Light-metal foams – history of innovation and technological challenges

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The history of metallic foams and the key innovations that have led to the variety of processing methods known today are reviewed. It is evident that the idea of foaming metals is very old and that most of the techniques used today have been proposed already in the 1950s. The most important milestones in the development of foaming technologies and the some of the attempts to commercialise metal foams are reviewed.

1. Introduction

Historically, the idea to create artificial cellular materials must have been motivated by natural materials such as pumice stone, wood or bone that have all been in use for a long time due to their unique properties. Since the 20th century, cellular materials are engineered from dense basic materials, their properties are investigated systematically and it is determined in which situations they are superior to their dense counterparts.[1,2] The matrix material of cellular materials – or, more specific, foams – can be a polymer or another organic material, a glass, a ceramic or even a metal[3].

Use of language in this area of research is often sloppy. Any kind of non-dense metallic material tends to be called 'metallic foam'. In this paper, a foam is defined as a mixture of a gas and a solid phase in which, (i) the gas bubbles are isolated from each other while the solid matrix is contingent and, (ii) which originates from a liquid precursor in which gas bubbles can arrange freely without help of a template. Other types of cellular, porous or spongeous materials shall not be considered. Those are governed by different rules and have been described elsewhere.[2,4]

The following outline of the most important innovations in metal foam processing technology will not be strictly chronological since such a presentation would be confusing due to the many side steps that have been taken. In fact, we shall group the known foaming techniques into various 'lines' as shown in Figure 1. Each method is named after a prototype of a process within a 'line'.

'Direct foaming' methods convert a liquid metal or alloy into foam without an interruption (1st line). For foaming, a gas source is needed and depending on the gas source we define different 'lines': gas can be injected into the melt ('Alcan line'), a chemical blowing agent can be added to the melt where it decomposes and liberates gas ('Alporas line') or gas can be first dissolved in the melt and then released during foaming ('Gasar line').

'Precursor foaming' (a.k.a. 'indirect foaming', 2nd line) involves melting of a solid material in which a gas source has been embedded that upon melting releases gas and drives the foaming process. Such precursors can be made both by powder pressing ('powder line') or by melt processing ('Formgrip line'). Mostly, the gas source is a blowing agent powder, but precursors are also made by entrapping gas in a powder mixture during densification and

expanding the compact by a subsequent thermal treatment.[4] Such methods have not yet matured sufficiently and are only briefly mentioned in Sec. 7.2.

In Figure 1, the different methods are also distinguished according to the way of bubble formation ('internal' from local sources or 'external' at the gas injection points) and to the state the base metal is in during processing (melt or powder).

This review covers different kinds of metal foaming technologies. The reference list contains about half of the journal papers and patents currently published. Papers found to be redundant or irrelevant have been omitted and, of course, there might be one or the other relevant paper that was simply overlooked. The 'Web of Science' lists 5600 publications when applying the search expression '(aluminum OR aluminium OR metal OR metallic) foam' in the search field 'topic'. This list contains many papers on cellular metals that are not foams and even more papers that describe properties (mostly mechanical) of cellular materials only.

2. Foaming metallic melts using gas-releasing blowing agents ('Alporas' line)

2.1. The early days in France

In many papers we read today, metallic foams are called 'novel materials' that have been invented 'recently'. More careful authors cite patents from the 1970s or even the 1960s in which many of today's concepts are already described, but it comes as a surprise that the principles of foaming metals have been developed much earlier. The earliest mention of metal foaming known to the author is by M.A. De Meller in 1925.[5] The process described in that patent comprises either, (i) the injection of inert gas into a molten metal, or, ii) the addition of a blowing agent such as a carbonate to a molten metal, during which the melt is stirred. In both cases foaming is initiated and a foamed body obtained. The author makes suggestions how to produce integral foams consisting of an inner foam core and a dense outer cover layer by either partially remelting the surface of a metal foam, by immersing a foam into a bath of molten metal or by centrifugal or pressing techniques that remove some liquid from a foam and form the outer cover layer. The inventor claims that complex parts such as the one drawn in Figure 2a can be made, but no real part is shown. The possibility to reinforce foams with wires or meshes is mentioned. Patents often contain pure ideas that have never been verified, but De Meller's knowledge of the feasibility of foaming aluminium with carbonates (later verified, e.g. by Ref.[6], see also Sec. 2.7) suggests that he talks about something that he has really worked on. On the other hand, De Meller does not describe a crucial step necessary to obtain stable bubbles, namely melt conditioning (also called 'melt thickening' or 'melt stabilisation'), which ensures that the bubbles created in a melt remain stable during processing and do not rupture or coalesce. Moreover, it is known that bubbling inert gas through an Al melt does not produce stable foam[7] and therefore the first variant proposed (inert gas injection) cannot work in such a simple way. De Meller mentions application of foams in building industry and in airplanes (wing elements, fuselage) but nothing is known about real attempts to industrialise the process and no other publications describing further technical details are found.

2.2. Restart in the USA – The Bjorksten Research Laboratories

The next steps in the development of metal foam are taken in the USA 20 years later. Benjamin Sosnick's process that involves melting aluminium/mercury mixtures to above the boiling point of mercury[8,9] appears rather poisonous but shows that the idea of making metal foams is still alive. In 1951, John C. Elliott of the Bjorksten Research Laboratories (BRL)[10] files a patent describing an improved version of De Meller's process.[11] He proposes to use TiH_2 or ZrH_2 as a blowing agent (BaH_2, LiH, $LiAlH_4$, $CaCO_3$ and other compounds are also claimed to work). The blowing agent (0.5 – 10 wt.% if using hydride) is added to a range of Al-Mg alloys either directly or after having been encapsulated in a low melting eutectic Mg-Zn alloy to avoid excessive oxidation or even burning. The blowing agent may be admixed to

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the liquid alloy at a lower temperature, after which the temperature is elevated for foaming. Mixing is assisted by mechanical action ('grinding'), e.g. by a pestle, to ensure wetting. Foaming is reported to be fast, taking 30 s for a batch of pure Al, and pore sizes range from 6 mm to 9 mm[11]. Liquid metal foam is reported to have an elevated apparent viscosity and to behave like whipped cream that can be poured into moulds and cast into shapes, although it is in general preferred to keep the expanding foam in the original vessel. Shaping of foam to sheets by moving belts or rollers is proposed. As De Meller, Elliott does not mention measures to stabilise the melt. The remark that oxidation has to be prevented by flushing with inert gas[12] indicates that the role of oxides in the melt has not been recognised at this stage. The reported necessity to cool foams quickly or even 'quench' them to prevent 'dissipation', i.e. decay, indicates poor stabilisation of those early foams. Moreover, the use of up to 10 wt.% or more blowing agent in the examples given[11] indicates non-optimal conditions.

In a later patent, further processing options are substantiated such as admixing the blowing agent under high pressure to delay its decomposition and triggering expansion by releasing the ambient pressure, or by expelling the metal/blowing agent mixture through an orifice into a low pressure environment where the alloy can foam.[13] The latter arrangement is claimed to be suitable for the continuous production of strips or boards.

Beside Elliott, William Stuart Fiedler, Stuart O. Fiedler (W.S.' father) and Johan Bjorksten are further inventors, first at BRL, later for the Lor Corporation to where the metal foam business is shifted for upscaling and commercial development around 1960.[14] These inventors publish more than 15 patents in the USA. Some of those describe the design of a continuous foaming process[15], where granulated base metal and blowing agent are continuously heated and foamed. How exactly this works is naturally not disclosed in the patents, but the picture in Figure 2d proves that an irregularly shaped strip of metal foam can be produced already in 1957, probably in an early version of the process. The technology of continuous foam production is carried on in later patents. There, worm screws and propeller blades ensur continuous distribution of blowing agents in a melt reservoir and a conveyor belt removes slabs of foam continuously,[12] see Figure 2c, or beater rods and blades are used to continuously disperse the blowing agent in the melt that is also continuously fed into the foaming vessel.[16] In the 1961 versions of Ref.[15] and in Ref.[13], the French patent from 1926[5] is mentioned for the first time. Possibly, it had been overlooked before.

As it is emphasised that metal foams have to be cooled quickly after foaming,[11,13] foam stability evidently is a problem, possibly leading to non-uniform pore sizes and a limitation of production to small foam components. The high fraction of blowing agent used inflates the pores but at the same time, ruptures the walls between bubbles and gives rise to very big pores as discussed by John Ridgway of the Standard Oil Company. He proposes a solution based on dispersing a finely divided, wetted inert powder in the molten metal which remains solid there.[17] For example, for foaming the magnesium alloy AZ92, addition of 12 wt.% of –325 mesh (< 44 µm) boron powder or 7% Si powder is suggested that is ball-milled together with some Mg powder before use. The added powders are speculated to cause a loss in liquid mobility when too many particles are constrained in a film of the thickness of the particles and an according 'stiffening' of the liquid film. Selection of size, type and volume fraction is empirical. It is recommended to use particles with a size ranging from 20% to 50% of the metal film thickness.

The necessity for foam stabilisation is addressed in another patent. It is first observed that the accidental entrainment of oxygen into the liquid metal during addition of the blowing agent, which is usually accompanied by stirring, is a prerequisite for foaming.[18] The entrained oxygen converts the blowing agent particles TiH_2 to TiO particles while hydrogen is being liberated. These oxide particles then stabilise the foam. This finding explains why foams are stable, although insufficiently, in earlier experiments although no stabilisation measures have been taken: The 'rapid rotative movements' during addition of the blowing agent[16] simply

lead to the formation of some stabilising particles. As a consequence, if the absence of oxygen is ensured, substantially no foaming is obtained.[18] Guided by this observation it is proposed to add MnO_2 to the aluminium alloy melt. MnO_2 reacts with Al and leads to the formation of alumina particles that are dispersed in the melt. The largely increased density of particles allows one to reduce the amount of blowing agent needed to 1/8 the amount needed for unstabilised melts and also provides more nucleation sites for bubbles. This leads to a more uniform distribution of more and smaller bubbles compared to the unstabilised foam.[18]

2.3. Ethyl Corporation

Metal foam development starts at the Ethyl Corporation in Baton Rouge in the late 1960s. As an alternative to the stabilisation measures discussed in the previous section[17,18], Currie B. Berry proposes thickening the metallic melts to be foamed by sparging oxygen, air or CO_2 through them[19]. The procedure described in the patent is exemplified by a liquid AlMg7 alloy that is treated by bubbling oxygen through the melt while running an agitator. Oxide particles are formed in the melt in-situ due to this treatment. After thickening to the level of 'heavy soap lather'[19], the melt is left for settling during which it becomes thinner again. After reaching the desired consistency, the melt is foamed by adding 0.6–1.2 wt.% ZrH_2 or other hydrides at a temperature of 620–650 °C. After solidification, the foam has not only gained stabilisation (reflected by smaller pores) but also strength by the oxide particles embedded in the base material. It is stated that the thickened mixture can be solidified to a foamable alloy and reheated later for foaming, i.e. an interruption is permitted between the thickening and foaming steps. Although the patent claims that pure Al can be foamed there is good reason to believe that the presence of Mg is beneficial for the formation of a sufficient density of particles (probably spinel and/or MgO). In pure aluminium, sufficient stabilisation is hard to achieve by in-situ oxidation[20] and perhaps intense oxidation by pure oxygen is necessary to produce the pure Al foams mentioned in Refs.[21,22]

Berry's further work draws additional attention to the key issue of foam stabilisation. He suggests to add to a melt prior to foaming 2–6 wt.% (or more) dross collected from surfaces of molten alloys. This stabilises the foam generated via the oxides contained in the dross and also reduces the cost of the process[23]. The action of dross addition is described as 'viscosity-increasing' but it is admitted that the mechanism is not known.

The foaming process is further elaborated in a later patent by Niebylski et al.[24] Details worth mentioning include: (i) The viscosity-increasing treatment reduces the amount of blowing agent required to 60% of the amount needed to foam an untreated melt (in analogy to Ref.[18]). (ii) The treatment should be rapid (15 s to 3 min) and its effect is temporary only. The higher the temperature, the faster the stabilisation effect levels off again. (iii) Moulds can be completely filled with foam. (iv) Preannealing in inert gas at up to 400 °C of the hydrides used for blowing reduces the amount of gas liberated and slows down kinetics. (v) The blowing agent (typ. 0.5 to 0.6 wt.%) can be wrapped into Al foil before being added to the melt. (vi) It may be useful to carry out thickening at a higher temperature than foaming.

What is questionable is the claim that thickening can be carried out with nitrogen and argon. It is not clear how this could stabilise a foam unless the gases contained some oxygen. Still, Ref.[24] contains many interesting observations related to the foaming process.

A lot is done to convert the bare foam into a product: casting of foams into moulds is investigated[25] as well as shaping or laminating solidified foams by compressive loading.[26] Foams are anodised to gain improved strength and to reduce surface porosity[27]. Age hardening aims at higher bulk (matrix) strength.[28] Fibre-reinforced foams are investigated[29] and metals other than aluminium alloys foamed, namely pure zinc (foamed with TiH_2)[30] and lead-zinc alloys with 1.5 to 5% Zn (thickened with CO_2 gas, foamed with TiH_2).[31] At least 12 patents in addition to the ones cited in this paper can be found. Work on metal foams at the Ethyl Corp. ends in the mid 1970s. Three scientific publications are known to deal with

properties of foams made by the Ethyl Corp.[21,22,30] The latter paper discusses application of Al foam for energy absorbing bumpers in cars. The samples shown in Figure 3 create an impression of the quality of the material.

2.4. 'Alporas' foams

The Shinko Wire Co. Ltd., Osaka, Japan, a subsidiary of Kobe Steel, invents a process that is closely related to the one developed at the Ethyl Corporation more than a decade earlier and files a patent in 1985 in Japan and later in Europe and the USA.[32,33] Here, metallic calcium (0.2 to 8% according to the patent,[32] 1.5% according to publications[34] is added to molten aluminium alloy at 680 °C[34] (or 720 °C[32]), after which the melt is stirred for several minutes (e.g. 6 min[34]) at ambient atmosphere. During stirring the viscosity increases.[34,35] After a predefined level has been reached, the thickened melt is poured into the foaming vessel and TiH_2 (1 to 3% according to the patent, 1.6% according to Ref.[34,36]) is admixed while stirring continues at 680 °C for some time. After this, the melt is left for foaming for ~15 min[34]. As soon as the foam has filled the foaming vessel the gas vents of the vessel are closed. The associated pressure increase is described as crucial for obtaining a uniform bubble size distribution especially near the foam surface.[32,33] Cooling the foam is done by air blowing. A typical foam made by the 'Alporas' technique is shown in Figure 4. Cell sizes of 'Alporas' vary from 2–10 mm with a mean of ~5 mm.[34]

The patent and subsequent publications do not emphasise that thickening is caused by the contact of the melt with air but it should be understood that oxidation causes the formation of particles that are crucial for foam stability (as pointed out in the previous section). This can be shown explicitly by comparing melts with and without Ca addition and thickening with and without stirring.[37] Ca allows one to obtain a sufficient number density of stabilising particles in the melt in a very short time and the 'Alporas' route seems to be more efficient than the methods described in Secs. 2.2 and 2.3. Other researchers report that pure Al can be foamed without Ca addition when using very fine TiH_2 powder (< 8 µm) as a blowing agent.[38] In this case, drainage is strong and cell size large and partial stabilisation might have come from the blowing agent particles.

Originally, there is not much literature on the foams Shinko Wire produced which are called 'Alporas' foams. Some mechanical properties and very little information on manufacture are communicated before 1993,[39-41] a bit more in the years after.[42-44] Some work goes into processing 'Alporas' into practical shapes by foaming inside complex moulds.[45,46] For this, the melt is poured into the mould after the addition of TiH_2 just before the expansion process sets in. However, 'Alporas' foam is mostly known as a product obtained by slicing large slabs of foam (typical batch size = 2050×650×450 mm^3, mass = 160 kg) into thin sheets.[34] Such sheets are primarily seen as good sound absorbers and electromagnetic wave shieldings.[32-34] Attempts to make such panels in a continuous casting and foaming operation have been reported.[46]

2.5. Studies of the 'Alporas' foaming process and its parameters

The first scientific studies of the 'Alporas' foaming process are published by a group in Nanjing, China. The viscosity during thickening of the melt with different levels of Ca is measured in-situ with a stirring paddle and related to the structure of the foam after manufacture. Melt viscosity is found to influence the foaming process but no microscopic explanation for the effects observed is given.[35,47] The expansion kinetics of 'Alporas' foam is measured in-situ using a mechanical expandometer and related to processing conditions.[48] Further analysis of the foam expansion process allows the authors to discuss the various forces governing foam expansion and to describe them by a model.[49] Melt properties are measured under defined conditions in a surface tensiometer and viscosimeter by researchers in Korea for both aluminium[50-52] and magnesium alloys.[52,53] Studies of the phases formed

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during melt treatment and still present in the solidified foam allow for assessing the mechanism of thickening and foam stabilisation[20,37,54-58] (such phases have also been analysed because of their suspected impact on foam fracture[59-62]). The interpretation of the phases found varies in the literature, some claiming that intermetallic phases are important, others holding oxides responsible for foam stability. The effect of process parameters such as foaming temperature,[34,63] stirring mode and velocity,[64] stirring time[65] and holding time[48,49] on the properties of the final product is studied by various researchers. The effect of Ca content[46,47] and cooling rate[46] are also discussed.

The possibility of using magnesium instead of calcium to promote thickening is investigated[38,66] with the background that the formation of stabilising particles might also be fostered by the presence of Mg during stirring. However, coarser and less uniform foams are obtained and a similar negative effect is observed for additions of lithium. Magnesium is found to lead to large gradients of cell size when used in addition to calcium.[67]

The effect of a pre-treatment of the blowing agent TiH_2 either by oxidation or by chemical filming is studied[38] (see Sec. 4.4. and Ref.[24] for the background). Unlike for the foams discussed in Sec. 4.4., no positive effect is found, just a slower expansion and a stronger coarsening of foams blown with pre-treated TiH_2 powder. The effect of the particle size of the blowing agent powder TiH_2 is investigated. Coarser TiH_2 particles lead to slower foaming, larger cells and increased drainage.

As the original 'Alporas' foams based on pure Al are not very strong, alloying with further elements is carried out. The problem encountered is that additional elements that strengthen the metallic matrix also influence foaming conditions due to their influence on surface tension and melting temperature.[63] AlZn5Mg1 alloy is found to lead to stronger foams than pure Al without compromising the foaming process (same for AlZn7Mg0.5[43] and AlZn10Mg0.3[46]) and so does Al-Sc.[68]

2.6. Alternate ways to stabilise melts

Melt treatment with Ca as it is done in the 'Alporas' process is only one option. Further research is carried out to find alternate particles that can stabilise a foam. It is realised that solid particles in a metallic melt stabilise metallic films because they are situated at the gas/liquid interfaces. The viscosity enhancement that gives rise to the expression 'thickening' for the melt treatment is not the only effect.[7] The particles also seem to influence the capillary pressure conditions in and the surface rheology of the films, although the exact mechanisms of stabilisation are not yet known.[7] Type, shape and properties of the particles play an important role.[20] Much of the work revolves around replacing expensive starting materials by cheap ones and improving foam stability to obtain more uniform foams with a more predictable structure.

A group in Hefei, China, thickens their melts with MnO_2,[69,70] thus following the suggestion by Graper.[18] A group in Taiwan uses recycled Al with a high oxide content that is melted and stirred into the melt to be foamed in open air to disperse the oxide films. Then, the melt is foamed by adding TiH_2 without adding additional thickening agents.[71] This is similar to what Berry suggests.[23,72] Later, in a related investigation, Al-Si-Mg casting alloy is melted and 5% Al powder added, after which the mixture is stirred until viscosity has increased to 1.7 times the original value. Then, TiH_2 is added for foaming.[73,74] A similar approach is reported in Ref.[75], where 3% Al powder are used for stabilisation and $CaCO_3$ for blowing a Al foam.

Other researchers foam an aluminium A356 (AlMg7Mg) melt containing 20% SiC particles (inspired by the melts used for the gas blowing process, see Sec. 3) by adding TiH_2 particles[20,76,77] and, optionally, Al powder[76]. The resulting foams are brittle, which is one of the disadvantages of using such materials. Something very similar is done using $CaCO_3$ as a blowing agent.[78,79] A direct comparison between stabilisation via the 'Alporas' route (with Ca) and by SiC reveals a slightly more stable foam for the latter.[20]

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7-µm thick Cu-coated carbon fibres are found to stabilise pure Al and Al-Mg foams.[80] An Al-Mg-Si alloy containing 5% AlN particles dispersed in the alloy matrix can be foamed with TiH_2 to a stable foam.[81] Here, the AlN particles act both as stabilisers and as reinforcement of the matrix. Fine fly ash particles (5 wt.%) are used to stabilise and foam a commercial 2014 (AlCu4Mg) alloy, for which 0.5 wt% CaH_2 is used as a blowing agent.[82] Finally, use of scrap swarf chips is demonstrated to give rise to uniform foams due to the oxide particles present in such melts.[83] An addition of Mg is found to be beneficial here.

It is hoped that finer particles of a higher particle density can give rise to even more stable foams than the ones created by the 'Alporas' process. One strategy is to disperse nanoparticles, e.g. SiC, by the help of ultrasound.[84] With such nanoparticles, a small volume fraction would lead to a high number density of particles and lower the threshold for stabilisation to lower values. This would reduce both costs and brittleness of the matrix.

Another possibility is to create nanoparticles in a melt by an in-situ reaction instead of adding them. Such reactions are also used to make grain refiners in a melt and it is shown that such melts can indeed be foamed.[85,86] Another route is based on an in-situ reaction that produces sub-µm spinel particles in a AlMg5 melt to which SiO_2 has been added.[87,88] 3.4 vol.% of such spinel particles are found to be sufficient for efficient foam stabilisation.

The attempt to stabilise a pure Al melt that contains neither calcium nor other oxidation promoters just by stirring in the presence of air is not successful.[20] The resulting foam is very instable and does not expand very much, thus showing the necessity to promote oxidation by adding suitable reaction partners.

2.7. Blowing agents other than TiH_2

Carbonates are suggested as a replacement of TiH_2 for reasons of safety and cost. The idea is not new – already DeMeller suggests to blow light metal foams with carbonates[5] – but the implementation of the technique is not straightforward. Of the carbonates, $CaCO_3$ appears especially suitable. In one study, the possibility of using $CaCO_3$ in the standard 'Alporas' process is demonstrated for the alloy AlSi7Mg. Reasonable results are obtained for $CaCO_3$ powders containing a chemical CaF_2 conversion layer on the surfaces of the powder particles which improves wetting by the melt.[6] Further alloys are foamed, including Al and Al-Mg-Zn-Cu (alloy 7075). Foams blown by $CaCO_3$ and TiH_2 are compared.[89-92] $CaCO_3$ leads to pores that are merely half the average size of the pores in TiH_2-blown foams. $CaCO_3$ is also used by other groups to foam pure Al[75] and the alloys ZnAl22[93] and AlSi9Mg.[78]

Dolomite $MgCa(CO_3)_2$ is used to foam pure Al without any additional stabilizer.[94] Here, the residues of the blowing agent (MgO and CaO) provide sufficient stabilisation. The foams obtained are less uniform than the original 'Alporas' foam. Within the family of hydrides, CaH_2 is used for foaming Al-Cu-Mg alloys[95] as well as ZrH_2 for foaming pure Al.[96]

The 'Alporas' process is further developed by The Aluminum Company of America (Alcoa).[97,98] Here, 2 – 8% $CaCO_3$ are used as a blowing agent. $CaCO_3$ not only liberates the blowing gas CO_2 and leaves behind CaO, but CO_2 also reacts with the Al-Mg-Si alloy and forms stabilising alumina, magnesia, carbide and other particles. As a result, the molten alloy can be turned into a foamable suspension by intense mixing and stirring. In this way, thickening and blowing can be combined in a clever way into an integrated process and AlSi7Mg2 alloys with very fine pores are created, see Figure 5. The process can be extended to a continuous casting process for sheets unlike most other Alporas-type foaming routes that convert a fixed batch of liquid into a block of foam.

Finally, it can be shown that melts can also be foamed without adding any blowing agent powder. The idea is to melt under normal ambient pressure pieces of scrap left over from Mg die casting and, after melting, to evacuate the recipient containing the melt.[99,100] As the scrap contains plenty of oxides, hydroxides and other impurities, stabilisation is guaranteed, while the gases adsorbed to the scrap or bound as hydroxides blow the foam as they are expanded

by the pressure drop. In a certain sense, these impurities in the melt are both the stabilisers and the blowing agent with the difference that they are contained in the starting melt already and do not have to be added.

2.8. Metals other than aluminium

Beside aluminium, magnesium alloys are in the focus of attention already in early work[17]. The vacuum foaming method described in the previous paragraph shows that such foams can be made from melts. The 'Alporas' process can be directly generalised to make pure Mg,[101] alloy AZ91 or AZ31 (Mg-Al-Zn) foams.[102,103] Ca metal is again used for melt treatment (2% wt.%,[102] 6 wt.%[103]), but TiH_2 is replaced by $CaCO_3$ as the blowing agent. The resulting foams have porosities up to 72% and pore sizes around 2 mm.[102] Their pore uniformities and properties are found to be superior to those of Al foams.[104] TiH_2 is not a suitable blowing agent for Mg alloys as shown in Ref.[53], where neither an AZ91 nor AM60 alloy stabilised with Ca or SiC addition exhibit satisfactory foaming.

Zinc-based ZnAl22 foams stabilised with SiC are blown with TiH_2[105,106] and $CaCO_3$[93]. Foamability is reported even without the need for melt conditioning.[93,105] The foams blown with $CaCO_3$ have small pores (of the order of 2 mm) and porosities up to 92%. It is very likely that the blowing agent particles act as foam stabiliser in non-conditioned melts, i.e. they have a dual function, blowing and stabilising. By adding a preform consisting of a compacted blend of milled ZnAl22, SiC and $CaCO_3$ powders to a ZnAl22 melt, stirring the mixture and foaming, reinforced Zn-base foams are manufactured in a slightly modified way.[107]

Foaming high-melting metals such as steel occupies three inventors from the US Steel Corporation.[108] They modify the stabilisation method proposed by Ridgway[17] and claim that iron can be foamed to more that 50% porosity by adding to a melt high-melting 'foam promoters' (i.e. stabilisers) such as tungsten powder and to foam the melt with TiH_2 or ZrH_2. However, no results are shown. An attempt to foam a Fe-Cr alloy by adding the blowing agent chromium nitride serving as a nitrogen source yields porous castings but no useful foams.[109]

2.9. Fast melt processing

Stabilisation is necessary for retarding degradation processes such as coalescence during foaming until the foam solidifies. The faster foaming can be carried out the less pronounced such degradation processes and the less difficult stabilisation will be. Already early researchers realised this.[11] Both the University of Erlangen, Germany, on one side[110] and the manufacturers of MgH_2, Goldschmidt GmbH in Essen, Germany, and of die casting machines, Bühler Druckguss GmbH, Uzwil, Switzerland, on the other[111] suggest to inject a melt into the mould of a die casting machine and to add a blowing agent powder shortly before the melt reaches the die. The parameters are set in a way that the melt that is intimately mixed with the blowing agent powder can expand and form a foam component in the mould. Goldschmidt and Bühler call their product that has a dense outer skin and a porous core 'Combal', see Figure 6. The University of Erlangen presents Al and Mg foams: Thixomolding or cold chamber die casting machines are used to foam Mg alloys,[112,113] die casting machines to foam Al alloys.[114] The blowing agent is MgH_2 in both cases. The resulting foams have a dense skin due to the solidification conditions in the die. One such sample is shown in Figure 7 and demonstrates that integral (or structural) foams with a closed skin can be produced. More details of the high pressure integral foam moulding technique are discussed in Refs.[115,116] Recently, it has been possible to manufacture integral foams with pore sizes well below 1 mm.[114] No stabilizing particles are added unlike in the slow foaming processes discussed previously. The very short processing times and some self-stabilisation of the melt in the semisolid range ('endogeneous stabilisation'[114,117]) can be assumed to be the reason for temporary stability.

2.10. Overview of processes of the 'Alporas' line

Many variants of foam processing following the principles of the 'Alporas' line – i.e. admixture of blowing agents to a melt – are now known. Beside by the general processing setup, the various methods differ by the kind of melt conditioning (a.k.a. thickening or stabilisation) used and by the blowing agent admixed. Some of the combinations found in the literature are summarised in Table 1.

3. Foaming metals by gas injection ('Alcan line')

Instead of using a gas-releasing blowing agent to blow metals to foams, gas can be injected from an external source through a nozzle into a metallic melt. This is suggested by A. De Meller[5] and later by W.S. Fiedler.[16] The former proposes inert gas, the latter oxygen or steam as blowing gas but it is doubtful whether metal foam has ever been produced in this way since no measures for stabilising the foam are addressed. The gas blowing approach promises to replace potentially expensive blowing agents by cheap gases but is not easy to implement. The same melt that can be foamed by adding a blowing agent powder (internal gas source) might not be easy to be foamed upon injection of gas from outside the melt.[118,119] The difference between the two approaches is that a multitude of gas bubbles are created locally in the former case, whereas in the latter, the gas bubbles are created at one – or few – points only and have to float through the melt from the injection point to their final position after detachment. Depending on the structure of the melt this might not happen and therefore no foam formed.

3.1. Bubble blowing in Canada and Norway

In the year 1989, patents are filed by researchers of the Aluminum Company of Canada (Alcan)[120] and of the Norwegian Norsk Hydro Company[121] almost simultaneously. Both describe essentially the same novel foaming method. For the Canadian side an accidental discovery during processing liquid aluminium matrix composites (MMC) is reported during which it is observed that gas bubbles are remarkably stable in such melts. It is realised that foam can be produced by injecting gas into MMC melts instead of adding gas-releasing blowing agents as described in the previous chapter. The basic layout of the process is given in Figure 8a. Gas is injected to below the surface of a melt and bubbles are formed that float to the top, accumulate there and form a metal foam layer. The particles dispersed in the liquid MMC act as stabilisers. They adhere to the gas/metal interfaces of the rising bubbles. Without them, the bubbles burst as soon as they reach the surface or merge with other bubbles. There is a minimum content of particles required for stability that depends on particle size (schematically visualised in Figure 8b) and also on the distance between the injection point and the surface:[122,123] The larger the particles are, the higher the particle volume fraction required. The larger the immersion depth of the injector is, the lower the necessary volume fraction. The foam layer forming on the melt surface can be drawn off continuously to form long slabs of foam. A further patent describes ideas how slabs of foam can be extracted from the surface of the melt.[124]

Gas injection is done by a rotatable air injection shaft connected to a number of outlet nozzles through which the gas (mostly air) escapes into the liquid. The cell size of the foam is said to be controlled by the gas flow rate and other parameters.[120] Beside the gas injection shaft shown in Figure 8a, use of a rotating shaft equipped with various blades is suggested. It creates a strong vortex through which gas is dragged into the liquid to form additional bubbles there.[125] It is claimed that the foam formed in this way has very fine pores and can be cast and shaped, even after an intermediary solidification step.[126]

The aspect of casting foam into shapes is substantiated in Ref.[127] Here, freshly produced liquid foam or remelted solidified foam is 'gently pressed' into moulds without compressing

or collapsing the foam. To which extend such pressing is actually successful cannot be specified.

The development at Norsk Hydro is very similar.[121] Al-based MMC alloys are foamed by injecting air or CO_2 into melts, after which the resulting foam layer formed on top of the melt is removed. Gas injection is through a rotor.

The foams produced in the 1990s by both companies have rather large pores and are not uniform[128], see also Figure 9. A gradient of pores size, shape and density from the bottom to the top of the slabs is mostly evident and mechanical properties are below the expectations (see next section). The processing opportunities claimed in the patent literature[120,121,124-127,129] do not appear to have been all verified.

3.2. Studies of processing parameters and physics of foaming

In the patents concerned, the details of the foaming process are not described. Questions of interest are related to the particle type (usually SiC is used), particle size (commonly 15 µm), composition of blowing gas (normally air), suitable alloys (often A356=AlSi7Mg alloy), melt temperature (typically, first 710 °C then decreasing to 650 °C), the distance between the gas injection point and the surface (varying from 50 mm[120] to 300 mm[130]).

The physics of foaming is first studied by Ip et al.[122] They find criteria for the stability of metal foams. Leitlmeier et al.[123] and Babcsán et al.[57] later continue these investigations. Some recent work is found in Ref.[131]. Empirical studies are undertaken to relate particle type,[132] size[132] and concentration[132,133] to properties of the foamed materials such as cell size and cell wall thickness.

Micro and macrostructures of Alcan-type foams are analysed[134,135] and density gradients and non-uniformities determined.[128] In view of the appearance of those foams it is plausible that their structure and properties are not well predictable. For the foams produced by gas injection in the 1990s, the mechanical properties, e.g. modulus or strength, are usually inferior to those of 'Alporas' foam of the same density and also below the theoretical predictions,[3] which is why many researchers prefer to used 'Alporas' foams for their studies of structure/property relationships.

Various authors study the structure of cell walls in order to discuss the stabilisation mechanism.[54,55,57,58,134,135] For example, high-resolution synchrotron X-ray tomography that provides enough phase contrast to distinguish between the SiC particles and the Al matrix allows one to visualise the distribution of SiC particles in the cell walls in 3D and to verify that most of the particles are located at the gas/metal interfaces and are not connected to the opposite side of a film.[136]

The role of oxygen in the blowing process is investigated.[57,137,138] Blowing with pure argon leads to markedly increased bubble coalescence and drainage. Oxidation of the inner surfaces of the bubbles during blowing is essential for foam stability. Therefore, stabilisation of these foams is caused by at least two mechanisms, by the segregation of particles to the gas/metal interfaces and by the oxide films that cover the interfaces.

3.3. Important discoveries in Austria

As mentioned above, dispersing bubbles by means of vibrating or rotating impellers is initially believed to be a prerequisite for good foam. Improved designs are suggested such as using porous frits to disperse gas more uniformly, to use mechanical choppers or stirrers to assist in detaching the gas bubbles from the injector or to create diverging gas jets.[130] In practice, operating such impellers is not easy and sealing can be a challenge.[139]

Research carried out at the Light Metals Competence Centre (LKR) in Ranshofen (Austria) shows that the ideas behind the impeller concepts are misleading. In order to obtain a uniform foam it is more favourable to carefully create and maintain individual equally sized bubbles instead of producing a statistical mixture by the techniques mentioned above. It is proposed to

use specially designed stationary injectors made of a ceramic material that have a defined conical geometry instead of applying vibrating or oscillating nozzles or vortices.[140] The new nozzle design provides stable bubble separation criteria and allows one to make foam with a plurality of bubbles with approximately the same volume. The key point is that the detachment of a bubble from a nozzle after it has been filled with gas often takes place at different filling stages for each bubble because the detachment conditions are irreproducible, i.e. different for each bubble, when mechanical agitation is applied to the melt. Bubble formation in a melt is studied experimentally by X-ray radiography and the detachment conditions discussed in terms of wetting conditions[141,142] and also by simulations.[143]

In a further patent it is proposed to blow bubbles from an array of the specially designed novel injectors mentioned above to increase the bubble formation rate[144]. The result of the combined effort is a clearly improved pore uniformity compared to foams made by 'traditional' gas injection techniques. Figure 10a shows such optimised foams. The foam not only looks more regular than previous ones but also has a narrower bubble size distribution, see Figure 10b.

The finding that stirring or agitation is detrimental to foam uniformity is reported by another inventor almost at the same time who suggests to foam Al-based MMC melt by a quiescent stream of argon gas through thin tubes immersed into a melt and obtains a 'surprisingly uniform cell structure',[145] thus confirming the effectiveness of the abovementioned techniques.

3.4. Further developments

The technologies described so far are mainly designed for making flat products. Manufacture of foam components with a complex 3D shape is also desirable. Pressing a liquid foam into a mould is the easiest way of shaping,[127] but damage of the fragile films in the liquid state is probably hard to avoid even if a more refined technique is used.[146] This problem can be avoided by allowing a metal foam to be generated directly inside a mould, e.g. by using an open mould that is immersed into the melt to be foamed and then bubbling gas into the melt and let the bubbles fill the mould without the need for any shaping.[147] One version of this mould-filling process comprises pressing molten metal into a die through an opening in the bottom die wall by applying a low external gas pressure and then filling the mould with foam by bubbling air through the melt during which the melt is drained off by controlling the gas pressure.[148]

In general, the outer surface of such shaped metal foam parts will have the thickness of an individual film within the foam, i.e. be very (too) thin. A procedure to overcome this limitation is disclosed in a further patent.[149] Here, the opening of a mould pointing downwards is first brought into contact with the meniscus of the melt to be foamed. By pushing the melt first up into the mould and then down again under the control of an external gas pressure, a dense outer skin is created in the mould because its inner walls are kept cold enough to solidify a thin skin of metal. After this and without an interruption, gas is sparged through the melt and bubbles are allowed to slide into the mould in a gentle way without exerting mechanical forces and bonding to the previously formed skin. The resulting parts, see Figure 10c, have a very uniform thick skin and a regular pore structure. Such parts are used as cores for low-pressure die casting, during which the foamed core is completed embedded in a dense casting.[123]

Another activity is directed towards overcoming the need for using expensive and brittle materials such as MMCs for foaming, while still using the gas injection principle. One approach is to combine the material used for the 'Alporas' process (e.g. Al melts thickened by adding Ca and stirring in the presence of oxygen) and the gas injection principle of this section. Babcsán[119] blow air through a variety of different melts including an 'Alporas'-type melt containing 3% Ca and find that foaming is inferior to the foaming of MMC melts. In

other words, 'Alporas-type' melts are not as easy to foam by gas injection through an injector as by addition of TiH$_2$ powder. However, by carefully tuning the thickening conditions it might be possible to make such foams and one embodiment of a process has been disclosed in a patent.[150] Thickening is carried out in one heated vessel here, after which the thickened melt is transferred to a foaming vessel where gas is injected and the foam floating up to the surface is continuously removed.

4. Metal powder based foaming processes ('powder line')

Another way to make metal foam is by first preparing a solid metallic precursor that can in a second step be expanded to a foam by thermal treatment (foaming step, foam 'baking'). Such precursors can be made by processing blends of metal and blowing agent powders. This approach is sometimes also called the 'powder metallurgical', the 'powder compact foaming' or just the 'powder' route.

4.1. Early trials in the 1950s

John F. Pashak of the Dow Chemical Corporation – at that time the chief producer of magnesium metal – proposes to mix Mg-base or Al-base metal powder with either MgCO$_3$ or other carbonates that can act as a blowing agent, extruding these mixtures and then heat treating the extrusions at temperatures below the melting temperature of the respective alloy. During this treatment, the blowing agent releases gas and the material expands in the solid state to form a 'foam' with densities down to 0.57 g/cm^3 for a Mg alloy. The cell structure of such cellular materials appears irregular.[151] It is not known why no attempt was taken to melt the extruded material and to achieve larger expansions and rounder pores. Still, this is an early mention of the possibility to expand solid precursors made by consolidating powder mixtures and even the possibility to fill closed moulds with the cellular material is referred to.

Benjamin C. Allen et al. of the United Aircraft Corporation further elaborates the powder method.[152] They propose mixing metal powder (e.g. aluminium) and a blowing agent (TiH$_2$, ZrH$_2$ or CaCO$_3$), extruding the mixture (Al powder at 482°C) after an optional cold pre-compaction step and then foaming the extruded precursor by controlled heating to at least the melting point of the metal or alloy. The latter step is the main difference to the work of Pashak who expands the precursor in the solid state. Allen at al. note that during extrusion the oxide films around each powder particle are broken and thus good consolidation is achieved. Axial hot pressing of the powders is said to be insufficient, i.e. extrusion is essential. For foaming, two arrangements are suggested: Zone foaming by induction heating to fill the inner section of a tube continuously and discontinuous foaming inside a shaped mould. The authors note that the latter variant has the disadvantage that the cooling rate in the centre of such a part is lower than at the surface and that larger pores may develop there.

Unlike many patents in which inventors claim exotic parameter combinations or process variants that might never work, the descriptions in the patent here[152] appear realistic and are in accordance with later experience. For example, the fact that increasing the amount of TiH$_2$ used for blowing pure Al foam does not lead to higher porosities above a threshold of 0.4 wt.%, is later exactly verified.[153] The observation that during cooling cell walls tend to break and create a partially open structure (connected pores) is also confirmed. The choice of all other parameters seems to have been guided by real experiments.

4.2. Rediscovery

The breakthrough for the method developed by Allen et al. does not come before 1990. Joachim Baumeister of the Fraunhofer-Institute in Bremen, Germany, redevelops the powder process, initially without having knowledge of the previous developments.[154] His process differs in small details from the previous one, namely that the compaction temperature of the powder is higher.[155-157] As a result, hot pressing yields a good enough compaction to ensure

very good foaming, in contrast to the statement by Allen et al.[152]. Initially, compaction is carried out uniaxially, either in a small die using a 10 to press, or in a 300 to press to disks of 15 cm diameter and 15 mm thickness. Later extrusion is used to make foamable material more efficiently. Extrusion is carried out either with or without precompacting the powders. In the former case, mixtures of Al powder, alloying elements and the blowing agent TiH_2 are filled into thin-walled aluminium cylinders. These are preheated to 400°C and inserted into the horizontal extrusion die with a lifting tool, after which they are extruded, mostly to flat plates or rods. The process is found to be insufficiently stable in the sense that the foamable material obtained varies in foamability over the length of the extrusion. Therefore, the powder mixtures are first precompacted to billets by cold isostatic pressing and then extruded which leads to a higher process stability and product quality.

Production of foamable precursor by continuous extrusion – sometimes called 'Conform extrusion' – is also developed, aiming at making large quantities of precursor material of small cross section. For this, powder is continuously fed into a channel leading to a rotating wheel (typ. 300 to 600 mm diameter) that conveys the powder to a die opening by frictional transport. During flowing to and through the die opening, the powder is heated up by friction, densified and shaped, e.g. to a wire of typically 9.5 mm diameter at a rate of 20 m/min.[158,159]

Another way to produce foamable alloy is by powder rolling.[160] Powders are filled into flat containers and are then hot rolled and therefore densified in various passes. The container material remains as a dense outer skin. Foamable material of acceptable quality is obtained, but no upscaling effort is known to have been successful up to now.

Although initial work concentrates on pure aluminium, it is quickly realised that aluminium alloys could offer advantages over pure metals. Al-Cu,[161] Al-Si,[162,163] Al-Mg,[163] Al-Si-Cu,[164] Al-Mg-Si,[163,165-168], Al-Mg-Zn[166,168] and Al-Sn[169,170] are studied, just to give some examples. It is found that it is neither necessary nor desirable to use prealloyed powders, but that one can mix elemental powders in the appropriate fractions. In this case the soft Al powder even facilitates compaction and the process of alloy formation takes place during melting and foaming.

4.3. Foaming other metals

Foaming of aluminium alloys is in the focus of most studies, but metals other than Al are also considered. The transfer of aluminium foaming technology to brass, bronze[154] and zinc,[153,171,172] or superplastic Zn-Al[173] merely requires minor adjustments of the hydride content and the pressing and foaming temperatures. Gold can be foamed with TiH_2 as a blowing agent, but only after adding some 2% silicon to lower the melting temperature.[174] Pure magnesium initially turns out to be difficult to foam, probably due to problems with compaction or the properties of the oxide layers on the powder particles[175]. Only after adding 33 wt.% Al good foams are obtained.[176] Attempts to use pure Mg precursors containing TiH_2 to produce a foam by solid-state expansion lead to poor pore structures.[177] Only recently, the conditions under which Mg foams can be made have been elucidated.[178] Lead and lead-tin foam can be produced by using lead carbonate as a blowing agent.[153,179] Using a salt of the metal to be foamed – e.g. $PbCO_3$ for foaming Pb – is an advantage whenever the absence of metallic impurities in the foam is an issue.[180] A lot of effort is put into the manufacture of iron and steel foam.[181-189] Due to the much higher melting range of steel, different blowing agents are required, e.g. carbonates with a high decomposition temperature. Manufacture of titanium foams using a gas releasing blowing agent is even more difficult due to the strong reactivity of Ti with all gases and success has been very limited.[188,190]

4.4. Selecting and tailoring the blowing agent

Many gas-releasing blowing agents are screened for their suitability to foam different metals, including the hydrides of Ti, Zr, Hf, Ca, Sr, Ba, Mg, La and Li, the carbonates of Mg, Ca, Sr,

Ba, Li, Pb, Zn and Co and the nitrides of Mn and Cr.[176] For foaming aluminium alloys, titanium hydride is still the most used and probably best suited blowing agent. Still, the mismatch between the melting range of most Al alloys and the decomposition range of TiH_2 causes problems because a gas pressure is built up in the precursor during heating before melting sets in. This can give rise to non-spherical and irregularly shaped pores as verified for example by X-ray tomography.[191-193] One possible remedy is to use alloys with a lower melting range that comes closer to the decomposition range of the blowing agent.[165,167]

Another possibility is to shift the range of hydrogen release to higher temperatures. One way to do this is to oxidise the TiH_2 powders. This is first suggested by Sidney Speed[194,195] and others followed[196-204] (Niebylski mentions pre-annealing of the blowing agent too, but without referring to oxidation[24]). The mechanism of hydrogen retardation is quite complex and linked to the phase transformations in the hydride during decomposition.[205-208] Other ways to retard hydrogen evolution from TiH_2 than by oxidation include: by chemical filming,[209] by coating the TiH_2 particles with a thin nickel layer[210] or by using a low melting alloying element such as Sn that encapsulates the TiH_2 particles during early melting of the precursor and leads to a more adapted release of hydrogen.[169] The effect of pretreatment of TiH_2 on foaming of powder compacts is studied by various authors.[165,202] The notable effect of the particle size of the blowing agent powder on hydrogen release and foaming behaviour is also reported.[211]

Besides TiH_2, other hydrides are explored. ZrH_2 is an obvious choice,[212] but does not seem to have an advantage over TiH_2, at least for Al alloys.[213] In a recent study, the compounds MBH_4 and $MAlH_4$, where M=(Li, Na, K), are shown to be possible potent blowing agents for Al foams.[214]

In addition to metal hydrides, carbonates are frequently proposed as blowing agents, initially motivated by the much lower costs. Carbonates release CO_2 upon heating and after decomposition leave behind an oxide, unlike hydrides where a metal atom remains that will form an alloy with the matrix. In addition to this, reactions between the gas released (CO and CO_2) with the liquid aluminium alloy[98,215] give rise to pronounced differences in the foaming characteristics between carbonate and hydride driven foaming.

Arnold et al. find that 1 wt.% of $CaCO_3$ in addition to 0.5 wt% TiH_2 leads to much higher expansions and very small cells and explain this by the drastically reduced melt mobility, i.e. increased viscosity of the melt, however, without specifying a mechanism.[216] Cambronero et al. use marble powder and $CaCO_3$ to foam aluminium alloys.[217] Comparing the foaming of 6061 alloy by these two blowing agents to foaming with TiH_2, they find smaller pores for the former than for the latter blowing agents and densities down to 0.53 g/cm^3.[218] This difference between TiH_2 and $CaCO_3$ is confirmed by other researchers.[91] Haesche et al. use $CaCO_3$ when they produce foamable precursor from two aluminium alloys by semisolid casting.[219] Kevorkijan et al. foam pure Al with $CaCO_3$ and achieve a reasonable foam.[220,221] Finally, Koizumi at al. compare different blowing agents from the group of carbonates, hydroxides and hydrides and foam an Al-Si-Cu alloy.[222] A mixture of dolomite and $MgCO_3$ is found to minimise shrinkage effects that may occur during foaming when just $CaCO_3$ is used.[223] The efficiency of dolomite can be improved by mechanochemical activation, i.e. milling in the presence of SiO_2.[224]

A recent development is foaming of metals without any of the usual chemical blowing agents. The starting point is the observation that metal powders release gas when they are heated due to the decomposition of reaction products on the powder surfaces, e.g. hydroxides. Compacted aluminium powder not containing any blowing agent is found to expand by as much as 15% when melted due to the liberation of such gases.[153] This is far below the level required for a foam at normal pressure. It is found that Al50Mg50 powder has a much larger potential to store and release gas than pure Al. Such powder is used to foam Al-Mg-base alloys made from a mixture of pure Al powder, Al50Mg50 powder and optionally other

elemental powders.[225,226] Very uniform and well expanded foams can be produced such as the one shown in Figure 11.

4.5. Continuous foaming and foam moulding

The first foaming experiments are carried out without using a mould (so-called 'free foaming') or in a mould, into which a piece of precursor is inserted, after which the mould is heated to a temperature high enough to let the foam expand and fill the mould. Such batch foaming processes are rather slow and uneconomical and improvements are sought. One concept includes a continuous foaming furnace in which many moulds filled with foamable precursor can be conveyed through various heating and cooling zones at the same time.[227,228] The aluminium foam spheres produced for the composite described in Sec. 4.6 (Figure 14) are produced using the furnace introduced in Ref.[228] For this, small pieces of precursor material are conveyed through the furnace on a belt during which they freely foam to small spheres. Another concept is to foam a long wire of precursor material continuously by pushing it through the coil of an induction heating and to squeeze the foam generated into a mould.[229,230] The feasibility of this process to produce metal foam structures remains to be shown. An alternate idea is to inject expanding metal foam from a reservoir into a mould instead of carrying out the entire foaming process inside the mould.[231-233] Such a strategy allows one to produce parts in a shorter time since the slow heating up of the precursor material can be separated from the foaming process inside a mould. Various moulds, for example a number of sand moulds, could be prepared and subsequently filled with expanding foam in a short time. On such foamed part is shown in Figure 12.

4.6. Composites based on aluminium foam

Use of bare metal foam alone is often not the optimal engineering solution as foams cannot bear tensile loads very well and are prone to damage or corrosion when exposed to the environment. It may therefore be desirable to manufacture composites of foam and metal sheets, tubes or other dense metal parts.

Aluminium or steel sections can be filled by foaming a foamable precursor inside the section. Various arrangements of the precursor are proposed[234] and foam filling studied.[235-237] If the sections are made of aluminium alloy, their melting temperature must be higher than the foaming temperature of the foam core alloy to prevent the section from melting, because the section and precursor have to be heated jointly to the foaming temperature. Interdiffusion of alloying elements during foaming can accelerate melting of the sections[238] and therefore a precise temperature control is mandatory.[239] With steel or other higher melting metals, melting is not an issue, but the high temperatures needed to foam aluminium might still deteriorate the mechanical properties of the section or lead to oxidation. The foam injection techniques discussed in Sec. 4.5. could improve the situation since in this case the section to be filled does not have to be at such high temperatures. To help keeping the hollow section to be filled at a low temperature, an induction heating technique could be applied in which the section exhibits a long slit perpendicular to the induction coil. This slit ensures that most of the heat is generated in the foamable precursor placed inside the section and little in the outer section, thus limiting the temperature increase there.[240] Instead of filling hollow sections with foamable precursor and expanding the precursor is it proposed to coat pieces of foamable aluminium alloy – e.g. a tube – by thermal spraying and to foam the composite after. The foam will then fill the dense sprayed coating and yield a composite part.[241]

Sandwich parts consisting of a foamed core and dense face sheets can be made by roll-cladding metal sheets to a sheet of foamable precursor and then foaming the composite.[242] Aluminium,[243] steel[244] or titanium face sheets can be used. By shaping the roll-clad three-layer precursor before foaming, 3D shapes are obtained.[234,243] Aluminium foam sandwich (AFS) with aluminium face sheets can be obtained in complex geometries such as that of the

rear bulkhead of a car.[234,245] The development of AFS technology has been documented in a series of publications.[239,243,246-248]

Precursor manufacture is a crucial step in the manufacture of foams and especially of large AFS sheets. Small defects in the precursor can evolve into large ones such as cavities, cracks etc. in the final foam. This can be demonstrated by deliberately inducing such defects and following foam evolution in-situ with X-ray radiography.[249] It is also found that the compaction conditions such as the atmospheric pressure influence subsequent foaming.[250] Building on such studies, the industrial fabrication of precursor material has been revised. By carefully degassing the powders and avoiding contaminations the quality of aluminium foam sandwich parts is notably improved.[248] The AFS sample shown in Figure 13a demonstrates foam uniformity over a large area.

Instead of roll-cladding previously densified foamable precursor material to face sheets, direct powder compaction between two face sheets could be an alternative to reduce the number of processing steps.[160,251,252] A similar strategy is described in Refs.[253-255] Making large panels in this way will be technologically difficult and feasibility remains to be demonstrated.

Another concept to reinforce metal foams is to integrate wires or meshes into them.[256] Stainless steel woven fabrics, perforated steel or expanded steel meshes are placed in the foaming mould and are subsequently incorporated into the expanding metal foam. Such reinforcing meshes are much lighter than sheets and strong enough to improve the tensile properties of the foam significantly. Especially the bending behaviour of sheets can be improved, see Figure 13b. The type of reinforcement to be used has to be adapted to the mode of loading.[257]

Another kind of composite is obtained by bonding together small spheres of aluminium foam to either ordered or disordered 3D stackings,[258-261] for the former see Figure 14. The spheres can be produced continuously at low costs. The composite can have complex shapes ore fill hollow sections.

4.7. Improving foam stability

Foams made from metal powders are stabilised by the natural oxide layers on the powder surfaces.[7] The idea to tailor the oxide content of the metal powders in order to obtain maximum stability is near at hand. It is indeed found that the oxide content influences stability of both Al[7,262,263] and Pb[179] foams, For less than 0.3% oxide in Al precursors poor stability was noted. More than 0.6% oxide content compromises foam expansion indirectly by its negative impact on powder compaction.[7,263,264] In general, it is difficult to separate the influence of the oxide layer on foam stability, i.e. stabilisation of liquid films, from other effects such as the quality of powder compaction.

Additional particles can be added in order to further promote foam stability. Particles used include SiC,[221,265-270] Al_2O_3,[265,268,271] TiB_2,[272] soot,[269] or metallic TiAl6V4.[273] Some of these additions are reported to lead to an increased expansion, less drainage and thinner cell walls. However, the cost efficiency of such additions remains to be shown.

Foam stability may also depend on the presence of alloying elements. This is not well investigated, mainly because alloying elements influence foaming in various ways, namely by shifting the processing temperature, their impact on powder compaction or by changing the rheological properties of the melt. Magnesium is usually ascribed a positive influence on Al alloy foam stability.[165,271,274]

4.8. Alternate routes for precursor or foam production

As pristine metal powder is expensive it is suggested to use recycled metal instead, e.g. foils, machining chips or swarf. Clearly, these are cheaper sources of metal, but their composition is not constant and also difficult to control and the morphology of such material is different from that of powders. Al-Mg-Si machining chips are used in a series of experiments in which the

mode of compaction and the influence of additional ceramic stabilizer powders are investigated.[275,276] An organic adhesive is used to improve mixing of the fine TiH_2 blowing agent powder with the coarse chips. It is found that additional compaction effort and stabilising additions are necessary for good foam expansion. Analogous experiments for the magnesium alloy AZ91 produced much less regular and expanded foams,[277] which can be related to the general difficulty of foaming Mg alloys.

Semisolid processing is proposed as an alternate way to compact metal powder/blowing agent mixtures.[249] Accordingly, the same powder mixtures as used for the route based on pressing or extrusion are used. The powders are first consolidated by cold isostatic pressing, then heated to a temperature at which the material is semisolid (e.g. 595 °C for alloy AlSi6Cu4), after which the billets are transferred into the sleeve of a horizontal cold-chamber die casting machine and are then pressed into a die. Foaming of the resulting precursor material leads to good expansion to foams exhibiting round bubbles with a uniform size distribution.[278] Application to a variety of alloys is reported, including a series of alloys containing various trace elements,[279] alloys based on recycled material and alloys foamed by using carbonates as a blowing agent.[219,280] For example, AlMg4.5Mn sawing chips or AlSi9Cu3 cutting chips are mixed with the blowing agent $CaCO_3$ and stabilising CaO powder. The mixture is first briquetted, heated to the semi-solid state and then cast. The resulting precursor show a reasonable foaming behaviour.[219]

Making a precursor by powder compaction is an additional processing step and it is proposed to eliminate this step by processing powders directly. Simply heating powder mixtures does not lead to any foam as the blowing gas can escape. Therefore, mixtures of powder and blowing agent are fed into the extrusion cylinder of a die casting machine where they are heated and plastified by a rotating screw. In a final step, the liquefying or already liquid mixture is injected into a mould by a coordinated axial movement. The mould is opened sufficiently to create a pressure drop and to allow the now expanding foam to fill it.[281] (see also Ref.[282]) Note that in later patents and publications a variant of this method is described: the blowing agent is not mixed with metal powder any more but admixed to liquid metal at the entrance of the die, a process that has been presented in Sec. 2.6.

A special technique is invented to create foams with a matrix that consists of an intermetallic compound. It exploits the exothermal reaction between many metals during formation of an intermetallic. The heat liberated can create foam during a self-propagating combustion reaction. In a first example, Al-Ni foam is made by mixing Al and Ni powders with the reaction enhancer B_4C, compacting the mixture and igniting the compact. Al_3Ni foam with more than 75% porosity is obtained.[283] The gas source for foam expansion is the gas adsorbed to the aluminium powder surfaces. In subsequent work, porous Ti composites are made in a similar way,[284,285] leading, e.g., to Al_3Ti composites with more than 60% porosity and a reasonably regular structure.[286] The technique is linked to the traditional manufacture of Al foam by mixing (Al – TiH_2) blends with a (Ti + B_4C) mixture. After igniting the compacted mixture, the latter mixture reacts and produces the heat needed to foam the former constituents.[287]

The phenomenon that aluminium powder surfaces contain adsorbed gases or hydroxides which can act as a gas source upon heating is exploited by a technique called pressure-induced foaming.[288,289] Aluminium powders are compacted and then melted under pressures up to 40 bar. After reaching the liquid state, the pressure is released to 1 bar within a few seconds. This pressure drop triggers expansion of gases contained in the precursor and expands the material so that it eventually grows to a foam.

4.9. Partially powder-based processes

Accumulative Roll-Bonding (ARB) is used to produce foamable precursors.[290] Two sheets of aluminium alloy are stacked with some TiH_2 powder in between. The stack is first rolled,

during which its height is reduced to 50%, the two sheets are bonded to each other and the TiH$_2$ powder is encapsulated between the sheets. The rolled sheet is then cut into halves that are stacked and rolled again. The procedure can be repeated various times. The resulting precursor then contains a multitude of TiH$_2$ particles encapsulated in an aluminium alloy matrix and can be foamed by melting. A variant of the process is called 'Accumulated Diffusion Bonding' and was used for aluminium[291] and magnesium[292] alloys. Here, the sheets are surface treated, stacked with some blowing agent in between, diffusion bonded, cut, and the procedure is repeated.

A related way to produce foamable precursor also starts from two aluminium alloy sheets that are stacked with some TiH$_2$ powder in between.[293] The stack is then intensely plastified by friction stir processing using a friction stir welding machine, yielding a dense material with TiH$_2$ particles distributed within. This material can be foamed in a second step. Foams are not well expanded in this basic configuration, but improvements are claimed to be possible by tuning process parameters or by adding stabilising Al$_2$O$_3$ powder in addition to the blowing agent.[294] It is worth mentioning – although it leads us to beyond powder processing – that castings can be used instead of wrought plates. Such castings contain so much dissolved and entrapped gas that they can be foamed without the need to add any blowing agent powder after thorough plastification by FSP.[295]

4.10. Tailoring and understanding the foam expansion process

The volume expansion process of aluminium precursors during foaming is governed by the temperature profile applied and is highly nonlinear as a function of time. Volume expansion occurs in distinct stages related to properties of the melt and the blowing agent.[153,165,202] Unexpected effects can be discovered such as a transient expansion stage during solidification of aluminium alloy foams.[296] It is found that during this expansion stage the occurrence of defects is more likely which is why this stage is practically relevant.[297] The temperature profile during heating of the precursor to the foaming temperature is also important. Even a short overheating at the transition between linear heating and isothermal holding can lead to largely decreased foam stability.[298]

The atmosphere surrounding a foaming precursor influences foaming. Oxygen in the atmosphere is found to retard foaming for both pure Al[299] and Al-Si-Mg.[300] The surrounding gas pressure also has a pronounced effect.[298,300,301] Underpressure (<0.1 bar) during foaming causes instability, whereas overpressure makes bubbles more stable, smaller and more uniform in size. This could be one way to manufacture microcellular metal foams.[302] Pressure changes during foaming lead to large expansions or compressions of the liquid foams.[298]

5. Foaming using precursors made by liquid metallurgy ('Formgrip line')

In the foaming processes described in Sec. 2 and 3 – 'Alporas' and 'Alcan' lines, – a liquid foam is created in a foaming vessel in one step. The liquid foam is usually solidified to a block unless it is cast into a mould (which is a challenging step). Therefore, net-shaping of foams to complex components or thin sheets is difficult. The precursor-based processes described in Sec. 4 avoid this problem since foam can be generated in moulds or between face sheets of a sandwich panel by expanding a precursor. However, the necessity to use metal powders makes the process more expensive. In order to combine the advantages of the melt-based routes of Secs. 2 and 3 and the precursor-based routes of Sec. 4, a combination was sought. The basic idea is to start processing along the line described in Sec. 2, i.e. by adding a blowing agent to a melt, but then to interrupt the incipient foaming process by swift cooling, e.g. by casting the liquid mixture into a cold crucible. The precursor obtained in this way will then be foamable upon reheating and can be further processed in analogy to the powder compacts described in Sec.4. This is exactly what William J. Ptashnik of the General Motors

Corporation proposes.[303] He admixes a blowing agent to an alloy melt held in the semi-solid state at a temperature at which the blowing agent does not decompose. The melt is solidified to a precursor in a second step. Foaming is done at a higher temperature than mixing, so that the blowing agent releases gas and creates bubbles. An example given is a ZnAl22 alloy to which 0.5 wt.% TiH$_2$ powder is admixed at 457 °C. Mixing and solidifying takes about 3 min and no visible foaming is reported. After solidification, the precursor is foamed at 471 °C – in the semisolid range – which takes about 15 min. Use of 20 µm carbonyl iron powder to thicken the melt is proposed. Such additional 'thickening' and the solid phase present in the semisolid range provide additional foam stabilisation, the latter mechanism being called 'endogeneous stabilisation'.[117]

Another way to make a foamable precursor is developed at the University of Cambridge, UK in 1998.[196,197] The starting point is a liquid Al alloy containing SiC particles, i.e. a liquid aluminium matrix composite. Such melts are also the starting point for the processes described in Sec. 3. TiH$_2$ is first added to the melt accompanied by vigorous stirring. The TiH$_2$ powder is preoxidised before admixture to prevent it from releasing too much gas during mixing. Moreover, to prevent burning of the hydride, the TiH$_2$ powder is mixed with some Al powder and pressed to pellets that are added to the melt. After stir-homogenising, the melt is cast into a cold crucible and heat is removed as fast as possible. The resulting solid composite material contains some porosity but is predominantly dense. This precursor is converted to foam in the subsequent foaming ('baking') step in analogy to the technique described in Sec. 4. Very uniform foams can be produced and all the advantages of the precursor route can be exploited. The acronym 'Formgrip' has been coined, standing for 'foaming of reinforced metals by gas release in precursors'. An analogous process based on the use of CaCO$_3$ as a blowing agent is known, called 'foaming of aluminium MMC by the chalk-aluminium reaction in precursors' ('Foamcarp').[215] It is found that the reactions between the metal and the carbonate contribute notably to foam stabilisation.

Another procedure was developed by Armin Melzer of the Fraunhofer-Institute in Bremen, also in 1998.[304] Aluminium alloy is injected into the die of a cold-chamber die casting machine. At the entrance of the die, a small reservoir contains TiH$_2$ powder and some aluminium powder. During melt injection, the powders and the melt are intensely mixed. In the die, the metal solidifies quick enough to avoid notable decomposition of the blowing agent and therefore a largely dense precursor with embedded blowing agent particles is obtained that can be foamed by reheating. As the oxide content in the cast material is low, the resulting foam is not very stable if too little aluminium powder is added. The process resembles the one described in Sec. 2.9, with the only difference that there the die is underfilled and the injected melt is allowed to foam in the die, whereas here, the die is completely filled and foaming is carried out in a separate step outside the die.

Babcsán, Kadoi et al.[119,305] propose a modification of the 'Alporas line' techniques described in Sec. 2.4 (stabilising an Al melt by adding Ca and foaming by adding a blowing agent). They suggest to interrupt the foaming process immediately after adding the blowing agent and to obtain a solid precursor which can be foamed upon reheating. Shang et al. describe this as 'two-step foaming'.[306,307] They melt an AlCu4 alloy, add Ca while stirring and then add untreated TiH$_2$, after which the foaming process is interrupted. The resulting precursors have considerable porosities but can be foamed to large volumes by reheating to a temperature about 100 K higher than applied during manufacture of the precursor. This technique appears like an 'interrupted Alporas' process. Kevorkijan et al. report a variation. They melt aluminium powder, admix stabilising SiC particles and CaCO$_3$ as a blowing agent, stir to homogenise the mixture and solidify to a precursor that is foamed in a second step.[221]

6. Foaming by gas precipitation from melts ('Gasar line')

Another potential gas source that could blow metal foams is gas dissolved in a melt. The solubility of most gases in metals is highly temperature dependent and shows abrupt changes at temperatures where phase transformations occur, e.g. at the melting point. Moreover, the solubility is pressure dependent according to Sievert's law. Therefore, if one charges a metallic melt with gas and solidifies it, possibly accompanied by a pressure drop, gas will precipitate, which can be utilised for foam formation.

At ambient pressure (1 bar) the solubility of hydrogen in aluminium drops by more than one order of magnitude at the solidification temperature (660 °C). This is more than for other elements such as Cu, Mg, Fe etc., but the absolute value of solubility is low. In order to blow foams with high porosity (e.g. >75%), the volume of the available gas has to be augmented by producing a pressure drop. This is demonstrated for Al, AlMg5 and AlSi9Mg5 alloys:[308,309] Melt charged with hydrogen is cast into a crucible in which during solidification the gas pressure is reduced from 1 bar to a few mbar. Even for pure Al a foam with 80% porosity can be obtained without adding stabilising particles. Additional stabilisation of the melt, e.g. by adding 5% SiO_2 particles, further improves stability and yields a more uniform distribution of smaller cells.

A different class of materials can be obtained by releasing gas from a gas-charged melt during solidification in a controlled way. Instead of allowing a free mixture of bubbles to be generated as described in the previous paragraph, bubble growth is controlled by directional solidification. If the solidification front is planar and advances along a temperature gradient, an initial pattern of bubbles that have nucleated heterogeneously at the bottom of the container will grow into an array of tubular voids as new gas preferentially nucleates at existing pores. This principle is first discovered by Vladimir Shapovalov in Dnepropetrovsk, Ukraine[310,311] and is later further developed by Hideo Nakajima in Osaka, Japan. The former scientist calls the material 'Gasar', whereas the latter choses the name 'Lotus Metal'. The variety of metals, alloys and ceramics that can be processed is large. Not only hydrogen, but also nitrogen and oxygen can be used as blowing gases.[312] Among the first successful gasar/lotus materials is Cu.[313-315] Later, Fe, Ni, Ag and brass are processed. In order to increase the available volume of gas that drives pore formation, a process variant is designed that uses additional gas liberated from TiH_2 powder that is added to a melt.[316] In this way, the density range can be extended to lower values. Gasars/Lotus structures are foams in the sense of the definition given in the introduction (free bubble arrangement in a melt without using a template). It is just the pore morphology that makes them look like a different class of material.

A related approach has been evaluated for aluminium alloys containing the alloying element lithium or for magnesium alloys. Pieces of casting alloy are heat-treated in a hydrogen atmosphere, during which hydrogen diffuses into the casting and forms a hydride compound there. The alloys charged in this way are heated to above their melting temperature in a second step, during which hydrogen is liberated and gives rise to the formation of porosity. The materials obtained in first tests are not usable yet and the potential of the method cannot be assessed.[317]

7. Further developments

A few still exotic methods shall be presented here to give an outlook on possible future developments.

7.1. Amorphous (metallic glass) foams

Amorphous metals (metallic glasses) shows exceptionally high strength levels compared to normal crystalline metals. Use of such metallic glasses as matrix material for metallic foams

promises extremely strong foams. Since metallic melts have to be cooled quickly to prevent crystallisation, an integration info a foam-making process is not straight forward. Schroers et al. successfully prepare a porous casting with a relative density of 24% from a Pd43Ni10Cu27P20 alloy that is one of the best glass formers. Hydrated B_2O_3 is used for fluxing and creating gas bubbles in the melt which are then expanded by lowering the ambient pressure.[318,319] A very similar alloy is successfully foamed by precipitating hydrogen dissolved in a melt.[320] Further details and variants can be found in Ref.[321]

7.2. Sputtering and deposition processes

Sputter deposition is used to manufacture a metallic material in which a multitude of gas atoms are entrapped. If this material is then heated to a temperature above the melting temperature of the metal and held there for a while, the gas will nucleate to small bubbles and form a porous body.[322]

Spray forming involves atomising a melt and depositing the metallic spray on a substrate, usually forming a dense material. If one adds a blowing agent to the spray, a foam can be obtained.[323]

8. Historical background of foam development

After the presentation of the basic innovations in metal foam technology some historical background especially of the industrial development shall be given. Nothing is known about the circumstances under which the early French pioneer M.A. de Meller carries out his research[5]. Some information is available about the Bjorksten Laboratories (BRL) where foaming of aluminium is developed in the 1950s. BRL received funding from the Wright Air Development Center to develop materials for light-weight sandwich constructions and publishes a report.[324] Moreover, BRL looks back on its own history[10]: 'In a program sponsored by the U.S. navy, the Bjorksten staff developed a process for foaming aluminum. The process was subsequently expanded to include other metals such as lead and zinc. A 20,000 square foot pilot plant for manufacturing experimental 4' × 8' × 1'' (1.2 m × 2.4 m × 2.5 cm) thick foamed aluminum building panels was constructed on the Bjorksten campus [in Fitchburg, a suburb of Madison, Wisconsin]'. Mike Maloney of BRL adds:[325] 'BRL entered into an agreement with the Lor Corp. to develop commercial uses for aluminium foam, e.g. crash bumpers for cars. In the late 1960s the entire operation was sold to the Ethyl. Corp and the pilot plant moved to Baton Rouge, Louisiana. BRL continued to study methods for foaming other metals (Pb, Zn etc.) and to produce fibre-reinforced foams for a few years until the chief metallurgist Edward Rock died' (see Refs.[326-328] for the fibre-reinforced foams).

Various sources report that other companies get licences to produce foam with BRL technology. Foamalum Corp. located near BRL[329] is reported 'to be going to business now' in 1958[330] with products costing between 1 and 2.25 USD [331]. Dynamic Metals in Houston, Texas, are also said to start metal foam production under a licence of BRL in 1958/59[330,332] with quite optimistic predictions both for the price of the product and the production quantities. It is difficult to verify today how far these activities have advanced, but nothing is found any more in the literature after 1962.

Most of the information on metal foam development in those years is disclosed in patents and press releases which are not always reliable sources. No scientific work is known with only one exception: A study conducted by Seliger and Deuther is published in 1965.[333] These researchers worked for a state-owned East-German company in Bitterfeld and carried out experiments to verify the disclosures of the patents and also to assess the commercial potential of metal foams. There publication seems to be the first scientific publication on metal foam manufacture. They are able to reproduce Al-Mg foam manufacture following the published recipes, but the samples shown are very inhomogeneous. They find mechanical properties inferior to the ones communicated before. They assess the properties of aluminium

foams and their potential to be used and conclude that aluminium foam is not strong enough to replace honeycomb structures in airplanes, too conductive for heat insulation applications and too expensive for architectural panels. They recommend to discontinue the development of such materials in their company.

Ethyl Corp. start working on metal foams in the late 1960s. The first to work in the project is Leonard M. Niebylski, while Currie B. Berry joins one year after. The project is one of many programs underway to replace Ethyl Corp.'s tetraethyl lead business that is jeopardised by the introduction of unleaded petrol in the USA. Ethyl has bought out the Bjorksten interests, primarily for their patents and builds on their technology. Ethyl produces slabs of foamed aluminium, about $1.2{\times}1.2$ m^2 large and 15 cm thick. While there is progress in the development of foaming technology, Ethyl never finds an application for foamed aluminium which would justify commercial scale production and therefore stops the product after a few years.[334]

Back to the 1950s and the development of the process described in Sec. 4: In the late 1950s, The Hamilton Standard Division of United Aircraft Corporation engages the Battelle Memorial Institute in Columbus, Ohio to explore methods to manufacture Al foam with a fine and regular morphology. The project engineer is Benjamin Allen, the supervisor Morris Mote and the expert for extrusion Alvin Sabroff. The latter provides the information presented here.[335] Inserts for lightweight piston-engine propellers and helicopter rotors are seen as possible applications for metal foam. First trials are based on the same principles exploited by the Bjorksten laboratories, namely the addition of gas forming additions to a melt, all with limited success, because coalescence of gas bubbles to large voids cannot be eliminated. Soon, the idea to extrude mixtures of metal powders and blowing agents comes up. The first foams produced in this way have an insufficient structure too, but an improvement is achieved by using the zone foaming process disclosed in the patent.[152] The fast heating and cooling largely prevents coalescence. After Battelle has delivered a report to United Aircraft, research continues there for some time, but is eventually discontinued, probably due to the lack of applications.

Shinko Wire develops 'Alporas' foams in the 1980s about 10 years after Ethyl. Corp. has stopped their research. Use of calcium as a thickener improves the quality of foams and makes it a product that can be sold. For a long time, 'Alporas' foams are the most uniform foams available and for many academic studies 'Alporas' is chosen because the scatter of its properties is lower than of other foams. 'Alporas' enters into an agreement with the company Gleich GmbH in Germany that becomes an active distributor in Europe. Still, in 2011 Shinko Wire stops the production of 'Alporas' foam due to poor business. At this time, the plant has been producing aluminium foam for 20 years but the operation has not become profitable.

Alcan and Norsk Hydro develop and patent the foaming of metal matrix composites almost simultaneously, which is the origin of a patent dispute that is finally solved by an agreement many years later. The foams produced by both companies are very brittle due to the presence of 15% SiC particles in the cells and the pore structure is rather inhomogeneous. None of the two companies successfully develops a market for aluminium foams that is big enough to meet the expectations of such large companies. Around the year 1997, the technology is transferred to Cymat Corp. in Mississauga, Canada[336] where up to present foams are being produced.[337] One product is 'Alusion' an architectural panel with a variety of surface designs. Other products include metal foam parts that are manufactured in a low-pressure mould filling process.

Work on metal foam made by melting compacted mixtures of metal and blowing agent powders continues in 1990 at the Fraunhofer-Institute in Bremen, Germany. The physicist Joachim Baumeister has heard a talk about the manufacture of metal foam under microgravity and want to prove that such foam can be made on Earth too.[154] It takes him just a few weeks to develop a process that, as he later realises, is very similar to the one invented in 1959 for

the United Aircraft Corp.[152] but has fewer restrictions. For example, powders compacted by hot pressing can easily be foamed. The author of this paper joins the Fraunhofer-Institute in 1991 and works there for 10 years, most of the time in a team of three to five scientists and two technicians. The response to initial press releases communicating the discovery of the aluminium foam that Fraunhofer calles 'Foaminal' is overwhelming. Hundreds of companies contact Fraunhofer to learn more about the material and many prototypes are developed with public and private funding. In 1996, a branch of Fraunhofer is opened in Newark, Delaware, to handle requests of companies in the USA.

Some of the companies that contact Fraunhofer are interested in becoming producers of aluminium foams. The Austria Metall AG (AMAG) in Ranshofen, Austria, is the first. In 1992, Helmut Wörz of the metal powder company Mepura, at that time jointly owned by AMAG and Ecka Granules in Fürth, Germany, decides to start an R&D program on aluminium foam, code name 'Hiporal'. Research is carried out under the supervision of Hans Peter Degischer in AMAG's R&D laboratory in Ranshofen. In 1994 the laboratory becomes an independent research centre called the Light Metals Competence Centre (LKR)[338] after AMAG has gone through a major financial crisis. After licensing negotiotions with Fraunhofer fail, the Austrian research centre starts a parallel development and it shall take more than 10 years to resolve disputes on intellectual property. In the meantime, Ranshofen is the birthplace of both the material 'Alulight' (identical to Fraunhofer's 'Foaminal') and the company Alulight.[339] Production lines for aluminium foam panels and some automotive parts are set up, the former in Bratislava.[340] Alulight has now been on the market for more than 15 years, first under the name 'Mepura' then as 'Alulight International'. Aluminium foam production never becomes profitable and since the world financial crisis in 2008 Alulight is going through a major restructuring process including changes of the ownership.

Back to 1998: The LKR also enters into a collaboration with the small Austrian company Hütte Kleinreichenbach (HKB) and develops an improved technology for making foams by gas injection into aluminium-based MMC melts (Alcan/Hydro process), see Sec. 3.3. First results are presented at the 2nd MetFoam conference in Bremen in 2001.[123] The prototype of an engine bracket for the car maker BMW causes a lot of attention, but the production capacity for large numbers of metal foam components is lacking at that time.

In 1993, Frantisek Simancik becomes the academic research partner of Alulight. After 1995, he works at (and today leads) the Institute of Materials and Machine Mechanics in Bratislava, Slovak Republic. He carries out the development of prototypes and new materials and operats a production line for foam panels. In particular, the foam injection process described in Sec. 4.5 is developed. The small Austrian company Neuman Alufoam builds a production line based on this technology that can produce 100,000 door sill reinforcement parts annually for the German car company Audi, but shortly before introducing the new car models in 2001, Audi decides not to use aluminium foam, after which Neuman Alufoam gives up their metal foam business.

After the unification of the two German states in 1990 a lot of public funding goes into the East to foster the ailing local industry. In cooperation with Fraunhofer, Walzwerk Hettstedt starts investigating the Alcan process and carries out experiments with a pilot plant in 1992. The small company Innovativer Werkstoffeinsatz (IWE) produces parts using Fraunhofer's technology after 1998.

Another company active for a few years is Schunk Sintermetalltechnik, Germany.[341] They initiate a joint R&D project with Fraunhofer in 1995. Later, Honsel AG in Meschede, Germany,[342] joins the consortium. Schunk is the powder specialist, Honsel has the expertise in extrusion and a small-scale production of Al foam parts is set up. Unfortunately, the market developes much too slowly so that the project is eventually stopped.

A further activity that evolves from a Fraunhofer cooperation is initially linked to the car manufacturer Karmann, Osnabrück, Germany. Jointly, the two institutions further develop the

aluminium foam sandwich (AFS) technology patented by Fraunhofer.[242] By 1998, large 3D shaped sandwich parts can be foamed such as a rear bulkhead or a front firewall.[243] In 2002, the metal foam activities are concentrated in the start-up company Applied Lightweight Materials (alm), first in Osnabrück, then in Saarbrücken, both Germany. After some restructuring, this company is now known as Pohltec Metalfoam GmbH in Cologne, Germany[343] where aluminium foam sandwiches (AFS) panels of all kinds are produced.

Alcoa also goes into metal foam business for a short time. After the development of the continuous foaming process based on $CaCO_3$ as a blowing agent[97] a pilot plant is built at the Alcoa Research Centre in Pittsburgh that can produce 30 kg of foam panel per minute. Alcoa wants to commercialise the technology in cooperation with the Aluminair Co. in Florida, but the plans to go into mass production of foam, mainly for building industry, do not materialise after this industrial sector faces problems in the 2008/2009 economic crisis.

Research on aluminium foams develops in China in 1994 or even earlier[344] and a bit later in Korea. Various companies start producing Al foams following the 'Alporas' route. Examples include Korea Metalfoam, Anyfoam, Foamtech and Dreametal, all of Korea. In China companies under varying names exist for a limited time.

9. Development of the academic world: conferences, books, reviews

No literature describing details of the manufacture of metal foams except Ref.[333] and very little on metal foam properties is available before 1990. Early papers include one by Niebylski[22] and two by Thornton and Magee.[21,30] The reason for this is clearly the commercial and military interest of the companies, funding agencies and research institutes involved and the decision not to disclose any technology. A change comes in the mid 1990s when a Multidisciplinary University Research Initiative is created in the USA (MIT, Harvard and Virginia Universities) and the UK (Cambridge University) which leads to a lot of systematic research on metallic foams, however, with an emphasis on their properties.[345] The principle researchers publish their results in a book.[3] In the frame of this initiative, specialised workshops take place that help to further disseminate the results of research. Together with the 1997 metal foam symposium 'Metallschäume' in Bremen, Germany,[346] (continued as 'Metallschäume 2000'[347]) the 1997 Fraunhofer workshop 'Metal Foams' in Stanton, Delaware,[348] and the 1998 MRS meeting in San Francisco, California,[349] the foundation for a series of International Conferences is laid: The MetFoam series of biennial conferences starting in the year 1999 in Bremen (Germany),[350] 2001 in Bremen again,[351] 2003 in Berlin (Germany),[352] 2005 in Kyoto (Japan),[353] 2007 in Montréal (Canada),[354] 2009 in Bratislava (Slovakia) , 2011 in Busan (Korea),[355] and scheduled for 2013 in Raleigh (USA). Moreover, the Cellmet (later Cellmat) series starts in the year 2005 (then 2008, 2010, 2012, all in Dresden, Germany).[356,357]

In Germany, a so-called priority program of the German Science Foundation (DFG) is initiated in 1998 by Robert F. Singer with funding for 6 years and support for more than 20 individual projects. The final report is published in conjunction with a conference proceeding.[358]

Currently two books treat the field of metal foams in a broader sense[3,359] and a number of review articles have been written, e.g.[4,360-364] More such literature is available in different languages and is likely to appear in the future.

10. Summary

The development of metal foams has a long history. Figure 16 reviews the historical development of metal foaming techniques and their logical evolution. Nowadays, a number of techniques is available that allow us to manufacture at variety of metallic foams that meet most expectations. The main reason that up to now metal foams have found niche market

applications only is their price. Whether there is a future mass market for metal foam depends on whether costs can be cut down in the future. Therefore the challenge of future process development is not only to improve foam properties but also to further reduce costs.
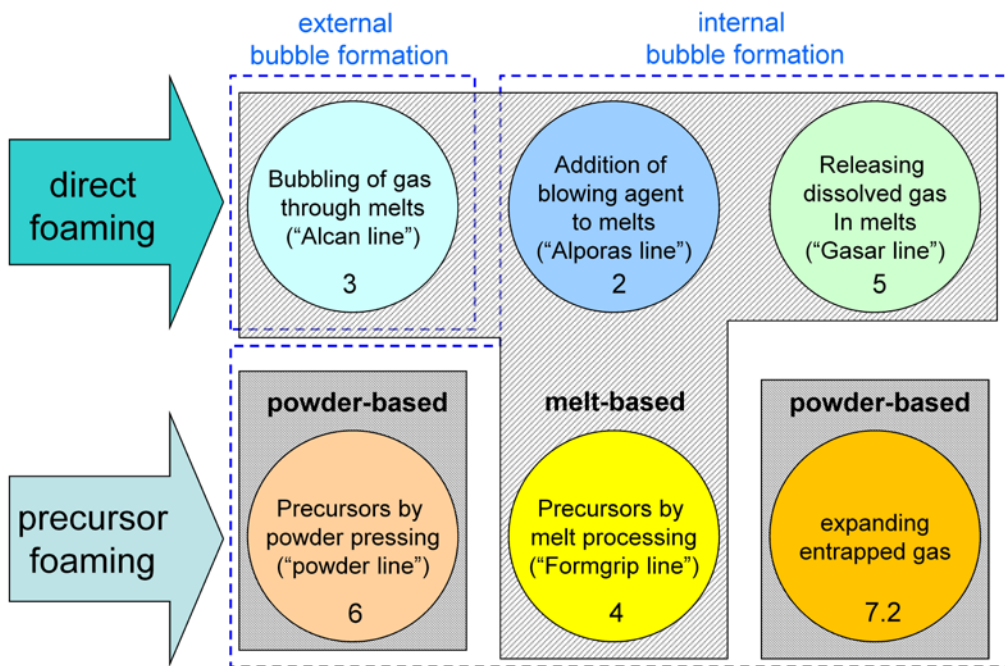
Figure 1. Principal methods for foaming metals. Numbers refer to the section in which the particular method is described.
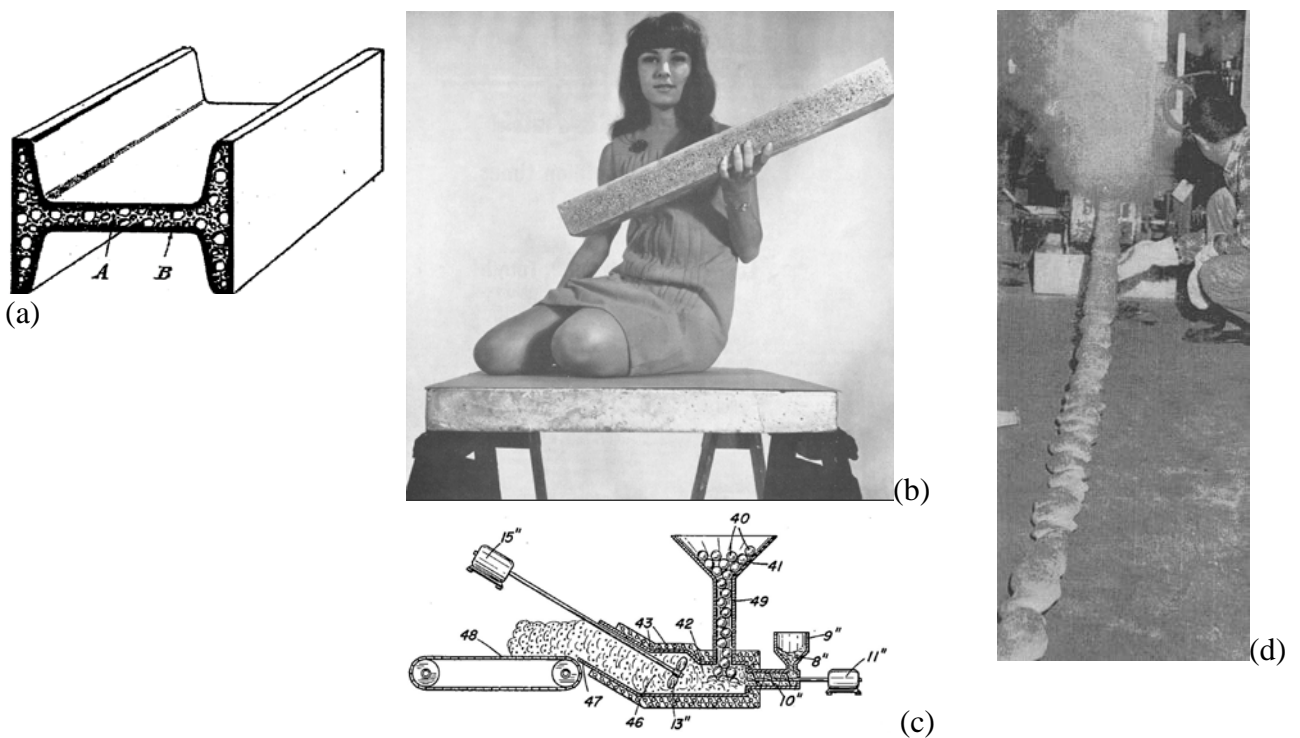

(a)

(b)

(c)

(d)

Figure 2. (a) Figure reproduced from French patent from 1926 showing metal foam core (A) with dense skin (B).[5] (b) Bjorksten demonstration of both lightness and stiffness of Al foam (unknown date, probably 1960s [10]). (c) depiction of continuous foam production[12] and, (d) photo of continuously cast metal foam slab made at Bjorksten.[365]

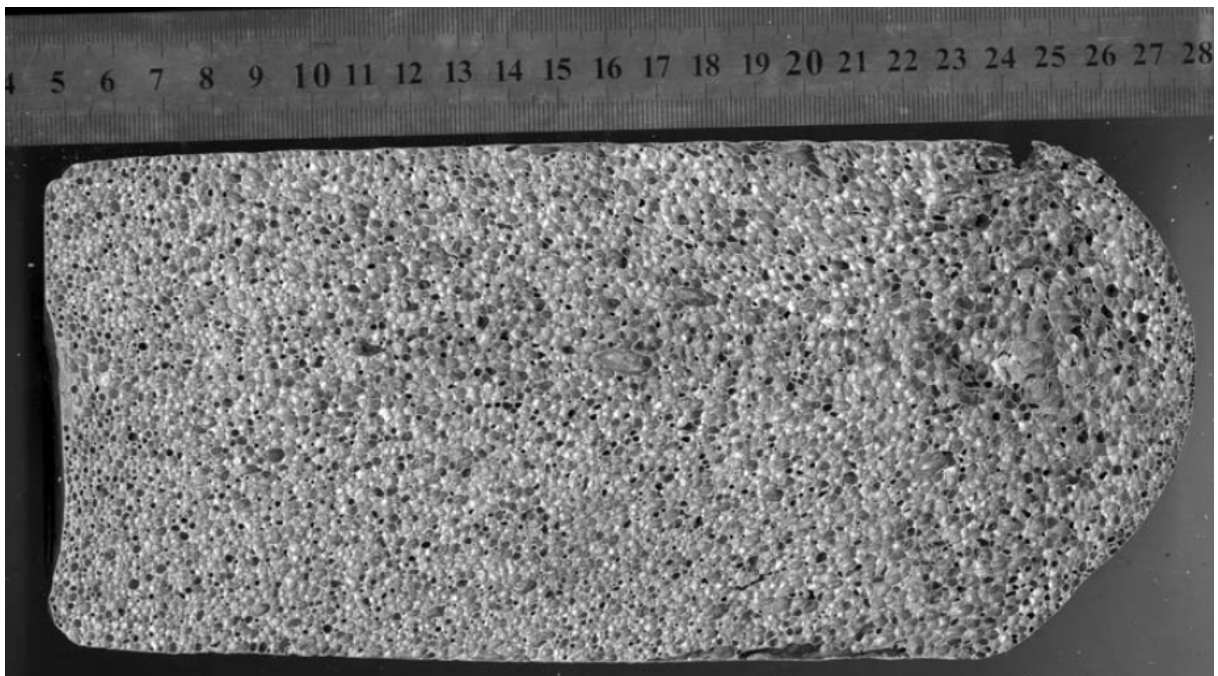*Figure 3. Aluminium foam blocks produced in the 1970s by the Ethyl Corp.[22]*

Figure 4. 'Alporas'-type material: Pure Al thickened with Ca and foamed with TiH_2.[49]
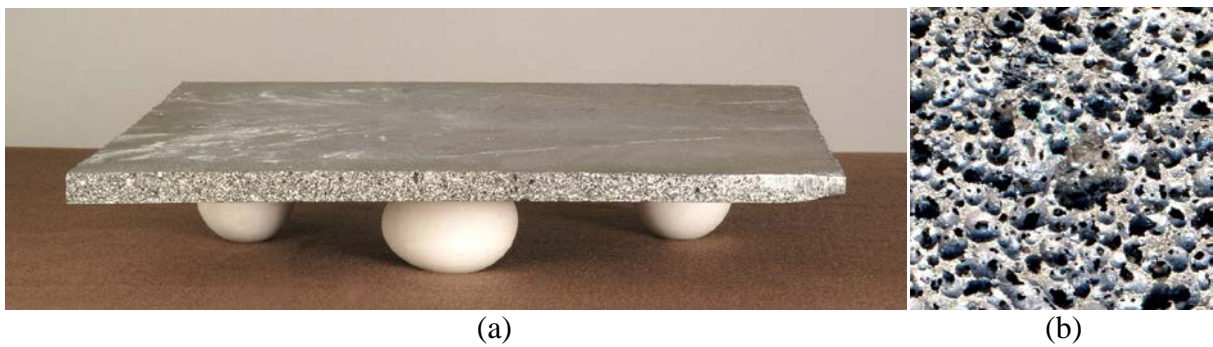

| (a) | (b) |

Figure 5. Aluminium foam panel made by Alcoa using $CaCO_3$ as a blowing agent. (a) panel suspended by eggs.(b) The cell morphology exhibits a sub-mm sized units with cell wall perforations (source: Dan Bryant).

Figure 6. Aluminium foam part made by the 'Combal' process.[366]
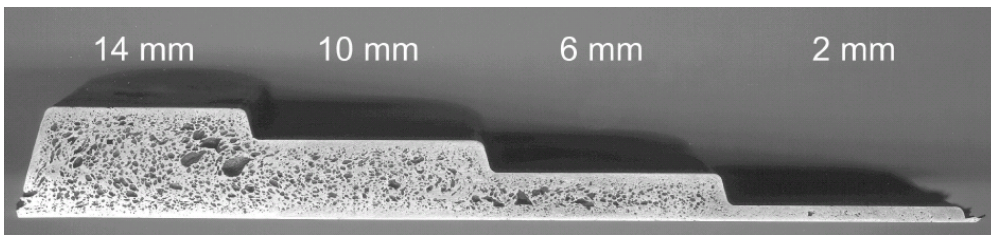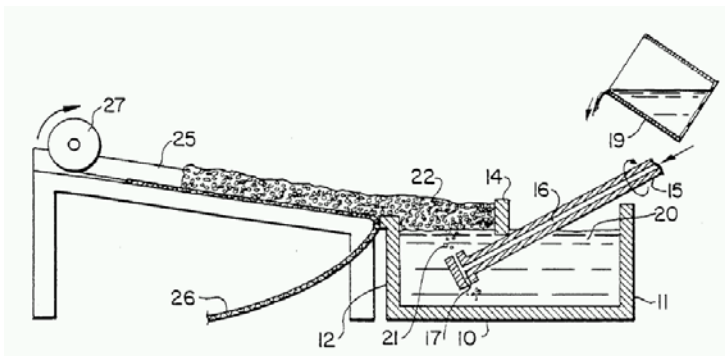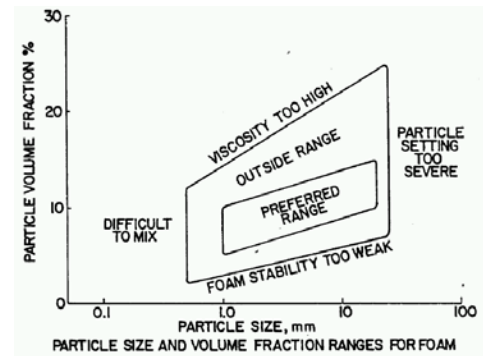

Figure 7. Step plate made by integral foam moulding of magnesium alloy AZ91.[113]

| (a) | (b) |

Figure 8. (a) Schematic of foam production taken from the patent of Alcan, (b) relationship between particle fraction and size required for good foaming, both from Ref.[120]

Figure 9. Foam samples made by Hydro Aluminium by blowing gas into SiC containing Al MMCs (Source: Fraunhofer).
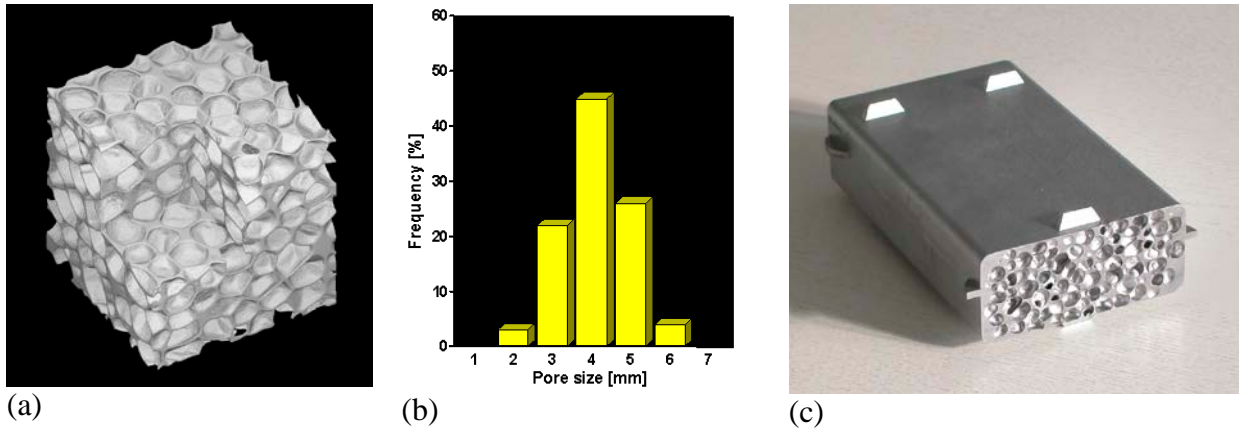
Figure 10. Foams made at the LKR from aluminium alloy in which SiC particles are dispersed. A novel gas injection principle was applied. (a) X-ray tomogram of a 34-mm long foam cube, (b) pore size distribution in that sample, (c) moulded part of Al foam with dense outer skin (courtesy of Dietmar Leitlmeier).
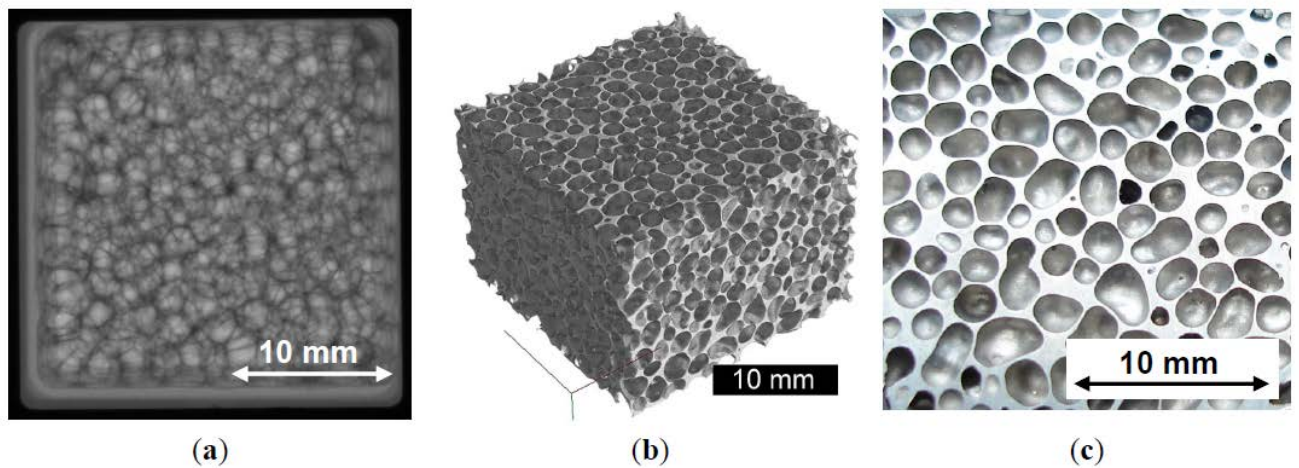

Figure 11. AlMg15Cu10 foam manufactured without using a blowing agent. (a) X-ray radiography of expanded liquid foam, (b) X-ray tomography of solid foam, (c) micrograph of section through solid foam.[235]
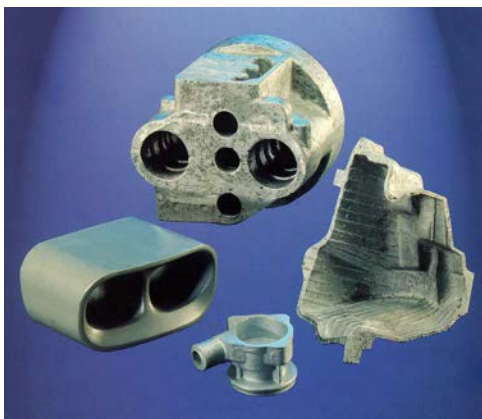
Figure 12. Aluminium foam parts produced by foam injection into complex sand moulds.[231]

Figure 13. (a) Aluminium Foam Sandwich (AFS) panel made by Pohltec Aluminium sliced in the central plane.[343] (b) Aluminium foam panel reinforced on the surface with stainless steel: (i) net, (ii) expanded metal sheet, (iii) woven steel wire, (iv) perforated sheet.[256]
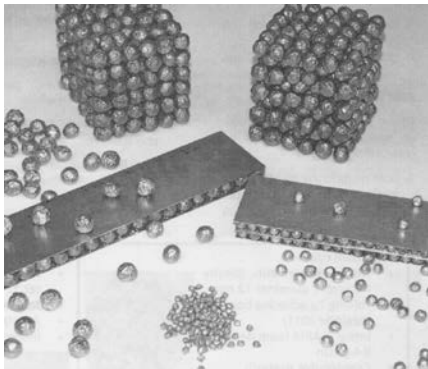
Figure 14. 'Advanced Pore Morphology' composite consisting of ordered arrays of aluminium foam spheres (Fraunhofer-Institute).
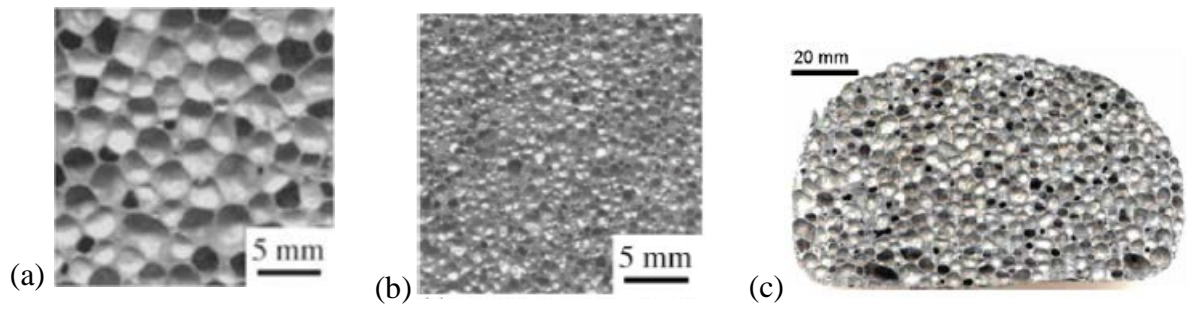
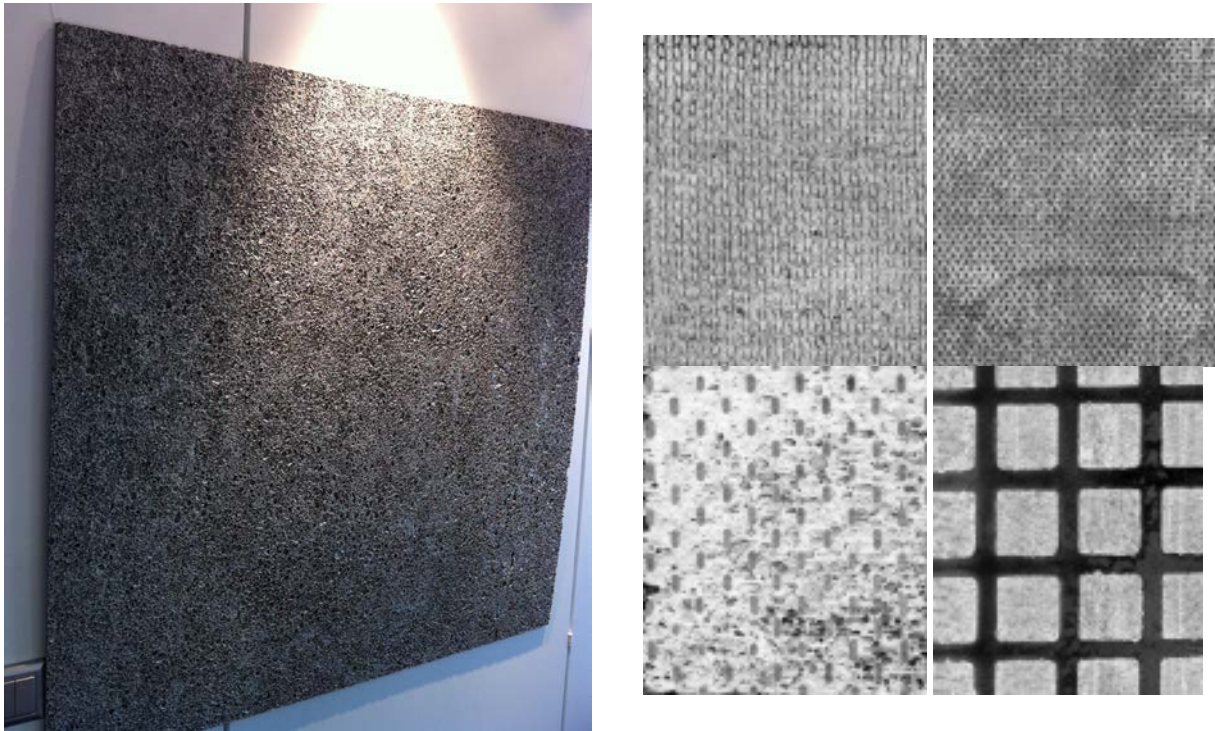*Figure 15. Foams made by the (a) 'Formgrip' process,[215] (b) 'Foamcarp' process.[215] In both cases the porosity is about 80%. (c) foam made by two-step (interrupted 'Alporas') foaming.[307]*

Figure 16. Overview of some of the important milestones in metal foaming technology until the year 2005 visualised as a tree. Vertical axis is time.

Table 1. Combinations of stabilization and blowing agent used for making foams by direct foaming of melts ('Alporas'-type processes) by addition of blowing agents.

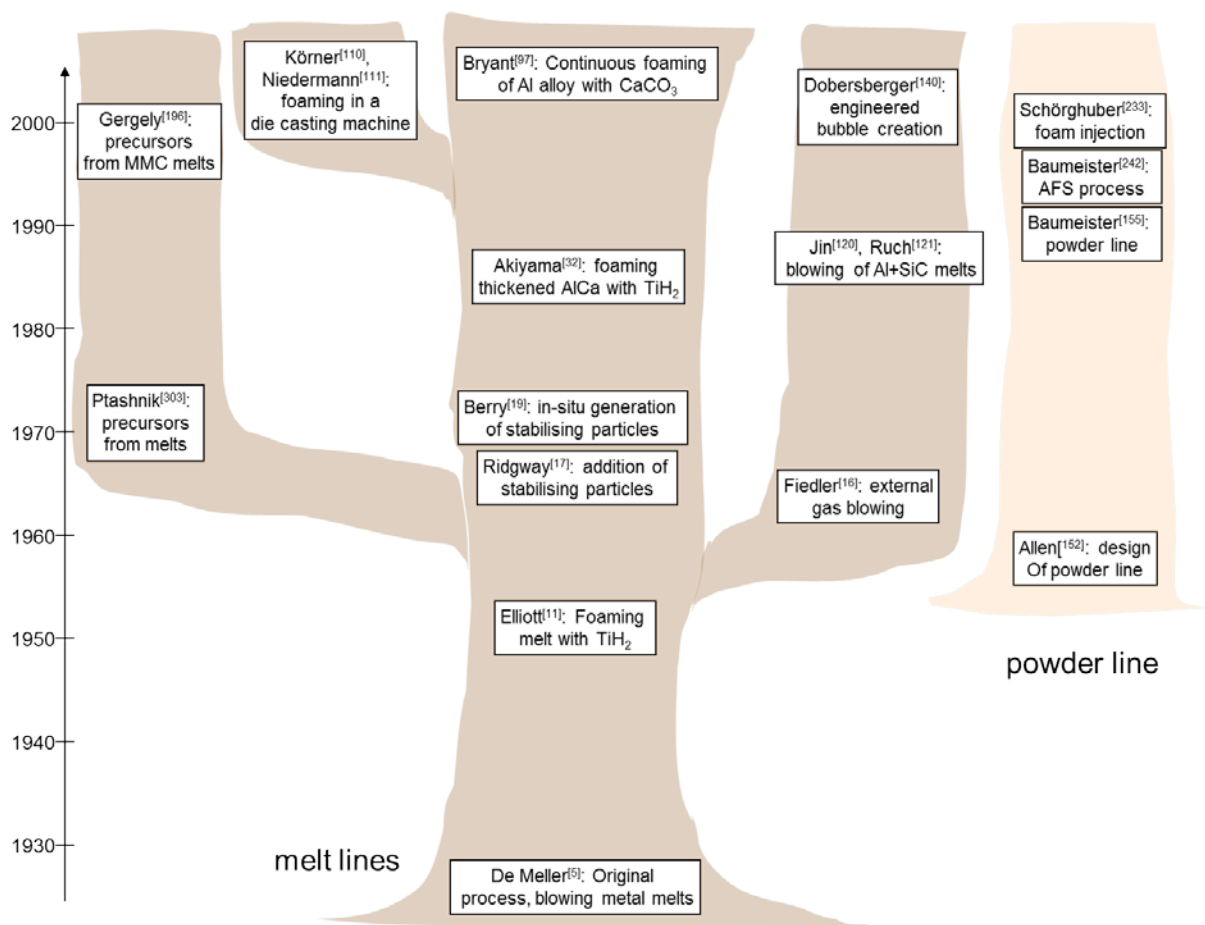|		blowing agent				
		TiH_2	ZrH_2	MgH_2	$CaCO_3$	$MgCa(CO_3)_2$
additions for stabilisation	none*	Al,[37,38] Al-Mg,[38] Al-Mg-Li,[38] AlSi7Mg,[91] AlSi9Cu3,[115,116] Al-Mg-Zn,[91,92] ZnAl22[105]		AlSi9Cu3,[114-116] Mg,[112] AZ91[113]	Al,[91] Al-Mg-Zn,[91,92] AlSi7Mg2,[98] ZnAl22[93]	Al[94]
	Ca	Al,[34-38,47-49,91,92] Al-Mg,[67] AlSi7Mg,[91] Al-Mg-Zn,[43,46,63,89,91,92] Al-Cu,[51] Al-Mg-Cu,[65] Al-Sc,[342] AZ91,[53] AM60[53]	Al [96]		Al,[90-92] AlSi7Mg,[6,90,91] Al-Mg-Zn[89-92] Mg[101,104] AZ91,[102] AZ31[102,103]	
	dross, scrap	unspec. alloy,[71] Al,[83] Al-Mg,[83]	unspec. alloy,[72] AlMg7[23]			
	oxygen		AlMg7[19]	CaH₂		
	MnO_2	Al,AlMg10,[69,70] AlSi13,[18] Al-Mg[18] (unspec. hydride)				
	SiC	AlMg7Mg,[76] AlSi7Mg,[77] AZ91,[53] AM60,[53] ZnAl22[106]		Al-Cu-Mg[95]	AlSi9Mg,[78] AlSi7Mg[79]	
	Al_2O_3					
	metal powder	AlSi7Mg [73,74]			Al [75]	
	Cu-coated fibres	Al [80]				
	AlN	AlSi4Mg [81]				
	fly ash			AlCu4Mg[82]		

* merely some mechanical action takes part which might contribute to foam stabilisation

References

(patents: year of filing in paranthesis)

[1]   M. F. Ashby, *Metallurgical Transactions A* **1983**, *14A*, 1755.
[2]   L. J. Gibson, M. F. Ashby, *Cellular solids: structure and properties*, 2nd ed., Cambridge University Press: Cambridge, **1997**.
[3]   M. F. Ashby, A. G. Evans, N. A. Fleck, L. J. Gibson, J. W. Hutchinson, H. N. G. Wadley, *Metal foams: A design guide*, Butterworth-Heinemann: Boston, **2000**.
[4]   J. Banhart, *Progress in Materials Science* **2001**, *46*, 559.
[5]   M. A. De Meller, Produit métallique pour l'obtention d'objets laminés, moulés ou autres, et procédés pour sa fabrication. French Patent 615,147, **1926** (1925).
[6]   T. Nakamura, S. V. Gnyloskurenko, K. Sakamoto, A. V. Byakova, R. Ishikawa, *Materials Transactions* **2002**, *43*, 1191.
[7]   J. Banhart, *Advanced Engineering Materials* **2006**, *8*, 781.
[8]   B. Sosnick, Process of making foamlike mass of metal. USA Patent 2,434,775, **1948** (1943).
[9]   B. Sosnick, Foamlike metal. USA Patent 2,553,016, **1951** (1947).
[10]   Bjorksten Laboratories. www.bjorksten.com [accessed: 15 October 2011].
[11]   J. C. Elliott, Method of producing metal foam. USA Patent 2,751,289, **1956** (1951).
[12]   J. C. Elliott, Metal foaming process. USA Patent 3,005,700, **1961** (1960).
[13]   J. C. Elliott, Metal foam and method for making. USA Patent 2,983,597, **1961** (1959).
[14]   J. Banhart, D. Weaire, *Physics Today* **2002**, *55*, 37.
[15]   S. O. Fiedler, J. Bjorksten, W. S. Fiedler, Production of metal foam. USA Patent 2,937,938, **1960** (1958) [see also 2,974,034 **1961** (1957) and 2,979,392 **1961** (1957) that are all similar].
[16]   W. S. Fiedler, Method of making metal foam bodies. USA Patent 3,214,265, **1965** (1963).
[17]   J. A. Ridgway, Cellarized metal and method of producing same. USA Patent 3,297,431, **1967** (1965).
[18]   L. G. Graper, Method of making metal foam. USA Patent 3,379,517, **1968** (1965).
[19]   C. B. Berry, Foamed metal. USA Patent 3,669,654, **1972** (1970).
[20]   K. Kadoi, H. Nakae, *Materials Transactions* **2011**, *52*, 1912.
[21]   P. H. Thornton, C. L. Magee, *Metallurgical Transactions A* **1975**, *6A*, 1253.
[22]   L. M. Niebylski, R. J. Fanning, Metal foams as energy absorbers for automobile bumpers, In *National Automotive Engineering Meeting*, Society of Automotive Engineers Inc. (SAE), New York, **1972**, p. 1676, paper 720490, doi:10.4271/720490.
[23]   C. B. Berry, Foamed metal. USA Patent 3,671,221, **1972** (1970).
[24]   L. M. Niebylski, C. P. Jarema, T. E. Lee, Preparation of metal foams with viscosity increasing gases. USA Patent 3,816,952, **1974** (1971) [similar to Patent 3,843,353].
[25]   C. P. Jarema, L. M. Niebylski, Method for quietly casting foamed metal. USA Patent 3,719,223, **1973** (1971) [similar to US 3,826,303].
[26]   L. M. Niebylski, C. P. Jarema, Pressure contouring and bonding of metal foams. USA Patent 3,873,392, **1975** (1973).
[27]   L. M. Niebylski, Anodizing aluminum foams. Patent 3,787,298, **1974** (1971).
[28]   L. M. Niebylski, C. P. Jarema, P. A. Immethun, Metal foams and process therefor. USA Patent 3,794,481, **1974** (1973).
[29]   L. M. Niebylski, C. P. Jarema, T. E. Lee, Reinforced foamed metal. Patent 3,940,262, **1976** (1974).
[30]   P. H. Thornton, C. L. Magee, *Metallurgical Transactions A* **1975**, *6A*, 1801.
[31]   L. M. Niebylski, C. P. Jarema, Lead-zinc foams. USA Patent 3,847,591, **1974** (1973).
[32]   S. Akiyama, H. Ueno, K. Imagawa, A. Kitahara, S. Nagata, K. Morimoto, T. Nishikawa, M. Itoh, Foamed metal and method of producing same. European Patent 0 210 803, **1989** (1986).
[33]   S. Akiyama, H. Ueno, K. Imagawa, A. Kitahara, S. Nagata, K. Morimoto, T. Nishikawa, M. Itoh, Foamed metal and method of producing same. USA Patent 4,713,277, **1987** (1986).
[34]   T. Miyoshi, M. Itoh, S. Akiyama, A. Kitahara, Aluminium foam 'ALPORAS': the production process, properties and applications, In *Porous and Cellular Materials for Structural Applications* (Eds: D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley), Materials Research Society, Warrendale, **1998**, pp. 133
[35]   L. Ma, Z. Song, *Scripta Materialia* **1998**, *39*, 1523.
[36]   T. Miyoshi, M. Itoh, S. Akiyama, A. Kitahara, *Advanced Engineering Materials* **2000**, *2*, 179.
[37]   K. Kadoi, N. Babcsán, H. Nakae, *Materials Science Forum* **2010**, *649*, 385.
[38]   A. A. Gokhale, S. N. Sahu, V. K. W. R. Kulkarni, B. Sudhakar, N. Ramachandra Rao, Materials issues in foaming of liquid aluminium, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 95

[39] M. Otsuka, N. Houjo, A. Kojima, M. Itoh, E. Ishii, Mechanical properties of aluminum foam, In *Light Materials for Transportation Systems (LiMat-93)* (Ed: N. J. Kim), Center for Advanced Aerospace Materials, Pohang, **1993**, pp. 435

[40] M. Otsuka, A. Kojima, M. Itoh, E. Ishii, Structure and mechanical properties of cellular aluminum, In *Science and Engineering of Light Metals (RASELM'91)*, Japan Institute of Light Metals, Sendai, **1991**, pp. 999

[41] E. Ishii, M. Itoh, Y. Morisawa, *Kobe Steel Engineering Reports* **1991**, *41*, 59.

[42] T. Mukai, H. Kanahashi, T. Miyoshi, M. Mabuchi, T. G. Nieh, K. Higashi, *Scripta Materialia* **1999**, *40*, 921.

[43] T. Miyoshi, T. Mukai, K. Higashi, *Materials Transactions* **2002**, *43*, 1778.

[44] T. Mukai, T. Miyoshi, S. Nakano, H. Somekawa, K. Higashi, *Scripta Materialia* **2006**, *54*, 533.

[45] T. Masuda, S. Kanbayashi, Method for manufacturing foam aluminum product and product. USA Patent 5,482,533, **1996** (1994).

[46] T. Miyoshi, S. Nishi, S. Furuta, T. Hamada, K. Yoshikawa, Current activities and new technologies of aluminum foam by melt route, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 255

[47] Z. L. Song, L. Q. Ma, Z. J. Wu, D. P. He, *Journal of Materials Science* **2000**, *35*, 15.

[48] Z. L. Song, J. S. Zhu, L. Q. Ma, D. P. He, *Materials Science and Engineering A* **2001**, *298*, 137.

[49] Z. L. Song, S. Nutt, *Metallurgical and Materials Transactions A* **2008**, *39A*, 2215.

[50] B. Y. Hur, S. H. Park, A. Hiroshi, *Materials Science Forum* **2003**, *439*, 51.

[51] S. H. Park, Y. S. Um, B. Y. Hur, *Solid State Phenomena* **2006**, *116-117*, 656.

[52] S. H. Park, Y. S. Um, S. Y. Kim, B. Y. Hur, Rheology of Al and Mg alloys for manufacturing metal foam, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 119

[53] S. H. Park, K. H. Song, Y. S. Um, B. Y. Hur, *Materials Science Forum* **2006**, *510-511*, 742.

[54] A. E. Simone, L. J. Gibson, *Acta Materialia* **1998**, *46*, 3109.

[55] J. Banhart, *JOM Journal of the Minerals, Metals and Materials Society* **2000**, *52*, 22.

[56] M. Nosko, F. Simančík, K. Iždinský, P. Švec, R. Florek, *Materials Letters* **2011**, *65*, 1378.

[57] N. Babcsán, D. Leitlmeier, H.-P. Degischer, J. Banhart, *Advanced Engineering Materials* **2004**, *6*, 421.

[58] N. Babcsán, D. Leitlmeier, J. Banhart, *Colloids and Surfaces A* **2005**, *261*, 123.

[59] E. Amsterdam, J. T. M. De Hosson, P. R. Onck, *Acta Materialia* **2006**, *54*, 4465.

[60] P. Onck, R. Van Merkerk, A. Raaijmakers, J. T. M. De Hosson, *Jornal of Materials Science* **2005**, *40*, 5821.

[61] A. E. Markaki, T. W. Clyne, *Acta Materialia* **2001**, *49*, 1677.

[62] Y. Sugimura, J. Meyer, M. Y. He, H. BartSmith, J. Grenstedt, A. G. Evans, *Acta Materialia* **1997**, *45*, 5245.

[63] T. Miyoshi, S. Hara, T. Mukai, K. Higashi, *Materials Transactions* **2001**, *42*, 2118.

[64] H. Hao, G. Q. Lu, M. A. Diop, F. Y. Wang, X. G. Zhang, Effects of stirring mode and processing parameters on the cell structure and uniformity of aluminum foam, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 115

[65] D. H. Yang, B. Y. Hur, D. P. He, S. R. Yang, *Materials Science and Engineering A* **2007**, *445*, 415.

[66] S. Suzuki, H. Murakami, K. Kadoi, T. Saiwai, H. Nakae, N. Babcsán, Aluminum fabrication through the melt route by adding Mg and Bi, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 3

[67] S. Y. Kim, K. H. Kang, Y. S. Um, B. Y. Hur, Foaming characteristics of Al-Mg alloy foam, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 115

[68] L. Huang, H. Wang, F. Ye, Z. P. Lu, D. H. Yang, Mechanical properties of cellular Al-0.2 wt.%Sc foams, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 301

[69] F. S. Han, Z. G. Zhu, J. C. Gao, *Metallurgical and Materials Transactions A* **1998**, *29A*, 2497.

[70] F. S. Han, J. N. Wei, H. F. Cheng, J. C. Gao, *Journal of Materials Processing Technology* **2003**, *138*, 505.

[71] C.-C. Yang, S.-C. Chueh, K.-C. Su, T.-H. Chiou, Method for manufacturing environmentally concious foamed aluminum materials. USA Patent 5,632,319, **1997** (1995).

[72] C. B. Berry, A. R. Valdo, Foamed Aluminum. USA Patent 3,725,037, **1973** (1971).

[73] C. C. Yang, H. Nakae, *Journal of Materials Processing Technology* **2003**, *141*, 202.

[74] C. C. Yang, H. Nakae, *Journal of Alloys and Compounds* **2000**, *313*, 188.

[75] W. M. Zhao, H. Zhang, H. P. Li, Z. F. Wang, Y. Zhao, R. Zhao, B. Y. Hur, *Advanced Materials Research* **2011**, *214*, 70.

[76] M. C. Gui, D. B. Wang, J. J. Wu, G. J. Yuan, C. G. Li, *Materials Science and Engineering A* **2000**, *286*, 282.

[77] N. V. Ravi Kumar, N. Ramachandra Rao, B. Sudhakar, A. A. Gokhale, *Materials Science and Engineering A* **2010**, *527*, 6082.

[78] S. R. Yu, Y. R. Luo, J. A. Liu, *Materials Science and Engineering A* **2008**, *487*, 394.

[79] M. Golestanipour, M. S. Abravi, M. Malekjafarian, H. Amini Mashhadi, Manufacturing of Al/SiCp composite foams using calcium carbonate as foaming agent, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 175

[80] Z. K. Cao, J. J. Du, G. C. Yao, *Materials Science Forum* **2010**, *650*, 320.

[81] Y. H. Song, M. Tane, T. Ide, Y. Seimiya, B. Y. Hur, H. Nakajima, *Metallurgical and Materials Transactions A* **2010**, *41A*, 2104.

[82] D. P. Mondal, M. D. Goel, S. Das, *Materials Science and Engineering A* **2009**, *507*, 102.

[83] G. S. Vinod Kumar, K. Heim, F. Garcia-Moreno, J. Banhart, A. R. Kennedy, *Advanced Engineering Materials* **2012**, *this issue*.

[84] A. H. Brothers, J. Banhart, Verfahren zur Herstellung eines Metallmatrix-Nanoverbundwerkstoffes, Metallmatrix-Nanoverbundwerkstoff und seine Anwendung [Process for manufacture of metal matrix nanocomposite and its application]. German Patent 10 2007 044 565, **2011** (2007).

[85] N. Babcsán, G. S. Vinod Kumar, J. Banhart, B. S. Murty, Verfahren zur Herstellung von Metallschäumen und Metallschaum [Process for the manufacture of metal foams]. German Patent 10 2006 031 213, **2007** (2006) [similar to European Patent EP 2 044 230, **2010** (2007)].

[86] N. Babcsán, G. S. Vinod Kumar, F. Garcia Moreno, B. S. Murty, J. Banhart, New foam-stabilizing additive for aluminium, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. C. Dunand), DEStech Publ., Lancaster, **2008**, pp. 27

[87] G. S. Vinod Kumar, F. Garcia Moreno, J. Banhart, Verfahren zur Herstellung von Metallschäumen und Metallschaum [Process to manufacture metal foam]. German Patent 10 2010 024 669, **2011** (2010).

[88] G. S. Kumar, M. Chakraborty, F. Garcia-Moreno, J. Banhart, *Metallurgical and Materials Transactions A* **2011**, *42A*, 2898.

[89] Y. Milman, A. Byakova, A. Sirko, S. Gnyloskurenko, T. Nakamura, *Materals Science Forum* **2006**, *519-521*, 573.

[90] S. V. Gnyloskurenko, A. V. Byakova, A. I. Sirko, A. O. Dudnyk, Y. V. Milman, T. Nakamura, Advanced structure and deformation pattern of Al based alloys foamed with calcium carbonate agent, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. C. Dunand), DEStech Publ., Lancaster, **2008**, pp. 399

[91] A. Byakova, A. Sirko, K. Mykhalenkov, Y. Milman, S. Gnyloskurenko, T. Nakamura, Progress in aluminium foaming technology: application of calcium carbonate as foaming agent for Alporas and powder compact techniques, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 273

[92] A. V. Byakova, S. V. Gnyloskurenko, A. I. Sirko, Y. V. Milman, T. Nakamura, *Materials Transactions* **2006**, *47*, 2131.

[93] S. R. Yu, J. A. Liu, X. Y. Zhu, Y. R. Luo, M. Wei, *Advanced Engineering Materials* **2007**, *9*, 679.

[94] D. P. Papadopoulos, H. Omar, F. Stergioudi, S. A. Tsipas, H. Lefakis, N. Michailidis, *Journal of Porous Materials* **2010**, *17*, 773.

[95] V. Rajput, D. P. Mondal, S. Das, N. Ramakrishnan, A. K. Jha, *Journal of Materials Science* **2007**, *42*, 7408.

[96] D. W. Li, J. Li, T. Li, T. Sun, X. M. Zhang, G. C. Yao, *Transactions of Nonferrous Metals Society of China* **2011**, *21*, 346.

[97] J. D. Bryant, J. A. Kallivayalil, M. D. Crowley, J. R. Genito, L. F. Wieserman, D. M. Wilhelmy, W. E. Boren, Method for producing foamed aluminum products by use of selected carbonate decomposition products. USA Patent 7,452,402, **2008** (2005).

[98] J. D. Bryant, M. Crowley, W. Wang, D. Wilhelmy, J. Kallivayalil, Development of Alcoa aluminum foam products, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. Dunand), DEStech Publ., Lancaster, **2008**, pp. 19

[99] R. Kretz, K. Renger, G. Rettenbacher, A. Hinterberger, Method for producing metal foam bodies. USA Patent 7,396,380, **2008** (2006).

[100] K. Renger, H. Kaufmann, *Advanced Engineering Materials* **2005**, *7*, 117.

[101] D. H. Yang, B. Y. Hur, S. R. Yang, *Journal of Alloys and Compounds* **2008**, *461*, 221.

[102] C. H. Seo, M. J. Jeong, I. Y. Jung, B. Y. Hur, *Materials Science Forum* **2008**, *569*, 273.

[103] H. H. Wei, W. M. Zhao, X. C. Xia, C. L. Qin, Z. G. Wang, Fabrication of Mg alloy foams by melt foaming method, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 533

[104] D. H. Yang, S. R. Yang, H. Wang, A. B. Ma, J. H. Jiang, J. Q. Chen, D. L. Wang, *Materials Science and Engineering A* **2010**, *527*, 5405.

[105] K. Sekido, H. Ishikawa, K. Kitazono, Superplastic deformation of Zn-Al22 alloy foam, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 133

[106] H. Ishikawa, K. Sekido, K. Kitazono, Superplasticity of particle dispersed Zn-22Al alloy foams, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 163

[107] S. R. Yu, J. A. Liu, Y. R. Luo, Y. H. Liu, *Materials Science and Engineering A* **2007**, *457*, 325.

[108] D. M. Albright, W. R. Chilcott, T. P. Floridis, Method of making foamed metal. USA Patent 3,360,361, **1967** (1964).

[109] A. Makaya, H. Fredriksson, Production of Fe-Cr-C-base foam: theoretical considerations and practical fabrication, In *Cellular Metals and Polymers* (Eds: R. F. Singer, C. Körner, V. Altstädt, H. Münstedt), Trans Tech Publications, Zürich, **2005**, pp. 49

[110] C. Körner, M. Hirschmann, R. F. Singer, Verfahren zur Herstellung eines Metallschaumkörpers [Process for manufacturing a shaped metal foam body]. German Patent 103 25 819, **2005** (2003).

[111] B. Niedermann, W. Knott, M. Recksik, A. Weier, Method for the production of metallic foam and metal foam bodies produced said method. European Patent 1 356 131, **2005** (2002).

[112] M. Hirschmann, C. Körner, R. F. Singer, Magnesium integral foam - A new metallic sandwich structure, In *7th International Conference on Sandwich Structures* (Eds: O. T. Thomsen, E. Bozhevolnaya, A. Lyckegaard), Springer, Netherlands, **2005**, pp. 845

[113] M. Hirschmann, C. Körner, R. F. Singer, *Materials Science Forum* **2007**, *539-543*, 1827.

[114] J. Hartmann, A. Trepper, C. Körner, *Advanced Engineering Materials* **2011**, *13*, 1050.

[115] H. Wiehler, C. Körner, R. F. Singer, *Advanced Engineering Materials* **2008**, *10*, 171.

[116] H. Wiehler, P. Heinl, C. Körner, R. F. Singer, High pressure integral foam moulding of aluminium, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. C. Dunand), DEStech Publ., Lancaster, **2008**, pp. 15

[117] C. Körner, M. Hirschmann, V. Bräutigam, R. F. Singer, *Advanced Engineering Materials* **2004**, *6*, 385.

[118] N. Babcsán, J. Banhart, In *Colloidal particles at liquid interfaces*, B. P. Binks, T. S. Horozov, Eds., Cambridge University Press, Cambridge, **2006**, p 445.

[119] N. Babcsán, F. Garcia-Moreno, J. Banhart, *Colloids and Surfaces A* **2007**, *309*, 254.

[120] I. Jin, L. D. Kenny, H. Sang, Method of producing lightweight foamed metal. USA Patent 4,973,358, **1990** (1989).

[121] W. W. Ruch, B. Kirkevag, A process of manufacturing particle reinforced metal foam and product thereof. European Patent 0 483 184, **1994** (1990).

[122] S. W. Ip, Y. Wang, J. M. Toguri, *Canadian Metallurgical Quarterly* **1999**, *38*, 81.

[123] D. Leitlmeier, H. P. Degischer, H. J. Flankl, *Advanced Engineering Materials* **2002**, *4*, 735.

[124] H. Sang, L. D. Kenny, I. Jin, Process for producing shaped slabs of particle stabilised foamed metal. USA Patent 5,334,236, **1994** (1992).

[125] I. Jin, L. D. Kenny, H. Sang, Stabilized metal foam body. USA Patent 5,112,697, **1992** (1990).

[126] I. Jin, L. D. Kenny, H. Sang, Lightweight metal with isolated pores and its production. USA Patent 5,221,324, **1993** (1992).

[127] L. D. Kenny, M. Thomas, Process for shape casting of particle stabilized metal foam. USA Patent 5,281,251, **1994** (1992).

[128] J. T. Beals, M. S. Thompson, *Journal of Materials Science* **1997**, *32*, 3595.

[129] M. Thomas, L. D. Kenny, H. Sang, Particle-stabilized metal foam and its production. USA Patent 5,662,542, **1997** (1994).

[130] M. Linke, W. Jungk, E. Fischer, G. Maurus, Verfahren und Vorrichtung zur Herstellung eines Metallschaums [Method and apparatus for producing metallic foam]. European Patent application 0 544 291, **1992**.

[131] X. N. Liu, Y. X. Li, X. Chen, Y. Liu, X. L. Fan, *Journal of Materials Science* **2010**, *45*, 6481.

[132] D.-Q. Wang, Z.-Y. Shi, *Materials Science and Engineering A* **2003**, *361*, 45.

[133] M. Malekjafarian, S. K. Sadrnezhaad, M. S. Abravi, M. Golestanipour, H. Amini Mashhadi, Manufacturing aluminum foams by melt gas injection process, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 195

[134] O. Prakash, J. D. Embury, H. Sang, C. Sinclair, P. Silvetti, Light weight cellular structures based on aluminium, In *Synthesis/Processing of Lightweight Metallic Materials 2* (Eds: C. M. Ward-Close, F. H. Froes, D. J. Chellman, S. S. Cho), The Minerals, Metals and Materials Society, Warrendale, **1997**, pp. 19

[135] O. Prakash, H. Sang, J. D. Embury, *Materials Science and Engineering A* **1995**, *199*, 195.

[136] A. Haibel, A. Rack, J. Banhart, *Applied Physics Letters* **2006**, *89*, 154102.

[137] N. Babcsán, D. Leitlmeier, H. P. Degischer, *Materialwissenschaft Und Werkstofftechnik* **2003**, *34*, 22.

[138] N. Babcsán, F. Garcia-Moreno, D. Leitlmeier, J. Banhart, *Materials Science Forum* **2006**, *508*, 275.

[139] S. Nichol, R. G. Manley, Sealed impeller for producing metal foam and system and method therefor. USA Patent 7,481,964, **2009** (2005).

[140] F. Dobesberger, H. J. Flankl, D. Leitlmeier, Device and process for producing metal foam. Patent 7,195,662, **2007** (2002).

[141] S. V. Gnyloskurenko, T. Nakamura, *Materials Transactions* **2003**, *44*, 2298.

[142] S. Gnyloskurenko, A. Byakova, T. Nakamura, O. Raychenko, *Journal of Materials Science* **2005**, *40*, 2437.

[143] D. Q. Wang, C. X. Sun, *Journal of Materials Science* **2008**, *43*, 2825.

[144] F. Dobesberger, H. J. Flankl, D. Leitlmeier, Process and device for manufacturing free-flowing metal foam. Patent 6,896,029, **2005** (2003) [see also US 7,144,636 (2006) and US 7,959,852 (2011)].

[145] C. D. Fuerst, Method for manufacturing closed-wall cellular metal. USA Patent 6,881,241, **2005** (2002).

[146] S. Nichol, Metal foam casting apparatus and method. USA Patent 6,998,535, **2006** (2005).

[147] P. Åsholt, G. Tokle, Method and means for producing moulded foam bodies. USA Patent 6,866,084, **2005** (2002).

[148] S. Nichol, J. K. Killingbeck, R. G. Manley, Method and apparatus for low pressure aluminum foam casting. USA Patent 6,840,301, **2005** (2002) [similar to US 6,932,146].

[149] F. Dobesberger, H. J. Flankl, D. Leitlmeier, A. Birgmann, Lightweight part, as well as a process and device for its production. USA Patent 7,137,433, **2006** (2003).

[150] B. Y. Hur, S. H. Cho, K. B. Kim, S. C. Bae, Method and apparatus for the continuous production of foamed metals. USA Patent 6,863,709, **2005** (2003) [similar to US 6,984,356].

[151] J. F. Pashak, Cellularized light metal. USA Patent 2,935,396, **1960** (1957).

[152] B. C. Allen, M. W. Mote, A. M. Sabroff, Method of making foamed metal. USA Patent 3,087,807, **1963** (1959).

[153] J. Banhart, J. Baumeister, M. Weber, Powder metallurgical technology for the production of metal foam, In *European Conference on Advanced PM Materials (Euro PM'95)*, European Powder Metallurgy Association, Shrewsbury, UK, **1995**, pp. 201

[154] J. Baumeister, Personal communication, **1991**.

[155] J. Baumeister, Verfahren zur Herstellung poröser Metallkörper. German Patent 40 18 360, **1991** (1990).

[156] J. Baumeister, H. Schrader, Verfahren zur Herstellung aufschäumbarer Metallkörper und Verwendung derselben [Process for manufacturing foamable metal bodies and use thereof]. German Patent 41 01 630, **1992** (1991).

[157] J. Baumeister, H. Schrader, Method for manufacturing foamable metal bodies. USA Patent 5,151,246, **1992** (1991).

[158] H. Wörz, H. P. Degischer, Process for the production of foamable metal elements. USA Patent 5,393,485, **1995** (1993).

[159] H. Wörz, H. P. Degischer, Verfahren zur Herstellung von Metallschaumkörpern [Process for the manufacture of metal foam bodies]. German Patent 42 06 303, **1993** (1992).

[160] J. Baumeister, Verfahren zur Herstellung von aufschäumbaren Metallkörpern durch Walzen [Process for the manufacture of foamable metal bodies by rolling]. German Patent 41 24 591, **1993** (1991).

[161] H.-D. Kunze, J. Baumeister, J. Banhart, M. Weber, *Powder metallurgy international* **1993**, *25* 182.

[162] J. Banhart, J. Baumeister, M. Weber, *Materials Science and Engineering A* **1996**, *205*, 221.

[163] F. Simancík, H. P. Degischer, H. Wörz, Foamed aluminium - Light structural and insulation material, In *Euromat '95*, Assoziazione Italiana di Metallurgica, Milano, 1995, **1995**,

[164] J. Banhart, J. Baumeister, *Journal of Materials Science* **1998**, *33*, 1431.

[165] H. M. Helwig, F. Garcia-Moreno, J. Banhart, *Journal of Materials Science* **2011**, *46*, 5227.

[166] M. Ota, M. Kobashi, H. Kanetake, Foaming behaviour of precursors made of various kinds of Al alloy powder, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 111

[167] D. Lehmhus, M. Busse, *Advanced Engineering Materials* **2004**, *6*, 391.

[168] D. Lehmhus, J. Banhart, M. A. Rodriguez-Perez, *Materials Science and Technology* **2002**, *18*, 474.

[169] L. Y. Aguirre-Perales, I. H. Jung, R. A. L. Drew, *Metallurgical and Materials Transactions A* **2012**, *43A*, 1.

[170] L. Y. Aguirre-Perales, I.-H. Jung, R. A. L. Drew, *Acta Materialia* **2012**, *60*, 759.

[171] J. Banhart, *Europhysics News* **1999**, *30*, 17.

[172] J. Banhart, D. Bellmann, H. Clemens, *Acta Materialia* **2001**, *49*, 3409.

[173] K. Kitazono, Y. Takiguchi, *Scripta Materialia* **2006**, *55*, 501.

[174] J. Banhart, *Gold Bulletin* **2008**, *41*, 251.

[175] F. W. Bach, D. Bormann, P. Wilk, R. Kucharski, Production and properties of foamed magnesium, In *Cellular Metals and Polymers* (Eds: R. F. Singer, C. Körner, V. Altstädt, H. Münstedt), Trans Tech Publications, Zürich, **2005**, pp. 77

[176] J. Banhart, unpublished work, **1992**.

[177] C. E. Wen, M. W. Barnett, J. Vella, Y. Yamada, Solid-state foaming of magnesium alloys, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 165

[178] T. Neu, M. Mukherjee, F. Garcia Moreno, J. Banhart, Magnesium and magnesium alloy foams, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 133

[179] A. Irretier, J. Banhart, *Acta Materialia* **2005**, *53*, 4903.

[180] J. Banhart, Verfahren zur Herstellung poröser Metallkörper und Verwendung derselben. German Patent 101 15 230, **2002** (2001).

[181] B. Kriszt, A. Falahati, H. P. Degischer, Machbarkeitsstudie zur Herstellung von Eisenschaum, In *Metallschäume* (Ed: J. Banhart), MIT-Verlag, Bremen, **1997**, pp. 59

[182] M. Weber, M. Knüwer, Evaluierung verschiedener Herstellungs- und Anwendungsmöglichkeiten für hochporöse Stahlwerkstoffe, In *Metallschäume* (Ed: J. Banhart), MIT-Verlag, **1997**, p. 73

[183] C.-J. Yu, H. H. Eifert, M. Knuewer, M. Weber, J. Baumeister, Investigation for the selection of foaming agents to produce steel foams, In *Porous and Cellular Materials for Structure Applications* (Eds: D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley), **1998**, pp. 145

[184] H. D. Kunze, M. Knüwer, *steel research* **1999**, *70*, 513.

[185] G. Rausch, M. Weber, M. Knüwer, *Materialwissenschaft Und Werkstofftechnik* **2000**, *31*, 424.

[186] C. Park, S. R. Nutt, *Materials Science and Engineering A* **2000**, *288*, 111.

[187] C. Park, S. R. Nutt, *Materials Science and Engineering A* **2001**, *297*, 62.

[188] G. Rausch, J. Banhart, In *Handbook of Cellular Metals*, H.-P. Degischer, B. Kriszt, Eds., VCH-Wiley, Weinheim, **2002**, p 21.

[189] M. D. Demetriou, G. Duan, C. Veazey, K. De Blauwe, W. L. Johnson, *Scripta Materialia* **2007**, *57*, 9.

[190] G. Rausch, T. Hartwig, M. Weber, O. Schulz, *Materialwissenschaft Und Werkstofftechnik* **2000**, *31*, 412.

[191] L. Helfen, T. Baumbach, H. Stanzick, J. Banhart, A. Elmoutaouakkil, P. Cloetens, *Advanced Engineering Materials* **2002**, *4*, 808.

[192] L. Helfen, T. Baumbach, P. Pernot, P. Cloetens, H. Stanzick, K. Schladitz, J. Banhart, *Applied Physics Letters* **2005**, *86*, 231907.

[193] A. Rack, H. M. Helwig, A. Bütow, A. Rueda, B. Matijašević-Lux, L. Helfen, J. Goebbels, J. Banhart, *Acta Materialia* **2009**, *57*, 4809.

[194] S. E. Speed, Process for controlled production of hydrogen gas by the catalyzed and controlled decomposition of zirconium and titanium hydride. USA Patent 3,676,071, **1972** (1970).

[195] S. E. Speed, Foaming of metal by the catalyzed and controlled decomposition of zirconium and titanium hydride. USA Patent 3,981,720, **1976** (1972).

[196] V. Gergely, T. W. Clyne, The effect of oxide layers on gas-generating hydride particles during production of aluminium foams, In *Porous and Cellular Materials for Structure Applications* (Eds: D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley), Materials Research Society, Warrendale, **1998**, pp. 139

[197] V. Gergely, T. W. Clyne, *Advanced Engineering Materials* **2000**, *2*, 175.

[198] A. R. Kennedy, *Scripta Materialia* **2002**, *47*, 763.

[199] F. von Zeppelin, M. Hirscher, H. Stanzick, J. Banhart, *Composites Science and Technology* **2003**, *63*, 2293.

[200] A. R. Kennedy, V. H. Lopez, *Materials Science and Engineering A* **2003**, *357*, 258.

[201] D. Lehmhus, G. Rausch, *Advanced Engineering Materials* **2004**, *6*, 313.

[202] B. Matijašević, J. Banhart, *Scripta Materialia* **2006**, *54*, 503.

[203] B. Matijašević-Lux, J. Banhart, S. Fiechter, O. Görke, N. Wanderka, *Acta Materialia* **2006**, *54*, 1887.

[204] D. Lehmhus, M. Wichmann, M. Busse, Kinetic analysis of foaming agent variants as a means towards optimised temperature cycles and foaming agent/matrix alloy combinations, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. Dunand), DEStech Publ., Lancaster, **2008**, pp. 51

[205] C. Jiménez, F. Garcia-Moreno, B. Pfretzschner, P. Kamm, T. Neu, M. Klaus, C. Genzel, A. Hilger, I. Manke, J. Banhart, *Advanced Engineering Materials* **2012**, in press.

[206] M. T. Malachevsky, C. A. D'Ovidio, *Scripta Materialia* **2006**, *61*, 1.

[207] C. Jiménez, F. Garcia-Moreno, B. Pfretzschner, M. Klaus, M. Wollgarten, I. Zizak, G. Schumacher, M. Tovar, J. Banhart, *Acta Materialia* **2011**, *59*, 6318.

[208] C. Jiménez, F. García-Moreno, A. Rack, R. Tucoulou, M. Klaus, B. Pfretzschner, T. Rack, P. Cloetens, J. Banhart, *Scripta Materialia* **2012**, *66*, 757.

[209] F. S. Han, Z. G. Zhu, J. C. Gao, W. H. Song, *Metallurgical and Materials Transactions B* **1998**, *29B*, 1315.

[210] P. M. Proa-Flores, R. A. L. Drew, *Advanced Engineering Materials* **2008**, *10*, 830.

[211] A. Ibrahim, C. Körner, R. F. Singer, *Advanced Engineering Materials* **2008**, *10*, 845.

[212] B. Matijašević, O. Görke, H. Schubert, J. Banhart, Zirconium hydride - A possible blowing agent for making aluminium alloy foams, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 107

[213] F. Baumgärtner, I. Duarte, J. Banhart, *Advanced Engineering Materials* **2000**, *2*, 168.

[214] P. H. Kamm, Alternative Hydride für das Schäumen von Metallen [Alternate hydrides for foaming metals], TU Berlin, **2011**.

[215] V. Gergely, D. C. Curran, T. W. Clyne, *Composites Science and Technology* **2003**, *63*, 2301.

[216] M. Arnold, C. Körner, R. F. Singer, PM aluminium foams: stabilising mechanisms and optimisation, In *Cellular Metals and Metal Foaming Technology (MetFoam2003)* (Eds: J. Banhart, N. A. Fleck, A. Mortensen), MIT Publishing, Berlin, **2003**, pp. 71

[217] L. E. G. Cambronero, C. Ranninger, Marble waste recovery as foaming agent for aluminium foams, In *Cellular Metals and Metal Foaming Technology (MetFoam2003)* (Eds: J. Banhart, N. A. Fleck, A. Mortensen), MIT Publishing, Berlin, **2003**, pp. 175

[218] L. E. G. Cambronero, J. M. Ruiz-Roman, F. A. Corpas, J. M. Ruiz Prieto, *Journal of Materials Processing Technology* **2009**, *209*, 1803.

[219] M. Haesche, D. Lehmhus, J. Weise, M. Wichmann, I. C. M. Mocellin, *Journal of Materials Science & Technology* **2010**, *26*, 845.

[220] V. Kevorkijan, *Aluminium* **2010**, *86*, 59.

[221] V. Kevorkijan, S. D. Škapin, I. Paulin, B. Šuštaršič, M. Jenko, *Materiali in Tehnologije* **2010**, *44*, 363.

[222] T. Koizumi, K. Kido, K. Kita, K. Mikado, S. Gnyloskurenko, T. Nakamura, *Materials Transactions* **2011**, *52*, 728.

[223] T. Koizumi, K. Kido, K. Kita, K. Mikado, S. Gnyloskurenko, T. Nakamura, *Metals* **2012**, *2*, 1.

[224] S. Gnyloskurenko, T. Koizumi, K. Kita, T. Nakamura, Development of dolomite foaming agent for Al-based precursors, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 121

[225] M. Mukherjee, C. Jiménez, F. Garcia Moreno, J. Banhart, Pulvermetallurgisches Verfahren zur Herstellung von Metallschaum [Powder metallurgical process for metal foam manufacture]. German Patent application 10 2009 020 004, **2009**.

[226] M. Mukherjee, F. Garcia-Moreno, C. Jiménez, J. Banhart, *Advanced Engineering Materials* **2010**, *12*, 472.

[227] J. Banhart, J. Baumeister, O. Irretier, J. Jöbstl, *Aluminium* **2000**, *76*, 491.

[228] J. Baumeister, A. Melzer, J. Banhart, M. Weber, O. Irritier, J. Jöbstl, *Metall* **1999**, *53*, 501.

[229] A. Schöne, N. Büngener, J. Baumeister, M. Weber, O. Belkessam, U. Fritsching, Continuous metal foam production within an adapted foaming equipment, In *Cellular Metals and Metal Foaming Technology (MetFoam2001)* (Eds: J. Banhart, M. F. Ashby, N. A. Fleck), MIT-Verlag, **2001**, pp. 161

[230] C. Umashankar, K. B. Khan, T. R. G. Kutty, K. N. Mahule, R. P. Singh, S. V. Kailas, Continuous casting of aluminium foam by controlled injection of TiH$_2$ powder, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 85

[231] F. Simančík, J. Kováčik, F. Schörghuber, Porosity in complex 3D-parts prepared from aluminium foam, In *Metallschäume* (Ed: J. Banhart), MIT-Verlag, **1997**, pp. 171

[232] F. Simančík, F. Schörghuber, Complex foamed aluminum parts as permanent cores in aluminium castings, In *Porous and Cellular Materials for Structure Applications* (Eds: D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley), **1998**, pp. 151

[233] F. Schörghuber, F. Simančík, E. Hartl, Method of producing molded bodies of a metal foam. USA Patent 5,865,237, **1999** (1997).

[234] C.-J. Yu, H. H. Eifert, J. Banhart, J. Baumeister, *Materials Research Innovations* **1998**, *2*, 181.

[235] F. Garcia Moreno, M. Mukherjee, C. Jiménez, A. Rack, J. Banhart, *Metals* **2012**, *2*, 10.

[236] M. Kobashi, S. Sato, H. Kanetake, Foaming and filling-in behaviour of porous aluminum in hollow components, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 169

[237] F. Garcia-Moreno, N. Raffaele, J. Banhart, Optimisation of mould filling during PM metal foaming, In *Cellular Metals for Structural and Functional Applications (CellMet)* (Ed: G. Stephani), Fraunhofer IFAM, Dresden, **2009**, pp. 133

[238] S. G. Shabestari, N. Wanderka, H. W. Seeliger, J. Banhart, *Materials Science Forum* **2006**, *519-521*, 1221.

[239] J. Banhart, H. W. Seeliger, *Advanced Engineering Materials* **2008**, *10*, 793.

[240] E. Keetman, K.-H. Süss, Vorrichtung und Verfahren zum in-situ Aufschäumen von Hohlprofilen mit Metallschaum [Apparatus and process to fill a hollow section in-situ with metal foam]. German Patent 101 61 563, **2003** (2001).

[241] E. Lugscheider, C. Liebscher, M. Maurer, L. Zhao, The new easy foam process - manufacturing and investigation of metal foam hybrid components, In *Cellular Metals and Polymers* (Eds: R. F. Singer, C. Körner, V. Altstädt, H. Münstedt), Trans Tech Publications, Zürich, **2005**, pp. 39

[242] J. Baumeister, J. Banhart, M. Weber, Verfahren zur Herstellung eines metallischen Verbundwerkstoffs [Process for manufacturing metallic composite materials]. German Patent 44 26 627, **1994**.

[243] J. Banhart, W. Seeliger, C. Beichelt, In *Handbook of Cellular Metals*, H.-P. Degischer, B. Kriszt, Eds., VCH-Wiley, Weinheim, **2002**, p 113.

[244] J. Baumeister, Production technology for aluminium foam/steel sandwiches, In *Metal Foams and Porous Metal Structures* (Eds: J. Banhart, M. F. Ashby, N. A. Fleck), MIT Verlag, Bremen, **1999**, pp. 113

[245] J. Banhart, J. Baumeister, A. Melzer, W. Seeliger, M. Weber, *Metall* **1998**, *52*, 726.

[246] H. W. Seeliger, *Advanced Engineering Materials* **2002**, *4*, 753.

[247] H. W. Seeliger, *Advanced Engineering Materials* **2004**, *6*, 448.

[248] J. Banhart, H.-W. Seeliger, *Advanced Engineering Materials* **2012**, *(in press, doi:10.1002/adem.201100333)*.

[249] H. Stanzick, M. Wichmann, J. Weise, L. Helfen, T. Baumbach, J. Banhart, *Advanced Engineering Materials* **2002**, *4*, 814.

[250] C. Jiménez, F. Garcia-Moreno, M. Mukherjee, O. Goerke, J. Banhart, *Scripta Materialia* **2009**, *61*, 552.

[251] S. Vatchiants, N. Manukyan, Technology of aluminium foam production using methods of powder metallurgy, In *Cellular Metals and Metal Foaming Technology (MetFoam2003)* (Eds: J. Banhart, N. A. Fleck, A. Mortensen), MIT Publishing, Berlin, **2003**, pp. 131

[252] S. Vatchiants, M. Manukyan, Structure development in aluminum foam manufactured by hot rolling, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 195

[253] B. N. Song, G. C. Yao, G. Y. Zu, L. Wang, H. Ding, *Advanced Materials Research* **2011**, *154-155*, 613.

[254] G. Y. Zu, B. Song, Z. Guan, L. Wang, G. C. Yao, *Journal of Wuhan University of Technology - Materials Science Edition* **2011**, 671.

[255] V. C. Srivastava, M. Singh, T. Kumar, K. L. Sahoo, Effect of Al alloy composition and foaming temperature on pore size, density and mechanical properties, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 21

[256] F. Simančík, Ľ. Lúčan, J. Jerz, Reinforced aluminium foams, In *Cellular Metals and Metal Foaming Technology (MetFoam2001)* (Eds: J. Banhart, M. F. Ashby, N. A. Fleck), Verlag MIT Publishing, **2001**, pp. 365

[257] E. Solórzano, M. A. Rodriguez-Perez, J. A. Reglero, J. A. De Saja, Improving the mechanical response of aluminium foams in compression by using internal reinforcements, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 509

[258] K. Stöbener, J. Baumeister, G. Rausch, M. Busse, *Metal Powder Report* **2005**, *60*, 12.

[259] K. Stöbener, D. Lehmhus, N. Zimmer, J. Baumeister, Aus Metallschaumbausteinen aufgebautes Bauteil und Verfahren zu seiner Herstellung. German Patent 10328047, **2005**.

[260] J. Baumeister, J. Weise, K. Stöbener, M. Busse, M. Haesche, Investigations on 4 new methods for aluminium foam production, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. C. Dunand), DEStech Publ., Lancaster, **2008**, pp. 11

[261] D. Lehmhus, J. Baumeister, L. Stutz, E. Schneider, K. Stöbener, M. Avalle, L. Peroni, M. Peroni, *Advanced Engineering Materials* **2010**, *12*, 596.

[262] S. Asavavisitchai, A. R. Kennedy, *Advanced Engineering Materials* **2006**, *8*, 810.

[263] S. Asavavisithchai, A. R. Kennedy, *Journal of Colloid and Interface Science* **2006**, *297*, 715.

[264] S. Asavavisithchai, A. R. Kennedy, *Advanced Engineering Materials* **2006**, *8*, 568.

[265] M. Haesche, J. Weise, F. Garcia-Moreno, J. Banhart, *Materials Science and Engineering A* **2008**, *480*, 283.

[266] S. Esmaeelzadeh, A. Simchi, D. Lehmhus, *Materials Science and Engineering A* **2006**, *424*, 290.

[267] S. Elbir, S. Yilmaz, A. K. Toksoy, M. Guden, *Journal of Materials Science* **2003**, *38*, 4745.

[268] A. R. Kennedy, S. Asavavisithchai, *Advanced Engineering Materials* **2004**, *6*, 400.

[269] L. Wei, Y. Sun, *Advanced Materials Research* **2012**, *146-147*, 370.

[270] K. Shinagawa, Methodology of adding agents for stabilising foaming behaviour, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 69

[271] S. Asavavisithchai, A. R. Kennedy, *Scripta Materialia* **2006**, *54*, 1331.

[272] A. R. Kennedy, S. Asavavisithchai, *Scripta Materialia* **2004**, *50*, 115.

[273] N. D. Karsu, S. Yuksel, M. Guden, *Journal of Materials Science* **2009**, *44*, 1494.

[274] L. Wang, Z. S. Hua, J. Ma, G. C. Yao, *Powder Metallurgy* **2011**, *54*, 385.

[275] S. Tsuda, M. Kobashi, N. Kanetake, *Materials Transactions* **2006**, *47*, 2125.

[276] N. Kanetake, M. Kobashi, S. Tsuda, *Advanced Engineering Materials* **2008**, *10*, 840.

[277] K. Mehara, M. Kobashi, N. Kanetake, *Advanced Materials Research* **2007**, *26-28*, 905.

[278] F. Garcia-Moreno, N. Babcsán, J. Banhart, M. Haesche, J. Weise, Analysis of metal foaming behaviour and development of foaming processes, In *Cellular Metals and Polymers* (Eds: R. F. Singer, C. Körner, V. Altstädt, H. Münstedt), Trans Tech Publications, Zürich, **2005**, pp. 31

[279] J. Weise, O. Marchetto, M. Haesche, F. Garcia Moreno, J. Banhart, Influence of alloying additions on foaming behaviour of thixocast AlSi11 precursor, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 123

[280] J. Baumeister, J. Weise, A. Jeswein, M. Busse, M. Haesche, Metal foam production from AlMg4.5Mn recycling machining chips by means of thixocasting and the effects of different additives for stabilization, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. C. Dunand), DEStech Publ., Lancaster, **2008**, pp. 83

[281] R. F. Singer, C. Körner, Method of producing a moulded body from foamed metal. USA Patent 6,733,722, **2004** (2003).

[282] M. Shiomi, Y. Tanino, Moulding of aluminium foams by using hor powder extrusion, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 127

[283] M. Kobashi, N. Kanetake, *Advanced Engineering Materials* **2002**, *4*, 745.

[284] N. Kanetake, M. Kobashi, *Scripta Materialia* **2006**, *54*, 521.

[285] M. Kobashi, K. Kuze, H. Kanetake, *Advanced Engineering Materials* **2006**, *8*, 836.

[286] M. Kobashi, N. Inoguchi, N. Kanetake, *Intermetallics* **2010**, *18*, 1039.

[287] M. Kobashi, N. Kanetake, *Materials Science Forum* **2006**, *519-521*, 1335.

[288] F. Garcia-Moreno, J. Banhart, Verfahren zur pulvermetallurgischen Herstellung von Metallschaumstoff und von Teilen aus Metallschaumstoff [Process for the powder metallurgical production of metal foam and of parts made of metal foam]. German Patent 10 2005 037 305, **2007** (2005) [also EP 1 915 226].

[289] F. Garcia-Moreno, J. Banhart, *Colloids and Surfaces A* **2007**, *309*, 264.

[290] K. Kitazono, E. Sato, K. Kuribayashi, *Scripta Materialia* **2004**, *50*, 495.

[291] R. Suzuki, K. Kitazono, Effect of layered microstructure of the aluminum precursor manufactured from sheet material on the foaming behaviour, In *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)* (Eds: B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun), GS Intervision, Seoul, **2012**, pp. 27

[292] Y. Kikuchi, K. Kitazono, E. Sato, K. Kuribayashi, Cell morphology of closed-cell magnesium foam manufactured by bulk foaming process, In *Porous Metals and Metal Foaming Technology (MetFoam2005)* (Eds: H. Nakajima, N. Kanetake), Japan Institute of Metals, Sendai, Japan, **2006**, pp. 355

[293] Y. Hangai, T. Utsunomiya, *Metallurgical and Materials Transactions A* **2009**, *40A*, 275.

[294] Y. Hangai, Y. Ozeki, S. Kawano, T. Utsunomiya, O. Kuwazuru, M. Hasegawa, S. Koyama, N. Yoshikawa, *Materials Transactions* **2010**, *51*, 548.

[295] Y. Hangai, T. Utsunomiya, *Metallurgical and Materials Transactions A* **2009**, *40A*, 1284.

[296] M. Mukherjee, F. Garcia-Moreno, J. Banhart, *Acta Materialia* **2010**, *58*, 6358.

[297] M. Mukherjee, F. Garcia-Moreno, J. Banhart, *Scripta Materialia* **2010**, *63*, 235.

[298] F. Garcia-Moreno, N. Babcsán, J. Banhart, *Colloids and Surfaces A* **2005**, *263*, 290.

[299] A. Dudka, F. Garcia-Moreno, N. Wanderka, J. Banhart, *Acta Materialia* **2008**, *56*, 3990.

[300] F. Simančík, K. Behulova, L. Borš, Effect of ambient atmosphere on the foam expansion, In *Cellular Metals and Metal Foaming Technology (MetFoam2001)* (Eds: J. Banhart, M. F. Ashby, N. A. Fleck), Verlag MIT Publishing, **2001**, pp. 89

[301] C. Körner, F. Berger, M. Arnold, C. Stadelmann, R. F. Singer, *Materials Science and Technology* **2000**, *16*, 781.

[302] F. Garcia-Moreno, M. Mukherjee, E. Solórzano, J. Banhart, *International Journal of Materials Research* **2010**, *101*, 1134.

[303] W. J. Ptashnik, Method for producing metal alloy foams. USA Patent 3,758,291, **1973** (1971).

[304] J. Banhart, J. Baumeister, A. Melzer, M. Weber, Verfahren zur Herstellung von Verbundwerkstoffbauteilen [Process for the manufacture of composite material components]. German Patent 198 13 176, **2000** (1998).

[305] K. Kadoi, N. Babcsán, H. Nakae, F. Garcia-Moreno, J. Banhart, Methodology for the in-situ observation of Alporas foams using X-ray radioscopy, In *Porous Metals and Metallic Foams (Metfoam 2007)* (Eds: L. P. Lefebvre, J. Banhart, D. Dunand), DEStech Publ., Lancaster, **2008**, pp. 111

[306] J. T. Shang, D. P. He, *Science in China Series B-Chemistry* **2005**, *48*, 523.

[307] J. T. Shang, X. M. Chu, D. P. He, *Materials Science and Engineering B* **2008**, *151*, 157.

[308] G. S. Vinod Kumar, F. Garcia Moreno, J. Banhart, Schmelzmetallurgisches Verfahren zur Herstellung eines Metallschaumkörpers und Anordnung zur Durchführung des Verfahrens [Metallurgical process to manufacture metal foam body and setup for manufacture]. German Patent application 10 2011 111 614.5, **2011**.

[309] G. S. Vinod Kumar, M. Mukherjee, F. Garcia Moreno, J. Banhart, *Metallurgical and Materials Transactions A* **2012**, *in press (doi: 10.1007/s11661-012-1398-8)*.

[310] V. I. Shapovalov, Method for manufacturing porous articles. USA Patent 5,181,549, **1993** (1991).

[311] V. I. Shapovalov, *Materials Research Society (MRS) Bulletin* **1994**, *19*, 24.

[312] H. Nakajima, *Progress in Materials Science* **2007**, *52*, 1091.

[313] V. Shapovalov, L. Boyko, *Advanced Engineering Materials* **2004**, *6*, 407.

[314] S. K. Hyun, K. Murakami, H. Nakajima, *Materials Science and Engineering A* **2001**, *299*, 241.

[315] S. K. Hyun, Y. Shiota, K. Murakami, H. Nakajima, Mechanical properties of porous copper fabricated by unidirectional solidification under high pressure hydrogen, In *International Conference on Solid-Solid Phase Transformations (PTM 99)* (Eds: M. Koiwa, K. Otsuka, T. Miyazaki), Japan Institute of Metals, **1999**, pp. 341

[316] H. Nakajima, *Advanced Engineering Materials* **2008**, *10*, 816.

[317] J. Weise, J. Baumeister, Study of the production of metal foams using maxima of hydrogen solubility of casting alloys, In *Cellular Metals and Polymers* (Eds: R. F. Singer, C. Körner, V. Altstädt, H. Münstedt), Trans Tech Publications, Zürich, **2005**, pp. 35

[318] J. Schroers, C. Veazey, M. D. Demetriou, W. L. Johnson, *Journal of Applied Physics* **2004**, *96*, 7723.

[319] J. Schroers, W. L. Johnson, T. Veazey, M. D. Demetriou, Method of manufacturing amorphous metallic foam. USA Patent 7,621,314, **2009** (2004).

[320] T. Wada, A. Inoue, *Materials Transactions* **2004**, *45*, 2761.

[321] A. H. Brothers, D. C. Dunand, *Materials Research Society (MRS) Bulletin* **2007**, *32*, 639.

[322] J. W. Patten, Closed cell metal foam method. USA Patent 4,099,961, **1978** (1976).

[323] J. Banhart, M. Knüwer, Powder Injection and Formation of Porosity in Spray Forming, In *1998 Powder Metallurgy World Congress and Exhibition*, European Powder Metallurgy Association, Shrewsbury, UK, **1998**, pp. 265

[324] J. A. Bjorksten, J. C. Elliot, J. R. Roth, *Foamed metal low density core material for sandwich construction*, Wright Air Development Center, **1953** [http://www.dtic.mil/dtic/tr/fulltext/u2/015741.pdf (accessed 14.10.2012)].

[325] M. Maloney, Personal communication, **2002**.

[326] J. Bjorksten, E. J. Rock, Method for foaming metals. USA Patent 3,707,367, **1972** (1971).

[327] E. J. Rock, J. Bjorksten, Method of mixing with inclined rotary kiln to provide metal foam. USA Patent 3,782,919, **1974** (1972).

[328] J. Bjorksten, E. J. Rock, Continuous process for preparing unidirectionally reinforced metal foam. USA Patent 3,941,182, **1976** (1973).

[329] Anon., *Materials in Design Engineering* **1957**, *46*, 200 & 202.

[330] Anon., *Revue des Produits Chimiques* **1958**, 561.

[331] Anon., *Modern Castings* **1959**, *35*, 37.

[332] Anon., *Chemical Engineering* **1959**, 120.

[333] H. Seliger, U. Deuther, *Freiberger Forschungshefte* **1965**, *103*, 129.

[334] C. B. Berry, Personal communication, **2011**.

[335] A. M. Sabroff, Personal communication, **2011**.

[336] J. T. Wood, Production and applications of continuously cast, foamed aluminum, In *Fraunhofer USA Metal Foam Symposium* (Eds: J. Banhart, H. H. Eifert), MIT-Verlag, Bremen, **1997**, pp. 31

[337] Cymat. Corp. www.cymat.com, [accessed: 20 April 2012].

[338] Leichtmetall Kompetenzzentrum Ranshofen (LKR). www.lkr.at, [accessed: 20 April 2012].

[339] Alulight International. www.alulight.com, [accessed: 20 April 2012].

[340] P. Schäffler, W. Rajner, *Advanced Engineering Materials* **2004**, *6*, 452.

[341] Schunk Group. www.schunk-group.com, [accessed: 20 April 2012].

[342] Honsel AG. www.honsel-ag.de, [accessed: 20 April 2012].

[343] Pohltec Metalfoam GmbH. www.metalfoam.de, [accessed: 20 April 2012].

[344] G. C. Yao, H. Liu, B. N. Song, *Advanced Materials Research* **2012**, *457 - 458*, 253.

[345] M. Judge, *New Scientist* **1997**, *27 September*, 34.

[346] *Metallschäume*, J. Banhart, Ed. MIT-Verlag, Bremen, **1997**.

[347] *Metallschäume 2000*, H. P. Degischer, Ed. Wiley-VCH (Issue 31 of Materialwissenschaft und Werkstofftechnik), Weinheim, **2000**.

[348] *Metal foams*, J. Banhart, H. H. Eifert, Eds., MIT-Verlag, Bremen, **1997**.

[349] *Porous and cellular materials for structural applications*, D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley, Eds., Materials Research Society, Warrendale, **1998**.

[350] *Metal Foams and Porous Metal Structures (MetFoam '99)*, J. Banhart, M. F. Ashby, N. A. Fleck, Eds., MIT Verlag, Bremen, **1999**.

[351] *Cellular Metals and Metal Foaming Technology (MetFoam2001)*, J. Banhart, M. F. Ashby, N. A. Fleck, Eds., MIT Verlag, Bremen, **2001**.

[352] *Cellular Metals: Manufacture, properties and applications (MetFoam2003)*, J. Banhart, N. A. Fleck, A. Mortensen, Eds., MIT Publishing, Berlin, **2003**.

[353] *Porous Metals and Metal Foaming Technology (MetFoam2005)*, H. Nakajima, N. Kanetake, Eds., Japan Institute of Metals, Sendai, Japan, **2006**.

[354] *Porous Metals and Metallic Foams (Metfoam 2007)*, L. P. Lefebvre, J. Banhart, D. C. Dunand, Eds., DEStech Publ., Lancaster, **2008**.

[355] *7th International Conference on Porous Metals and Metallic Foams (MetFoam2011)*, B.-Y. Hur, B.-K. Kim, S.-E. Kim, S.-K. Hyun, Eds., GS Intervision, Seoul, **2012**.

[356] *Cellular Metals for Structural and Functional Applications (CellMet2005)*, B. Kieback, G. Stephani, Eds., Fraunhofer IRB Verlag, **2005**.

[357] *Cellular Metals for Structural and Functional Applications (CellMet2008)*, G. Stephani, Ed. Fraunhofer IFAM, **2009**.

[358] *Cellular Metals and Polymers*, R. F. Singer, C. Körner, V. Altstädt, H. Münstedt, Eds., Trans Tech Publications, Zürich, **2005**.

[359] *Handbook of cellular metals: Production, processing, applications*, H. P. Degischer, B. Kriszt, Eds., Wiley-VCH, Weinheim, **2002.**

[360] G. J. Davies, S. Zhen, *Journal of Materials Science* **1983**, *18*, 1899.

[361] J. Banhart, J. Baumeister, Production methods for metallic foams, In *Porous and Cellular Materials for Structural Applications* (Eds: D. S. Schwartz, D. S. Shih, A. G. Evans, H. N. G. Wadley), Materials Research Society, Warrendale, **1998**, pp. 121

[362] J. Banhart, *International Journal of Vehicle Design* **2005**, *37*.

[363] C. Körner, R. F. Singer, *Advanced Engineering Materials* **2000**, *2*, 159.

[364] J. Banhart, *Mrs Bulletin* **2003**, *28*, 290.

[365] Anon., *Chemical and Engineering News* **1957**, 56.

[366] U. Binder, B. Fritsche, W. Knott, *Advanced Engineering Materials* **2006**, *8*, 778.