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Porous Metals from Powder Metallurgy Techniques

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Abstract

Porous metals are in use in many technical applications like filters, membranes, structural parts, sound absorbers, gasification units, sleeve bearings, electrochemical devices or biomedical implants. A well-defined network of interconnected pores defines the function of these components. Due to the broad range of possibilities for tailoring pores, powder metallurgy techniques are the preferred method of manufacturing porous metals. This book chapter highlights specific advantages of porous metals, introduces the basic principles of their manufacturing by selected powder metallurgy techniques and explains their potential by means of current applications. Finally, the chapter summarizes standard methods for characterization of porous metals.

1. Introduction

Many technical applications like filters, membranes, structural parts, sound absorbers, gasification units, sleeve bearings, electrochemical devices or biomedical implants rely on porous metals. Powder metallurgy techniques are preferred to manufacture such components resulting in a welldefined network of interconnected pores and therefore defining the function of these components. Adapted processing and sintering parameters enable tailoring of the pore morphology to large extent. Different kinds of powder metallurgy techniques and alloying systems are in use to adjust the properties with respect to the required mechanical strength, ductility, corrosion resistance, pore size, porosity, flow rate, selectivity and others. Development of innovative novel techniques further broadens the range of applications. Examples are porous components for electrochemical devices like substrates for solid oxide fuel cells or porous transport layers for electrolysis cells. Here, advantageous combination of metal properties like mechanical stability, resistance against high differential pressures, vibrations or mechanical impacts and joining ability by soldering/welding with the performance of electrochemically active ceramic or polymer membranes defines the function of the part. Another important field of application are biomedical implants. Adjustment of pore size and porosity enables stable fixation of implant in the human skeleton due to enabling adaption of Young's modulus and bone ingrowth. In this book chapter, we introduce the motivation of using porous metals for numerous applications in a more general way at first. By means of selected examples with high relevance to industrial application, subsequent sections explain how to produce these components by specific adaption of suitable powder metallurgy techniques. Finally, standard methods for characterizing components with functional or structural porosity are presented.

2. Specific advantages of porous metals

If aiming on to manufacture porous metals, there is no best practice method, which fits for all applications and materials (Atwater et al., 2018). Generally, there is a difference providing porous parts for functional or structural applications. If kind of porosity dominates the function of component, powder metallurgy techniques are often the only option for manufacturing. Powder metallurgy offers a broad range of possibilities to control porosity, pore size and pore shape. In the case of functional applications, an open network of pores interacts with a surrounding medium. The amount, size and shape of each single pore play a significant role for the function of the whole component. Closed pores, which do not have any interconnection to the surrounding medium or do not allow flow of the medium through the pore network, are useless and unwanted.

In contrast, preferential applications of materials with structural porosity are construction elements for heavy machinery or architecture (**Atwater et al., 2018**). The focus lies on an optimum combination of mechanical performance at low density usually aiming on lightweight parts with high specific stiffness and energy absorption capacity. Here, closed porosity might be even advantageous due to e.g. avoiding penetration of the structure with corrosive media. Aluminum foams already produced on industrial scale are typical representatives of materials with structural porosity. They are usually manufactured by entrapping gas bubbles in a high viscous melt, but due to use of Al and TiH₂ powders as starting materials they have a relevance here as well (**Banhart, 2001**). In general, it must be considered that components with structural porosity can be often realized by other solutions like honeycomb structures with at even lower costs and specific weight than metal foams. Due to comparably high costs and limitations regarding realization of large parts, classical powder metallurgy techniques like pressing and sintering are often not competitive for structural applications.

Functional porous metals compete against porous ceramics and polymers, especially if pore sizes below $0.8 \mu m$ are aspired. If applying established PM techniques, powder particle sizes below five

µm are usually required to achieve such pore sizes. Risk of self-inflammation due to the high specific surface and the need of applying specifically adapted protective conditions limits the application of fine metal powders for such applications and prefers the application of ceramic powders. An attractive alternative are metal/ceramic composites, which combine advantages of metals and ceramics in one component as discussed in more detail later. Fine porous polymers are less expensive than metals or ceramics, but have restrictions with respect to higher temperatures and higher differential pressures. Furthermore, their long-term stability is limited in contact with corrosive media or cleaning agents. Nevertheless, in some cases polymer parts are preferred as single—use component, e.g. if cleaning of metal or ceramic components does not work properly like in the case of membranes for artificial lungs.

If pore sizes above $0.8 \mu m$ are the aim, porous sinter metals made by powder metallurgy techniques offer a number of specific properties, which in sum can lead to advantages compared to ceramic or polymer parts:

- Dimensional stability, even in the case of high differential pressure
- High mechanical stability in the case of impacts, pressure drops, vibrations and thermo shocks
- Long-term stability at elevated temperatures (bronze up to 400°C, high alloyed steels up to 600°C, special alloys up to 1000°C)
- Providing the use of suitable alloys, chemical stability against acids and caustic cleaning agents
- Wide spectrum of cleaning methods like stripping, supersaturated hot steam, chemical agents or thermal treatment
- Wide spectrum of pore sizes, ranging from 0.8 to 2000 μm
- Green technology due to the potential of long-term application, re-use and recycling
- Shaping by conventional methods like milling
- Ease of joining, e.g. by soldering or welding

If suitable powders are available, almost every metal and alloy enables the manufacturing of components with functional porosity. For giving an overview of porous metals and alloys, we refer to the respected literature (GKN Sinter Metals, 2020). In addition, Section 4 shows some examples of material selection for specific applications.

3. Ways to adjust pore sizes by powder metallurgical means

Influence of the starting powders: The shape and the size of the starting powders has a significant influence on the kind of porosity in the sintered part. For detailed description of powder processing, we refer to related literature (Schatt and Wieters, 1997). In most cases, producers of metal powders use atomization of melts. Varying the pressure of the atomization medium enables to adjust the mean particle size of the powders to a certain extent. Depending on atomization medium, specific surface tension of the melt and time until solidification of the melt, spherical or irregular shaped powders result. Gas atomization with inert gas like Argon usually leads to formation of spherical particles and fits for metals or alloys, which are sensitive to oxygen (e.g. titanium and its alloys). Gas atomized powders exhibit a smooth surface and are less suitable for powder compaction techniques. Therefore, their shaping requires methods, which distinguish themselves by a good flow ability like pouring, wet powder spraying, tape casting or screen-printing. To preserve the shape of the part, such methods require in most cases a multicomponent binder system combined with the need to remove it by a separate debinding step before sintering. Contrary, water atomization leads to rapid solidification of the melt resulting in irregular shaped particles. It is suitable to metals and alloys, which are less sensitive to oxygen or which form oxides easily to reduce by adapting the sintering atmosphere. Other methods for production of irregular shaped powders comprehend reduction of oxides, established in industrial scale for the production of Febased powders and refractory metal powders, hydrogenation – milling – dehydrogenation (HDH) for titanium powders and last not least electrolytic deposition of metals like Cu or Ni. Irregular shaped powders usually have a good compaction ability due to interlocking of the particle contacts supported by plastic deformation of surface roughness and cold welding. In the case of shaping by pressing, there is no need of binders but pressing aids can be helpful to increase homogeneity of the microstructure by reducing die wall and inter particle friction.

Particle size distribution has a significant influence on the resulting pore size. Therefore, fractioning of starting powders by sieving or air classifying – aiming on a narrow Gaussian distribution of particle sizes – is an important processing step after powder production. For spherical powders, median pore size is in a rough approximation one fifth of the median particle size. Considering that the closest packing density of spheres is 74 vol. %, overall porosity of

sintered parts usually can be expected in the range of 20-30 vol. %. In the case of irregular shaped powders, the morphology of resulting pores is hard to define and therefore it is often difficult exactly giving a pore size. Therefore, we recommend characterizing such structures by their specific properties like particle retention ability or flow resistance. Interlocking of particles and cold welding enables to produce parts with porosities up to 50 vol. %. **Figure 1** shows typical pore structures of parts made of spherical powders or irregular shaped powders.

In general, porous metals made by powder metallurgy techniques require a sintering step to achieve the final properties (Schatt and Wieters, 1997). If shaping has been done by wet chemical methods, all organic compounds have to be removed before sintering by an additional debinding step, which can be done e.g. by solving or thermal decomposition. Debinding requires care to avoid contamination of the sintered part with interstitials like oxygen or carbon, which can in worst case significantly deteriorate mechanical properties. Driving force of sintering is the reduction of free surface area, grain boundaries and lattice defects. For keeping an open porous structure, sintering process has to interrupt at an early stage after the formation of stable sintering necks between the particles. Typically, sintering temperatures suitable for preserving the porous state are lower than sintering temperatures required for full densification. At these temperatures, gas phase and surface diffusion mechanisms dominate, which are mainly responsible for sintering neck formation. Depending on the material and particle size of the starting powders, sintering temperatures are usually in the range of 800 - 1300°C and dwell times may range between 0.5 and 5 hours. To reduce uptake of interstitial elements like oxygen to a minimum, sintering requires inert or reducing conditions. Typical sintering atmospheres for industrial production are endogases, N2, N2/H2, H2 or vacuum.

<Figure 1 near here>

The following part introduces the most important powder metallurgy techniques to produce netshaped parts with well-defined porosity. **Figure 2** summarizes all techniques by schematic sketches. Loose powder sintering: Loose powder sintering is the simplest method to produce porous metals since only the powder, a suitable mold and a furnace are required. The process starts by pouring the starting powder into the mold. Optional tapping or vibration enables to increase the packing density of the powder. Then, sintering necks form between the powder particles during sintering preserving the shape defined by the geometry of the mold. For achieving homogeneous pore structures, spherical particles are preferred.

Shaping by binder based and wet chemical methods: There are a couple of powder metallurgy methods, which enable the manufacturing of net-shaped parts by adding a binder system. Commonly, spherical particles are preferred for these methods due to better flow ability, but they can be – as discussed in more detail later – even applied for irregular shaped powders if higher porosities are the aim. Net-shaping of components can be done by metal injection molding, extrusion, tape casting, wet powder spraying, screen-printing, dip coating and others. Final porosity depends on adapting the temperature and dwell time of the final sintering step accordingly.

Shaping by pressing: Production of porous metals on industrial scale often uses pressing and sintering. To improve compaction behavior and homogeneity, adding pressing aids like lubricants to the starting powder is helpful. Application of multiaxial pressing devices enables to achieve complex shapes. In addition, isostatic pressing with flexible molds enables to produce porous parts with a large height/diameter ratio, which is e.g. attractive for tubular shaped filters. In general, pressing clearly improves the particle bonding and the flexural strength of the parts, but high compaction pressure in combination with subsequent sintering leads to a loss of porosity.

Application of sacrificial templates and space holders: If porosities higher than 50 vol. % are the aim, established PM techniques fail due to not achieving sufficient strength. To overcome this restriction, application of temporary templates or space holders is a promising approach. In the first case, coating a net-shaped template with the metal powder replicates its shape. A well-recognized example is replication of a polymer foam by dip coating technique. The second case comprises mixing of the metal powder with a space holder material and subsequent shaping of the mixture by powder metallurgy techniques (e.g. pressing or metal injection molding). After shaping, removal of template or space holder by leaching or thermal decomposition follows and then sintering as

final step. Advantageously, sintering temperatures usually required for full densification are suitable since the template/space holder introduces porosity. Low residual porosity of the sintered struts is prerequisite to achieve suitable mechanical stability of the highly porous parts. With the template technique, porosities higher than 90 vol. % and pore sizes up to several mm has been demonstrated (Li et al., 2002). With the space holder technique, porosities in the range of 70 - 80 vol. % and pore sizes in the range of 200 - 500 µm are reasonable (Imwinkelried, 2007).

Hollow spheres: Another related method to achieve highly porous structures is to produce hollow spheres by coating a template sphere (e.g. expanded polystyrene with diameter in the mm range) with metal powder, removing the template by thermal decomposition and sintering the remaining sphere. Application of hollow spheres encompasses filling lightweight structures or direct combination to a three-dimensional part by applying another heat treatment. Hollow spheres are preferentially attractive for structural applications.

Cellular structures by design: In the last years, additive manufacturing techniques starting from metal powders have gained a lot of attraction for the manufacturing of porous metals (Sames et al., 2016). Direct replication of a digitally designed part starts with slicing it into separate layers and then printing the part layer by layer in a powder bed. Most commonly used are selective laser melting and electron beam selectively melting the powder bed. Recently, binder jetting has attended increasing interest. Here, a liquid adhesive printed on the powder bed binds the powder particles together. Filament printing is another attractive method to build up three-dimensional structures. After terminating the printing process, consolidation of parts requires debinding and sintering. In general, additive manufacturing techniques enable periodic lattice structures as well as stochastic foam replications. Furthermore, individual adaption of customer needs are easily feasible.

<Figure 2 near here>

4. Examples of applications of porous metals made by powder metallurgy techniques

4.1 Sintered Bronze

Loose powder sintering is an established method for manufacturing porous Bronze parts on industrial scale. Therefore, the process starts with pouring spherical Bronze powders (alloy Cu89Sn11) in the cavity of a graphite mold followed by increasing the packing density by vibration. The molds pass through a continuous sintering furnace heated to 820°C in the hottest zone. Reducing hydrogen atmosphere avoids oxidation of the powder particles. At 820°C, formation of stable sintering necks takes place, which are responsible for the mechanical stability. Since shrinkage of the parts remains marginal, ease remove from the mold after sintering is possible. Optional, loose powder sintering enables sintering connection to flanges, sockets, threads or hexagonal bolts by directly placing them in the mold before charging the furnace. Figure 3a shows examples of parts made by loose powder sintering of Bronze powders. In principle, this method can be even adapted to other metals or alloys, but it is often difficult to find a suitable mold material, which does not react with the sintered part especially at higher sintering temperatures. Main use of sintered Bronze parts is in pneumatic or hydraulic devices. Examples of application are filtration of particulate materials from hydraulic oil, lubricants or liquid fuels as well as separation of aerosols from gas streams. Furthermore, such structures enables to distribute, throttle or settle streaming gases or liquids. As side effect, noise level of streaming gases reduces significantly.

4.2 Filters

The standard methods for manufacturing porous parts from metals and alloys, which require higher sintering temperatures (e.g. Fe- and Ni-based alloys, steels), are axially or cold isostatic pressing. As mentioned before, irregular shaped powders are preferred for these methods. The powders are compacted to a degree that enables handling and charging them in the sintering furnace. Uniaxial pressing is used for the manufacturing of components with planar shape. Here, it must be considered that coarse powder fractions and larger dimensions of the part require high compaction forces (up to 1000 tons) restricting the maximum size of the plates to approximately 200 x 300 mm². Optionally, larger parts can be realized by welding of single plates. Multiaxial pressing allows the manufacturing of parts with enhanced geometrical complexity like hollow cylinders

with moderate height/diameter ratio. Maximum ratio is limited to approximately 3:1 due to increase of wall friction. If exceeding a critical value, cracking of the compact during ejection results. For enlarging the height/diameter ratio, cold isostatic pressing comes into play. Here, an elastic rubber mold is filled with the powder and sealed by a cap. Then the mold is placed in a pressure vessel, which is filled with water or hydraulic oil. After closing the vessel, the powder is isostatically compacted by compressing the pressure transfer medium via a compressor. If manufacturing of porous tubes is aspired, a metallic mandrel is placed in the center of the elastic mold and the powder is pressed on it. The mandrel is removed after ejection, resulting in a porous tube, optionally with open or closed end. The maximum length of the tubes is up to 1.8 m, the maximum diameter is around 300 mm. Cold isostatic pressing enables to directly introduce flanges, sockets or threads in the elastic mold. Depending on the production output, sintering of pressed compacts is conducted in a chamber furnace or a continous furnace under protective atmosphere. **Figure 3b** gives an overview of porous components made by uniaxial pressing.

<Figure 3 near here>

In most cases, porous metals made of Fe- or Ni-based powders are applied for filtration and separation processes. End users come from chemical industry, food and beverage industry, pharmaceutics, cellulose and paper industry, petrochemical industry, producers of liquid and gaseous fuels, polymer industry and automotive industry. Beyond filtration, porous compacts are used for gassing and fluidization of liquids and granulates. Compressed gases are fed through the porous part and are homogeneously distributed to the surrounding medium. Further applications are flame arrestors and explosion protection. Here, spreading of flames is stopped by the pore network. High thermal conductivity, shock resistance and low flow resistance are other attributes distinguishing porous metals for this application. Last, not least, isostatically pressed tubes are in use as pulley for processing of polymer tapes.

Application of pure metal filters is limited if pore sizes below 1 µm are the aim. To overcome this restriction, multilayered filter systems with a stepwise gradient in porosity are an established solution. Furthermore, thin fine porous functional layers on coarse porous substrates have clear advantages due to significantly reduced flow resistance without changing the separation behavior.

Furthermore, graded filter concepts enable to combine different classes of materials like metal-ceramic composites, combining the advantages of metal substrates (mentioned before) and ceramic functional layers (higher chemical stability, lower pore sizes). An established method for manufacturing multilayered filters is to produce the metal substrate with established powder metallurgy routes (uniaxial or cold isostatic pressing, tape casting) and to deposit the functional coatings by wet chemical methods like wet powder spraying or dip coating (Zhao et al., 2004). Specific techniques enable to even realize pore sizes in metals down to the nano meter range. Due to being out of scope of the present work, we refer to the related literature (Zhu et al., 2018; Huang et al., 2019).

4.3 Structural Applications

Porous metals combine lightweight, strength, stiffness and energy absorption, which make them attractive for many structural applications as well. Here, structures with closed pores are favored due to their improved mechanical properties. Commercialization of porous aluminum started in the 1990ies and it remains the most used porous metal for structural applications caused by its high stiffness/weight ratio. Examples of application include crash elements for cars, lifting arm for element platform, wagon floor and crash absorption structures for trains (Lefebvre et al., 2008). As alternative, development of porous iron, nickel and titanium deals with application in particularly extremely harsh environments where aluminum has not enough strength, chemical or temperature resistance. Porous metals are in use as core of sandwich panel further increasing stiffness at moderate weight. In spite of being more expensive than the honeycomb structures traditionally used for lightweight constructions, sandwich panel filled with porous metal offer some specific advantages such as improved energy absorption, acoustic properties and vibration damping (García-Moreno, 2016). There is an expected growth of applying porous metals in the automotive industry triggered by increasing electrification of vehicles. Lightweight materials are key to increase transport autonomy. Another important consideration is the fact that electrical cars do not have a heavy combustion engine in the front part of the car. Therefore, an alternative crash absorption system is required. This system should be as light and compact as possible. Recent tests of tubes and pillars filled with porous aluminum (Figure 4a) recommend them as crash system in electric vehicles. Increase of specific strength and stiffness had the expected impact on energy absorption and therefore on safety (Hanssen et al., 2016; Banhart et al. 2019). Another promising application of porous aluminum is the battery compartment of electrical cars. Replacing current multilayer structure made of bulk aluminum and steel sheets by porous aluminum sheets will decrease weight while increasing the protection of the battery against impact, consequently increasing safety in case of a collision (Banhart et al., 2019). Porous metals with multifunctionality might be a cost-effective solution for aerospace applications as well. Sandwich panel filled with porous metals would increase damping of vibration and sound of turbines as well as temperature isolation compared to traditional dense aluminum sheets used in airplane fuselage. Porous metals are especially attractive in the hot section of aircrafts, where the temperature limits the use of polymer reinforced composites. Other possible application is to increase impact protection against collisions with birds in airplanes or with micro-meteorites in satellites (García-Moreno, 2016; Banhart et al., 2019). In future, additive manufacturing will play an important role in the manufacturing of porous structural parts for aerospace, especially for parts made of titanium alloys and superalloys.

4.4 Vibration and sound damping

Porous materials are promising candidates for dissipating acoustic wave soundproofing. In general, soundproofing capacity of porous metals is lower than that of porous polymers and ceramics. Furthermore, they are more expensive. However, porous metals have other attractive properties like higher stiffness, vibration damping, lightweight construction, fire protection, chemical stability and 100% recyclability, which combined to acoustic damping make them suitable for soundproofing in harsh environments when other kinds of foams fail. Tuning the microstructure of porous metals increases the absorption range. In general, an open porosity and pore sizes in the order of 10 to 1000 µm are optimal for acoustic absorption (Banhart, 2001). Recently, space holder method enabled manufacturing of porous aluminum parts with a significant absorption in the audible range. Adding an air gap between the sample and the rigid back surface improved their sound absorption (Hakamada et al., 2006). Warmuth et al., 2017 demonstrated that porous titanium struts produced by electron beam melting had a phonic band gap (in the range of 100 kHz), which can be adjusted by modifying the struts thickness. Aerospace industry can particularly take benefit of porous metal sound absorbers applied in the fuselage or turbines to reduce noise and vibration.

4.5 Heat exchangers

Heat exchangers made of porous metals are in use as compact cooling system for high power electronics and other small system where water-cooling would not be possible and fan would not be convenient due to noise. Porous aluminum with open porosity (Figure 4b) is the most used metal as heat exchanger due to low density, high surface area and heat conductivity. Besides aluminum, porous nickel and porous copper are also attractive for industrial heat pipes due to their improved heat exchanger performance. Other authors report on testing heat exchangers made of porous metal in fuel cells, solar panels and hydride tanks for hydrogen storage. Odabaee et al., 2013 replaced the water-cooling system of polymer electrolyte membrane-fuel cell (PEM-FC) by an air-cooling system based on porous aluminum. This system required less pumping power and resulted in more uniform distribution of temperature in the bipolar plate. Afshari et al., 2017 demonstrated that the addition of a porous aluminum layer attached to the bipolar plates in a PEM-FC stack increase the uniformity of temperature distribution while keeping a low pressure drop. Jouybari et al., 2017 applied a porous metal part in a solar collector. This component acts as heat exchanger by absorbing solar energy and converting it into heat. Another promising application for heat exchangers made of porous metals are metal hydride tanks for hydrogen storage (Figure 4c). Mellouli et al., 2009 showed that the use of porous aluminum significantly accelerates heat transfer and therefore reduces the storage time by 60 %.

<Figure 4 near here>

4.6 Sliding materials and bearings

Sliding materials and bearings belong to the group of porous metals manufactured on large industrial scale for many mechanical engineering applications like electro motors, pumps, tooling machines, door hinges and many others. The main task of bearings is to keep a moving part in position while absorbing load and reducing the energy losses due to friction to a minimum (Schatt and Wieters, 1997). In most cases, porous metals based on Fe, Cu or Bronze are used for the production of bearings. After powder conditioning, established powder metallurgy techniques like pressing and sintering are in use for fully automated production of bearings. To improve the performance characteristics, bearings are sized (e.g. by a calibration step) and vibratory grinded to improve the surface quality at the interface being in contact with the moving part. To enable the

formation of a liquid film during operation, which reduces friction to a minimum, in most cases impregnation of bearings directly follows powder metallurgy processing. Typically, suitable oils with adapted viscosity and thermal stability are in use as lubricants. Bearings have to fulfill a complex requirement profile ranging from good running-in behavior, low coefficient of friction, high load capability, good lubrication breakdown behavior and wear resistance, high thermal conductivity, adapted thermal expansion coefficient, good absorption of vibrations and many others.

4.7 Porous implants

Porous implants are attractive to improve long-term fixation in the human skeleton due to stimulating cell attachment and bone ingrowth. An established method to tailor the surface roughness of load bearing part of implants like the shaft of hip or knee implants is vacuum plasma spraying of metal powders. By suitable adapting the spraying parameters, the surface roughness can be tuned stimulating cell attachment and bone ongrowth (**Ryan et al., 2006**). To achieve a real interlocking between implant and bone, ingrowth of bone in the porous implant is advantageous. To achieve this goal, a percolating network of pores with pore sizes in the range of $300 - 1500 \,\mu m$ and porosity beyond 60 vol. % are required. These conditions arise from the diameter of blood vessels, which must penetrate the porous network as well for enabling bone growth.

There are several established methods to produce implants with open porosity. Already in the 1980ies, **Bobyn et al.**, **1980** introduced implants coated with a porous sintered layer of coarse spherical Ti powders (beads). Such kind of implants are still on the market, but they have drawbacks regarding the inherent risk of tissue irritation or inflammation in the case of losing particles to the surrounding tissue. Such kind of implants are often brittle with low fracture toughness and are prone to crack formation already at low stresses or impact energies. Furthermore, high temperature sintering of the powders leads to microstructural changes of the substrate causing significant degradation of strength and corrosion resistance (**Ryan et al.**, **2006**).

A more promising method is the adaption of the space holder method for the manufacturing of netshaped implants with well-defined porosity and pore size. Here, adding a suitable space holder to the starting powder enables to realize interconnected macro pores, which are prerequisite for the bone ingrowth. Usually, fractionizing of the space holder particles e.g. by sieving, adjusts the pore size. Systematic studies showed that a space holder content beyond 60 vol. % is required to ensure

interconnection of pores (Imwinkelried, 2007). If amount of space holder is varied, implants with a functional gradient in porosity become accessible. Laptev et al. 2004 demonstrated that powder compacts with space holder had sufficient stability in the green state to net-shape them by conventional methods like milling, turning or sawing (Laptev et al., 2004). After net-shaping, removal of space holder by decomposition or leaching and sintering as final processing step follows. Not unexpected, reduced mechanical strength with increasing porosity makes such implants only suitable for primarily compression loaded applications like hip cups, spine cages, bone augments or dental implants. A positive side effect of the high porosity is the low Young's modulus in the range of 3 – 5 GPa, which is well-adapted to Young's modulus of human bone (Gibson and Ashby, 2003). Therefore, risk of stress shielding – loosening of the implant due to not adapted elasticity – reduces to a minimum. Another promising method to produce porous implants with complex shape and tailored porosity is additive manufacturing. This technology has gained a lot of interest in the last years due to enabling manufacturing of three-dimensional implants with periodic lattice structures or stochastically distributed pores. Individual adaption to the patient's physiognomy based on tomography analysis methods with no need of tooling becomes possible. Therefore, based on a sliced computer model, the implant is build layer by layer connecting the powder particles either by selective melting (preferentially with electron beam) or by ink-jet printing of a liquid binder system with subsequent debinding and sintering (Sames et al. **2016**).

<Figure 5 near here>

4.8 Porous components for electrochemical devices

Similar to graded composite filters, metal supported solid oxide fuel cells (MS-SOFC) consist of a metal substrate coated with the electrochemically active layers anode, electrolyte and cathode (Tucker, 2010). For effective operation of the MS-SOFC, the metal substrate has to fulfill a number of requirements: i.) Thermo shock resistance in the case of fast heating rates ii.) Sufficient electrical conductivity iii.) Thermal expansion adapted to the functional layers iv.) Corrosion and oxidation resistance up to temperatures of 800°C in wet reducing atmospheres v.) Redox stability if air succeeds to the anode side vi.) Long-term stability up to 40,000 h for stationary applications and up to 8,000 h for mobile applications. The first requirement is one of the main challenges of

this technology, in especial for mobile applications as discussed in more detail later. There are several production routes for the manufacturing of MS-SOFCs including plasma spraying and laminating of tapes with subsequent infiltration of the electrodes (Tucker, 2010). As example, Figure 6 shows a schematic sketch and microstructure of a MS-SOFC mainly produced by powder technological means. For more details, see the work of Rojek-Wöckner et al., 2016. The concept uses a porous metal substrate made by tape casting and subsequent sintering. Typical substrate thickness of MS-SOFCs lies in the range of $300 - 1,000 \,\mu\text{m}$. The porosity is around 40 vol. % and the pore size is in the range of $20 - 60 \,\mu\text{m}$. Multi-layered anode with gradient in porosity and surface roughness – made by screen-printing and sintering – enables coating of a 4 μ m thick electrolyte by magnetron sputtering, a specific physical vapor deposition (PVD) technique. Processing of anode and electrolyte requires protective atmospheres to avoid strong oxidation of the metal substrate during cell manufacturing. As final step, screen-printing of cathode and in-situ activation in the electrochemical setup by feeding air through the cathode compartment at 850°C follows. After in-situ activation of cathode, the MS-SOFC is ready for operation.

MS-SOFCs are preferentially suitable for mobile applications due to their resistance against harsh heating and cooling cycles. Main application of this cell concept are fuel cell generators, which are attractive for i.) Auxiliary power units (APUs) in heavy-duty vehicles like trucks, power shovels, wheel loader and others and as ii.) Range extender for battery electric vehicles (Rechberger et al., 2018). APUs have a maximum power output in the range of 5 kW providing the increasing energy demand for power electronics and comfort functions for the driver like air condition, refrigerator, lights and others. In 2016, Nissan Motor Co., Ltd. presented a novel concept of range extender system for battery electric vehicles based on MS-SOFC technology. Amongst others, the device tolerates operation with bio-ethanol and bio-ethanol water mixtures accessing already existing infrastructures in countries like Brazil. The range extender continuously charges the batteries. With this concept, driving range of the BEV increases up to 600 km. In general, fuel cell generators deliver a wide flexibility regarding the fuel ranging from diesel reformates liquid natural gas to hydrogen from renewable sources. Compared to combustion engines, higher efficiency of fuel cell systems directly corresponds to reduced CO₂ emission.

<Figure 6 near here>

Porous metals are attractive for battery electrodes since they require materials with high corrosion resistance, high electrical conductivity, mechanical strength and the ability of acting as support for catalysts. Furthermore, the high surface to volume ratio of porous metal alloys enables the fabrication of compact electrodes with high specific performance. For many years, electrodes made of porous nickel are in industrial use for Ni-metal hydride batteries. Currently, other alloys are under development to further increase of energy density. Most recently, there is a development of porous metal alloys for application as electrodes in lithium ion batteries. For instance, Shin et al., 2005 produced negative electrode of rechargeable lithium batteries from a porous Cu₆Sn₅ alloy, significantly increasing rate capability and storage capacity compared to dense electrodes.

5. Characterization of porous metals

Porous metals can combine very different properties depending on alloy composition and size, amount and distribution of pores. Therefore, characterization of porous metals requires a large number of specific methods. We briefly summarize the most important characterization methods for evaluating their microstructure, mechanical, electrochemical, thermal, electrical and acoustic properties. For more details, we refer to related literature (e.g. Banhart, 2001 and Gibson and Ashby, 1999).

Microstructure and porosity: Pore morphology is largely characterized using optical and scanning electron microscopy. For that, metallographic methods are in use for sample preparation similar to procedures applied for bulk samples. Analysis of pore shape and pore size distribution is often supported by commercial image analysis software. However, pores usually are randomly orientated in the space. It must take into consideration that measured 2D images are not a real representation of the whole sample. Therefore, measurement of overall porosity utilizes geometrical calculations referring to the weight of the sample or Archimedes principle based on the buoyancy of materials in liquid media. In the last years, X-ray computed tomography has become an important tool for 3D characterization of porous metals. With advanced tomography techniques, high-resolution images resolve pores down to the nanoscale. Such techniques help tracking morphological details of porous metal electrodes, where porosity is a key factor for improved efficiency (Lefebvre et al, 2008). Control of porosity by X-Ray tomography enables improvement of mechanical properties, amongst other by a better understanding of the relationship between deformation mechanisms and

mechanical properties (Lefebvre et al, 2008). Furthermore, bubble point method, Mercury porosimetry, and gas absorption techniques based on the principle of Brunnauer Emmet Teller (BET) enable sound conclusions on characteristic pore size distribution and specific surface of porous structures. For filtering applications, particle retention measurements with standardized particle size distributions enable conclusions on effectiveness of irregular shaped pores. To characterize the flow resistance of porous structures for gases or liquids, permeability measurements with respective gases and liquids are useful.

Surface defects: Surface defects of porous metals, i.e. cracks and holes, are often characterized by non-destructive techniques like dye penetration. Eddy current method enables analysis of local density fluctuations.

Mechanical properties: Comprehensive characterization of mechanical properties is required for any structural application of porous metals. The applied techniques are the same as for bulk materials. However, some specific factors must considered. Testing of porous metals samples usually leads to a larger scattering of measurement values compared to bulk samples and thus it is necessary to analyze a larger number of samples to increase the mean of the results. When samples have large porosity and pore size, which is common e.g. for bone implants, compression tests are more accurate than tensile tests, once clamping of the samples is not required. Fatigue behavior of porous metals is one of the main concerns for bone implant and structural applications. Again, literature recommends tests in compression-compression mode for the same reason discussed before (Banhart, 2001). Fatigue tests in compression-tension, tension-tension and cyclic bending mode are possible, but require some specific sample preparation and fixation of samples. Other mechanical tests such as creep failure, hardness and fracture toughness have also employed for porous metals characterization.

Damping: As discussed before, porous metals have large potential for vibrational damping. Vibrational analysis techniques enable measurement of Young's modulus and damping loss factor of porous metals. In the simplest version of this technique, vibrations are excited on the samples, supported on one or two ends, by a magnetic field. An impedance coil enables to characterize the sample response regarding damping of these vibrations (Banhart, 2001). Sound absorption measurements throughout impedance tube method is the standard method to characterize acoustic properties of porous metals. (Banhart, 2001).

Electrical conductivity: Four point measurements based on the Van der Pauw principle enable characterization of electrical properties of porous metals.

Corrosion behavior: Established techniques applied for bulk metals enable characterization of corrosion resistance of porous metals as well. Here, it must considered that inside of pores, corrosion conditions might become significantly different from the surrounding medium, e.g. by diffusion limitation. Methods for characterizing corrosion behavior of porous metals are measurement of polarization curves, moisture and salt spray chamber tests as well as differential thermoanalysis/thermogravimetric analysis to measure high-temperature oxidation.

6. Summary and conclusion

Porous metals have a wide spread range of applications ranging from filters to electrochemical devices and biomedical implants. With exception of structural applications, where application of porous metals aims on construction, damping or crash elements, powder metallurgy techniques are preferentially suitable for applications, where exact size, morphology and distribution of the pore network defines the function of the component. Compared to metal parts made by melting techniques, porous metals made by powder metallurgy techniques are often niche products, but often with high commercial benefit like in the case of biomedical implants. The book chapter summarizes most important powder metallurgy techniques for manufacturing porous metals and gives an overview of current applications with high relevance for the society. In detail, the chapter introduces sintered Bronze parts, filters, structural parts, damping elements, heat exchangers, sliding materials, bearings, porous implants and components for electrochemical devices. Finally, we introduce established characterization methods for porous metals in compact form.

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Figure captions

Figure 1: Microstructure and pore morphology of porous metals (here 316 L steel) made by **a**, **b.**) spherical powders (tape casting and sintering) and **c**, **d.**) irregular shaped powders (pressing and sintering).

Figure 2: Overview of powder metallurgical techniques to manufacture net-shaped components with functional porosity **a.**) Loose powder sintering **b.**) Pressing and sintering **c.**) Sacrifical template method **d.**) Space holder method with green machining **e.**) Hollow sheres **f.**) Cellular structures by design (additive manufacturing).

Figure 3: Application of powder metallurgy for the manufacturing of filters **a.**) Bronze filters made by loose powder sintering in graphite die **b.**) Porous steel parts made by uniaxial pressing (Courtesy GKN Sinter Metals).

Figure 4: Applications of porous Aluminum **a.)** Cross section of aluminum foam-filled A-pillar (**Hansen et al., 2006**) Reprinted with permission of Taylor & Francis **b.**) Prototype of finned metal foam heat sink (**Feng et al., 2015**) Reprinted with permission of American Society of Mechanical Engineers ASME **c.**) Schematic sketch of porous aluminum applied as heat exchanger in a metal hydride tank (**Mellouli et al. 2009**) Reprinted with permission of Elsevier.

Figure 5: Examples of porous implants made by powder metallurgical means a.) Spine implant with stepwise gradient of porosity achieved by temporary space holder (Bram, 2013). Reprinted with permission of Forschungszentrum Jülich Verlag b.) Representative microstructure of porous titanium made with temporary space holder, modified from (Golovin et al., 2004) c.) Individual implant made by additive manufacturing (Murr, 2017) Reprinted with permission from Elsevier.

Figure 6: Schematic sketch and real microstructure of a metal supported fuel cell consisting of a porous metal substrate made by tape casting coated with electrochemically active layers by screen-printing and physical vapor deposition, modified from (**Rojek-Wöckner et al., 2016**).