

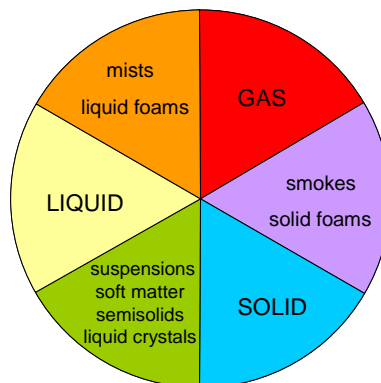
# On the road again: metal foams find favor

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## Gas, liquid, solid...

The three states of matter are well represented by earth, sea and sky. God saw that it was good, and so did many generations of physics lecturers. But purity is obscurity, as Ogden Nash reminded us. The rich variety of combinations of gas, liquid and solid that are found in nature's creations and man's artefacts present us with an infinity, rather than a trinity, of possibilities (**Figure 1**).

Today solid state physics has extended its horizons to encompass all of condensed matter and the wide world of materials science. We share with the physical chemist and the industrial engineer an eclectic interest in the exceptional properties that can emerge from mixed phases. For example, an ice cream, consisting of crystalline solids, liquid and gas, is much more than the sum of its parts. Offered separately they might provide the same nutritional value but the pleasure of consumption would be lost. Here structure is as important as composition, and it owes more to culinary artifice than the laws of thermodynamics. In this metastable world of mixed-phase structures, science meets art. The current interest in such things was heralded in the fifties by the MIT metallurgist Cyril Stanley Smith, whose testament was *A Search for Structure* [1].



**Figure 1.** Examples of mixed-phase states.

Smith was particularly attracted to the elegant liquid/gas system that is called a *foam*, as a prototype for much of materials science. It is typically disordered and each sample is a product of its particular history, yet its internal local arrangements are not arbitrary. They

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conform to rules dictated by surface tension, that were expounded by the blind Belgian physicist Joseph Plateau in the 19<sup>th</sup> century. These rules require that only three of the thin films that separate bubbles may meet on a line (a Plateau border), and only four of these lines can meet at a point. Films and lines meet symmetrically, at equal angles. Strictly the rules apply only in the limit of zero liquid fraction, but foams often have low liquid fractions and conform well to these requirements [2].

The beautiful structure described by Plateau is common to most liquid foams, and hence also to the solid foams that result from freezing them. Those encountered in everyday life include polyurethane and polystyrene products for cushioning, packaging and insulation. Many other materials, such as ordinary glass, can be foamed. Even metals are produced in this form. A comparatively new entry in the foam catalogue, they are attracting a lot of attention, as promising applications are identified.

### **Light, stiff, crushable**

The relative density of a solid metal foam (density divided by that of its solid constituent) is typically less than 15 percent. It consists primarily of a network of thin frozen Plateau borders, meeting at junctions which usually have the prescribed tetrahedrally symmetric form.

In their classic book on solid foams Lorna Gibson and Michael Ashby pursued many simple scaling relations for physical properties of relevance to engineering [3]. An important example is Young's modulus, since this determines the stiffness of a panel or a beam. Assuming that the thin struts make the dominant contribution to elastic properties, the Young's modulus  $E$  is predicted to scale as

$$E \approx (\text{relative density})^{1.5}.$$

For real foams the empirical law that one finds is closer to

$$E \approx (\text{relative density})^2.$$

The stiffness of a panel, i.e. its resistance to bending, varies as its thickness *cubed*. So if a dense metal panel is replaced by a foam panel of the same weight but five times thicker, its bending stiffness increases by the same factor of five. The stiffness/weight ratio is often an important figure-of-merit for the structural engineer.

Metal foams offer another benefit, having to do with their deformation under high loads. Different types of solid foam behave in different ways when large deformations are imposed and the network buckles. In a polyurethane cushion the struts undergo the familiar Euler buckling of an elastic beam under compression, so that the original structure is recoverable upon removal of the applied load and remains undamaged. Metal foams fail irreversibly. Depending on the type of alloy the foam is made of, the cells either suffer brittle fracture or deform plastically without breaking, or even show a more complicated deformation pattern. In each case there is a certain yield stress at which strongly non-linear effects enter into play. Which foam is selected depends on the application in question.

Most foams collapse gradually under the critical compressive load, until a high degree of compaction is achieved. This process absorbs a great deal of mechanical energy, and herein lies the second main attraction of metal foams, which have a high yield stress compared to polymer foams. Add to this the compatibility with much of existing automobile technology of

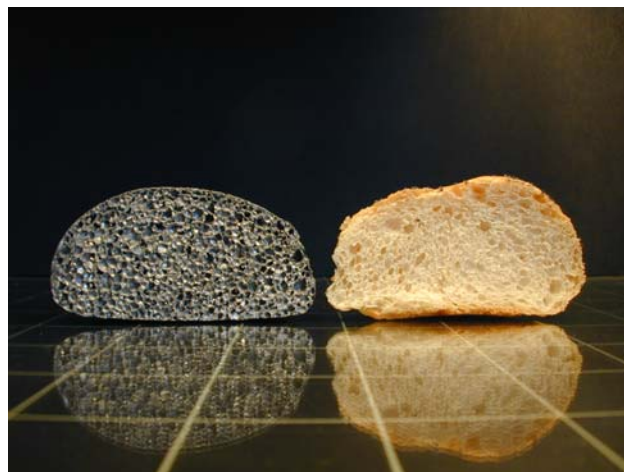
metal forming and welding, and the motivation for current research becomes obvious. The intended fate of some metal foam is to be crushed in a crash, as one of those sacrificial elements of modern vehicle design that are deliberately intended to collapse, in order to save the passenger from experiencing something similar. It might be termed “heavy-duty polystyrene” as one cubic centimetre of aluminium foam can absorb up to 10 Joules of mechanical energy if crushed to 20% of its original length.

### **But can we make it?**

In 1943 Benjamin Sosnick [4] attempted to foam aluminium with mercury. He first melted a mix of Al and Hg in a closed chamber under high pressure. The pressure was released, leading to vaporisation of the mercury at the melting temperature of aluminium and to the formation of a foam.

Less hazardous processes were developed in the 1950's when it was realised that liquid metals could be more easily foamed if they were pretreated to enhance viscosity. This could be done by oxidising the melt or by adding oxide particles. William Elliott and Stuart Fiedler at Bjorksten Research Laboratories (BRL) developed an aluminium foaming process for the U.S. Navy in the late 1950's. BRL subsequently entered into an agreement with the LOR Corporation to develop commercial uses for foamed aluminium. A pilot plant was constructed at BRL to produce 4' × 8' × 1" thick wall panels. Other potential uses, such as crush bumpers for cars, were also investigated. In the late 1960's, the entire operation was sold to the Ethyl Corporation and the pilot plant was moved to Baton Rouge. BRL continued for several years to investigate methods for foaming other metals such as lead and zinc.

Two methods for foaming metals were used in those early days, and they are still current today. In the first of these, gas is injected continuously to create foam. In the second method, gas-releasing propellants are added to the melt, akin to the blowing agents of the plastic foam industry or indeed the yeast of the baker (see [Figure 2](#)). Aluminium was found to be particularly amenable to foam production. The Ethyl Corporation produced material of remarkably high quality around 1972 which was given to the Ford Motor Company for evaluation. Why was this initial development not successful? Certainly it was not the time for light-weight materials in the era of seemingly unlimited energy supply, and issues of safety and recycling were not so important as now. Perhaps also the disordered nature of the material caused some raised eyebrows in Quality Control. Whatever the reason, the excitement and the level of R&D activities both declined after 1975.



**Figure 2.** Zinc foam and bread roll, both 8 cm wide (HMI Berlin)

By the end of the eighties there was a resurgence in metal foam research throughout the world. Japanese engineers at Shinko Wire Co. developed what is now known as the *Alporas* process. Norsk Hydro in Norway and Alcan Corp. in Canada independently developed a foaming process for particle-stabilised melts. In 1990 an old powder-compact foaming route developed in the late 1950's by Benjamin Allen at the United Aircraft Corporation in Delaware was rediscovered by German physicist Joachim Baumeister and brought to a considerable level of sophistication at the Fraunhofer Laboratory in Bremen, Germany. These and other variants have been continually refined up to the present day.

The accompanying box (including **Table 1**) summarises processes which have the potential to be used to make large slabs and structural components [5]. Most of the resulting foam products have closed cells. A certain degree of open porosity can be achieved by such post-treatments as rolling. Alternatively, there is a quite different process, that of investment casting, by which metal foams are made as replicas of open-celled plastic foams.

Industrial processes for metal foam production					
	metal foams				
foaming route	direct foaming of melt			indirect foaming via precursor	
stabilization	ceramics added to melt	oxide formation in melt	viscosity of melt	oxides in powder compact	ceramics added to melt
gas source	external gas source	blowing agent	dissolved gas	blowing agent	blowing agent
name of process	Hydro / Alcan / LKR-HKB	Alporas	Gasar	Foaminal / Alulight	Formgrip

**Table 1.** Practical methods for making large quantities of metal foam

In the *Alcan/Hydro* process, liquid metals - usually aluminium alloys – are foamed directly by injecting gas. Silicon carbide is commonly added in volume fractions as high as 10-20%. Foam can be continuously drawn off the surface of the melt on a conveyor belt, and slabs with a cross section of 100×400 mm<sup>2</sup> can be produced in lengths up to 16 m. Foam densities range from 0.07 to 0.54 g/cm<sup>3</sup>, average bubble sizes 3 to 25 mm. The Canadian company Cymat is industrializing the process.

The *Alporas* process foams a pool of aluminium by adding titanium hydride powder which serves as blowing agent. The aluminium melt is thickened by adding calcium that forms fine mixed oxides in the melt. The foaming vessel in use at Shinko Wire produces blocks of size 2050 x 650 x 450 mm<sup>3</sup>.

The *Gasar* process foams metal by supersaturating a liquid with hydrogen under high pressure and temperature, after which it is solidified. Gasar is a Russian acronym which stands for “gas-reinforced”.

The *Alulight/Foaminal* process, starts from a compacted mixture of metal and blowing agent powders, e.g. aluminium and titanium hydride. Re-melting the precursor leads to in-situ gas evolution within the metal as the blowing agents sets free hydrogen gas. *Alulight* and *Foaminal* are commercial trade names for the resulting solid material. Closed moulds can be filled with foam and structural foam parts of complex shape can be manufactured as well as shaped sandwich panels with two dense face sheets and a cellular core [5][6].

The *Formgrip* process starts from a melt in which blowing agent powder is dispersed after which it is solidified to form a solid precursor which can later be foamed by re-melting [7]. “Formgrip” means “foaming of reinforced metals by gas release in precursors”.

**Box 1.** Industrial processes for metal foam production

**The physics of metal foaming**

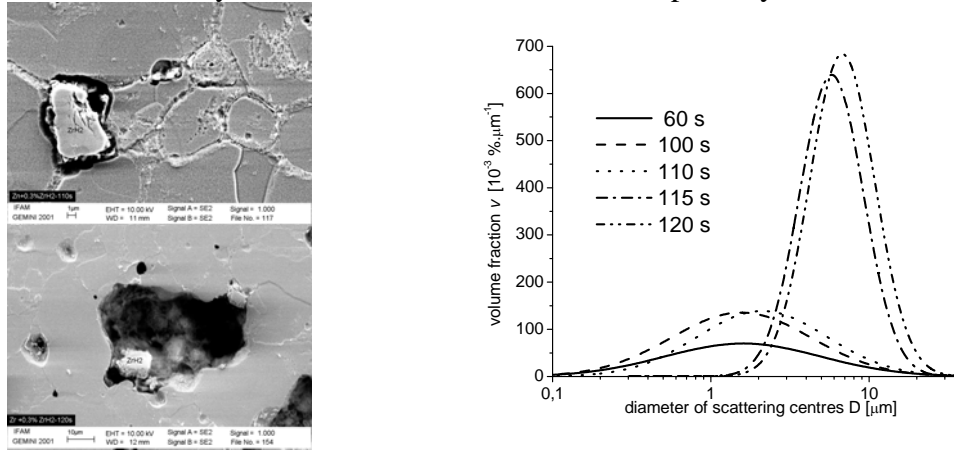
In making a foam from compacted powder mixtures, five stages can be identified, all of which offer opportunities for research.

1. *making of precursor*, for example by compacting a mix of metal powder and gas-releasing blowing agent powder. The densification has to be such that each blowing agent particle is encapsulated in the metallic matrix. Evolving gas must not be allowed to escape via some residual porosity.
2. *initial pore formation* after heating: the gas evolves in the precursor and forms nuclei. Depending on the decomposition range of the blowing agent and the melting range of the alloy, nucleation may take place in the solid, semi-solid or liquid state.
3. *pore (bubble) inflation*: driven by the ongoing gas supply from the decomposing blowing agent the nuclei are enlarged and come together to form the foam. Whereas temperature may be constant in the foaming of aqueous liquids it is not so here because the precursor is being heated continuously.
4. *foam degradation*: while pores are being inflated, degradation begins. Drainage is caused by the downward flow of liquid through Plateau borders under gravity, and bubbles coalesce as films become thin and unstable.
5. *solidification*: to save the unstable foam from collapsing the metal has to be solidified quickly at exactly the right time. Sudden cooling can lead to deformations of the films or create cracks in the cell walls, especially if heat flow is non-uniform.

In striving to prevent collapse there is not much that can be done to speed up the heat extraction. It remains only to slow the drainage process by increasing viscosity, and this is the primary role of many additives that are used in commercial processes. Usually these are finely dispersed non-metallic components such as oxides or carbides which remain solid in the liquid and make it highly viscous. Another trick is to use alloy compositions for which the melt has a “mushy” semisolid character in a certain temperature range. Popular choices are Al-Si or Al-Mg alloys. Additives are often considered to play a further role in acting as surfactants, together with dissolved oxygen, but this is not well established. These notional surfactants are presumed to stabilise the thin films.

A range of sophisticated physical instrumentation has already been brought to bear on this process. Pore nucleation can be investigated by quenching the foaming sample before foam formation sets in. Neutron scattering at extremely small angles (USANS) can measure the pore size distribution as an average over the entire sample [8]. SEM images have revealed the mechanism of initial pore formation in zinc foamed with zirconium hydride (**Figure 3**). After 110s of heating, blowing agent particles are surrounded by an annular void which has been formed by the evolving hydrogen gas. Just ten seconds later the voids have grown considerably. Most blowing agent particles are found on the walls of bubbles. Bubbles can also be formed in the absence of a particle, due to the diffusion of hydrogen gas through the metal. The pore size distributions measured by USANS confirm this picture. The distribution function is centred around 2  $\mu\text{m}$  for short foaming times and gradually moves to higher values before rapid pore growth sets in. Zinc shows a comparatively simple behaviour because the

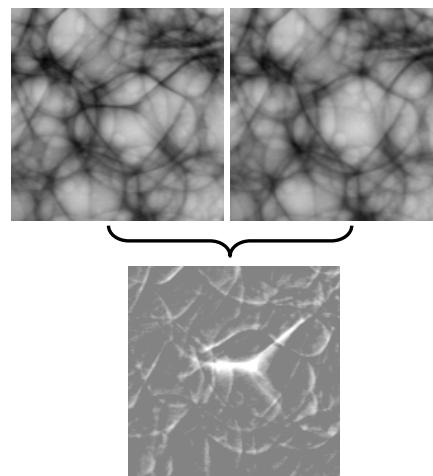
decomposition temperature of the blowing agent and the melting point of metal are nearly the same (420°C). Therefore, pore formation takes place in the liquid state and the bubbles are spherical. In aluminium foamed with titanium hydride the situation is different. As gas evolution already starts in the solid state, the initial porosity has a more complex morphology.



**Figure 3.** Scanning electron microscopic images and pore size distributions measured by ultra-small angle neutron scattering (USANS) [8]. Top SEM picture: Zn foam after 110 seconds of foaming at 440°C, bottom: 120 s.

The rapidly developing technique of synchrotron x-ray radioscopy enables the evolution of bubbles to be directly monitored *in situ*. In an experiment at the European Synchrotron Radiation Facility in Grenoble foams were generated in a furnace which was equipped with water-cooled Al windows through which the synchrotron X-ray beam could pass. The beam had a cross section of 40×15 mm<sup>2</sup> and 33 keV energy. Absorption radiographs were captured with an electronic detector system based on a 1024×1024 pixel CCD camera. Spatial resolutions between 10 and 40 μm have been achieved, with the camera being read out at frequencies between 2 and 18 Hz. The entire foaming experiment took a few minutes, corresponding to 500-900 radiographs.

If samples are chosen which have a thickness of only a few bubble diameters in the beam direction, a wealth of details can be detected. This can be seen from **Figure 4**, which shows the rupture of a cell wall [9]. These beautiful pictures rival anything that has been produced in the more traditional context of aqueous foams.



**Figure 4.** Cell rupture observed in an AlSi7 foam. The two successive radiographs (500 ms apart) show an area of 4.5×4.5 mm<sup>2</sup>. The difference was calculated to visualise the change (bottom) [9].



Quite clearly, the foam structure suddenly changes within the 500 ms that separate the two images. The change can be seen best if one calculates the difference between the two pictures, as shown. One observes the sudden spontaneous rupture of three films. They disappear very quickly but leave the remaining structure unchanged.

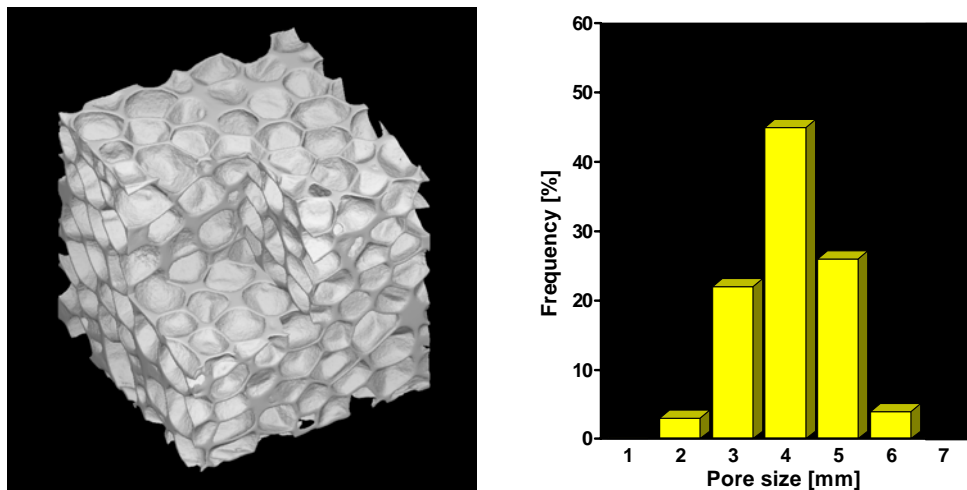
The solidification process can also be monitored by x-ray radioscopy by cooling the foam while observing it. Moreover, moulds made of thin titanium foil which absorb x-rays only weakly may be used to enable foam flow to be visualised.

Because of the importance of drainage, which can make metal foam formation a race against time, the microgravity environment of space offers a promising new dimension for experiments. Some have been carried out already on parabolic flights but the long term goal of a research team funded by the European Space Agency is to foam metals on board the International Space Station.

### The future for metal foams

The second surge of research on these new materials has begun to produce much more reliable and homogeneous products.

In the latest development, Light-Metals Competence Centre and Hütte Kleinreichenbach (LKR-HKB), both located in Austria, have found a new way to produce extremely uniform aluminium foam structures stabilized with ceramic particles. The trick is a novel bubble generation device which allows for the creation of a nearly mono disperse bubble spectrum. **Figure 5** shows a tomographic image of such a sample and the corresponding size distribution function.

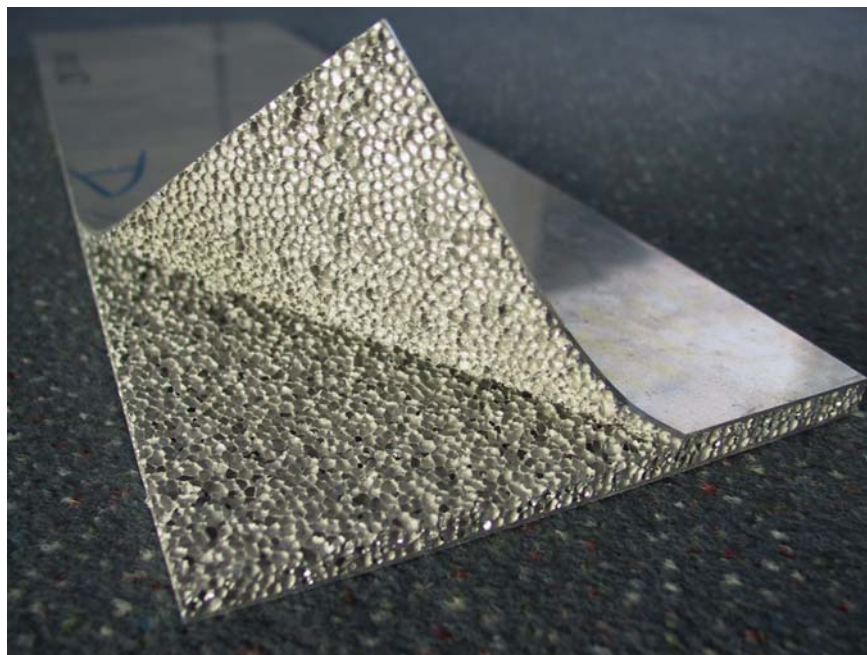


**Figure 5.** State of the art: aluminum 6061 foam stabilized with alumina particles produced by LKR/HKB (size 34 mm<sup>3</sup>). The distribution function of pore sizes makes evident the very narrow size spectrum (Courtesy of LKR/HKB).

As for applications, a recently published design guide provides a comprehensive framework for their evaluation [10]. Proceedings of the latest conferences [11][12] and a new handbook on metallic foams [13] indicate the wide range of possibilities, which arise in the automotive, aerospace, nautical, railway, building, civil engineering and medical industries. To give examples of the latter: ship builders could use large panels of aluminium foam for doors, escape hatches or walls exploiting the high stiffness-to-weight ratio, vibration damping capacity and non-inflammability of the material. Foam-filled columns or sandwich panels

could replace conventional dense metal, e.g. in rotating printing rolls or quickly moving platforms or crossbeams in machines in order to reduce their inertia and to damp vibrations. Biomedical industry could use foams based on titanium as dental implants since titanium is biocompatible and the elastic properties of the foam can be adapted to the modulus of the bones by selecting appropriate porosities [5].

The automotive industry has been most active in recent years. Karmann (Germany) that has developed a foam sandwich technology in collaboration with Fraunhofer Institute in Bremen [13]. One of their so-called AFS components is shown in Figure 6. It is a flat sandwich panel with a foamed aluminium core between two aluminium face sheets. More complex shapes can be manufactured as well without using any adhesives. Such components are damage tolerant and easy to integrate into an aluminium space frame. Incorporated into prototypes that are currently under testing, metal foams are truly back on the road.



**Figure 6.** Example for a lightweight aluminium foam sandwich (AFS). The face sheet has been partially torn off to show the quality of bonding between foam and sheet (Courtesy of Karmann).

Work on the AFS technology started about eight years ago. A rule of thumb says that it usually takes fifteen years for a new technology to develop from a laboratory curiosity to a marketed product; the next few years may see the completion of that evolution for AFS. Without such a major implementation, industry and the scientific community may again lose interest in metal foams. But for the time being the road ahead looks clear.

### Acknowledgements

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See also web site <http://www.metalfoam.net> for information about metal foams.