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Current state of metal foaming technology

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Abstract

Metallic foams have become an attractive research field both from the scientific viewpoint and the prospect of industrial applications. Various methods for making such foams are presented and discussed. Some techniques start from specially prepared molten metals with adjusted viscosities. Such melts can be foamed by injecting gases or by adding gas-releasing blowing agents which cause the formation of bubbles during their in-situ decomposition. A further way is to prepare supersaturated metal-gas systems under high pressure and initiate bubble formation by pressure and temperature control. Yet a further class of techniques starts from metal powders. One mixes such powders with a blowing agent, compacts the mix and then foams the compact by melting. The various foaming processes, the foam stabilising mechanisms and some known problems with the various methods are addressed and some possible applications for metallic foams presented.

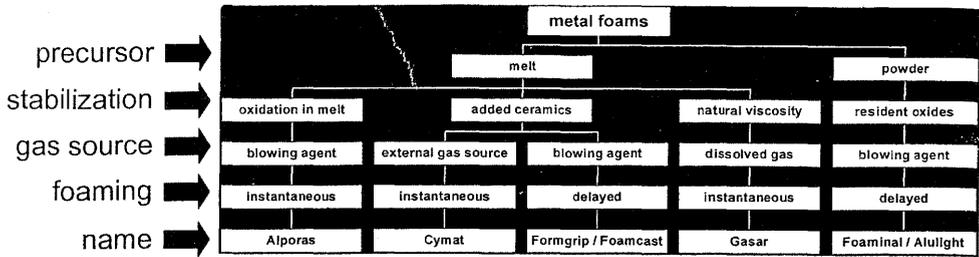


Figure 1. „Family tree“ of metal foams [1].

various methods as will be explained later. Some methods have been given a name, others are named by the manufacturer.

Production methods for metallic foams

Under certain circumstances metallic melts can be foamed by creating gas bubbles in the liquid. Normally, gas bubbles which are formed in a metallic melt tend to quickly rise to its surface due to the high buoyancy forces in the high-density liquid, but this rise can be hampered by increasing the viscosity of the molten metal. This can be done by adding fine ceramic powders or alloying elements which form stabilising particles in the melt, or by other means. Currently there are three ways for foaming metallic melts: firstly, by injecting gas into the liquid metal from an external source, second, by causing an in-situ gas formation in the liquid by admixing gas-releasing blowing agents to the molten metal, third, by causing the precipitation of gas which was previously dissolved in the liquid.

Foaming of melts by gas injection („Cymat“)

The first way for foaming aluminium and aluminium alloys was originally developed by Hydro Aluminium in Norway[2] and Alcan International in Canada. Cymat Aluminium Corp. [3] has taken over the activities and is currently exploiting this foaming technology. According to this process described schematically in Fig. 2a, silicon carbide, aluminium oxide or magnesium oxide particles are used to enhance the viscosity of the melt. Therefore, the first step comprises the preparation of an aluminium melt containing one of these substances. This step reportedly requires some sophisticated mixing techniques to ensure a uniform distribution of particles. A variety of aluminium alloys can be used.

The melt is foamed in a second step by injecting gases (air, nitrogen, argon) into it using specially designed rotating impellers or vibrating nozzles. These generate very fine gas bubbles in the melt and distribute them uniformly. The resultant viscous mixture of bubbles and metal melt floats up to the surface of the liquid where it turns into a fairly dry liquid foam as the liquid metal drains out. The foam is relatively stable owing to the presence of ceramic particles in the melt. It can be pulled off the liquid surface, e.g. with a conveyor belt, and is then allowed to cool down and solidify. The resulting solid foam is in principle as long as desired, as wide as the vessel containing the liquid metal allows it, and up to 10 cm thick. Cymat Corp. claims that they can make panels up to 16.66 x 1.33

final product. This obviously has a pronounced effect on the mechanical properties which become anisotropic [8]. The situation could be improved, e.g. by pulling the foam off vertically. 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. Owing to the high content of ceramic particles, machining of MMC-foams can be a problem.

Advantages of the direct foaming process include the large volume of foam which can be continuously produced and the low densities which can be achieved. MMC foams are therefore probably less expensive compared to other cellular metallic materials. A possible disadvantage of the direct foaming process is the eventual necessity for cutting the foam, thereby opening the cells. This disadvantage, however, could be possibly removed if one could pour the semi-liquid foam into moulds to make complex near-net shape parts. This would also allow to fill tubes with foam without having to cut the filler out of a larger block and bond it to the tube with adhesives.

In order to avoid some of the unwanted side effects of stabilising additives to metallic melts (e.g. brittleness), it was suggested to foam pure, additive-free metallic melts with inert gases [1]. In order to keep viscosity low the foaming process has to take place at temperatures very close to the melting point. This can be done by bubbling gas through a melt which is constantly cooled down, e.g. in a continuous casting process. The bubbles are then caught in the solidifying liquid and form a foam-like structure. In the liquid state such systems are very unstable in contrast to particle-stabilised metals which can be kept liquid for some time.

Foaming of melts with blowing agents („Alporas“)

A second way for foaming melts directly is to add a blowing agent to the melt instead of injecting gas into it. The blowing agent decomposes under the influence of heat and releases gas which then propels the foaming process. This is shown in Fig. 3a for a currently used implementation of the method [9]. Shinko Wire Co., Amagasaki (Japan) has been producing foams in this way since 1986 with production volumes reportedly up to 1000 kg foam per day. In a first step about 1.5 wt.% calcium metal are added to an aluminium melt at 680°C. The melt is stirred for several minutes during which its viscosity continuously increases by a factor of up to 5 owing to the formation of calcium oxide (CaO), calcium-aluminium oxide (CaAl_2O_4) or perhaps even Al_4Ca intermetallics which thicken the liquid metal. Fig. 3b shows the effect of stirring on the viscosity of aluminium melts with various calcium additions [10]. After the viscosity has reached the desired value, titanium hydride (TiH_2) is added (typically 1.6 wt.%) which serves as a blowing agent by releasing hydrogen gas in the hot viscous liquid. The melt soon starts to expand slowly and gradually fills the foaming vessel. The foaming takes place at constant pressure. After cooling the vessel below the melting point of the alloy the liquid foam turns into solid aluminium foam and can be taken out of the mould for further processing. The entire foaming process can take 15 minutes for a typical batch (2050 x 650 x 450 mm³). It has been shown that a careful adjustment of process parameters leads to very homogeneous foams (see Fig. 3c). In fact, the foams produced in this way - trade name "Alporas" - seem to be the most homogeneous aluminium foams currently available. There is an empirical relationship not only between average cell diameter and the viscosity of the melt but also between the final foam density and viscosity [10]. Typical densities after

Solid-gas eutectic solidification ("Gasar")

A method developed about a decade ago [11] exploits the fact that some liquid metals form a eutectic system with hydrogen gas. By melting one of these metals in a hydrogen atmosphere under high pressure (up to 50 atms.), one obtains a homogeneous melt charged with hydrogen. If one then lowers the temperature, the melt will eventually undergo a eutectic transition to a heterogeneous two-phase system, "solid + gas". If the composition of the system is sufficiently close to the eutectic concentration, there will be a segregation reaction at one temperature. As the melt is solidified gas pores precipitate and are entrapped in the metal. The resulting pore morphologies are largely determined by the hydrogen content, the pressure over the melt, by the direction and rate of heat removal and by the chemical composition of the melt. Generally, largely elongated pores oriented in the direction of solidification are formed (see Fig. 4). Pore diameters range from 10 μm to 10 mm, pore lengths from 100 μm to 300 mm, and porosities from 5 to 75%. The pore size distribution is non-uniform because of concurrent growth of small and large pores and coalescence. Pores may be conical or even corrugated. For the porous materials formed by solid-gas eutectic solidification, the word „*gasar*“ was coined meaning „gas-reinforced“ in a Russian acronym.

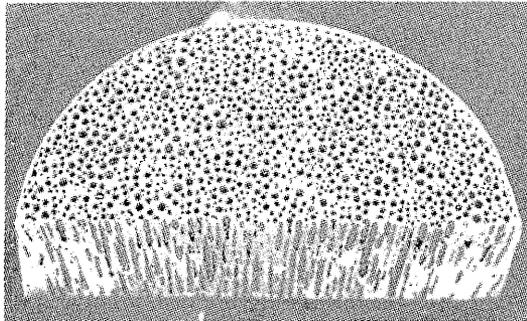


Figure 4. „Gasar“ showing largely elongated pores (source: V. Shapovalov).

Foaming of powder compacts („Foaminal/Alulight“)

Foamed metals can be also prepared from metal powders [12][13]. The production process begins with the mixing of metal powders - elementary metal powders, alloy powders or metal powder blends - with a blowing agent, after which the mix is compacted to yield a dense, semi-finished product (see diagramme in Fig. 5a). In principle, the compaction can be done by any technique that ensures that the blowing agent is embedded into the metal matrix without any notable residual open porosity. Examples of such compaction methods are uniaxial or isostatic compression, rod extrusion or powder rolling. The manufacture of the precursor has to be carried out very carefully because residual porosity or other defects will lead to poor results in further processing. Heat treatment at temperatures near the melting point of the matrix material is the next step. The blowing agent, which is homogeneously distributed within the dense metallic matrix, decomposes. The released gas forces the melting precursor material to expand, thus forming its highly porous structure. The time needed for full expansion

depends on temperature and the size of the precursor and ranges from a few seconds to several minutes. The method is not restricted to aluminium and its alloys: tin, zinc, brass, lead, gold and some other metals and alloys can also be foamed by choosing appropriate blowing agents and process parameters.

Foaming a piece of precursor material in a furnace results in a lump of metal foam with an undefined shape unless the expansion is limited in certain directions. This is done by inserting the precursor material into a hollow mould and expanding it by heating. In this way near-net shaped parts can be obtained which have a closed outer skin and a highly porous cellular core [14]. Quite complicated parts can be manufactured by injecting the still expanding foam from a reservoir into suitable moulds [15].

Sandwich panels consisting of a foamed metal core and two metal face sheets can be fairly easily obtained by bonding the face sheets to a piece of foam with adhesives. Alternatively, if pure metallic bonding is required, conventional sheets of metal - aluminium or steel - are roll-clad to a sheet of foamable precursor material [16][17]. The resulting composite can be deformed in an optional step, e.g. by deep drawing. The final heat treatment, in which only the foamable core expands and the face sheets remain dense, then leads to sandwich structures such as the one shown in Fig. 5b. Aluminium foam can be combined with steel or titanium face sheets as well as with aluminium face sheets. In the latter case, care has to be taken not to melt the face sheets during foaming, e.g. by choosing alloys with different melting points of the core material and the face sheets. A large aluminium/aluminium foam sandwich was developed in a joint effort by the German car maker Karmann in Osnabrück and Fraunhofer-Institute in Bremen for a concept car in which structural aluminium foam applications were demonstrated [18]. Such sandwiches are 3D-shaped, up to 2 metres in length and about 1 metre in width.

The powder compact melting method is now in the stage of a small-scale commercial exploitation by the German companies Schunk (Gießen) and Honsel (Meschede) and the Austrian companies Alulight (Ranshofen) and Neuman Alufoam (Markt). The names "Foam-in-Al" and „Alulight“ have been coined for these foams.

Foaming of ingots containing blowing agents („Foamcast/Formgrip“)

A recent development concerns a modification of the powder compact melting process. One tries to prepare a foamable precursor material by incorporating titanium hydride particles directly into an aluminium melt instead of using powders. To avoid premature hydrogen evolution the melt has to be either quickly cooled down below its melting point after mixing or the blowing agent has to be passivated to prevent it from releasing gas already in the stage of mixing. The former route was carried out in a die-casting machine. The powdered hydride is injected into the die simultaneously with the melt [19]. Normal casting alloys such as A356 without ceramic additives have been used. The resulting cast part is virtually dense and can be foamed by re-melting in complete analogy to the powder-based route described in the previous section. However, achieving a homogeneous distribution of TiH_2 powders in the die is challenging. The latter route requires that TiH_2 powders be subjected to a cycle of heat treatments that form an oxide barrier on each particle and delay decomposition. The powders are then added to a melt and can be cooled at comparatively slow rates after stirring [20]. In order to obtain stable



Figure 7. Microstructure of a foam made by injecting gas into a SiC reinforced melt („Alcan”-foam).

- of the foam films with perhaps a slight tendency for an accumulation at the film surfaces.
- Al-, Ca- or mixed oxides which are *formed* in the melt by internal oxidation after adding Ca metal and stirring in the Alporas process. The source of oxygen could be alumina or other oxides which are in the melt already before adding calcium or air which is dragged into the melt during agitation. A micrograph of a foam of type „Alporas“ is shown in Fig. 8. One can distinguish two different types of precipitates: light grey precipitates, the majority of which is about 10 μm in diameter and a small fraction of smaller dark grey inclusions which are connected to the light grey particles and which are about 3 μm in diameter. Energy-dispersive X-ray analysis yields an estimate for their composition: the light grey areas contain roughly 5 at.% Ca, 12.5 at.% Ti and 5 at.% O, the dark areas 12 at.% Ca, 2 at.% Ti and 6 at.% O. The measurements of the dark areas, however, should not be taken too literally because of their small size. The values obtained are in a reasonable agreement with values found in the literature [7]. Thus it can be suspected that the precipitates contain various mixed oxides of Al, Ca and Ti such as Al_2CaO_4 or $\text{Al}_2\text{Ca}_3\text{O}_6$, or oxide mixes $\text{Al}_2\text{O}_3+\text{TiO}_2$ [23], or intermetallic compounds of the type Al_4Ca , Al_2Ca or Al_3Ti [24], see also Ref. [25]. There is no evidence that the precipitates are concentrated on or near the interface bubble/air but they seem to be fairly evenly distributed over the cross-section of the cell walls. One can easily find parts of the bubble surface which do not contain any precipitates. This casts doubts on the



Figure 9. Lead foams made from two different lead powders. Left: low-oxygen powder (0.06 wt.%), right: higher oxidised powder containing 0.46 wt.% O) [28].

- (i) *where* are the solid particles located in the foam? Are they incorporated into the metal or do they rather segregate? Their behaviour is governed by the wettability of the particles by the melt commonly described by the contact angle between the two. This angle is primarily determined by the chemical composition of the particle but probably also by its size, shape, surface roughness and concentration in the liquid. For the SiC stabilised Al foams of the „Hydro/Alcan“- and Formgrip-type it has been claimed that particles actually accumulate on the inner walls of bubbles and are partially wetted [20][22]. This view, however, is not supported by the work of the author (Fig. 7) and the micrographs shown in Ref. [7] are not definite on this either. For the foams made by powder compact melting the oxides have not yet been seen by direct observation. All one knows is that aluminium powder compacts have oxide contents up to 1 wt.% and that the foams show oxide layers on their surfaces which are 30 nm thick after foaming under argon [27]. However, part of this oxide might have formed by reactions with residual oxygen in the foaming chamber. Recent real-time X-ray observations of the foaming process of aluminium foams have revealed that oxidation of evolving foams increase the apparent viscosity of films which are near to the surface and are therefore exposed to oxygen [29]. However, this effect should not be confused with the postulated effect of particles accumulating on the film surface.
- (ii) *how* does a given configuration of ceramic particles and metal films influence foam stability? Various mechanisms have been proposed:
 - uniformly dispersed solid particles increase the bulk viscosity of melts. This slows down the vertical motion of liquid metal and contributes to kinetic foam stability. Especially in thin films there could be a progressive effect when the solid particles touch and built barriers. As the films get thinner, these barriers build up and become less penetrable to the melt thus creating a self-stabilising mechanism by a kind of additional „structural viscosity,. Moreover, as viscosity drops with rising temperature, liquid metallic foams are more stable if one keeps them at temperatures close to the melting point.
 - it was suggested [22] that solid particles lead to flatter curvatures around the Plateau borders and therefore to a reduced suction of metal from the films into the borders. However, no experimental verification for this is known and no theoretical explanation for this effect was given.
 - It has been derived that the wetting angle has to be in a certain range to ensure that i) the bubble/particle interfaces are stable when the bubbles rises through the melt, i.e. the particles are not stripped off the bubbles, ii) that the particles on the interface lower the total energy of a pair of bubbles with particles in between, i.e. stabilise

- databases and design guidelines for metallic foams have to be created and disseminated. There has been some movement on this field recently [30],
- *foams are too expensive.* Mass production will lead to lower prices but metal foam will never be a really cheap material. Therefore, the selection of applications where the specific properties of foams are fully exploited is indispensable. Because this search cannot be done without a detailed knowledge of the properties of foams and of the limits of foaming processes design engineers will not start such a search: a vicious circle.

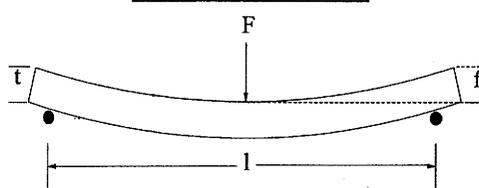
Properties

The properties of metal foams stem both from the properties of the matrix metal or alloy and from the specific morphology of the foam. The microstructure of the alloy is more complex than that of conventional dense metal both due to the stabilising particles dispersed in the solid and also because the solidification of the material after foaming is somewhat undefined and non-uniform. The morphology of foams varies a lot between different types of foams but also between the same foam type but different densities. For this reason metal foams show very complex relationships between properties and the parameters describing the foam, making it very hard to summarise foam properties in data sheets. However, there has been a lot of research on this field and rules could be derived which have some universality. For many properties, e.g., power laws of the form $A \propto \rho^n$ have been established, which link the property A of a foam with its density ρ . However, one usually observes a large scatter in the observable A if one compares

Table 1. Some of the most relevant quantities used for characterising metallic foams.

class	sub-class	observable	
mechanical	elastic	Young's modulus	E
		shear modulus	G
	anelastic	loss factor	η
		plastic	compressive/tensile strength
	shear strength		σ_s
	bending strength		σ_b
	toughness		K_{IC}
		indentation resistance	F_i/a
	energy absorption	E_{abs}	
electrical	conduction	electrical conductivity	σ
thermal	expansion	expansion coefficient	α
	conduction	thermal conductivity	κ
acoustic	absorption	sound absorption coefficient	$\alpha(v)$
hydro/aero-dynamic	flow	filter parameters	α, β

Deflection of rectangular beam

$$m = \frac{1}{2} \sqrt{\frac{Fl^5}{f} \left(\frac{\rho}{\sqrt{E}} \right)}$$


Example: $l=1\text{m}$, $f=1\text{cm}$, $F=800\text{N}$

material	ρ g/cm ³	E GPa	ρ/\sqrt{E} g cm ⁻³ MPa ^{-1/2}	m kg	t mm
steel	7.8	200	17.4	2.5	18
aluminium	2.7	69	10.3	1.5	24
concrete	2.5	47	11.5	1.6	25
glass	2.5	69	9.5	1.3	23
CFRP (ud)	2.0	40	10.0	1.4	26
GFRP (ud)	1.5	270	2.9	0.4	16
Al foam	0.5	5	7.1	1.0	45
PU foam	0.1	0.06	12.9	1.8	134

Figure 10. Potential of aluminium foams for light-weight construction .

SLK. The concept is to use AFS-sandwich panels as shown in Figure 11. These sandwich panels are 3D-shaped and very stiff at a relatively low weight. In combination with new constructional principles they could replace conventional stamped steel parts in a car. At the same time they could also reduce the number of parts in the car frame, facilitate assembly and therefore reduce costs while improving performance because such sandwich panels act as vibration dampers.

- *Energy-absorption*: owing to their structure foams can absorb a large quantity of mechanical energy when they are deformed while stresses are limited to the compression strength of the material. Metal foams with their high strengths can therefore act as high-capacity impact energy absorbers. Examples include front impact or side impact absorbers for cars or underride protectors for lorries.
- *Acoustic and thermal control*: Foams can damp vibrations and absorb sound under certain conditions. Moreover, their thermal conductivity is low. These properties are not outstanding – polymer foams are much better sound absorbers – but they could be useful in combination with other features the foam shows.

Currently automotive industry has various applications in mind that exploit one or more typical properties of metal foams. Other industries, such as building industry, machine construction and even aerospace industry has similar ideas.

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Further source of information include:
32. URL <http://www.metalfoam.net> . This site contains literature, links, news etc. and is updated regularly.
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