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Porous Metals and Metal Foams Made from Powders

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1. Introduction

Porous materials are found in natural structures such as wood, bone, coral, cork and sponge and are synonymous with strong and lightweight structures. It is not surprising that man-made porous materials have followed and those made from polymers and ceramics have been widely exploited. The commercialisation of porous metals has lagged somewhat behind, but has received a boost following a surge in worldwide research and development in the early 1990's.

The unique combination of physical and mechanical properties offered by porous metals, combinations that cannot be obtained with dense metals, or either dense or porous polymers and ceramics, makes them attractive materials for exploitation. Interest mainly focuses on exploiting their ability to be incorporated into strong, stiff lightweight structures, particularly those involving Al foams as the "filling" in sandwich panels, their ability to absorb energy, vibration and sound and their resilience at high temperature coupled with good thermal conductivity.

The applications for porous metals (metals having a large volume of porosity, typically 75-95%) and metal foams (metals with pores deliberately integrated into their structure through a foaming process) depend on their structure. Closed cell foams, which have gas-filled pores separated from each other by metal cell walls, have good strength and are mainly used for structural applications. Open cell foams, which contain a continuous network of metallic struts and the enclosed pores in each strut frame are connected (in most cases these materials are actually porous or cellular metals), are weaker and are mainly used in functional applications where the continuous nature of the porosity is exploited. Examples of structures for both these types of porous metals are shown in Figure 1.

Table 1 summarises the potential uses for porous metals and metal foams, highlighting the relevant attributes that make them suitable for that particular application (Ashby et al., 2000). Specific examples of current applications for porous metals and metal foams can be found in (Banhart, 2001), but it should be remarked that this is a dynamic area and new applications and components are continually being developed.

This short review describes the main powder metallurgy-based manufacturing routes, highlighting the key aspects of the relevant technology involved and the types of foam structures that result.
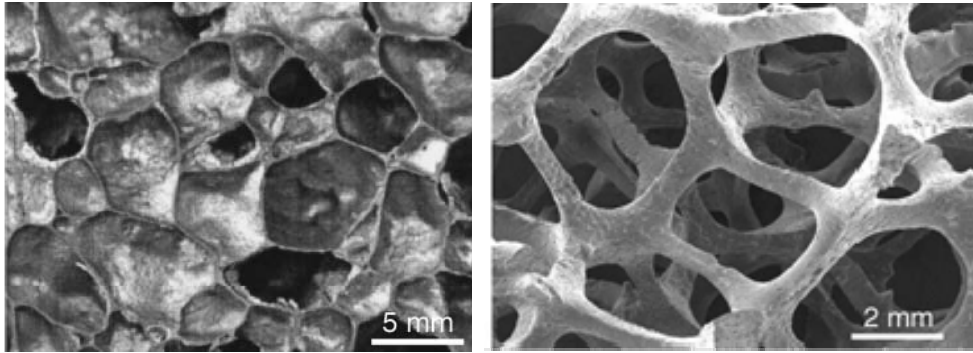
Fig. 1. Micrographs of (left) a closed cell foam and (right) an open cell foam, or more correctly, a cellular metal (Zhou, 2006).

Application	Relevant Attributes
Lightweight structures	Excellent stiffness-to-weight ratio when loaded in bending
Mechanical damping	Damping capacity is larger than solid metals by up to 10x
Vibration control	Foamed panels have higher natural flexural vibration frequencies than solid sheet of the same mass per unit area
Acoustic absorption	Open cell metal foams have sound-absorbing capacity
Energy absorbers / packaging	Exceptional ability to absorb energy at almost constant pressure
Heat exchangers	Open-cell foams have large accessible surface area and high cell-wall conduction giving exceptional heat transfer ability
Biocompatible inserts	Cellular texture stimulates cell growth
Filters	Open-cell foams for high-temperature gas and fluid filtration

Table 1. Potential application areas for porous metals and metal foams adapted from (Ashby et al., 2000).

2. Processing methods for metal foams

There are many different ways to produce porous metals and metallic foams and these methods are usually classified into four different types of production, using liquid metals, powdered metals, metal vapour or metal ions. The use of powdered metals as the starting material for foam production offers the same types of advantages (and often the same limitations) as conventional powder metallurgical processes. If a particular metal or alloy can be pressed and sintered, there is a high likelihood that it can be made into a porous metal or metal foam.

2.1 Porous metals produced by powder sintering

2.1.1 Pressureless sintering

Loose pack, pressureless or gravity sintered metal powders were the first form of porous metals and are still widely used as filters and as self-lubricating bearings. The porosity in these components is simply derived from the incomplete space filling of powders poured

into and sintered in a die. With packing densities broadly in the range of 40-60%, but affected by particle shape, size and vibration, the porosities in these structures are well below those for most porous metals. The simplicity of the process means that porosity can be included in a wide range of metals, limited only by the ability to sinter the metal in an appropriate die. The process is most commonly used to sinter bronze powders to make bearings, an example of which is shown in Figure 2, but porous structures from titanium, superalloys and stainless steel have also been made in this way.
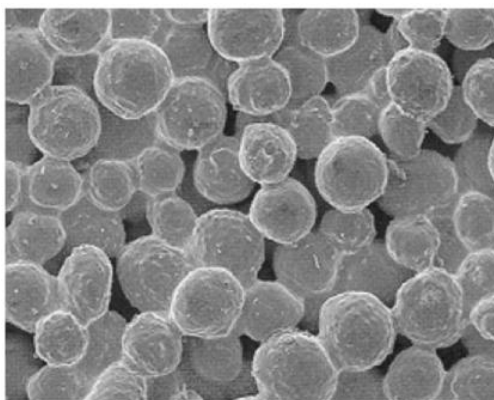

Fig. 2. Porous bronze made by pressureless sintering of approximately 100 µm diameter powders [Eisenmann, 1998].

In the case of Al alloys, where sintering is made difficult by the surface oxide layer covering the powder particles, milling of the powder with sintering aids such as Sn and Mg is required. The limitations imposed by the need to sinter in a die, principally on the size of the product and the productivity, can be mitigated by performing die (or other) compaction processes to increase the green strength of the compact so that it is sufficient to perform containerless sintering. The inevitable consolidation that is involved will, of course, decrease the already low porosity.

In an effort to increase the porosity in these parts, powders have been replaced by metal fibres, made by processes such as melt spinning, which with higher aspect ratios, exhibit lower packing densities, making them suitable for a wider range of applications (Anderson and Stephani, 1999). A further development of this, leading to much higher porosities, is the sintering of hollow metal spheres (which themselves are made via a powder route – to be described later). Spheres with diameters ranging from 1.5 to 10 mm, with wall thicknesses from 20 to 500 µm can be arranged to produce both open and closed pore structures. Open structures can be obtained in the same way as for powders and compaction can be used to deform the spheres to polyhedral bodies, reducing the degree of open porosity. True closed pore structures can be obtained by filling the interstices between the spheres with metal powder followed by a sintering treatment. Porosity is contained both within and between the hollow spheres and porosities in the range of 80-97% are reported (Anderson et al., 2000). Examples of an open cell sintered hollow sphere structure and the spheres in cross section, showing their thin walls, are presented in Figure 3.
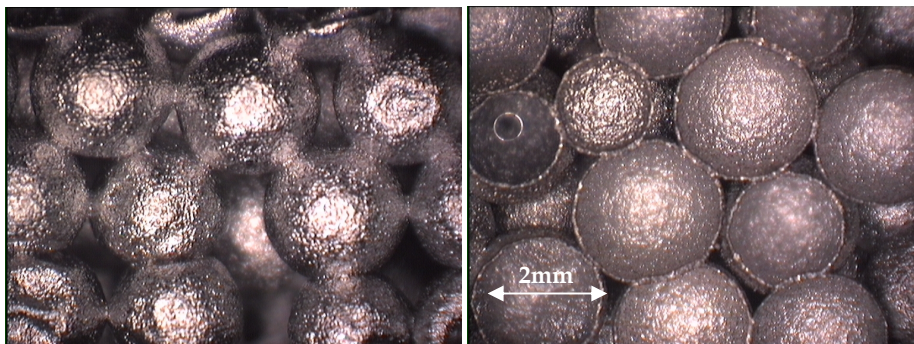
Fig. 3. Steel hollow spheres (left) sintered to form an open cell foam and (right) sectioned.

The advantage of porous structures made from sintered powders or hollow spheres is that there is good control of the volume fraction and to a lesser extent, the geometry and size of the pores, leading to reproducible structures and properties. Sintered metal powder and fibre structures are mainly suited to applications based on filtration, catalysis or heat exchange. The low density structures that can be made from sintered hollow spheres can be used for lightweight structural parts and for energy and sound absorption.

2.1.2 Gas entrapment

Internal porosity can also be developed in metal structures by a gas expansion (or foaming) process based on hot isostatic pressing (HIPing) (Martin and Lederich, 1992). Initially, following the standard method for HIPing of metal powders, a gas-tight metal can is filled with powder and evacuated. In a deviation from common practise, the can is then filled with argon gas at pressures between 3 and 5 bar before being sealed, isostatically pressed at high temperature and then worked to form a shaped product, normally a sheet. Porosity is generated by annealing the part. When holding at elevated temperature, the pressurised argon gas present within small pores in the structure causes the material to expand (foam) by creep. As HIPing is an effective method for sintering and the can material can be made from the same material as the powder, this process could be used for many different metal powders. The use of a can means that sandwich-type structures, consisting of a lightweight foam core and thin, solid face sheets are produced. These types of structures are ideal for lightweight construction.

Porous bodies with typically 20–40% of isolated porosity are obtained and theoretical considerations show that no more than 50% porosity can be expected (Elzey and Wadley, 2001). Figure 4 shows a schematic representation of the process, which has been used to make porous titanium sandwich structures for the aerospace industry, without the need for complex joining methods. Disadvantages include low porosity and irregular-shaped pores.

2.1.3 Reactive processing

In contrast to the gas entrapment method, porosity is evolved much more rapidly when foaming occurs in highly reactive multi-component powder systems such as those which undergo self-propagating high temperature synthesis (SHS). The highly exothermic
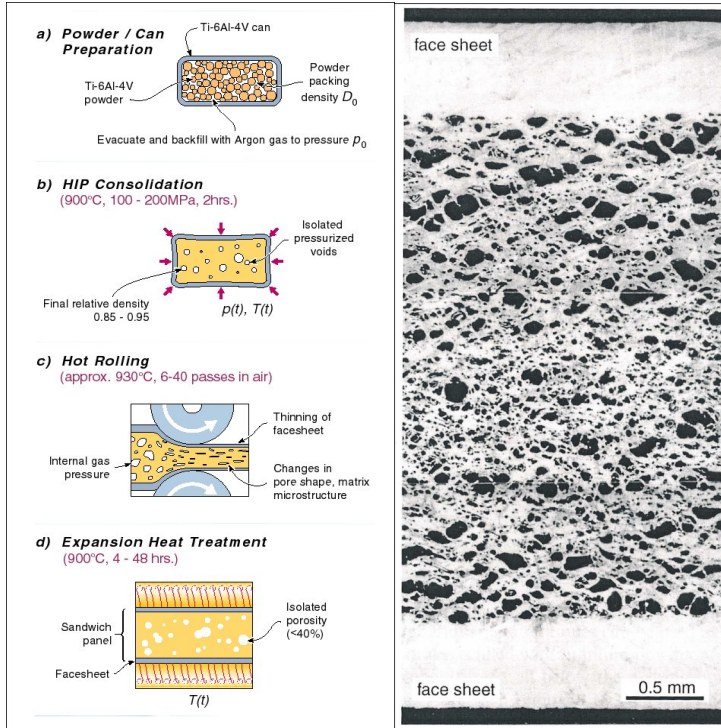
Fig. 4. A schematic (left) of the processing steps used to manufacture titanium alloy foam sandwich panels by gas entrapment (Ashby et al., 2000) and (right) the morphology of a TiAl6V4 sandwich structure (Banhart, 2001).

reactions, initiated either by local or global heating of compacted powder mixtures to the reaction ignition temperature, lead to vapourisation of hydrated oxides on the powder surfaces and the release of gases dissolved in the powder. The reacting powder mixture heats up rapidly to form a liquid containing (mostly hydrogen) gas bubbles and when the reaction is complete, cools rapidly, entrapping the gas to form a foam. A schematic of this process is shown in Figure 5 (Kanetake and Kobashi, 2006).

Gas formation and foam expansion can be augmented by the addition of vapour forming phases such as carbon (which burns in air to produce CO) or foaming agents which react together to increase the reaction temperature and produce fine particles that stabilise the foam. As foaming takes place in the liquid state, stabilisation of the bubbles is needed to avoid rapid collapse of the foam structure. Figure 5 shows how a reactive Ti+B_4C foaming agent increases the porosity in a Ni-Al powder mixture from 30 to 90% by 5% addition. It can be seen that the pores are irregular in shape, as is the shape of the expanded foam. Although the process is relatively simple, the production of foams is limited to combinations of materials that react exothermically, some metal-metal systems but typically metals and carbon or carbides, or metals and oxides. These limitations, coupled with the difficulty controlling the expansion process and defining the shape of the expanded foam, mean that few, if any, commercial foam products are made this way.
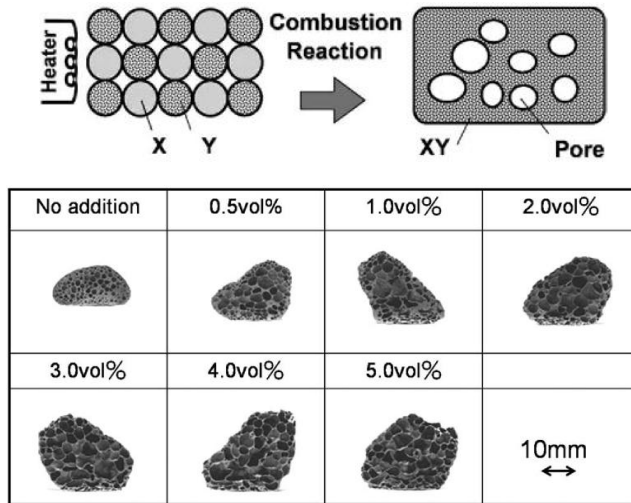
Fig. 5. A schematic (top) of the reactive powder process used to make metal foams and (bottom) cross-sections of $NiAl_3$ foams containing different addition levels of a Ti + B_4C foaming agent mixture, after (Kanetake and Kobashi, 2006).

2.1.4 The addition of space-holding fillers

Many of the processes already mentioned have shortcomings in either the rather limited levels of porosity that are achievable, or in the formation of pores that are highly irregular with a wide distribution in sizes. A simple development of standard PM practices, but incorporating a volume of sacrificial space fillers, offers a solution to both these problems.

Porous metals are produced by mixing and compacting metal powders with a space holder which is later removed either during or after sintering, by dissolution or thermal degradation, to leave porosity (Zhao and Sun, 2001). A schematic of this process is shown in Figure 6. This simple method has the advantage that the morphologies of the pores and their size are determined by the characteristics of the space holder particles and the foam porosity can be easily controlled by varying the metal/space holder volume ratio. Addition levels of the space holder are typically between and 50% and 85%. These are sufficiently high that they are interconnected and hence can be removed easily. Above 85% the structure of the struts is unlikely to be continuous and below 50%, residual space filler will be enclosed within the structure, making removal very difficult.

Commonly, space fillers take the form of polymer granules and water soluble salts, but can also be metal powders and ceramic or polymer hollow spheres (if the hollow spheres aren't removed then these materials are, strictly speaking, syntactic foams). Two distinct approaches may be taken. In the first, the space filler can either thermally decompose, sublime or evaporate below the sintering temperature of the metal matrix. This requires the resulting skeletal metal structure to have good strength, which is affected during the compaction stage. Polymer powders (for example PMMA), carbamide granules or Mg grains are commonly used. In the second approach, the space filler has a higher melting point than the sintering temperature and is removed, after sintering, by dissolution in a
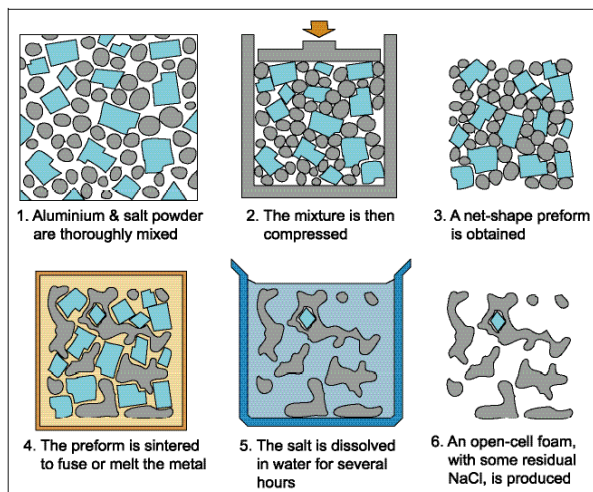
Fig. 6. Production of an open cell foam by sintering a mixture of metal powder and a removable agent (Ashby et al., 2000).

suitable solvent in which the metal matrix should be unaffected, most commonly water. In the case of Al alloys, NaCl is the favoured space holder as it melts at approximately 800°C and can be dissolved fairly rapidly in warm water. For higher melting point metals, $NaAlO_2$, with a melting point of 1800°C, is used.

In addition to the decomposition or melting temperature and general ease of processing, including solubility in the solvent, space fillers are also selected based on their inertness and lack of solubility in the matrix, as well as the availability in the size and shape desired (typically in the range of hundreds of μm to a few mm and often spherical space fillers are preferred). As salts (such as NaCl) are brittle materials and, particularly when ground, are angular in shape, melting and granulation methods have been used to produce them in spherical form (Goodall and Mortensen, 2007). If these granules are porous, this has the additional benefit of more rapid removal from the sintered part due to the granule being able to disintegrate as well as dissolve. Figure 7 shows porous beads made by the controlled agglomeration of fine salt particles and the structure of the resulting porous metal (Jinnapat and Kennedy, 2010). The cell structure is clearly interconnected via windows between neighbouring pores, the number and size of which are dependent upon the co-ordination number and contact area for the packed spheres.

Processing difficulties can arise during mixing the metal powder with the often much larger space holders. Segregation results in defects in the final product, usually in the form of incomplete struts and cells. Liquid binders are used to promote homogeneous mixing, often by ensuring that the space filler is coated with the metal powder. An alternative approach is to vibrate the finer metal powders into the interstices within a packed bed of the larger space holder particles. The metal powder – space holder mixtures are then compressed to form a compact with sufficient strength to be sintered free-standing and, in the case of Al to disrupt surface oxide films so that sintering can take place. Compaction processes can include all of those used in standard metallurgical practices, including metal injection moulding.
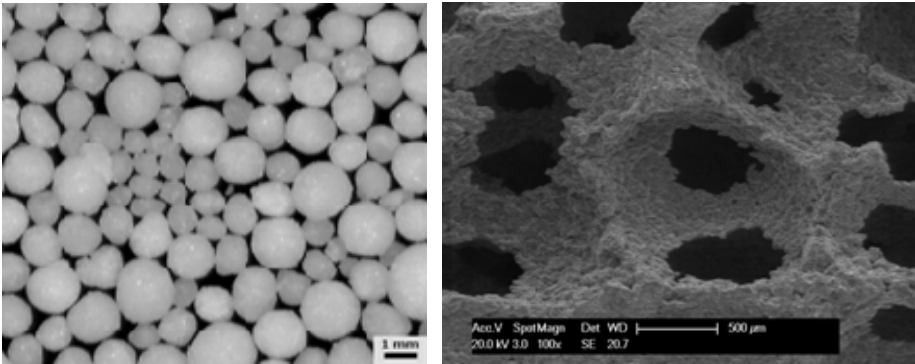
Fig. 7. Images showing (left) porous spherical salt beads and (right) the microstructure of the resulting cellular stainless steel (Jinnapat and Kennedy, 2010).

Despite a few drawbacks, for example if space fillers such as NaCl are not completely removed this can lead to corrosion and the size of parts produced is rather limited, in part due to slow dissolution of the space fillers which might take days even for small parts, this method is a favoured route for the manufacture of porous metals from a wide range of materials. It is particularly suited to those metals with high melting points and is a common route for the production of porous biomedical devices made from Ti or NiTi.

2.1.5 Additive manufacturing

Porous metal structures can be built, layer upon layer, using processes such as selective laser sintering (SLS), direct metal typing or 3D direct metal printing. 3D parts are constructed by stacking these layers, the geometry of which is defined by a CAD model.

Direct metal laser sintering uses a high power laser to sinter metal powders on the surface of a powder bed. After each cross-section is scanned, the powder bed is lowered by one layer thickness, a new layer of material is applied on top, and the process is repeated until the part is completed. Two-component powders can be used, comprising metals coated with a polymer, where the laser only melts the coating. Products made in this way, however, still need a secondary sintering step to produce sufficiently robust parts. Steel and titanium foams can be made by both these methods, although with polymeric binders, contamination of Ti with carbon occurs and direct metal laser sintering is, therefore, preferred.

Direct metal printing works in a similar way, spraying a polymeric binder, which is dispensed through a print head, over a powder bed. 3D metal typing or screen printing uses a metal powder mixed with a binder which is then spread over patterned masks and cured layer by layer (Andersen et al., 2004). For both these processes, subsequent polymer-removal and sintering steps are required. Figure 8 shows cellular structures made from 316L stainless steel by direct typing. Among the benefits of these processes are high levels of design flexibility, including small, precise cellular structures with complex internal geometries.
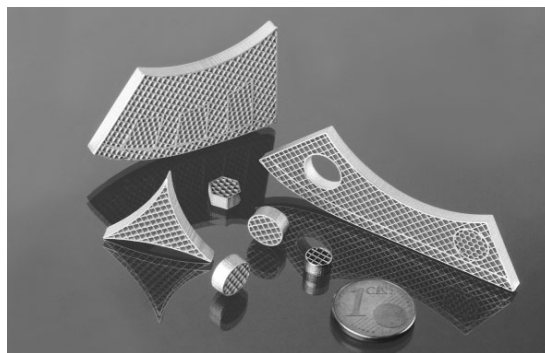
Fig. 8. Cellular structures made from 316L stainless steel by direct typing (Andersen et al., 2004).

2.2 Metal powder slurry processing

2.2.1 Metal powders slurries

Slurry processing of ceramics has been used for many years to produce bulk products, coatings, films and foams. The wealth of scientific research and resulting literature pertaining to this area is not mirrored for metal powders slurries, the need for processing in this way is perhaps not so great given the many alternative forming methods for metals. The production of stable (non-agglomerated, non-sedimenting) slurries containing metal powders provides significant challenges. Metal powders are larger in size than those used for ceramic processing and have a higher density, making them more difficult to keep suspended. Metal powder slurries, like their ceramic counterparts, are usually based on aqueous systems to which a suspending agent (to increase the viscosity) and dispersants (to prevent particle flocculation) are added (Kennedy and Lin, 2011). Other additions may be needed to lower the surface tension, change the pH or facilitate gelation.

The advantages of using metal slurries as the basis for producing foams is that constraints imposed by poor compressibility are removed, shaping can be performed by gelling in simple rubber moulds and gas bubbles can be introduced into the system by whisking or through the addition of gas-forming agents (although this means that the foam has to be stabilised). Although not well established, there are likely to be limitations to the materials that can be used based on interactions between the metal and the solvent (corrosion or reaction) and the ability to form a stable slurry.

2.2.2 Slurry coating of polyurethane foams

Porous metals can be produced by a replication method using an open cell polyurethane (PU) foam or sponge as a template (Quadbeck et al., 2007). In this process the polymer foam is first coated with a metal powder slurry, usually performed by immersion or by spraying. Excess slurry is removed by squeezing the foam, often by passing it through rollers. Without this, the cells may become partially closed due to the formation of liquid films bridging the cell struts. After coating and drying, the template is removed by thermal degradation and the resulting, fragile metal skeleton is further heated to sinter the metal powder particles, forming a rigid cellular metal structure.

Figure 9 shows a sintered porous stainless steel structure alongside the polymer foam used in the replication process. The strut structure is also shown and it is clear from the cross section that the struts are hollow (due to the space vacated by the polymer) and the walls of the struts are porous. Open cell structures with cell sizes between 10–80 pores per inch (about 2.5-0.2 mm) can be produced with precise pore structures with total porosities as high as 96%. This total porosity also includes the porosity in the sintered metal struts, but open cell porosities as high as 90% can be achieved.

This type of approach can be used to make metallic hollow spheres (which are themselves sintered to produce cellular metals as was described earlier). To make hollow spheres, expanded polystyrene spheres are coated with a metal powder slurry and then sintered, during which the polystyrene is removed and the metal forms a dense metal shell (Andersen et al., 2000).
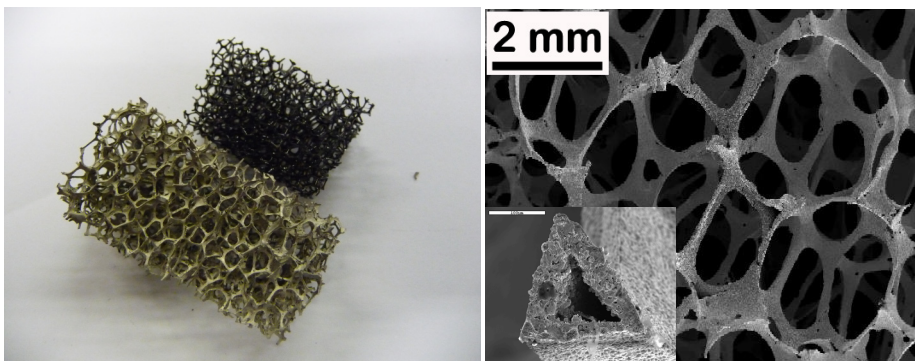

Fig. 9. Images (left) showing a PU foam and a stainless steel foam made by slurry coating and (right) the microstructure of the struts showing, inset, their hollow nature.

2.2.3 Slip reaction foam sintering

Metal powder slurries can also be foamed by the insitu generation of a gas. In the slip reaction foam sintering (SRFS) process, the slurry (or slip) contains additives which stabilize the slip during processing (Angel et al., 2004) and to this a solution of ortho-phosphoric acid in either water or alcohol is then added. The hydrogen generated by the metal-acid reaction creates bubbles in the slip causing it to foam. As the solvent evaporates during the drying process, the pores formed by the hydrogen bubbles, which were originally closed, turn to interconnected porosity and an open cell green part is obtained. Figure 10 shows the typical structure for a steel foam which has irregular primary pore sizes as large as 3.5 mm and secondary pores between 0.05-0.3 mm. After sintering the total porosity is typically 60%. Foams have been produced from both steel and aluminium powders but for high porosities the green strength is low and cracks form in the foamed material.

In a variation on this process the slurry is an aqueous polymer solution that has the ability to form a gel (Shimizu and Matsuzaki, 2007). Gelation of the slurry is carried out by a freezing and thawing process and after gelation, it is heated until the foaming agent (hexane) decomposes, forming a gas, causing the gel to expand. The resulting foam is then dried and sintered.
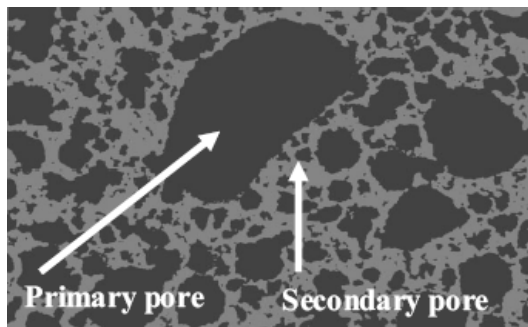
Fig. 10. Micrograph of a steel foam produced by the slip reaction foaming process (Angel et al., 2004).

2.2.4 Foaming by mechanical whisking

Foams have been produced from ceramic slurries by introducing air into the slurry, in much the same way as whisking cream (Sepulveda, 1997), and this method has recently been translated to metal systems (Lin, 2011). In the same way as for ceramics, in order to stabilise the air bubbles that are introduced during whisking, a surfactant must be added to the metal powder slurry. Through sufficient aeration, a foam can be formed which can be poured into a shaped mould made from almost any material. Despite the addition of surfactant, drainage of the liquid from the network of pores does occur, inevitably leading to collapse of the foam. To preserve the foam structure, slurry systems are designed to either gel by heating (cellulose systems) or cooling (agarose systems) or be polymerised by the addition of an initiator (acrylamide systems). The foamed body is then dried, further heated to burn out the polymer and finally sintered to densify the matrix.

The pore structures for these foams are surprisingly uniform given the simplicity of the process, showing round pores connected by small windows. Figure 11 shows a cross section through a stainless steel foam in the gelled and dried condition, which demonstrates good
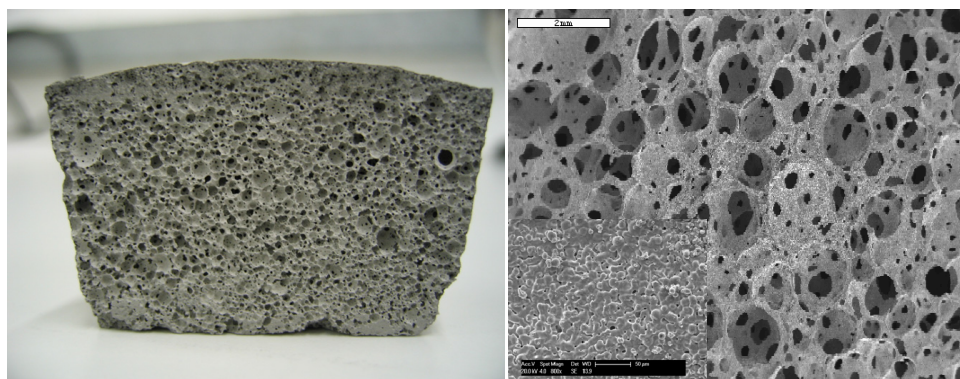

Fig. 11. A cross section (left) of a gelled and dried foam before sintering and (right) the foam microstructure showing an open cell structure and (inset) the porous nature of the cell struts (Lin, 2011).

green strength, and also presents the sintered microstructures for the cells and the porous cell struts (inset). Porosities up to 90% have been achieved in sintered parts but work to date has shown that it is difficult to vary the pore size beyond the range of 0.5-1.5 mm. It is thought that this simple foaming process has the potential to produce foams that are suitable for both structural and functional applications.

2.3 Foaming of compacted powder precursors

2.3.1 Foaming process

Metal foams can be produced by encapsulating a foaming (or blowing) agent into a precursor made from compacted metal powder, followed by melting (Baumeister, 1990). The foaming agents are fine powdered compounds that, when heated, decompose to form a gas (typically they are metal hydrides or carbonates). When the compact is heated, usually in a mould, above the solidus temperature of the alloy, which should also be above the decomposition temperature of the foaming agent, the gas evolved causes expansion of the precursor. Expansion is rapid but collapse occurs, requiring fast cooling to "freeze-in" the foam structure. A schematic of the process used to make and foam powder precursors is shown in Figure 12.
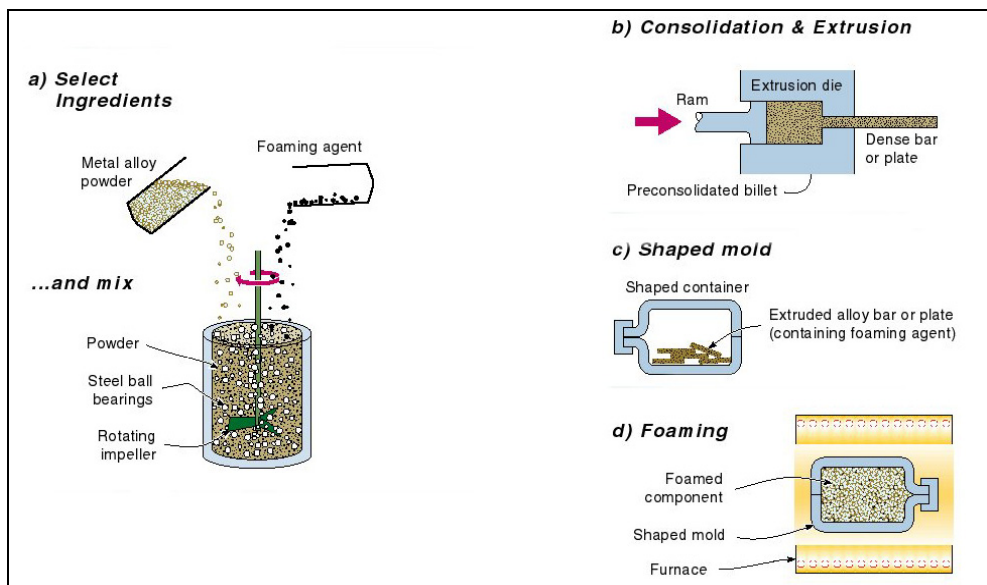

Fig. 12. The sequence of steps used to manufacture metal foams made from compacted powder precursors (Ashby et al., 2000).

Figure 13 shows an expanded precursor that has been foamed in a metal mould, thereby defining its cylindrical shape. Also shown is a radiograph of the sample, revealing the porosity inside the part. The cross section of the foam, also shown in this figure, reveals that although the pores are reasonably spherical, a large variation in the pore sizes is observed. The closed porosity in foams made in this way is typically below 90%.
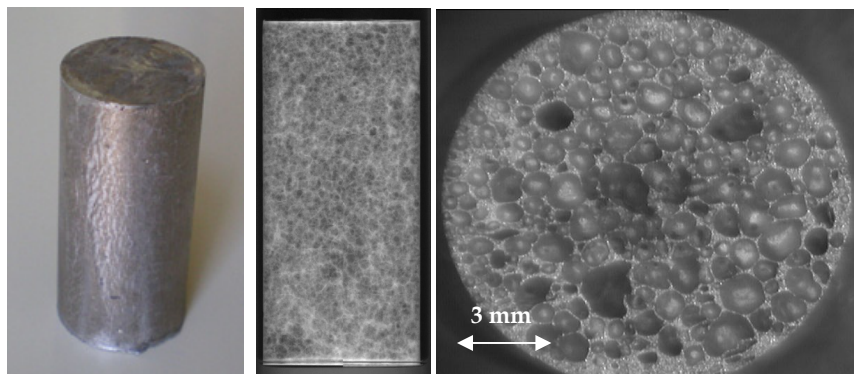
Fig. 13. Images of (left) a foam produced by the expansion of a melted PM precursor in a mould, (centre) an X-ray radiograph of the foam structure and (right) a cross section of the foam showing the pore structure.

2.3.2 Advantages and limitations of the process

The foaming of compacted powder precursors has several key advantages. It is one of the few processes that can make closed cell foams, with the ability to produce near-net-shape and complex foam parts, including foam plates and sandwich structures. Lightweight Al foam parts made in this way are being used in a number of applications where their high strength at low mass and excellent energy absorbing ability are exploited. The main disadvantages are that large 3D parts are difficult to make and, in part due to the rapid nature of the foam expansion process, the uniformity and reproducibility of the pore structure can be unsatisfactory, leading to concerns over the reproducibility of the mechanical performance (Kennedy, 2004).

Limits to the range of metals that can be foamed in this way arise due to several factors. There is a requirement for the blowing agent to only start to decompose when the metal or alloy is semi-solid. If decomposition occurs when the precursor is still solid, gas evolution can cause cracking of the precursor and escape of the gas without it contributing to foam expansion. It is, therefore, difficult to find suitable foaming agents for all metals. TiH_2, which starts to decompose at around 450°C (Kennedy and Lopez, 2003), is used to foam low melting point metals, such as Al and Mg, despite decomposing below the melting point of most of their alloys. This requires the compacted precursor to contain very low (<2%) porosity to contain the gas (Kennedy, 2002). This is not readily achieved by conventional PM compaction methods and so to achieve the target densities, the use of high strength, pre-alloyed powders is avoided, favouring mixed elemental powder additions, and powder consolidation is either performed by hot die compaction, cold isostatic pressing followed by extrusion or continuous powder rolling or extrusion processes. The foaming of reactive metals and those with high melting points is not that practical, given the need for a conductive metal mould to produce shaped parts, but $SrCO_3$ has been used to produce Fe-based foams.

Foams produced by melting compacted powders are stabilised (at least temporarily) by oxide films introduced into the liquid from the surface of the metal powders. The fraction of

these oxides in the expanding liquid is critical to achieving good foam structures and stable foams. Variations in oxide content for different powder sizes, from different suppliers or even for different batches of powders (due to variations in the atomising or storage conditions) can be the reason behind highly variable foaming responses (Asavavisithchai and Kennedy, 2006a). Varying the processing conditions during hot compaction can also affect the oxidation of the metal powder and alter the foaming behaviour (Asavavisithchai and Kennedy, 2006a, 2006b). Figure 14 shows the effect of oxygen content on the foam expansion for an Al powder, too low and foam collapse is severe, too high and the liquid is too viscous to foam. It should be noted that the way in which this oxygen (or oxide) level is achieved, through heat treatments at different temperatures or through atomisation, is not important.
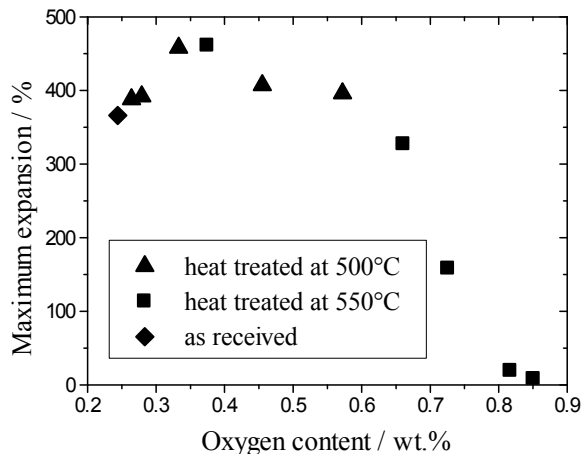

Fig. 14. The effect of oxygen content on the foaming of pure Al powder compacts, showing that an optimum level is required (Asavavisithchai and Kennedy, 2006a).

3. Summary

An overview of some of the many and varied methods for making porous metals and metal foams from metal powders has been presented. With research and development into metal foams being vibrant and dynamic, pioneered by institutes like the Fraunhofer IFAM centres in Bremen, Chemnitz and Dresden in Germany, the state-of-the-art is continually evolving as the understanding behind powder processing, foaming and foam stabilisation improves.

For established foaming processes, research conducted within academia and industry has a strong emphasis on eliminating problems which would otherwise limit the wider use of these materials. This includes; improving the uniformity and reproducibility of the foam structures, aiming to achieve uniform pore sizes and densities throughout the component and similar foam structures from part to part; decreasing the processing and materials costs, through improved or new processing routes, reduced waste and cheaper starting materials and developing compelling case studies based on innovative design, simulation and testing to demonstrate to end users that despite higher prices for some foams or components containing foam elements, that these costs can be more that offset by the weight and energy savings offered by these novel materials and structures.

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