crushing, milling, pressing in the magnetic field and subsequent sintering. Sm-Co is a brittle and hard material with a high energy product. These magnets are very resistant to a demagnetizing field acting.

A drawback of Sm-Co magnets is a high content of cobalt, which makes the final price going-up considerably. Therefore they are mainly used for applications, where small-size magnets with high energy are needed at high temperatures. The work temperature of SmCo_5 magnets is up to 250 $^{\circ}\text{C}$ and of $\text{Sm}_2\text{Co}_{17}$ magnets up to 300 $^{\circ}\text{C}$.

8.11.3 Ferrites

Ferrites are magnetic materials manufactured from metal oxides. Except from different magnetic characteristics, they feature high specific resistance, contributing to a loss decrease by eddy-currents and low apparent density of 3.8 to 5.1 g.cm⁻³. In general, ferrites are divided as follows:

- 1. Soft magnetic spinel ferrites with a rounded hysteresis loop** (MeO.Fe₂O₃; Me - Ni, Zn, Fe, Cu, Li, Co) – are characterized by high structural and phase sensitivity to magnetic properties. They feature low H_c , high μ_B , low I_s value, relatively low Curie temperature and resistivity $\sim 10^{-3} - 10^{10}$ Ω.cm. Applications – radiotechnics in a range of frequencies 100 Hz to 100 MHz, magnetostrictive materials for conversion of electromagnetic energy and mechanical vibrations etc.
- 2. Hard magnetic hexagonal ferrites** (MeO.6Fe₂O₃, Me - Co, Ba, Pb, Sr) – feature high H_c , lower B_r , resistivity $\sim 10^9$ Ω.cm and considerable brittleness. Applications – permanent magnets, rotors, stators of direct-current and asynchronous motors.
- 3. Ferrites with a rectangular hysteresis loop** (MeO.Fe₂O₃, Me - Mn, Mg) – feature a high coefficient of rectangularity and a very short re-magnetization time. Applications - computer technology (memory elements) and automatized control systems.
- 4. Soft magnetic ferrites for very high frequencies** (MeO.Fe₂O₃, Me - Ni+Cu, Mg+Mn, Ni+Zn, Y₂O₃) – must meet requirements for high resistivity of $10^8 - 10^{11}$ Ω.cm (a decrease of magnetic losses), high density, stability of properties within a specified temperature interval, high sensitivity within a range of operation frequencies. Applications – waveguides.

The manufacturing technology for ferrites involves the following steps:

- wet milling and homogenization of the initial raw materials in a form of synthetic oxides of iron, nickel, zinc, manganese, copper and magnesium, for hard magnetic ferrites barium and strontium carbonates in ball mills (powder size $\sim 5 \div 10$ μm);
- drying;
- calcination (thermal decomposition) at 800÷1000 °C (formation of the ferritic structure);
- wet milling (powder size $\sim 1 \div 2$ μm);
- drying;
- forming of the powder mixture by pressing in dies in a magnetic field under pressure of 100 to 200 MPa, or by extrusion; dry as well as wet powders can be used, so that they align themselves along the direction of the applied magnetic field;
- sintering at temperatures 1100÷1400 °C (large shrinkage up to 30%);
- surface finishing (polishing, diamond cutting).

8.12 Carbon materials

Owing to their properties, carbon materials hold a special position between metals and ceramics. The products can be divided to coarse-grained (< 12 mm) and fine-grained (< 0.1 mm). They feature a more or less oriented structure, high electrical and thermal conductivity and low thermal expansion. Graphite is an only material the strength and modulus of elasticity of which increases with temperature to 2300 °C. This phenomenon relates to processes of removal of structure defects at high temperatures.

Carbon- or graphite-based products find their use in various technical fields. Generally, these products can be divided into brushes for rotating electrical machines and other components and devices. Brushes for rotating electrical machines represent important components serving for power supply from a stationary machine part to a movable one – a commutator or a ring, by which an energy-

saving regulation of speed is ensured in traction motors, electrical devices in vehicles and electrical machines in power industry, metallurgy and other industrial branches. Good friction properties and resistance to melting and welding-on are utilized for a manufacture of contacts and friction materials. Other equipment and parts of carbon include above all moulds for horizontal and vertical semi- and continuous metal casting. These materials exhibit particularly high thermal and chemical stability, high thermal conductivity and favourable sliding and lubricating characteristics. This type of material is advisable mainly for non-ferrous metals which have high wetting angle in a combination with carbon. Using carbon materials, higher casting speeds, higher homogeneity of a casting and higher surface quality can be achieved. Carbon materials are significant and, in a way, preferred in a manufacture of electrodes for spark machining.



Summary of terms

PM steel

Filter

Self-lubricating bearing

Cemented carbides

Cermet

Ferrites

Dispersion hardened materials



Questions to the topic

- 8.1. What is the application of Fe-based PM materials?
- 8.2. How are the self-lubricating bearings produced?
- 8.3. What are the requirements on friction composites?
- 8.4. What is the suitable particle shape for the production of metal filter?
- 8.5. What are the main components of cemented carbides?
- 8.6. Which material is characteristic with the highest value of the maximum energy product $(BH)_{\max}$?



Solved tasks

Exercise 8.1

5 tons/year of WC cemented carbide are produced in a plant. As a binder, 8 wt.% of Co is used, which is gained from $(COO)_2Co$ oxalate by reduction of H_2 with the process efficiency 50 % + 5 % of Co loss through manufacturing. Assume 360 days per year for computations purposes. Hydrogen is manufactured by water electrolysis.

In the plant, there are:

12 furnaces where $W + C \rightarrow WC$ reaction takes place in the hydrogen atmosphere. Hydrogen consumption is 3 l/min.

10 furnaces for sintering in hydrogen Hydrogen consumption is 5 l/min.

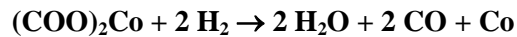
Calculate:

- Hydrogen consumption per day / per year
- W and C consumption

♦ **Solution**

Ad a) Hydrogen consumption per day / per year

The oxalate decomposition occurs in accordance with the reaction:



$$M(\text{Co}) = 58.93 \text{ g/mol}$$

$$M(\text{H}_2) = 2 \text{ g/mol}$$

$$V_m(\text{H}_2) = 22.4 \text{ dm}^3 = 0.0224 \text{ m}^3$$

Cobalt consumption:

$$100 \% \dots\dots\dots 5 \cdot 10^6 \text{ g (WC + Co)}$$

$$8 \% \dots\dots\dots m_{\text{Co}}$$

$$m_{\text{Co}} = 400 \cdot 10^3 \text{ g} + 5 \% \text{ loss} = \mathbf{420 \cdot 10^3 \text{ g}}$$

$$m_{\text{H}_2} = m_{\text{Co}} \cdot 2M(\text{H}_2)/M(\text{Co}) = 420 \cdot 10^3 \cdot 2 \cdot 2 / 58.93 = \mathbf{28.5 \cdot 10^3 \text{ g}}$$

$$m_{\text{H}_2} = \frac{2M_{\text{H}_2}}{M_{\text{Co}}} = 420 \cdot 10^3 \cdot \frac{2 \cdot 2}{58.93} = \mathbf{28.5 \cdot 10^3 \text{ g}}$$

$$V_{\text{H}_2} = \frac{m_{\text{H}_2} \cdot R \cdot T}{M_{\text{H}_2} \cdot p} = \frac{28.5 \cdot 10^3 \cdot 8.314 \cdot 273.15}{2 \cdot 1 \cdot 101325} = \mathbf{319.38 \text{ m}^3}$$

$$\text{The process efficiency is } 50 \% \Rightarrow 2 \cdot 319.38 = \mathbf{638.76 \text{ m}^3/\text{year} \dots \mathbf{1.77 \text{ m}^3/\text{day}}}$$

The consumption in the furnaces:

$$\text{- synthesis: } V_{\text{H}_2} = 12 \cdot 0.003 \cdot 60 \cdot 24 \cdot 360 = \mathbf{186 \ 62.40 \text{ m}^3/\text{year} \dots \mathbf{518.40 \text{ m}^3/\text{day}}}$$

$$\text{- sintering: } V_{\text{H}_2} = 10 \cdot 0.005 \cdot 60 \cdot 24 \cdot 360 = \mathbf{25 \ 920.00 \text{ m}^3/\text{year} \dots \mathbf{72.00 \text{ m}^3/\text{day}}}$$

$$\Sigma V_{\text{H}_2} = 638.76 + 18 \ 662.40 + 25 \ 920 = \mathbf{45 \ 221.16 \text{ m}^3/\text{year} \dots \mathbf{125.61 \text{ m}^3/\text{day}}}$$

Ad b) W and C consumption

5 t WC + Co....8 %Co, 92 % WC

$$m_{\text{WC}} = 0.92 \cdot 5 \cdot 10^6 = \mathbf{4.6 \cdot 10^6 \text{ g/year} \dots \mathbf{12 \ 777.78 \text{ g/day}}}$$

$$m_{\text{W}} = m_{\text{WC}} \cdot M_{\text{W}}/M_{\text{WC}} = 4.6 \cdot 10^6 \cdot 183.85/195.86 = \mathbf{4.32 \cdot 10^6 \text{ g/year} \dots \mathbf{11.99 \cdot 10^3 \text{ g/day}}}$$

$$m_{\text{C}} = m_{\text{WC}} \cdot M_{\text{C}}/M_{\text{WC}} = 4.6 \cdot 10^6 \cdot 12.01/195.86 = \mathbf{0.28 \cdot 10^6 \text{ g/year} \dots \mathbf{783.52 \text{ g/day}}}$$



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