

# Metal Foams: the Mystery of Stabilisation

John Banhart<sup>1,2</sup>

<sup>1</sup>Department of Materials Science, Hahn-Meitner-Institut, Glienicker Str. 100, 14109 Berlin, Germany

<sup>2</sup>Department of Materials Science and Technology, Technical University Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Liquid metal foam can be generated by creating gas inside a liquid or semi-liquid metallic melt which has been pre-treated in a suitable way. Such foams are self-supported disordered structures in complete analogy to aqueous foams. The stabilisation mechanism of metallic foams is still not fully understood. In order to facilitate discussion of foam stabilisation the various methods for making such foams are classified with respect to the mode of gas generation and the type of melt used for foaming. Metal foams can be produced by gas injection from an external source or by in-situ nucleation of gas bubbles in the melt for which various possibilities are known. Melts amenable to foaming range from almost pure molten alloys to melts to which particles have been added, formed by in-situ reactions or which have been already present in the solid precursor prior to melting. Some interactions present in aqueous and metallic foams are reviewed and their possible contribution to foam stability discussed. Then, some of the available experimental evidence for the action of stabilising particles in metallic foams is presented. It is found that although stabilisation seems to be based on the presence of a solid constituent in all the foaming processes, the mechanisms might vary. At present it is not possible to fully understand the nature of stabilisation and many questions remain open.

**Keywords:** metallic foam, stabilisation, oxide particles, surface tension

## 1. Metal foams – past, present and future

Liquid metal foams are mixtures of gas bubbles and a molten alloy<sup>1</sup>. Upon solidification a highly porous metallic material is obtained which can exhibit unique combinations of properties<sup>2</sup>. Cellular metals made by sintering, casting, electroplating or chemical vapour deposition<sup>3</sup> shall not be considered in this article since these are different classes of materials from the viewpoint of materials processing.

### 1.1 Historical remarks

The history of metal foams dates back to the 1940s<sup>1</sup>. A large number of patents were issued from the late 1950s to the 1970s and many variants of foaming processes were proposed. As hardly anything was ever published beside these patents, it is difficult to assess whether all the ideas proposed actually worked. A second surge of scientific activities starting in the late 1980s led to the re-establishment of some of the old techniques and to a much higher publication activity. Nowadays the operability of some of the proposed metal foaming processes has been shown and commercialisation has begun.

Much of the research and development work on metal foams in the past seems to have been carried out on a mainly empirical basis without a detailed knowledge of the underlying mechanisms of the foaming process. This procedure quickly led to limits when applied to a very complex area such as metal foaming and no real scientific understanding was ever developed.

### 1.2 Manufacture of metal foams today

There are two fundamental strategies for making metallic foams (Table 1). *Direct foaming* methods start from a specially prepared molten metal containing uniformly dispersed non-metallic particles to which gas bubbles are added to create foam. This can be done in various ways: through a capillary or porous frit, by adding a chemical

agent which decomposes in the melt or by making use of gas dissolved in the metal which is precipitated into bubbles by temperature or pressure control.

*Indirect foaming* methods start from a solid precursor which consists of a metallic matrix containing uniformly dispersed blowing agent particles, for Al-based alloys mostly titanium or zirconium hydride. Upon matrix melting, this precursor expands and forms a foam.

#### 1.2.1 Direct foaming of melts

Silicon carbide, aluminium oxide or other ceramic particles can be used to make aluminium alloys amenable to foaming. Typical volume fractions of the reinforcing particles range from 10 to 20%, mean particle sizes from 5 to 20  $\mu\text{m}$ . Gas injection (usually air) is done through specially designed capillaries, frits etc, some of which are described to rotate or vibrate (see Fig. 1). During gas injection gas bubbles rise to the surface of the foam. The particles present in the melt are collected by the rising bubbles, attach to the metal/gas interfaces and prevent them from bursting when they reach the top surface of the metal. A foam layer is built up which can be pulled off, e.g. with a conveyor belt. Alternatively, the foam can be guided into a mould where it is allowed to cool and solidify.

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 which can be quite cumbersome due to the hard particles in the matrix. Advantages of this foaming process include the large volumes of foam which can be produced and the low densities which can be achieved<sup>4,5</sup>.

An alternative way of foam generation implies adding calcium to an aluminium alloy and stirring in the presence of air which leads to an in-situ creation of solid particles in the melt. After this,  $\text{TiH}_2$  powder is admixed which then triggers the foaming process by gas evolution<sup>6,7</sup> (Fig. 2).

Table 1: Fundamental strategies for making metal foams, current manufacturers of aluminium-based foams and names of their products.

<b>direct foaming</b>		<b>indirect foaming</b>	
	melt alloy make alloy foamable create gas bubbles collect foam solidify foam		prepare foamable precursor remelt precursor create foam solidify foam
manufacturers (products)	Cymat, Canada ( <i>SAF</i> ) Foamtech, Korea ( <i>Lasom</i> ) Hütte Kleinreichenbach (HKB), Austria ( <i>Metcomb</i> ) Shinko-Wire, Japan ( <i>Alporas</i> ) (Distributor: Gleich, Germany)	manufacturers (products)	alm, Germany ( <i>AFS</i> ) Alulight, Austria ( <i>alulight</i> ) Gleich-IWE, Germany Schunk, Germany

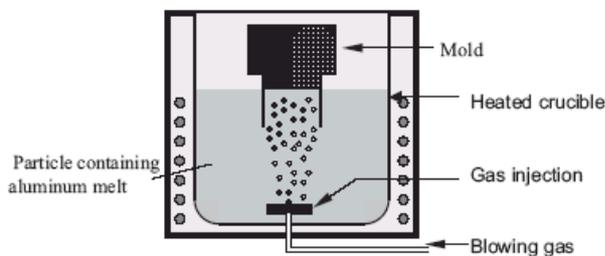


Fig. 1 Sketch of a facility for foaming aluminium-based alloys reinforced with ceramic particles<sup>5</sup>.

Adding calcium is just one possibility. Manganese oxide<sup>8</sup> or aluminium powder<sup>9</sup> have also been reported to generate the required effect when added to the melt before stirring in the presence of air.

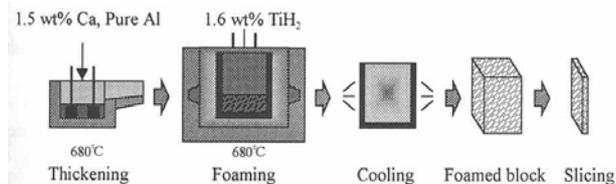


Fig. 2 Steps in foaming aluminium-based alloys by thickening via addition of calcium and foaming by adding  $TiH_2$  powder<sup>6</sup>.

### 1.2.2 Indirect foaming of precursors

Precursor-based indirect foaming implies heat-treating a piece of metal containing a blowing agent as shown in Fig. 3. Foamable precursor materials can be produced in various ways:

- by mixing aluminium powder and titanium hydride and compacting this mix e.g. by hot pressing, extrusion or powder rolling to a dense precursor<sup>10</sup>. If alloy foams are required, powdered alloying elements have to be added to the mix accordingly (“*Foam-in-Al*” or “*Alulight*” process),
- by pre-compacting powder mixtures to billets, heating these billets to the semi-solid state and thixocasting them to shaped precursor parts<sup>11</sup>,

- by adding blowing agent powder to an aluminium alloy melt after which the melt is solidified. This can be done in a die-casting machine<sup>12</sup>) or in an ordinary crucible in which case, however, the blowing agent powders have to be pre-treated to prevent them from premature decomposition<sup>13</sup>) (“*Formgrip*”-process).
  - by producing a liquid aluminium spray and allowing for deposition in the presence of a blowing agent.
- In all cases the actual foaming (or baking) process is very similar.

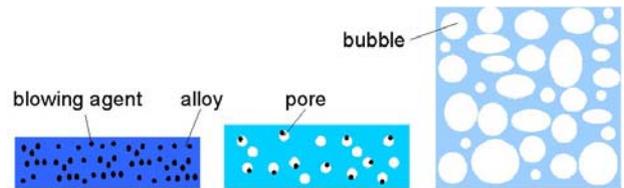


Fig. 3 Indirect foaming method via solid precursor.

Beside these foam production processes others exist: the Lotus (or Gasar) process relies on gas precipitation from a gas-charged melt during solidification<sup>14</sup>). Combustion reaction of aluminium with a second component, e.g. Ni., can also drive foaming<sup>15</sup>).

Foaming processes can also be classified according to the way the gas bubbles are brought into the metal<sup>16</sup>). *Internal* gas sources include decomposing blowing agent particles, in-situ chemical reactions, heterogeneous nucleation of dissolved gas etc. In these cases gas bubbles are created at many locations instantaneously. *External* gas injection takes place through capillaries or frits which means that gas bubbles are created in a small region of the melt and have to be dispersed after. The type of gas injection is important since the distribution of bubbles depends on the rheological properties of the melt. As a rule, internal gas injection seems to be more likely to create a stable foam than external injection<sup>17</sup>).

### 1.3 Status of technology

Foaming aluminium or aluminium alloys by gas injection (see Fig. 1) is already in the state of commercial exploitation.

Cymat, Canada, produces its foam – called *Stabilised aluminium foam (SAF)* – in this way<sup>4)</sup>. The metallurgical plant in Kleinreichenbach (HKB), (Austria) is currently setting up a production facility based on a new concept of gas injection which leads to foams with an excellent uniformity of cell sizes<sup>5)</sup>. By casting the foam into moulds, complex-shaped foamed parts with a closed outer skin can be generated. This type of aluminium foam is called “*Metcomb*” (see Tab. 1).

Shinko-Wire has been producing metal foam based on the process shown in Fig. 2 for many years. Other companies are following with similar technologies, e.g. Foamtech in Korea offering a product called “*Lasom*”.

Foam making based on one of the indirect foaming methods (first in the list in Sec. 1.2.2) is now in the stage of a small-scale commercial exploitation by the companies Schunk (Gießen, Germany), Applied Light-weight Materials *alm* (Saarbrücken, Germany), Innovativer Werkstoffeinsatz *ive* (Stralsund, Germany) and the Austrian company Alulight (Ranshofen)<sup>18)</sup>.

Fig. 4 shows AFS panels produced by *alm*. Such panels can be manufactured in sizes up to 1.7×1.3 m<sup>2</sup> with various thicknesses<sup>19)</sup>. Alulight produces aluminium foam panels without face sheets and has announced to be able to make panels up to 1×1,50 m<sup>2</sup> large soon<sup>20)</sup>.

A list of further companies supplying cellular metals can be found in Ref. 18. An overview of the state of applications especially in automotive industry can be found in Ref. 22.



Fig. 4 Production of Aluminium Foam Sandwich at alm GmbH, Saarbrücken (Courtesy: H.-W. Seeliger).

### 1.4 Challenges for the future

Although the development of metallic foams looks back on a long history none of the processes available nowadays has been brought to a level of sophistication comparable with that of polymeric foams. It is obvious that there are difficulties in finding applications for metallic foams outside niche markets. Deficiencies of the various metal foaming techniques can be found on many levels, namely, e.g.

- Lack of *understanding of the basic mechanisms* of metal foaming: Knowledge is still speculative and some points remain unclear, e.g.: what is the reason for the existence of a critical cell wall thickness?
- Insufficient ability to make foams of a *constant quality* with pre-defined parameters, i.e. the lack of control of

structure and morphology. Limited stability of emerging metal foams is one reason for these problems,

- The interrelationship between *morphology* and *structure* on the one hand, and mechanical (or other) *properties* on the other is not sufficiently understood,
- *Physical properties of foams are not good enough*: There seems to be still some potential for an improvement of properties by optimising foaming processes and materials selection,
- *Knowledge of foam properties is insufficient*: further characterisation of properties is necessary,
- *Transfer of research results to design engineers is insufficient*: Databases and design guidelines for metallic foams have to be created and disseminated,
- *Foams are still too expensive*. Mass production will lead to lower prices but metal foam will never be a really cheap material.

The selection of applications in which 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 which has to be interrupted. One key research field is that of metal foam stability because it can help in making the processes more reliable and economically viable.

## 2. Stability of metal foams

### 2.1 Phenomena

Liquid metallic foams are systems which go through a series of transient states and change their morphology constantly throughout their lifetime. They are hardly ever stable, at the best metastable. While some of the rapid changes in a foam are an essential part of the process, others are deleterious and limit the applicability of metal foam technology. A foam can be called (kinetically) *stable*, if it does not change considerably in the time span between completion of the blowing process and solidification.

The forces acting on a foam are:

- **Gravity**
- External atmospheric and internal *gas pressure*
- **Mechanical forces**
- Forces from within the metallic phase (*surface tension, capillary forces* etc.)

Any imbalance of these forces will lead to a movement of the foam. Changes in foam morphology can be classified according to the terms given in Fig. 5:

- **Flow** is the movement of bubbles with respect to each other caused either by external forces or changes in the internal gas pressure, e.g. during foaming,
- **Drainage** is the flow of liquid metal through the Plateau borders – the intersection of three foam films – driven by capillary forces and gravity,
- **Rupture** (or coalescence) is a sudden instability in a film leading to its disappearance.
- **Coarsening** (or Ostwald ripening) is slow diffusion of gas from smaller bubbles to bigger ones driven by a pressure difference.

The effects described are not independent as indicated by the arrows in Fig. 5. Bubble flow during growth of a foam, e.g., can trigger rupture of cells. Drainage can lead to thinning of films and to rupture. Körner et al. use the terms *growth*

*coalescence* and *drainage coalescence* to distinguish between these two mechanisms<sup>23</sup>.

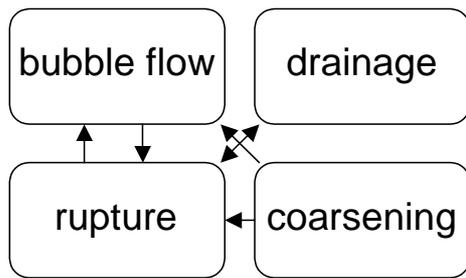


Fig. 5 Different effects limiting the stability of foams<sup>21</sup>.

The phenomena mentioned are well-studied in aqueous foams<sup>24</sup>. Studies in metal foams are more difficult due to their intransparency, high processing temperature and the chemical reactivity of liquid metals. In this paper we shall examine two of the deleterious effects which limit liquid metal foam stability, namely drainage and rupture. We shall present the experimental evidence for these effects and try to discuss the underlying mechanisms.

## 2.2 Role of particles

Metal foams can not only be made using different processing variants as described in Sec. 1.2 but also starting from a variety of different types of metallic melt. This makes discussion of the physics of foaming a bit confusing because processing issues and physical mechanisms tend to be mixed. There seem to be at least four different types of melts which have been used in foaming experiments<sup>16</sup>:

- pure metallic melts near their melting point or alloys in the semi-solid state,
- melts, to which non-metallic particles have been added, consisting, e.g., of ceramic particles dispersed in an aluminium alloy matrix (so-called metal-matrix composites “MMCs”),
- melts in which solid components have been created in-situ by chemical or metallurgical reactions. Examples are reactive alloys through which oxygen has been bubbled,
- melts which have been obtained by re-melting powder compacts.

Both morphology and volume fraction of the particles created by the different techniques are quite different in the various cases. MMCs usually contain fairly equiaxed particles with diameters in the order of around  $10\ \mu\text{m}$ <sup>25,26</sup>. In-situ reacted melts such as the melts used for the *Alporas* process (see Fig. 2) contain thin ( $\approx 1\ \mu\text{m}$ ) oxide bi-films which are smaller than SiC particles<sup>27</sup>. Powder compacts exhibit a network of oxide skins which covered the individual powder particles prior to foaming<sup>23</sup>. Alloys in the semi-solid state contain primary grains which are some tens of micrometers large.

It has been shown that melts without a solid phase are not foamable. Foaming of exotic undercooled metallic melts in highly viscous states has been reported<sup>28</sup> but these results could be also interpreted by assuming that particles were present, stemming from, e.g., reactions of the blowing agent.

## 2.3 Models of foam stability

Foam stability has been discussed in the literature on aqueous systems for a long time. Aqueous films owe their stability to the presence of at least one further component. Surfactants are one possibility. They form charged layers of molecules on each side of a surface and start interacting strongly through the aqueous film whenever it gets sufficiently thin. Simple theory assumes an attractive van der Waals force which is counterbalanced by a repulsive disjoining pressure caused by said surfactant films<sup>29</sup>. Therefore at a certain thickness a film can be stable against further thinning under static conditions. If dynamic conditions apply, the re-distribution of surfactants creates additional forces via the so-called Gibbs-Marangoni effect.

Another type of aqueous foam is stabilised by macroscopic particles<sup>30</sup>. Silica particles, e.g., can stabilise aqueous foams even in the absence of surfactant molecules<sup>31</sup>. These foams have similarities with metal foams which do not seem to contain any stabilisation agent on a molecular level either.

Interestingly, the mechanism of foam stabilisation via particles has not yet been explained convincingly. It is clear from fundamental considerations that a particle attaches to an interface between a liquid and gas if it is partially wetted. Very small particles can become so tightly bound to interfaces that adsorption is irreversible<sup>31</sup>. Depending on the wetting angle the liquid will arrange around the particle. If the film is much thinner than the diameter of the particles, particles can bridge the liquid in the way shown in Fig. 6. If the particles are wetted (top) they will stabilise a film, if wetting is poor, the film will be destabilised.

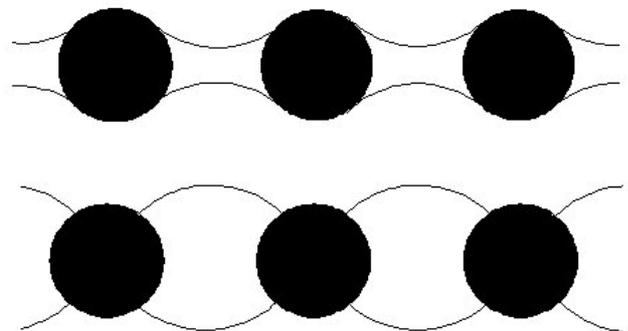


Fig. 6 Effect of particle wettability on film stability. Top: particles are partially wetted ( $\Theta < 90^\circ$ ); bottom: particles are poorly wetted ( $\Theta > 90^\circ$ ) (after Ref. 32)

Thus, Fig. 6 could represent a stabilisation (and destabilisation) mechanism. However, as in many cases the particles are much smaller than the film thickness, this picture cannot be used in all cases. Other explanations were therefore proposed such as the one depicted in Fig. 7 which reflects an idea given by Kumagai et al.<sup>33</sup>. They suggest that whenever particles are adsorbed to a surface they modulate the originally flat film (right) and introduce a vaulted structure (middle). This would indeed have an influence on the pressure difference  $\Delta p$  between the Plateau borders (PB) and the films.  $\Delta p$  is responsible for the flow of liquid out of the films and into the PBs and is given by  $\Delta p \propto (R_{PB})^{-1} - (R_F)^{-1}$ . For flat films  $R_F$  is infinite, while  $R_{PB}$  is small and  $\Delta p$

can therefore be quite large. If, however,  $R_F \approx R_{PB}$ ,  $\Delta p$  could become very small which would prevent capillary driven flow in the foam and would stabilise a film. Of course this does not work for non-wetting particles as shown on the left in Fig. 7. The problem is that the modulated surfaces predicted by this model are not observed in cross-sections of real metallic foams and it therefore uncertain whether the model applies.

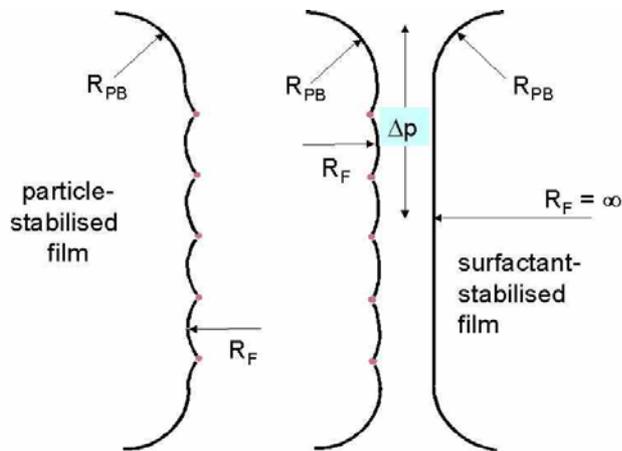


Fig. 7 Proposed stabilisation of foams by solid particles (partially adapted from Ref. 33), left: non-wetting, right: wetting particles.

Kaptay analysed a number of particle arrangements in a film – including the one in Fig. 6 (top) – and evaluated their capability to stabilise films<sup>34</sup>. Some are shown in Fig. 8: Configuration a) consists of a dense packing of particles on each side of the film. As the particles are firmly bound to the interface these two layers are stable. However, there is no disjoining force in this model since the two layers are not connected.

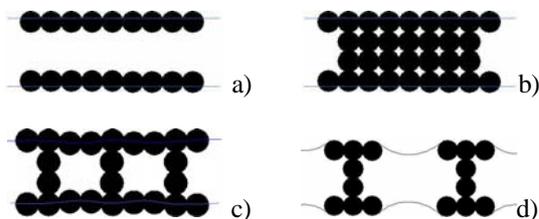


Fig. 8 Proposed stabilisation of foams by solid particles (adapted from Ref. 34).

Therefore, it was proposed that the space between the two layers be filled with particles (b). The disjoining force is now transmitted mechanically via this dense particle packing. This variant requires a very high particle density which is unrealistic in view of the situation in real soams. Therefore, variant (c) was proposed, in which the disjoining force is transmitted only locally via particle bridges. Finally, the requirement that the layer be dense was relaxed and variant (d) was suggested. Here, particles cover only parts of the surface of a film. In order to transmit forces the particles are again connected by bridges. In this way films could be stabilised against rupture with particle volume fractions close to the ones found in some real metal foams ( $\approx 10\%$ ).

### 3. Experimental approaches to characterise stability

We shall briefly review how the stability (or instability) of metal foams has been characterised by various researchers. A typical stability experiment consists of making foams under defined conditions and varying parameters considered important for foam stability. A number of methods can be applied to derive a quantitative measure for stability. We shall first describe which parameters are usually varied to characterise stability and then list the characterisation methods used in these experiments.

#### 3.1 Foaming experiments

##### 3.1.1 Foaming by gas creation in liquid alloys

One way to make foams is to blow gas into a particle-stabilised melt through a nozzle or a porous frit (see Fig. 1). Parameters which can be varied to influence foam stability include:

- composition of alloy<sup>35</sup>,
- type and volume content<sup>32,35</sup> of particles,
- temperature of melt<sup>32</sup>,
- composition of blowing gas, especially oxygen content<sup>35,36,37</sup>,
- immersion depth of injector<sup>5,38</sup>.

The foaming experiment itself can be quite variable. Bubbling can be turned off and free drainage of the standing foam observed in analogy to aqueous foams. Alternatively, one can sparge a fixed volume of gas through the liquid and measure the height of the foam (“Bikerman test”)<sup>24</sup>. One possible test is to sparge bubbles through a liquid and wait until the foam column no longer rises<sup>32</sup>.

An alternative way of foaming is to add blowing agent to a melt which has been stabilised by in-situ creation of particles (see Fig. 2). The parameters which have been varied include:

- content of calcium addition to melt<sup>6,39</sup>,
- stirring time prior to  $TiH_2$  addition<sup>6,9,39</sup>,
- holding temperature during thickening and foaming<sup>40</sup>,
- blowing agent content<sup>40</sup>.

This foaming method is less flexible since gas evolution is controlled by thermal decomposition of the blowing agent and one cannot easily manipulate the foaming process.

##### 3.1.2 Foaming of solid precursors

A solid precursor is foamed by heating it to above its melting temperature and holding it there (Fig. 3). There are many parameters which have been varied in such foaming experiments:

- composition of alloy<sup>41</sup>,
- oxide content of precursor<sup>23,42-44</sup>,
- type and content of additional ceramic particles<sup>13,45,46</sup>
- type<sup>47-49</sup>, pre-treatment<sup>13,50</sup> and content of blowing agent,
- manufacturing parameters of precursor<sup>41</sup>, e.g. pressure, pressing temperature and time,
- temperature profile during foaming. This often includes varying the heating rate<sup>41,51</sup> up to the foaming temperature and the holding temperature/time during foaming<sup>23</sup>,
- pressure profile during foaming<sup>27,52-54</sup>,
- level of gravity<sup>43,44</sup>.

### 3.2 Characterisation methods

The foams manufactured in one of the experiments described in Sec. 3.1 have to be analysed in order to derive data describing foam stability. Two types of experiments can be distinguished.

#### 3.2.1 Ex-situ investigations

In this type of experiment a foam is blown under pre-defined definitions. Foam evolution is interrupted by quenching to obtain samples representing various stages of foam life. Samples are characterised with respect to their

- volume (i.e. density),
- morphological parameters such as pore sizes, orientations, cell wall thicknesses - in 2D by investigating sections or in 3D by X-ray tomography<sup>55)</sup>,
- pore diameters as a function of density to study growth coalescence<sup>52)</sup>,
- microstructure of films and Plateau borders (LOM, SEM, TEM).

#### 3.2.2 In-situ investigations

The evolving foam is characterised in its liquid state during evolution. The methods which have been applied include:

- simple volume measurements<sup>41,56)</sup> (“expandometer”),
- X-ray<sup>57,58)</sup> and neutron<sup>58,59)</sup> radioscopy to obtain morphological information such as cell sizes and shapes, cell wall thicknesses, rupture rates,
- thermo-gravimetry or mass spectrometry to detect weight losses associated with blowing agent decomposition<sup>50)</sup>.

Regarding studies of stability the following parameters have been considered useful:

- density profiles to quantify the effect of drainage<sup>59)</sup>,
- minimum cell wall thickness distributions to derive a limit until which metallic films can be stretched<sup>11)</sup>,
- coalescence rates to quantify rupture phenomena<sup>60)</sup>.

### 4. Stability of foams – selected results

We shall now present a selection of experimental studies related to the stability of metal foams.

#### 4.1 Particle containing aluminium melts blown with gas

Little is known about the early work on the foaming of Al + SiC composite melts as this work was carried out in the laboratories of Alcan and Hydro Aluminium in the 1980s and hardly anything has been published. Some of the inventors at Alcan have described a relationship between particle content and foam stability in a qualitative way<sup>61)</sup>, showing that particle size and volume fraction play an important role. Fig. 9 states that about 10 vol.% of roughly 5  $\mu\text{m}$  large particles yield the best results for aluminium. Deviating from these parameters too much creates problems with foam stability or makes processing too difficult. Kaptay has discussed this diagramme theoretically by considering interfacial forces between particles and melt<sup>62)</sup>.

Prakash et al.<sup>25,63)</sup> and Simone et al.<sup>64)</sup> gave a description of the morphology and microstructure of such foams. They characterise the spatial distribution of SiC particles in the foam and discuss foam stability in terms of particle accumulation at the gas/metal interfaces. Their stabilising

action is explained by a reduction of coalescence activity and their influence on the rheology of liquid in the interfacial region. The arguments are motivated by the literature on the stabilisation of aqueous systems by colloidal particles. No proof is provided that the same mechanisms actually apply to metals.

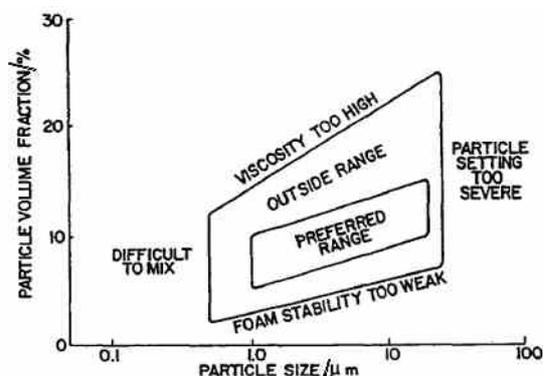


Fig. 9 Aluminium foam processing window as given by Jin<sup>61)</sup>.

Ip et al.<sup>32)</sup> were the first to carry out a quantitative study on foam stabilisation in Al-SiC systems. They inject nitrogen into Al melts containing various volume fractions of SiC particles through a lance positioned 3 cm below the melt level. Bubbling is continued until the bubbles at the surface break, after which the foam is solidified and the height of the column is measured. They find that a minimum content of SiC particles is needed to create a foam at all – between 8 and 10 vol.%, depending on temperature – and that increasing the contents of SiC lead to increasing heights of the column (see Fig. 10).

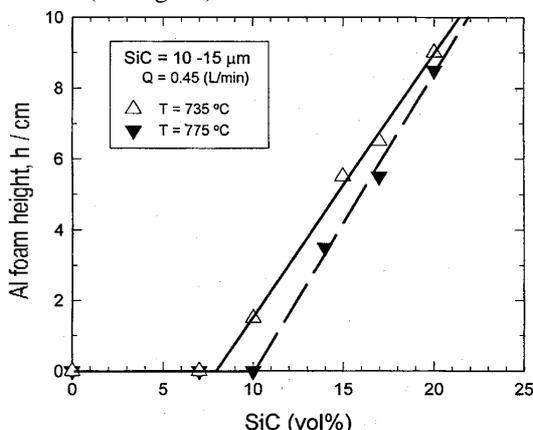


Fig. 10 Influence of SiC particle content on aluminium foam stability expressed by the height of a column blown with nitrogen<sup>32)</sup>.

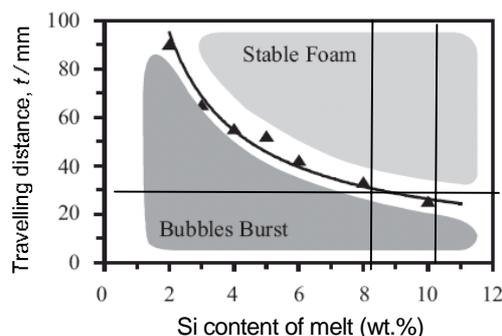


Fig. 11 Criterion to obtain stable Al foams<sup>32)</sup> (alloy A356, T=727°C). Lines: stability boundaries as given by Ip et al.<sup>32)</sup> (see Fig. 10).

Leitmeier, Babcsán et al. carried out further studies on aluminium alloy foams stabilised with SiC particles. They found that a bubble has to collect a minimum amount of particles while travelling through the melt to be stable as shown in Fig. 11 which is another proof for the necessity for adding particles<sup>5</sup>.

Aluminium-based foams were made from different alloys (with Cu, Mg, Si and/or Ni additions), containing different types of particles (Al<sub>2</sub>O<sub>3</sub> and SiC) in various volume fractions (10-22%) and using blowing gases containing different levels of oxygen<sup>17,35,36</sup>. The alloying elements Si and especially Mg were found to decrease cell wall thickness. A pronounced influence of the type of atmosphere was found. Nitrogen-blown foams were less stable than air- or oxygen-blown ones. For oxygen-containing foams the distribution of cell wall thicknesses was found to be unchanged ( $\approx 50 \mu\text{m}$ ) when foams were held for 100 minutes indicating a pronounced stability of these foams. The effect of oxygen could be seen in metallographic images: oxygen created a dense surface oxide layer and kept the SiC particles away from the gas/metal interface. The oxide films are about 30 nm thick<sup>5</sup>. Reactions between the stabilising particles with the melt could be observed in some cases, e.g. the formation of spinel in Al-foams stabilised with Al<sub>2</sub>O<sub>3</sub> and having a low Si:Mg ratio<sup>38</sup>.

#### 4.2 Aluminium alloy melts foamed by TiH<sub>2</sub> addition

There are not many publications treating the stability of *Alporas*-type foams. Some studies relate the viscosity of the melt as it emerges from the thickening process (first stage in Fig. 2) to foam properties. In a fairly simple experiment the torque on a paddle rotating in a Al melt to which calcium metal is added is measured<sup>6,39</sup>. The measured torque is then related to the bulk viscosity of the melt. Its impact on foaming behaviour – e.g. expansion height – or foam properties, e.g. cell size and cell uniformity, is investigated. A pronounced influence is found but no explanations are given in the various studies.

A microscopic investigation of cell walls shows that oxide bi-film networks are created during thickening. They extend throughout the sample<sup>65</sup> and are obviously responsible for stability.

Wübben measured the viscosity of some compacted and re-melted lead powders with different oxide contents and found a clear relationship between oxide content and viscosity<sup>66</sup>. Yang and Nakae added aluminium powder to an aluminium alloy melt and find an increase in viscosity and foamability after<sup>9,40</sup>. Park et al. compare pure and recycled aluminium and find that recycled aluminium has both a higher viscosity and a better foamability<sup>67</sup>. From these data it seems plausible to assume that viscosity and foam stability are correlated. However, as we shall discuss later, viscosity might be just an indicator for the presence of particles and not the primarily interesting physical quantity.

#### 4.3 Foaming of aluminium alloy precursors

##### 4.3.1 Phenomenology of drainage and coalescence

During growth and after maximum expansion metal foams evolve rapidly. The presence of drainage and coalescence is obvious from series of foams prepared by freezing the foaming process (see e.g. Ref. 41). During

foaming one can see bursting films and an accumulation of liquid at the bottom of the vessel containing the film<sup>57</sup>.

The extent to which *drainage* takes place can vary very much. Foams have been found which exhibit extremely strong drainage (e.g. Ref. 59), in other cases very little drainage is observed (e.g. Ref. 23). Gergely et al. produced a series of *Formgrip* foams in which foaming time was varied and measured the vertical density profile after. They do find significant drainage and construct a model to explain it<sup>47</sup>. Garcia-Moreno et al. measure drainage profiles in a foam made from a thixocast precursor as a function of time by in-situ X-ray radiography. The system is found to exhibit strong drainage occurring within a very short period<sup>27</sup>.

*Coalescence*, in contrast, is ubiquitous in metal foams during expansion. This is most obvious in in-situ X-ray experiments in which the rupture of individual films can be observed directly. These experiments allow one to measure critical film thicknesses  $d_{\text{crit}}$ . Whenever a film is stretched to such an extent that the film becomes thinner than  $d_{\text{crit}}$ , or drainage leads to a loss of liquid that the film becomes too thin, it ruptures. The existence of a critical thickness can of course also be derived from sections of foams by ex-situ analysis.

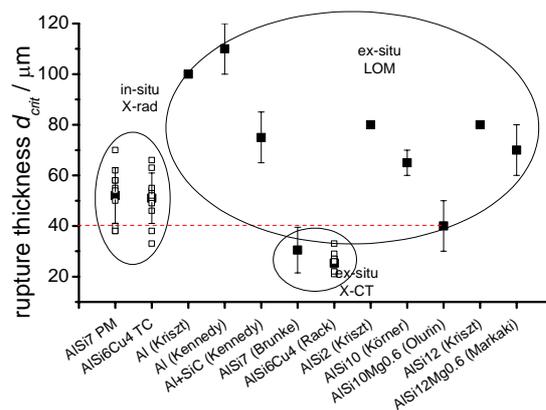


Fig. 12 Critical cell wall thickness of various aluminium alloys made by foaming a precursor (from Ref.11 with some updates).

Some data obtained either by conventional metallography or by computed tomography on solidified samples, or from in-situ image sequences of liquid foam are compiled in Fig. 12. Despite the considerable scatter one can conclude that pure aluminium foams have the thickest films and that alloying with silicon and copper lowers this limit notably. Tomography seems to be able to detect thinner films than radiography or light microscopy.

Data from ex-situ analysis can be used to prove the existence of coalescence by plotting the average cell diameter  $D$  as a function of inverse density  $\rho$ . The argument is as follows: whenever bubbles are blown in a fixed metal volume and the films are stable, conservation of the liquid requires that the thickness of films decreases with expansion while the size  $D$  of the fixed number of bubbles increases. If, however, a critical cell wall thickness exists, below which a film ruptures, the number of bubbles will reduce and the

mean pore diameter  $D$  will grow more quickly. One can show that:

$$D \propto \sqrt[3]{\rho^{-1} - 1} \quad \text{for coalescence-free growth}^{68),}$$

$$D \propto 6d_{crit}(\rho^{-1} - 1) \quad \text{growth with rupture at } d_{crit}^{23),}$$

where the second eq. has been slightly modified by the author. These functions are shown in Fig. 13 together with some experimental data by Körner et al. It becomes clear that growth is accompanied by film rupture and that the model of a critical thickness describes the real situation quite well.

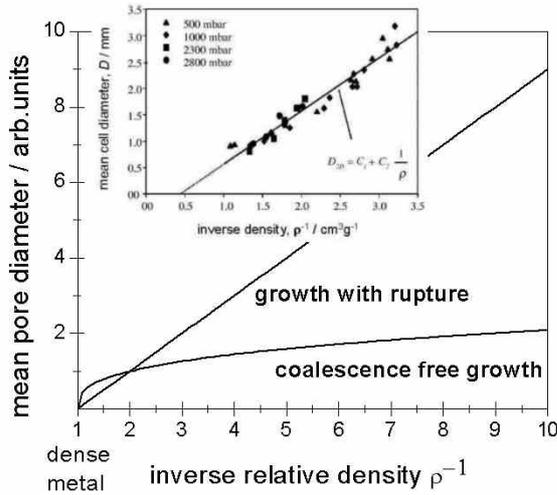


Fig. 13 Relationship between mean pore diameter  $D$  and density  $\rho$  of foams expanded under two different conditions. Inset: data for aluminium foams foamed under various pressures and up to different expansion stages<sup>23,52</sup>.

#### 4.3.2 The role of oxides in foaming powder compacts

The first to point out the role of the oxides contained in the powders used for making precursors for aluminium foam stabilisation was Weber<sup>69</sup>. He postulated an accumulation of oxide particles in regions close to the surface of films and a corresponding increase in surface viscosity caused by these particles. The increased surface viscosity is then thought to slow down drainage. Spontaneous oxidation of fresh metal films by traces of oxygen present in the pressed precursors causing the formation of a supporting skin was postulated as a second stabilising effect.

A few years later Weigand carried out the first quantitative study by varying the oxide content in the powders used<sup>42</sup>. Fig. 14 shows the influence of the oxide content of the powder used for making foamable precursors on the maximum expansion of pure Al foams as determined from expansion curves. Six different powder sources were used. For two powders (“Rheinfelden” and “EckaAS”) the oxide content was varied by annealing powders at 600°C in air for 30 to 180 minutes. Weigand finds that the oxide content significantly influences maximum expansion. In contrast, kinetics of foaming (applying the same heating profile) and the degree of collapse after expansion to the maximum value are hardly influenced. The data shown can be interpreted such that within a range between 0.2 and 0.8 wt.%  $\text{Al}_2\text{O}_3$  the foam expands to a maximum value, while oxide contents

below and above this range lead to lower expansions, i.e. reduced foamability. Oxidation of the low-oxygen “Rheinfelden” powder increases the foam expansion factor from 280 to 410%. Annealing of the EckkaAS powder, in contrast, leads to a reduction in expansion for times above 30 minutes.

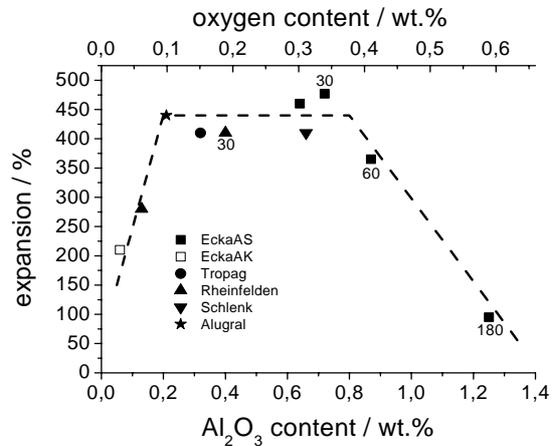


Fig. 14 Influence of oxide content of aluminium powder on expansion factor of foam. Numbers are annealing times prior to pressing of the powder in minutes at 600°C (redrawn using data of Ref. 42, Tab.8.1.1 and Fig. 8.1.1.).

Weigand’s interpretation of this result assumes that oxides are surface active and cover the surface of the aluminium films. If the content is too low, the growing inner surface of the liquid foam cannot be covered completely and surface tension rises locally, triggering rupture events which then decrease the surface area and prevent the foam from reaching maximum expansion. Within the optimum range found the oxide content is thought to be sufficient to cover the inner surface of a foam within the normal expansion range. Above 0.8 wt.% the increasing difficulties with obtaining a dense, gas-tight precursor are held responsible for the decrease in foamability.

A very similar conclusion was drawn from tests with lead powders which were foamed using lead carbonate as a blowing agent<sup>43,70,71</sup>. It was shown that powders with very low and very high oxide contents did not foam well, whereas intermediate oxide contents allowed for making stable foams. Especially at low oxide contents drainage was very pronounced which lead to the destruction of the foam already during its manufacture. Wübben carried out foaming experiments under microgravity in order to prevent the unstable foams from collapsing<sup>44</sup>. By measuring the total inner surface of foams made from powders with different oxide contents he could show that the ratio of surface and oxide content is a constant. The interpretation given was that coalescence leads to a reduction of surface area during foaming until a minimum coverage has been reached to prevent the films from further rupture.

Körner et al. discuss the role of oxides in stabilising aluminium foams by various experiments<sup>23</sup>. First, by using Al powders with different oxide contents. Low-oxide powders were found to lead to foams with a lower expansion and a higher degree of drainage. Second, by metallographic analysis of powder particles, precursor materials and foams. As oxide films are very thin they can be made visible only

after careful preparation. Körner et al. observe irregular structures which are shown to be enriched in oxygen by EDX. The oxides seem to form an interconnected network. No accumulation at the gas/metal interfaces is observed in contrast to the situation in SiC-stabilised foams and in contradiction to the assumptions by Weigand<sup>42)</sup>, Wübber and Odenbach<sup>44)</sup>. In order to explain the mechanism of particle stabilisation Körner et al. develop a model based on the following assumptions:

- The original oxide network in the pressed powder is fractionated during foaming. Fragments cluster together and form *network particles* which freely float in the melt.
- These network particles are infiltrated by liquid and can bear mechanical forces.
- The network particles are completely wetted by the melt and are therefore confined between the two interfaces of each film.
- The confinement together with the mechanical stability of the network particles creates a repulsive force which prevents the films from thinning.

The model is supported by experimental observations in which it is found that in many cases in bulges of the cell wall oxide agglomerations are found, whereas thin parts of films are oxide-free. In terms of the stabilisation models available, the model depicted in Fig. 8d is preferred.

#### 4.3.3 Stability of cast Al/SiC precursors

Stability of foams made by baking cast precursors containing TiH<sub>2</sub> as a blowing agent and SiC as stabilising particles – so-called *Formgrip* precursors - was investigated by various methods. In-situ X-ray radioscopy revealed that precursors containing large SiC particles (mean size 70 μm) showed much stronger coalescence during foaming than precursors containing 3 μm or 13 μm particles<sup>72)</sup>. Ex-situ analysis of the resulting foams containing 13 μm large particles showed films 85 to 100 μm thick with surfaces entirely covered by particles. In contrast, for the 70 μm particles the films were up to 300 μm thick and have surfaces only sparsely populated with particles<sup>65)</sup> (see Fig. 15 for images).

The surface layers observed for the former case can be used to discuss stability in terms of the models given in Fig. 8. Fig. 15b does not yield any evidence for the existence of bridges which could transmit forces from one layer to the other. Haibel et al. carried out an extensive study applying high-resolution synchrotron tomography to answer the question whether the surface layers are connected by continuous particle bridges which might be not visible in two dimensions. They found that the individual silicon carbide particles on opposing two gas/metal interfaces did have contact only with particles on the same side. None of the layers was connected through a continuous bridge through the cell wall<sup>73)</sup>.

As it had been speculated that the arrangement of particles might change during solidification, in-situ tomography was carried out during foaming and after solidification of a single *Formgrip*-type metal foam<sup>74)</sup>. The correlation curve between pores and SiC particles specifies the likelihood to find a SiC particle at a certain distance from a pore (see Fig. 16). It shows that there are some re-arrangements of SiC particles during foaming, but these do not justify the

assumption that particle bridges between the two interfaces exist in the liquid state and are destroyed during solidification.

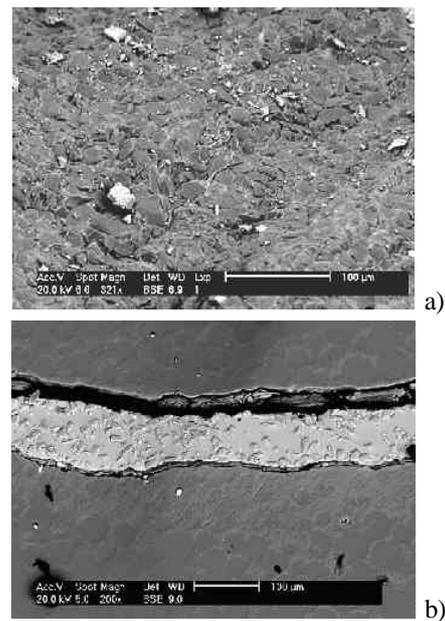


Fig. 15 a) Top-view and b) cross-sectional view of a cell wall in a Al+10 vol.% SiC (13 μm) *Formgrip* foam<sup>65)</sup>.

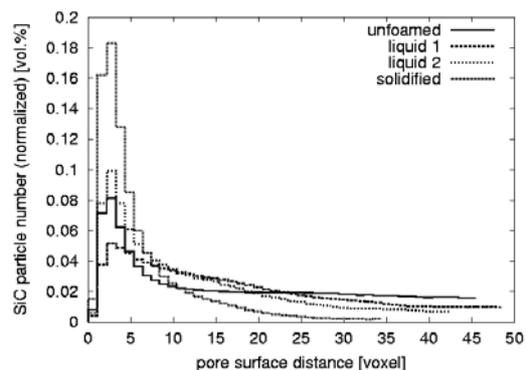


Fig. 16 Correlation between pores and SiC particles in *Formgrip* foams containing 13 μm large particles<sup>74)</sup>.

#### 4.3.4 Stability of hybrid foams

Aluminium foams have been manufactured following the powder compact route but with additional ceramic particles added to the powder blend prior to solidification<sup>45,46)</sup>. It is observed that precursors foamed for a given time reach higher expansions whenever they contain either 3 vol.% of SiC, Al<sub>2</sub>O<sub>3</sub>, or TiB<sub>2</sub> as compared to particle-free aluminium<sup>45)</sup>. These particles also retard collapse of the foam but only SiC leads to some degree of long-term stability while foams stabilised with the other particles collapse quite considerably. Particles also lead to less coalescence during foaming expressed by thinner films in samples analysed ex-situ after foaming: all the particles-stabilised foams have a minimum cell thickness from 70 to 80 μm as compared to 100 to 120 μm for pure aluminium. Only SiC particles are wetted by the Al melt, while Al<sub>2</sub>O<sub>3</sub> and TiB<sub>2</sub> particles are not wetted and protrude

into the gaseous phase. SiC particles are also efficient in reducing drainage as seen from micrographs of foams foamed for a long time. Foams containing no particles of  $\text{Al}_2\text{O}_3$  or  $\text{TiB}_2$  exhibit a thick layer of metal at the bottom of the foams after 10 minutes, while this layer is thin for SiC particles. If the content of  $\text{TiB}_2$  particles is increased to 6 vol.% some drainage reduction is reported even for this system<sup>46</sup>. The authors stress that the function of particles is to reduce the critical cell wall thickness but do not give an explanation for the mechanism.

Another possibility to improve stabilisation of aluminium foams blown with  $\text{TiH}_2$  is to use a second blowing agent which releases gas during decomposition and influences cell wall stability at the same time. Arnold et al. find that 1 wt.% of  $\text{CaCO}_3$  in addition to 0.5 wt%  $\text{TiH}_2$  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 without specifying a mechanism<sup>48</sup>. Gergely et al. fabricate *Formgrip*-type precursors containing 10% SiC particles and about 3.5 wt.%  $\text{CaCO}_3$  as a blowing agent (no  $\text{TiH}_2$ )<sup>49</sup>. Foams with much smaller cells compared to hydrogen-blown foams are obtained. The cell wall stabilising mechanism is investigated. It is found that foams blown with  $\text{CaCO}_3$  exhibit a thin solid reaction layer at the gas/metal interface which prevents the SiC from protruding into the pores. In fact no SiC particles can be found at the interface while in hydrogen-blown foams SiC particles can be seen at the surface (see Fig. 15). The film was found to contain alumina, magnesia and spinel. No explanation was given for the mechanism the surface layer improves foam stability.

## 5. Discussion and some speculations

The presence of non-metallic particles in metallic foams makes them stable and prevents films from rupturing and liquid from draining out too quickly. The mechanism of stabilisation has been discussed in different ways in the literature. Some authors explain stability by the reduction of drainage in liquid foams caused by the presence of particles (e.g. Ref. 47), others stress that particles primarily prevent films from rupturing (e.g. Ref. 44)

As the structure of the non-metallic constituent is very different for various metal foam types these will be discussed separately.

### 5.1 Melts stabilised with SiC particles

Foams containing SiC particles are easy to investigate due to the size of the particles. Whether the foams are blown with an external gas source (“*Metcomb*”-type, see Fig. 1) or are made from precursors (“*Formgrip*”-type, see Fig. 3) does not influence the basic structure of the cell walls. In both cases they exhibit layers of SiC particles sitting at the gas/metal interfaces. There are some particles between the interfaces but these do not fill the space in between and do not even connect the layers mechanically. It is therefore unclear how the particle layers can give rise to a repulsive force (“the so-called disjoining pressure”) known from aqueous foam physics. One can speculate about possible explanations for the origin of the disjoining force:

- The repulsive force is generated by an additional constituent of the melt not yet known. This could be

traces of aluminium oxides which are present in the blowing gas (for “*Metcomb*”-type foams) or in the blowing agent or additional aluminium powder which is added to the melt (“*Formgrip*”-type). These oxides would act similar to the oxides in the foams made from powder compacts, i.e. maintain the observed minimum distance  $d_{\text{crit}}$  between the two interfaces.

- The repulsive force is generated by a capillary effect not yet explainable stemming from the particle layers.
- There is no repulsive force at all and it is not needed because there are no notable attractive forces which have to be balanced. Van der Waals interactions between the two gas/metal interfaces – an important attractive force in aqueous foams – have a very short range and could be negligible over the large film thicknesses found in metal foams. The particles at the interfaces increase surface viscosity, the particle within the films bulk viscosity and all together – perhaps assisted by residual oxide filaments – are sufficient to slow down drainage and to prevent films from losing too much liquid.

The observed increase in foam stability when the gas/metal interfaces are oxidised – either after using air as blowing gas or blowing powder compacts with  $\text{CaCO}_3$  – could be also discussed in terms of melt viscosity. This is made clear in the schematic in Fig. 17. Comparing two films of the same thickness – 50  $\mu\text{m}$  in the example – one sees that if the particles – average size 13  $\mu\text{m}$  in the case discussed – float on the interface and are partially wetted, the bulk liquid layer is thicker than if the surface is covered by an oxide layer pushing the particles into the film. Moreover the particles could be more mobile on the non-oxidised interface since the oxide layer might pin the particles and preventing them from moving downwards. Together, these effects could largely reduce drainage.

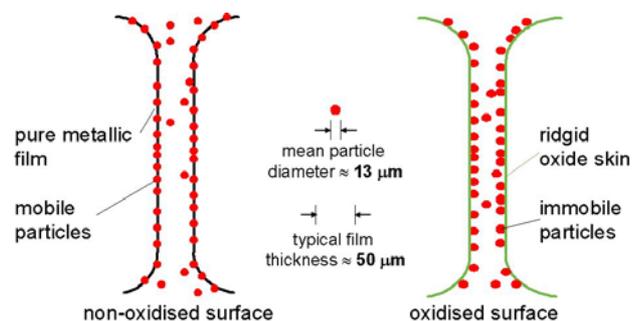


Fig. 17 Sketch of the particle arrangement in SiC-stabilised Al foams having a non-oxidised or an oxidized interface.

An alternative explanation has been proposed by Babcsán et al.<sup>36</sup>. He concludes that the oxid film damps surface waves in the liquid metallic films which are caused by mechanical or thermal perturbations and can lead to the rupture of a film. According to this picture the oxide film would therefore primarily prevent rupture and not influence drainage.

### 5.2 Melts from powder compacts

Foams made from powder compacts have a special melt structure as the metal contains nanometre-thick oxide filaments which covered the individual powder particles

prior to melting. Stabilisation of such foams has been discussed in terms of viscosity<sup>57,70)</sup> motivated by experiments with aluminium powder. An easy experiment shows how a melt can be stabilised by the presence of oxides. The sample of Fig 18a was made by pressing pure aluminium powder without any addition. After melting the sample does not behave like a liquid but maintains its shape almost without alterations (Fig 18b). The molten alloy is not mobile because each grain is separated by the oxide skin which surrounded the former powder particles.

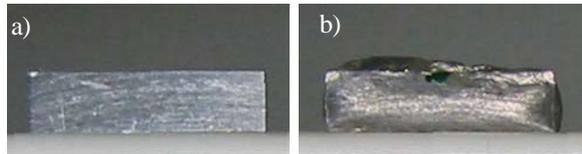


Fig 18: Al powder compact a) before melting, b) after melting at 680°C. Width of sample is 10 mm (courtesy of F. García Moreno)

In a liquid metal film the former surfaces of the powder particles can be very efficient in blocking metal flow. This effectively corresponds to viscosity approaching infinity. This hypothesis is supported by the observation that if the oxide network is damaged liquid metal runs out of the foam. One can, e.g., poke into a liquid foam with a needle and highly fluid aluminium will sometimes run out, indicating a breakdown of the oxide network and a sudden transition to low viscosity. This will also happen after sudden stretching of a cell wall leading to fast rupture. Fig. 19 highlights these ideas. The micrograph on the right shows a bamboo-like structured cell wall of a foam. One can see the individual Al-rich grains which have maintained their original shape during foaming.

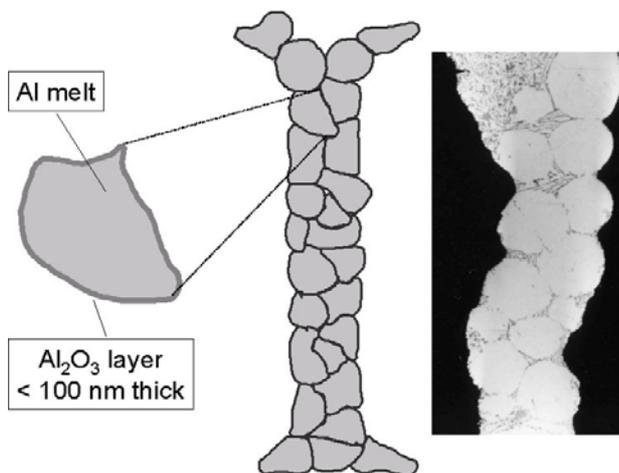


Fig. 19 Model of a cell wall in a foam produced by melting a powder compact. Micrograph: cell wall in a AlSi7+0.6wt.% TiH<sub>2</sub> foam<sup>42)</sup>. Foaming was in the semi-solid range at 600°C for 780s.

Körner et al. have investigated the structure of the oxide network in detail<sup>23)</sup> and concluded that network particles stabilise the foam by keeping the two films apart and holding the liquid in between by capillary action. Although this explanation sounds different it could in the end be equivalent to the viscosity-based model described above.

From their microgravity experiments Wübben et al. concluded that the function of oxides cannot solely be to increase bulk viscosity but also to stabilise the metal films

since the oxide content is proportional to the inner surface of the foams<sup>43,44,66)</sup>. The increase in bulk viscosity which is measured is therefore not the primary effect of the oxides. Viscosity is merely an indicator for the presence of a solid phase, the physical action of which is more complex.

Another interesting problem is that of the minimum cell wall thickness. Its existence means that films thinner than this limit disappear and the ones which are thicker survive. The question is what causes the rupture of films thinner than  $d_{crit}$ . The author has suggested that a film is prone to rupture whenever the interfaces move so close together that a non-wetting solid constituent bridges the films and causes the melt to recede from the particle<sup>57)</sup> (see Fig. 6b). Körner point out that the size of the individual network particles and the curvature of the liquid between them determine the critical thickness. Whenever the particles are far apart or large, a film ruptures at a larger  $d_{crit}$ <sup>23)</sup>. The discussion resembles the arguments for aqueous foams<sup>75)</sup>. Babcsán discusses rupture in terms of surface waves which make a film dynamically instable if it becomes too thin<sup>36)</sup>.

### 5.3 Is there an endogeneous stabilisation mechanism?

The idea that  $\alpha$ -grains present in a semisolid alloy act like particles and can stabilise or destabilise foams has been brought forward in the literature<sup>42,57,68)</sup>. Weigand foamed powder compacts of AlSi7 alloy in the semi-solid state and found that these foams were extremely stable<sup>42)</sup>. It is plausible that solid particles present in the liquid could have contributed to stability, in addition to the oxide network. However, whether this is a pure effect of viscosity of whether the  $\alpha$ -grains are surface active can not be answered definitively. Körner et al. have foamed Mg alloys by injecting semi-solid melt into a die together with some TiH<sub>2</sub>. No particles were added. They explain the observed foam stability with the presence of  $\alpha$ -Mg particles in the melt and call this effect *endogeneous stabilisation*<sup>68)</sup>. However, as injection was done into an air-filled mould, one could also speculate that oxides were foamed in-situ and that these oxides provide the stabilisation mechanism. Further investigations using an oxygen-free environment could help clarifying this question.

### 5.4 Is there a universal stabilisation mechanism for all foams?

Most authors are vague about the stabilisation mechanism of the type of foam they investigate and usually give explanations in terms of surface activity or viscosity. Körner at al. claim that there is a universal stabilisation mechanism for all kinds of metal foams<sup>23)</sup>. Accordingly, either solid ceramic particles,  $\alpha$ -grains in a semi-solid liquid or oxide network particles stabilise a metal foam film by adhering to the gas/metal interface and creating a direct mechanical bridge which counteracts the forces trying to thin the film. The present author is in doubt whether this is actually true, since there are stable foams in which no obvious mechanical forces exist. To the author it seems more likely that there is a complex and varying interplay between different effects in various types of metal foams and that both viscosity-enhancing effects and surface activity of particles play an important role.

## 6. Conclusions

The stabilisation of metal foams is still in parts a mystery. More knowledge about stability would allow to tailor foams such that they could be processed more reliably, exhibited smaller and more uniformly distributed cells and correspondingly showed a smaller variance of mechanical properties. Such foams are hoped to be more accepted by application engineers and to lead to a breakthrough in metal foam technology.

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