Production Methods for Metallic Foams

J. Banhart

Fraunhofer-Institute for Applied Materials Research, Bremen, Germany

Abstract

The possibilities for making metallic foams or similar porous metal structures are reviewed. The various processes are classified according to the state of the starting metal - liquid, powdered, ionised. The most important advantages and disadvantages are presented. In some cases examples of the resulting pore structure are shown.

1. Introduction

Cellular materials are widespread in everyday life and are used for cushioning, insulating, damping, constructing, filtering purposes and many other applications. Highly porous materials are also known to have a high stiffness combined with a very low specific weight. For this reason cellular materials frequently occur in nature as constructional materials (e.g. woods and bones). The fact that even metals and metallic alloys can be produced as cellular solids or metal foams is not as well known as the possibility to foam more traditional engineering materials such as polymers, ceramics or glass. Metallic foams offer interesting perspectives due to the combination of properties which are related to the metallic character on the one and to the porous structure on the other hand.

In the past 40 years many attempts have been undertaken to foam metals or to produce porous metallic structures. In the present review some of the more important and successful procedures are described.

There is no clear cut and generally accepted definition for the term "foam". First of all, one has to distinguish between liquid and solid foams. A liquid foam is a fine dispersion of gas bubbles in a liquid. Cooling down a liquid foam beneath the melting point of the respective material yields a frozen liquid foam which is then clearly a solid foam. What is generally meant in the context of metallic foams are in general solid metallic foams. One could restrict usage of the word "solid foam" to materials which originally emerged from a liquid foam. However, customarily other porous structures such as sintered metal powders are often also called "foams" although they never were in a liquid state. So one often extends the usage of the word "foams" to porous metal structures which are not actually foams but resemble foams regarding their high porosity, the inter-connectivity of the solid material and their irregular structure.

2. Production of foams from metallic melts

A first group of foam making processes starts from the molten metal which is processed to a porous material by foaming it directly, by using an indirect method via a polymer foam or by casting the liquid metal around solid filler materials which reserve space for the pores or which remain in the foam.

2.1. Direct foaming of melts

Metallic melts can be foamed directly under certain circumstances by injecting gases into the liquid. Normally, the gas bubbles which are then formed in the metallic melt will tend to rise to its surface quickly due to the high buoyancy forces in the highdensity liquid but this rise can be impeded by increasing the viscosity of the molten metal. This can be done by adding fine ceramic powders or alloying elements which form particles in the melt.

It should be noted that numerous attempts to foam liquid metals have been undertaken in the 60s and 70s (e.g. [1]), but apparently the processes then invented could not be sufficiently optimised to yield foams of a satisfactory quality and price. In the past ten years, however, a number of new developments have taken place so that nowadays better production routes are available.

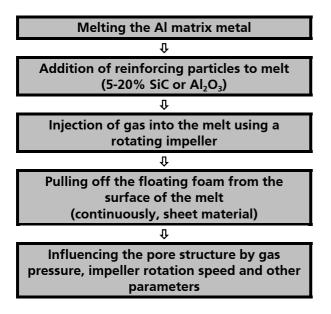


Fig. 1: Direct foaming of melts (MMC foams)

Currently there are two ways for directly foaming metallic melts. One line is being exploited by Cymat (originally by Alcan) in Canada and Hydro Aluminium in Norway [2-5] for foaming aluminium and alloys. According aluminium to this process which is depicted in schematical form in Fig. 1, silicon carbide, aluminium oxide or magnesium oxide particles are used to enhance viscosity. Therefore, the first step consists of making an aluminium melt containing one of these substances. The problem to be solved resembles the one encountered in making ordinary MMCs, namely the problem of wetting the particles by the melt and of achieving homogeneous distribution of the а reinforcing particles [6].

The liquid MMC melt is foamed in a second step by blowing gases (air, nitrogen, argon) into it using specially designed rotating impellers. These impellers have to produce very fine gas bubbles in the melt and distribute them homogeneously. The foam which is generated this way floats up to the surface of the liquid where it can be pulled off by means of a conveyor band. Care has to be taken not to damage the foam structure by

shearing the semi-solid foam too much. The resulting material is in principle as long as desired, as wide as the vessel containing the liquid metal allows it and typically 10 cm thick. The foamed material is either used in the state it comes out of the casting machine having a closed outer surface or is cut into the required shape after foaming. Due to the high content of ceramic particles, machining of the MMC-foams might be a problem. The advantage of the process is the ability of producing large volumes at a rather low price and the low density which can be achieved. Porosities range from 80 to 97%. A possible disadvantage is the eventual necessity for cutting the foam and therefore opening the cells and the brittleness of the MMC foam due to the reinforcing particles contained in the cell walls. However, attempts for making shaped parts by casting the semi-liquid foam into moulds or by shaping the emerging foam with rolls have been undertaken [7,8] thus removing one of these disadvantages. Some properties of such metal foams have been investigated and are given in literature [9,10].

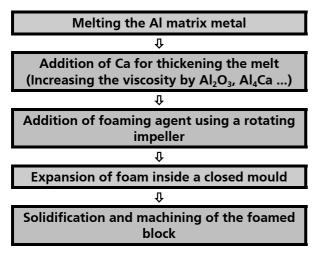


Fig. 2: Direct foaming of melts (ALPORAS-Process)

The second way for foaming melts directly is to add a foaming agent to the melt instead of blowing gas into it [11]. The foaming agent decomposes under the influence of heat and releases gas which then propels the foaming process. For the process which is currently in a state of a small-scale commercial exploitation at Shinko-Wire in Japan, calcium metal is used to stabilise the melt (probably forming an Al₄Ca intermetallic) and titanium hydride TiH₂ serves as the foaming agent releasing hydrogen gas when heated. The foamed aluminium is produced in batches of approximately 2000x1000x600 mm. Typical densities are 0.25 to 0.33 g/cm³. The blocks are cut

into sheets of the required thickness (5 mm to 250 mm, standard thickness 10 mm [12]). The pore structure of the material - named ALPORAS - is rather uniform [13]. Mechanical [13] and sound absorption properties [14] have been measured. The material has been reported to be more expensive than the MMC foams described above.

2.2 Solid-gas eutectic solidification (GASARS)

A method which was developed some years ago in the Ukraine [15] exploits the fact that some liquid metals form a eutectic system with hydrogen gas. By solving hydrogen in these metals under high pressure (typically 50 atms) one first prepares a melt which is pore free with the hydrogen completely solved in the metal (see Fig. 3). If one then reduces temperature and pressure, one forces the melt to go through the two-phase regions. Beneath the eutectic temperature one arrives at a two-phase field corresponding to a solid plus the gas. If the process parameters - cooling rate and pressure profile - are chosen appropriately the gas will accumulate in fine gas bubbles in

the solid, thus forming a foam [16]. The possibility of solidifying the liquid directionally offers the advantage of making foams with elongated pores. If the casting vessel is cylindrical, radial and axial pores can be made [17]. The maximum porosities which can be achieved by this process are not very high (5-75%) but metals with medium and high melting points such as copper and nickel can be foamed. The pore structure of such foams - called *GASARS* - is somewhat problematic [18,19] so that further improvements have to be awaited. The mechanical properties (compression and tension) of GASARS have been characterised recently [20-22].

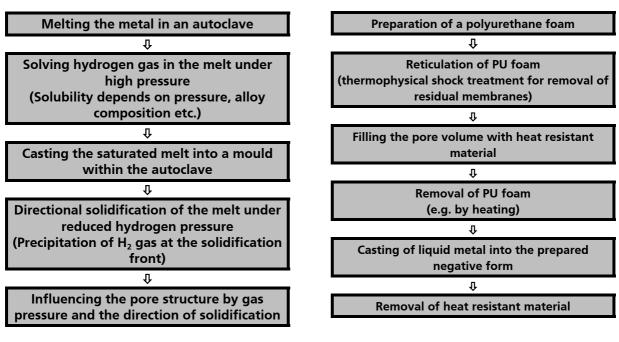


Fig. 3: Foaming metals by the GASAR process

Fig. 4: Making metallic foams by investment casting

2.3. Investment casting

Metal foams can also be fabricated without directly foaming the metal [23,24]. For this a polymer foam is used as a starting point (Fig. 4). The polymer foam is processed into a structure with open pores by manipulating the foaming process or by a subsequent

reticulation treatment. The resulting foam is then filled with a slurry of heat resistant material, e.g. a mixture of mullite, phenolic resin and calcium carbonate [24]. After drying the polymer is removed and molten metal is cast into the resulting open voids which exactly represent the original foam structure. After removal of the mould material (e.g. by water under high pressure) a metallic foam is obtained which is an exact image of the original polymer foam.

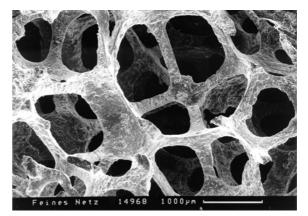


Fig. 5: SEM image of a metal foam made by investment casting (DUOCEL)

Fig. 5 shows a micrograph of such a foam which is being sold by ERG in California under the trade name DUOCEL. Various grades are available ranging from 2.5 to 16 pores per cm (10 to 40 ppi). Complex shaped parts can be fabricated by pre-forming the polymer foam. Prices have been reported to be high. Aluminium alloys are usually used but other metals can also be processed. The densities and foam morphologies are of course determined by the polymer foam. Porosities typically range from 80 to 97%.

2.4. Syntactic foams using filler materials

Light-weight porous metals can be produced by casting around inorganic granules or hollow spheres of low density or by infiltrating such materials with a liquid melt. A loose bulk of expanded clay granules, foamed glass spheres of aluminium oxide hollow spheres can be used for this [25,26]. The granules are then introduced into the melt or the melt is poured over the bulk of filler material. The heat capacity and conductivity of the granules is very low and therefore does not disturb the flow of the metal too much. Due to the high surface tension of the liquid metal wetting of the granules is a problem and in general the interstices between the granules will not be filled completely. Creating a slight vacuum or an external pressure facilitates infiltration significantly. A wide range of metals can be processed this way including aluminium, magnesium, zinc, lead, tin etc. Parts of a predefined shape can be fabricated by designing a mould of the appropriate geometry. Sandwich panels have also been made [27].

3. Foams made from metal powders

Instead of the molten metal, metal powders can be used to make porous metallic structures.

3.1. Fraunhofer Process

Foamed metals can be produced by a powder metallurgical method invented and patented [28-30] at Fraunhofer-Institute in Bremen (Fig. 6).

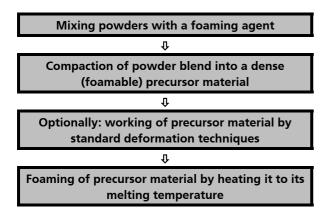


Fig. 6: Powder metallurgical process for making foamed metals

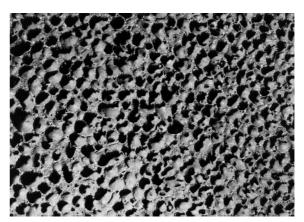


Fig. 7: Lead foam made from metal powder (scale approx. 4:1)

For the production of foamed aluminium commercial powders of aluminium or aluminium based alloys are mixed with a foaming agent and are then compacted. As a result a semi-finished product is obtained in which the foaming agent is homogeneously distributed within a dense, virtually non porous metallic matrix. This foamable material can be processed into sheets, rods, profiles etc. by conventional techniques like rolling, swaging or extrusion. Finally, foamed metal parts are obtained by merely heating the material to temperatures above the melting point of the matrix metal. The density of metal foams can be controlled by adjusting the content of foaming agent and several other foaming parameters. The porosity ranges between 50 and 92%, but for aluminium the preferred range is from 80 to 85%. If metal hydrides are used as foaming agents, a content of less than 1% is sufficient in most cases. The method is not restricted to aluminium: tin, zinc, brass, bronze and lead can also be foamed by choosing appropriate foaming agents and process parameters. An example for the pore structure of a metal foams made in this way is shown in Fig. 7.

A more detailed description of the process is given elsewhere [31-34]. The mechanical and other physical properties have been characterised [35-37]. The process is now being extended to metals with higher melting points, e.g. iron and steel [38,39].

3.2. Gas Entrapment

Metals can be foamed without using a propelling agent by compressing powders to a precursor material and allowing gas to be entrapped in the metal structure during compaction [40,41]. Heating the precursor material then leads to an expansion of the metal due to the internal pressure created by the entrapped gas. The process has mainly been designed for making porous titanium structures. For this titanium powder is filled into a can which is then evacuated and refilled with argon gas. The filled can is densified by hot isostatic pressing, subsequently worked and finally foamed by means of an appropriate heat treatment.

3.3. Foaming of Slurries

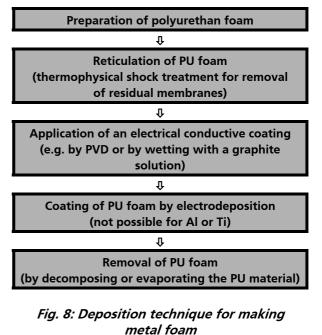
Metallic foams can also be produced by preparing a slurry of metal powder mixed with a foaming agent. The slurry is poured into a mould after mixing and dried there at elevated temperatures. The slurry becomes more viscous and starts to foam as gas begins to evolve. If sufficient stabilising measures have been taken the expanded slurry can be dried completely thus obtaining a metal foam. Such foams have been produced from aluminium powders using orthophosphoric acid with aluminium hydroxide or hydrochloric acid as a foaming agent [42]. Relative densities down to 7% have been achieved but there are problems with low strength [43] and cracks in the foamed material.

3.4. Other techniques

There are many ways to make porous metallic products from metal powders, fibres or hollow spheres. The easiest way is to sinter loose powder fillings in a canister yielding a porous material with open porosity. Mixtures of metal powders and polymer binders can be extruded and then heat treated to produce porous parts [44]. Reaction sintering of metal powder mixtures is also known to yield porous products. Finally, hollow spheres made from titanium or steel, e.g., can be used to build highly porous structures by sintering. Ordered and disordered arrangements can be realised.

4. Deposition techniques

Deposition techniques start from the ionic state of metals. The metal is galvanically deposited on a polymeric foam with open cells [45,46]. This process and the investment casting process therefore have in common that the actual foaming does not take place in the metallic state but with a polymer which is then replaced by a metal. Galvanic deposition on a polymer foam requires some electrical conductivity of the initial polymer foam. This is achieved by dipping the polymer foam into graphite solutions or by coating it with a thin conductive layer bv metal vaporisation. After electroplating the polymer can be removed from the metal/polymer composite by thermal treatment. Foams of various grades can



be fabricated ranging from 2 to 30 cells per cm (6 to 70 ppi). The preferred metal is nickel or a nickel-chrome alloy but copper foams can also be fabricated. Foams have been offered on a commercial basis under the name RETIMET (Dunlop Ltd., GB) and

CELMET (Sumitomo, Japan, [46]). Recently material has also been offered by a Belorussian company [47]. Sheets with thicknesses between 2 and 10 mm are available with densities ranging from 0.2 to 0.5 g/cm³.

Summary

There is a large variety of methods for producing metallic foams or similar porous metal structures starting from liquid metal, powdered metal or from an electrolyte containing metal ions. Each process works for a selection of metals or alloys and produces foams of a typical morphology and density range. The development of aluminium-based foams has been especially promoted by the request for certain structural light-weight applications so that the widest range of foams is available for this metal and its alloys. The cost effectiveness of each process is different meaning that only few methods are suited for a high-volume mass production. Many of the methods will always be restricted to specialised applications where cost is not the most important parameter.

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