Remark: references to other chapters of the handbook were numbered according to the section numbers given in the outline by Degischer/Kriszt and may change after printing. Such references are underlined and printed in **red**

2.1 Al-Foaming

2.1.1 Industrialisation of powder compact foaming technique

(J. Banhart and F. Baumgärtner)

2.1.1.1 Principles of foam production

There are many different ways to manufacture cellular materials [1]. One of the available processes has become increasingly popular in the past few years and is in the stage of industrial implementation now. The method is sometimes loosely called the "powder metallurgical route", but the term "powder compact foaming technique" seems more appropriate. The technique consists of mixing aluminium or aluminium alloy powders with appropriate blowing agents and compacting this mix to a dense product called "foamable precursor material", e.g. by hot pressing, extrusion, powder rolling or combined methods (see Figure 1). Heating the precursor to its melting point turns the metal into a semi-liquid viscous mass and simultaneously makes the blowing agent decompose. The associated release of gas first leads to the formation of pores and then, in a later stage, to an expansion of the metal to a lowdensity foam structure [2][3].

The method is not restricted to aluminium and its alloys: tin, zinc, lead, gold and some other metals and alloys can also be foamed by choosing appropriate blowing agents and process parameters (see <u>Sec. 2.1.2</u>.). The most common alloys for foaming, however, are pure aluminium or wrought alloys such as aluminium 2XXX, 6XXX or 7XXX alloys, e.g. AA 2014, 6060, 6061, 6082 or 7075. Casting alloys such as AlSi7Mg (A356) and AlSi12 are also frequently used because of their low melting point and good foaming properties, although in principle virtually any aluminium alloy can be foamed by carefully adjusting the process parameters.

Quite complex shaped metal foam parts can be manufactured by expanding the foam inside a mould thus confining spatial expansion. An example for one such part is shown in **Figure 2**. The part, developed in the framework of a feasibility study, is a novel pantograph horn of an electrical locomotive. This light-weight solution based on aluminium foam replaces traditional cast aluminium parts with 30% more weight.

A nice feature of the technique is that composite structures consisting of an aluminium foam and bulk metal parts can be realised without using adhesives. Examples are foam filled aluminium sections and sandwich panels with an aluminium foam core and metallically bonded steel, aluminium or even titanium face sheets. For making such composites the foamable precursor material is first bonded to the solid section or sheet by co-extrusion or roll-cladding, respectively, after which the foamable core layer is expanded by heat treatment [4][5] (see also <u>Sec. 3.3</u>).

The advantages of the powder compact route are obvious and are listed in **Table 1**: Beside the first two features already mentioned, the flexibility arising from the preparation of the precursor from powders is important. Alloys can be made by simply mixing inexpensive elementary powders. No ceramic additives are needed to stabilise the foam in contrast to some of the liquid metal foaming processes in which up to 15% silicon carbide have to be added [1][6]. However, if required, ceramic powders, metal fibres or ceramic fibres can be added to the powder blend for special applications, e.g. for matters of reinforcement or increase of wear resistance. Naturally, there are also some disadvantages which are inherent to the process. Metal powder is more expensive than bulk metal. This rules out applications which ask for very cheap materials. Moreover, the size of aluminium foam parts which can be manufactured is smaller than for some of the competing liquid foaming processes. The largest sandwich components which have been manufactured until now using the powder compact foaming technique are about $2m \times 1m \times 1cm$ in size (possibly larger in future). At LKR in Ranshofen a part of similar size was produced without face sheets. True 3D-volume parts are usually no thicker than 30 cm, a limit which is hard to shift to higher values. A large aluminium foam column produced at Fraunhofer IFAM was 1m high, and 18cm in diameter while weighing 13 kg. In contrast, the liquid metal route allows for making panels with 15 meters length [7] and 100 cm thickness [8]. However, as these processes cannot be used for near-net shape production and only permit making very simple geometries, they aim on different fields of applications.

The middle column of **Table 1** lists some of the problems which are still encountered when foaming aluminium with the powder compact melting method but which can in principle be solved, thus not being a principle limitation of the technique.

2.1.1.2 Practical aspects of foam production

Powder selection

The appropriate selection of the raw powders with respect to purity, particle size and distribution, alloying elements and other powder properties is essential for successful foaming. Commercial air-atomised aluminium powders were shown to be of sufficient quality. However, powders from different manufacturers lead to notable differences in foaming and empirical criteria have been derived to facilitate the selection of powders. The cost of powders and the ability of a manufacturer for providing large amounts with a constant quality are also crucial. As already pointed out, alloys can be obtained in different ways. The frequently used alloy AlSi7, e.g., can be either prepared by atomising a AlSi7 melt, or by blending pure aluminium powder with 7 wt.% silicon powder, or, in a third way, by mixing 58% of standard AlSi12 powders with 42% aluminium powder.

Mixing

The mixing procedure should yield a homogeneous distribution of alloying elements and the blowing agent to ensure that high quality foams with uniform pore size distributions are obtained. Powders are mixed in batches of 500 kg at Schunk-Honsel in commercial large-scale tumbling mixers with parameters determined in technological tests. Alternatively, powder mixes can be obtained by aerodynamic mixing. Eckart Austria, e.g., mixes aluminium and titanium hydride in large containers with 50-80 short pulses of pressurised nitrogen gas.

Densification

Powder consolidation can be carried out by various techniques. It has to be ensured that the blowing agent is completely embedded in the metal matrix and no residual open porosity remains. One way to obtain foamable precursor material with nearly 100% theoretical density is the combined use of cold isostatic pressing and ram extrusion. Cold isostatic pressing (CIP) is first applied to consolidate the powder mix to billets with a relative density of about 70-80% and a mass of typically about 50 kg. These billets are used in the following extrusion step. Although CIPping is not absolutely necessary powders have been filled into thin-walled aluminium cartouches and inserted into the extrusion machine without prior conolidation - it bears additional advantages such as the prevention of powder contamination and powder de-mixing. The CIP-billets themselves are not foamable because of their large content of residual porosity which causes massive hydrogen losses when the material is heated. To obtain foamable material, the billets are pre-heated to 350°C and extruded to rods or any other profile. For this a horizontal 25MN direct extrusion machine is used by Schunk-Honsel. The extrusion machine is operated in cycles with a new billet inserted after each extrusion step. This way rather high outputs can be achieved. The advantage of producing the raw materials on a full-scale industrial machine already in the R&D phase of technology development is that scaling up into mass production will be easier in a later phase.

Foamable material has also been manufactured by rotary continuous extrusion in the so-called *CONFORM-process* by Mepura (Ranshofen). Here a rotating wheel is used to drag the powder into the consolidation chamber from which it is pulled off in radial direction as a solidified wire. Foamable wires with some 8 mm diameter were manufactured from wrought alloys containing titanium hydride.

Further processing of foamable material

The extruded material can be foamed as it is after consolidation or it can be worked to the required shape. By conventional rolling foamable sheets with thicknesses down to about 2 mm are produced. Optionally, the foamable raw material can be cladded to conventional sheets of metal, e.g. of steel or aluminium, by attaching two sheets to each side of the foamable precursor before rolling. This way a purely metallic sandwich structure is obtained. By deep drawing, the sheets and the sandwiches may be transformed to 3-D-shaped sheets for special applications. In all cases it is favourable to start from near-net shape precursors in order to minimise foam flow [9].

Foaming

Heat treatment at temperatures near the melting point of

the foamable matrix is necessary to produce the foam structure. The gas released by the decomposing blowing agent forms bubbles and the matrix expands up to a maximum volume, i.e. to a minimum density. The density and density distribution of the growing foam can be controlled by several parameters. The blowing agent content in the precursor material is obviously important, but furnace temperatures and heating rates also have an influence [10]. The mould material, the mould shape and the type of furnace naturally influence the heating rate and have therefore also to be considered. A careful control of the heating conditions during foaming is essential for obtaining high quality foams. The difficulty is that the liquid foam is thermodynamically unstable and conditions change constantly during foaming. There are various intermediate stages: at first only the mould is heated directly, whereas the foamable material receives heat only indirectly via heat conduction through the mould. Initially there are merely some point contacts between the piece of foamable material in the mould and the mould walls. However, as the temperature increases, the precursor softens and assumes the contour of the mould thus increasing the transfer of heat. Moreover, heat transfer via radiation gains importance with rising temperatures. The reflectivity of the mould and precursor surfaces may change during the process and add a further variable. Finally, after foaming has started, the thermal conductivity of the precursor rapidly decreases thus reducing heat flow. As soon as the mould has been filled with foam it has to be cooled down below its melting point to stabilise the foam structure. The phenomena during cooling are also quite complex and difficult to describe for similar reasons mentioned for the heating phase.

Typical densities of aluminium foams range from 0,4 to 0.8 g/cm^3 including the closed skin around the foam body. The final density of a foamed part can be simply predicted if the volume of the hollow mould and the mass of the inserted

precursor material are known. The foaming mould may be loaded with several small pieces or one single piece of precursor. Choosing the latter method which is preferred by LKR and the Bratislava group [11] one has to take into account that each piece of the expanding foam has a dense aluminium oxide layer on its surface and the individual foam pieces may remain separated even after the foaming process has come to an end unless there is a certain overpressure in the mould and a relative movement of the foam pieces relative to each other helping to break up the oxide films. Figure 4 shows an example for a successful formation of a foamed body from various pieces of the precursor and an example for failure. In the former case the location of the original individual foam pieces can still be identified from the contrast in grey scales between the various regions – darker grey identifies extruded surfaces, brighter grey is the new (expanded) surface. This effect is currently exploited to create foam panels and other foamed parts for making designer objects.

2.1.1.3 State of commercialisation

Currently the foaming technique described is still in the stage of industrial implementation. Nevertheless, a number of companies have already made commitments for a future production and are building up facilities [12]. The joint effort of *Schunk Sintermetalltechnik* (Gießen) and *Honsel* GmbH&Co KG (Meschede) is one example. Due to their collaboration with Karmann the activities are preferentially directed towards foam and foam sandwich parts with a complex 3D geometry (see <u>Sec.</u> <u>3.3</u>). *Alulight* is another example. This small Austrian company works exclusively on the field of aluminium foams. It is owned by *SHW* (Germany) and *Eckart Austria*. The company offers aluminium foam panels in sizes up to 625 x 625 mm, with thickness ranging from 8 to 25 mm. *Neuman AluFoam*, another

Austrian company, also offers foamable precursor material (extrusions) and foamed parts.

2.1.2 Making cellular metals from metals other than aluminium

(G. Rausch and J. Banhart)

The previous section was dedicated exclusively to aluminium foams. For many applications one would like to use cellular materials made from other metals or alloys than aluminium. There have been some attempts to manufacture metal foams by simply adapting the powder compact process originally developed for aluminium to other metals by adjusting the properties of the blowing agent and the process parameters. This procedure was successful in some cases. However, for high melting alloys the powder compact foaming technique is difficult to implement and especially for titanium no very promising results could be obtained. Here alternative routes based on advanced powder metallurgy yielded better results. Therefore, in the current section the topic will be slightly extended from "foams" to "cellular metals" in a more general sense.

2.1.2.1 Zinc

Zinc can be foamed by a straight-forward modification of the powder compact technique. The blowing agent used for aluminium - TiH_2 - can be used, although ZrH_2 seems to yield slightly better results. Powder properties and mixing procedures are quite similar to aluminium. Only the pressing and foaming temperature has to be chosen slightly lower than for aluminium due to the melting temperature of zinc at 419°C. Foamed zinc shows a very uniform pore structure. This can be attributed to the fact that the decomposition temperature of the blowing agents and the metal match. Therefore, melting and pore formation occur simultaneously and round bubbles are created from the very beginning. In contrast to aluminium there is no extended solid state expansion range with corresponding crack formation. **Figure 5** shows an example for a zinc foam.

2.1.2.2 Lead

Lead and lead alloys such as Pb-Sn and Pb-Sb can be foamed by another modification of the process. TiH₂ and ZrH₂ cannot be used as blowing agents because of the low melting temperatures of pure lead (327°C) and the alloys mentioned (even lower). Quite good foams have been obtained by using lead(II)-carbonate as a blowing agent. This chemical decomposes above about 275°C and releases CO₂ and water which act as blowing gas. Figure 5 shows an example for a lead foam

2.1.2.3 Titanium

Due to its high melting temperature (1670°C) and relatively low density (4,51 g/cm³) titanium and its alloys are excellent materials for lightweight applications at elevated temperatures and are widely used, e.g. in aeronautic applications. Porous titanium structures bear an additional potential for weight reduction and could even be suitable for functional applications if the pore structure were open.

In principle, there are many possible production methods for cellular materials based on titanium, most of them starting from metal powders:

- 1. consolidation of slurry saturated plastic foam
- 2. foaming and sintering of powder slurries
- 3. reaction sintering of element powder mixtures
- foaming of powder compacts containing blowing agents (powder compact melting process)

- 5. hot isostatic pressing and creep expansion of titanium compacts with entrapped inert gas
- 6. sintering of hollow spheres.
- 7. sintering of compacted or loose powder-filler mixtures

While some of these methods (1-3) have not yet been investigated very intensively, the feasibility of the blowing agent process (4) for titanium has been demonstrated [13]. However, owing to the high temperatures during foaming titanium, the reactivity of this metal with practically any noninert gas and the lack of appropriate foaming moulds, this method is not suitable for producing shaped titanium foam components. Hot isostatic pressing of titanium powder with gas entrapment (5) has been successfully developed for some aircraft applications [14]. Metal hollow spheres (6) can be produced using wet chemical methods for coating styrofoam spheres [15]. Shaping and sintering of these hollow structures typically result in materials with very low porosity.

One of the most promising methods for manufacturing open porous titanium materials is the sintering of compacted or extruded mixtures of powders and fillers which contain removable space holder materials. The materials are mixed and shaped by conventional PM techniques. After removal of the space holder the green samples are sintered at temperatures between 1100 and 1400°C. Bram and co-workers use urea and ammonium hydrogen carbonate as space holder [17] which can be removed by thermal treatment below 200°C. Depending on the size and shape of the space holder powder, spherical and angular pores in the range of 0.1 and 2.5 mm can be obtained resulting in overall porosities between 70 and 80 %. It was found that the sintering activity can be increased by partially substituting titanium by titanium-hydride, thus yielding an increased compression strength.

At Fraunhofer IFAM polymer granules were used as space holder. They were removed by a chemical process at temperatures around 130°C after pressing. After space holder removal, samples are sintered in vacuum at temperatures between 1100 and 1250°C. Depending on the particle size of the granules average pore diameters in the range of 200-3000 µm can be obtained. Figure 6 shows some typical samples. Figure 7 shows the typical pore structure of samples based on spherical space holder granules. Beyond the primary pore structure, some microporosity (secondary pores) inside the sintered network is visible. It was shown that the secondary porosity has a strong influence on the overall strength of the samples and can be reduced by either changing the sintering parameters and/or partially replacing titanium powder by titanium hydride [17]. As for all porous materials, the mechanical properties of cellular titanium are a function of density. Figure 8 shows the strength and Young's modulus obtained from bending and tension tests as a function of density.

2.1.2.4 Steel

Blowing agent technique

The long experiences in making aluminium foams from PM precursors encouraged researchers to transfer this process to higher melting materials such as iron based alloys and steels. The major requirements for an adaptation of the blowing agent process to this group of materials are:

- 1. Selection of suitable blowing agents
- 2. Development of alloys, qualified for good 'foamability'
- 3. Evaluation of proper compaction methods
- 4. Adaptation of the foaming process.

The basic requirements for blowing agents are: point of gas emission above 1000°C-1200°C (depending on the alloy

composition), broad temperature range of gas emission (up to 1550°C for nearly pure iron) and sufficient volume of gas release. It was found, that especially metal nitrides and certain carbonates show a significant gas emission and qualify for being useful as blowing agents. Examples are manganese nitride, chromium nitride, molybdenum nitride, calcium carbonate, strontium carbonate and barium carbonate [18][19]. Theoretical investigations [20] have shown that both the iron-carbon and the iron-boron system are able to meet the basic requirements for being foamed to iron-based metallic foams, namely: 1. low melting point matching the decomposition temperature of the blowing agent and, 2. a broad two-phase semi-solid region in the phase diagramme, thus creating a wide foaming interval. As for the production of Al-based foamable precursor material, extrusion has been successfully used for compacting iron powder mixtures. The resulting samples are shown in Figure 9.

Experiments with powder mixtures of iron and carbon have shown that free carbon without any additional blowing agent already leads to a certain degree of porosity. Carbon is oxidised during the foaming process and the resulting gaseous CO and CO₂ creates pores. However, pore size distributions are not uniform and pore shape is usually rather irregular. The porosity mainly results from large, isolated pores (see Figure **10**). Adding 0.25% SrCO₃ leads to an increase of porosity to 55.5%. The pore structure at this composition appears to be more homogeneous and the average pore size is obviously lower. Increasing the amount of SrCO₃ results in a further increased porosity (64.3 %). From that it can be concluded that SrCO₃ has a significant influence on the achievable porosity and the maximum expansion. The blowing agent technique has therefore been shown to be feasible for steel. However, foaming of stainless steel or even super alloys has not yet been successful and the general state-of the art of foaming steel with the blowing

agent method is still far beyond the aluminium foaming technology.

Steel foams from powder-filler mixtures

All foams obtained from the blowing agent process have closed cells. For certain applications (filters, membranes, biomedical applications) open porosity is required. For this class of materials the space holder technique can be used. The process used for steel is very similar to the one described in the titanium section. The process starts with a mixture of metal powders and the filler powder. The mixture is compacted, usually by axial compression in a conventional powder press. If necessary, an additional bonding agent is used in order to achieve a better strength of the green samples. After pressing an additional drying step is optional. After this the filler/bonding agent phase is removed from the samples, e.g. in a chemical (catalytic) or thermal process. After complete filler removal the samples are sintered in a furnace under hydrogen atmosphere. Either urea [17] or plastic granules [21] can be used as space holders. In Figure 12 examples of porous 316L and INCONEL 600 materials are given, developed by Forschungszentrum Jülich GmbH. The porosity of these materials is about 70 % with an average pore size of 1-1.4 mm.

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Figures



Figure 1: Foam production by powder compact foaming technique



Figure 2: Aluminium foam part (Schunk Sintermetalltechnik, Giessen)



Figure 3: Rear wall of an automobile made of aluminium foam (LKR Ranshofen and DaimlerChrysler AG)



Figure 4: Left: aluminium foam part made by inserting various pieces of foamable material into the mould. Right: foam part made of two pieces of precursor without achieving bonding between the two pieces.



Figure 5: Zn and Pb-foam (width of images is about 5 cm)



Figure 6: Open porous Titanium made by space holder technique. Left: Pore size 1-4 mm, right: pore size approx. 500µm, Porosity 55-80%.



Figure 7: Pore structure of open porous Titanium with 67% Porosity.



Figure 8: Strength and Young's Modulus as a function of density obtained from bending and tension tests [13].



Figure 9: Iron foams obtained from the blowing agent process



Figure 10: Iron-based metal foams made from extrusion pressed powder mixtures of Fe + 2,5% C. Left: 0,0% SrCO₃, middle: 0,25% SrCO₃, right: 0,50% SrCO₃



Figure 11: Average porosity as a function of foaming agent content (SrCO₃).



Figure 12: SEM images of sintered specimen. Left: stainless steel 316L, 1100°C, 1h, particle size $16 < \mu m$. Right: Inconel 600, 1250°C, 1h, particle size 100-200 μm . [17]

Tables

Table 1: Characteristics of powder compact foaming method: advantages and disadvantages which are inherent are listed together with points which are a problem presently but can be solved in principle.

Advantage	Problem	Disadvantage
near net-shape foaming possible	uniformity of pore structure still not satisfactory	cost of powders
composites can be manufactured	process control must be improved	very large volume parts difficult to make
flexibility in alloy choice		
no stabilising particles have		
to be added		
ceramics and fibres can be		
added		