METAL FOAMS – MANUFACTURE AND PHYSICS OF FOAMING

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Abstract − The various ways to produce metal foams are reviewed. An analogy to aqueous foams is drawn and exploited to discuss the principle mechanisms responsible for foam stability. Experimental work based on ex-situ metallography and in-situ radioscopy of metal foam formation is used to answer some questions associated with the physics of foaming and to define areas where further research is still needed.

Keywords: metal foams, production, stability

1. INTRODUCTION

Metal foams are very challenging materials as their manufacture involves the simultaneous occurrence of solid, liquid and gaseous phases at varying temperatures and the morphology of the solidified foam is quite complex.

Quite some manufacturing technologies for foamed metals are now known. However, despite the quality improvement over the past 10 years the resulting metal foams still suffer from non-uniformities and other deficiencies. In order to improve the cellular structure of the materials and also to make the production technologies more reliable and reproducible, foam stability of liquid metals, i.e. avoidance of rupture and drainage, has to be understood and controlled. In developing production methods empiricism has been usually applied instead of relying on profound scientific knowledge. Therefore a clear understanding of foam stability is expected to allow one to improve foam quality and process control more easily.

In the literature and in practical use there is some confusion concerning the term *metallic foam which* is often used for any kind of non-dense metallic material. In the field of aqueous foams the term *foam* is usually reserved for dispersions of gas bubbles in liquids [1] and the foams are produced in the liquid or semisolid state. For metallic systems we define:

- *cellular metals*, which are materials with a high volume fraction of voids made up of an interconnected network of struts and plates,
- *porous metals*, which have isolated, roughly spherical pores and a porosity level of usually less than about 70%. Mechanically, pores do not interact if the porosity is less than about 20%,
- *metal foams* are a subgroup of cellular metals, usually having polyhedral cells, but shapes may vary in cases where, e.g., directional solidification creates

different morphologies. Cells may be either closed with membranes separating adjoining cells, or open, if there are no membranes across the faces of the cells so that the voids are interconnected. The expression *metal foam*, strictly valid only for the liquid phase, is often also used to describe the solid product. Thus the liquid counterpart is defined as *liquid-metal foam*.

- Solid foams originating from liquid foam are closed. Some prefer to call open-cell metallic structures *metal sponges*, not metal foams.

2. METAL FOAM PRODUCTION METHODS

The manufacture of cellular metals in the most general sense is described in review articles and conference proceedings [2-6]. A dedicated web page offers up-to-date information [7]. The present paper will be restricted to metallic closed-cell foams. These are low-density liquid-gas mixtures at some stage of their evolution which are then solidified to yield solid foams. As surface tension governs morphology in the liquid state – isolated gas bubbles separated from each other by metal films – the corresponding solid metal foams show a similar morphology. We shall first review different manufacturing routes and then discuss the physics of foaming.

2.1. Foaming liquid metals

Metallic melts can be foamed by creating gas bubbles in the liquid provided that the melt has been prepared such that the emerging foam is fairly stable during processing. This can be done by adding fine ceramic powders or alloying elements to the melt, which form stabilising particles, or by other means.

Currently three ways for foaming metallic melts are known: firstly, by injecting gas into the liquid metal, second, by causing an in-situ gas release 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.

2.1.1. Foaming melts by gas injection ("Cymat/ Metcomb")

The first way for foaming aluminium and aluminium alloys is already being exploited commercially by Cymat Aluminium Corp. in Canada [8]. Silicon carbide, aluminium oxide or magnesium oxide particles are used to enhance the

viscosity of the melt and to adjust its foaming properties. The base metal is usually an aluminium alloy. The volume fraction of the reinforcing particles typically ranges from 10 to 20%, the mean particle size from 5 to 20 μm. The melt is foamed by injecting gases (air, nitrogen, argon) into it using specially designed rotating impellers or vibrating nozzles which generate 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 and solidify [9].

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 these foams can be a problem. Advantages of this direct foaming process include the large volume of foam which can be continuously produced and the low densities which can be achieved.

Quite recently the melt foaming route has been revolutionised by scientists working at the Light-metals Competence Centre (LKR) and the metallurgical plant Hütte Klein-Reichenbach GmbH, both in Austria [10]. The key point is a new concept of gas injection which leads to foams with an excellent uniformity of cell sizes. Moreover, by casting the foam into moulds, complex-shaped foamed parts with a closed outer skin can be generated. Commercial exploitation of this type of aluminium foam –called "*Metcomb*" – is on the way.

2.1.2. Foaming 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 [11]. The blowing agent decomposes under the influence of heat and releases gas which then propels the foaming process. 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. The Chinese company Jiangsu Tianbo Light-Weight Materials in Nanjing has also set-up a production plant recently. In a first production step about 1.5 wt.% calcium metal is 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 oxides, e.g. $CaAl_2O_4$, or intermetallics which thicken the liquid metal. After this, titanium hydride (TiH_2) is added (typically 1.6 wt.%) which acts as a blowing agent as it releases hydrogen gas. The melt soon starts to expand slowly and gradually fills the foaming vessel. The entire foaming process can take 15 minutes for a typical batch of about 0.6 m^3. 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 foams produced in this way - trade name "*Alporas*" – have a very uniform pores structure.

CaF_2 coated $CaCO_3$ foaming agent was applied in an Alporas-like process by Nakamura et al. [12]. Carbonate foaming ensured smaller pores but similar densities as foaming with TiH_2.

2.1.3. Solid-gas eutectic solidification ("Gasar/Lotus")

A method developed about 15 years ago exploits the difference in gas solubility of liquid and solid metals [13]. A melt is first charged with gas under high pressure (up to 50 bar), e.g. with hydrogen or nitrogen. If the temperature is then lowered to below the melting point of the metal the gas will precipitate. Under favourable conditions gas bubbles are entrapped in the metal. The resulting pore morphologies are largely determined by the gas 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. Pore diameters range from 10 μm to 10 mm, pore lengths from 100 μm to 300 mm, and porosities from 5 to 75%. The word "gasar" was coined for such materials which means "gas-reinforced" in a Russian acronym. Recently the method has been adapted in Japan [14] where the material was named "lotus-structured" for its resemblance with lotus roots.

2.2. Foaming metallic precursors

A second class of metal foaming techniques adds an additional step to the process chain. Instead of foaming the melt directly, a precursor is prepared which contains a uniformly dispersed blowing agent. The foam is created in a second step by melting the precursor during which the blowing gas evolves and bubbles are created. The advantage of this process is that complex shaped parts can be manufactured by filling moulds with the precursor and foaming. Foamable precursors have been prepared in three ways: by densifying mixtures of powders containing a blowing agent in the solid state, by shaping such powder blends by thixo-casting in the semi-solid state and by admixing blowing agent powders to melts which are then solidified.

Instead of using gas-releasing blowing agents, powders can be added to the metal to be foamed which react with a second component during foaming and create gas that way. Alternatively, crystal water bound in a powdered component can propel foaming when it evaporates [15].

2.2.1. Foaming of powder compacts ("Foaminal/ Alulight")

The production process begins with the mixing of metal powders - elementary metal powders, alloy powders or metal powder blends - with a powdered blowing agent, after which the mix is compacted to yield a dense, semi-finished product [16]. 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 during further processing. The next step is to melt the matrix material causing the blowing agent to decompose. 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. Aluminium and its alloys, tin, zinc, brass, lead, gold and some other metals and alloys been foamed by choosing appropriate blowing agents and process parameters.

Sandwich panels consisting of a foamed metal core and two metal face sheets can be obtained by roll-cladding conventional sheets of metal – aluminium, steel or titanium - to a sheet of foamable precursor material. The resulting composite can be shaped 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 [17].

The process is now in the stage of a small-scale commercial exploitation by the German companies Schunk (Gießen), Karmann (Osnabrück), Applied Light-weight Materials ALM (Saarbrücken) and the Austrian company Alulight (Ranshofen). The names ”*Foam-in-Al*” and “*Alulight*” have been coined for these foams. The term *AFS* is used for **A**luminium **F**oam **S**andwich.

2.2.2. Foaming thixo-cast precursor material (“Thixofoam”)

Instead of consolidating the metal powder mixtures in the solid state by powder pressing one can carry out the densification by thixo-casting in the semi-solid state [18]. For this the powder blend is first pre-densified to billets by cold isostatic pressing, yielding densities of about 80%. These billets are then heated to a temperature at which the respective alloy is semi-solid and are then cast to shapes in a die-casting machine. The resulting precursor can be foamed as described in the previous section by re-melting the precursor. The advantage of this route is that the precursor can have a complex shape and does not have to be further worked. Moreover, compared to the powder densification method, casting leads to a more isotropic precursor material and therefore to foam with a very uniform pore structure.

2.2.3. Foaming of ingots containing blowing agents (“Formgrip/Formcarp”)

Foamable aluminium-based precursor material can be prepared without using metal powder at all. For this titanium hydride particles are admixed to liquid metal after which the melt is solidified. The resulting precursor can then be foamed in the same way as described in the previous two sections. To avoid premature hydrogen evolution during mixing, solidification has to be either rapid or the blowing agent has to be passivated to prevent it from releasing too much gas at this stage.

One way is to use 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. However, achieving a homogeneous distribution of TiH_2 powders in the die is challenging. Alternatively, TiH_2 powders can be added to a melt by comparatively slow stirring and subsequent cooling provided that they are subjected to a cycle of heat treatments that form an oxide barrier on each hydride particle to delay their decomposition [20]. In order to obtain stable foams, melts containing 10-15 vol.% SiC particles are used. The process has been baptised “*Formgrip*” which is an acronym of “Foaming of reinforced metals by gas release in precursors”.

Gergely et al. reinvestigated foaming of aluminium alloys by means of $CaCO_3$. A sister of “Formgrip” process was developed and named “*Foamcarp*” [21]. During foaming $CaCO_3$ releases CO_2 that is reduced to CO and oxidises the surface of the cells [22] creating an oxide layer [21].

2.2.4. Foaming by gas generation during foaming

Instead of using a blowing agent which generates a gas by decomposition, foam-propelling gas can be created by reaction of two components in a powder compact. Steel foam can be manufactured by admixing fine carbon powder to steel powders containing some iron oxide. This leads to the in-situ formation of CO gas upon melting of the compacts [23].

2.2.5. Foaming by combustion reaction

Al-Ni intermetallic foams can be produced by mixing aluminium and nickel powders with Ti, B_4C and TiC additives [15]. After blending and compacting the precursor is heated to above the melting point of Al where a self-propagating exothermal reaction takes place between the components. The oxide-hydrate in the powder surfaces leads to the formation of the blowing gas in this case. Quite uniform foams with porosities ranging up to 85% have been obtained.

3. PHYSICS OF FOAMING

The physics of foams comprises many phenomena associated with their birth, life and death [24]. In this article we are concerned with the stabilisation of foams and with processes leading to sudden, unwanted changes in foams. Bubble formation as the birth of foams and the variety of drainage phenomena are not investigated.

We first review the stabilisation of aqueous foams before we try to understand liquid-metal foam stability by discussing results of ex-situ metallography and in-situ radioscopy on aluminium-based foams.

3.1 General

The term *foam stability* is related to the absence of rupture of cell walls and to a limitation to drainage in the foam. Rupture is a spontaneous and almost instantaneous phenomenon while drainage is time consuming. Several factors influence foam stability, including the geometry of Plateau borders, cell wall thickness, surface adsorption,

surface mobility, dilatational viscosity and elasticity. One can consider foam as a viscoelastic system. The elastic parameters of aqueous systems can be characterized by dilatational elasticity measurements [25].

Pure single-component liquids cannot be foamed. Bubbles, e.g. in mineral water or pure aluminium, immediately rupture when they arrive at the surface. Stability cannot be achieved by merely choosing a large bulk viscosity or a low surface tension of a single-component liquid. To prevent a film from thinning until rupture, a local force is necessary which acts against local destabilisation caused by perturbations such as thermal fluctuations or surface waves. Water can be foamed if it contains a second, *surface-active component*. Stable soapy water films can be made as thin as 6 nm (black film) [26]. The second component reduces surface tension but its main effect is to increase what is called *surface elasticity*. In many types of foam the stability derives from a pair of locally acting phenomena associated to the names of two 19th century scientists, namely J.W. Gibbs and C.G.M. Marangoni. The Gibbs effect dictates that a stretched film will try to contract like an elastic skin. The Marangoni effect acts temporary. It arises because a certain amount of time is required for surfactant molecules to diffuse to the surface of a newly stretched film. These two effects act such that foams are stabilised whenever the surface layers in the lamellae can rapidly compensate for surface tension gradients that develop from disturbances during foam ageing.

The force balance in films is quite complicated: beside attractive van der Waals forces there are repulsive forces – called disjoining forces – opposing film contraction. Electrical double layers on the film surfaces can generate such forces. The balance of these two forces describes foam stability in the so-called DLVO theory [27]. However, other forces such as hydration forces, steric forces, structural forces, peristaltic or hydrodynamic forces can also be important.

The rupture of liquid films is closely connected with interfacial waves caused by external effects. These can be generated by sound waves, mechanical vibrations, temperature fluctuation and the heterogeneous exchange of components with the environment. The Gibbs and the Marangoni effects stabilise the films in foams against fluctuation in thickness. If a perturbation increases the area of film locally, the surface tension will also increase. This will stiffen the surface against growth of the fluctuation. The absence of Gibbs and Marangoni effect in a pure liquid is the main reason, why a pure liquid cannot foam: the films in the foam of a pure liquid are unstable to infinitesimal fluctuations [28].

Aqueous foams can be also stabilised by *solid particles*: a) wetting particles present in Plateau borders slow down foam drainage; b) partially wetting particles form layers on the surface of the liquid films and therefore can be considered as surfactants [29]; c) colloidal particles forms long-range ordered microstructures in the liquid films which are stabilised by a non-DLVO surface force called structural force [30]. The structural force appears during the thinning of thin liquid films containing colloidal particles, e.g.

surfactant micelles, macromolecules or solid particles. It origins from the long-range interaction force in concentrated colloidal dispersions. It is still a question how the particles – their action described by their concentration, their contact angle with the liquid-gas system, their size and shape – affect the stability of liquid foams. Foam stability of a model system of water and 3.88 μm surface modified polystyrene particles was characterised by Wilson [31] as a function of the contact angle. The contact angle was set either by salt addition or by surfactants. Between 0-33° no foaming, between 33-67° slight foaming, between 67-85° good foaming and above 85° very good foaming was observed. In the presence of surfactants Johansson et al. examined the foam stabilising effect of micrometre-sized quartz particles. A stabilising effect was found in the range of 60-90° with an optimum at 75°. Below 44 μm particle size foam stability was enhanced with respect to larger particles [32]. Sun and Gao examined the effect of 1-75 μm PTFE, PE and PVC particles in surfactant free ethanol-water solution. The wetting angle of particles is tuned by setting the ethanol concentration. An optimum wetting angle range of 75° to 85° for obtaining stable foams was found. Smaller particles produced more stable foams [33]. Sethumadhavan et al. stabilised aqueous liquid films with 3-38.6 nm silica particles. It has to be noted that non-wetting particles are used even as antifoaming agents where the defoaming ability depends on both the contact angle - contact angles >90° leading to good defoaming - and the surface roughness of the particles [34]. An increase of particle concentration decreases the apparent surface tension of a water suspension [35].

3.2 Metal foams

The open question currently dividing metal foam scientists is, which chemical and processing parameters are essential to obtain stable metal foam. From the experimental evidence it seems clear that all metal foams are stabilised by solid additions – e.g. particles – but the way these particles create disjoining forces has not been explained in a convincing way. Moreover, the role of viscosity or surface tension of the metallic melt is under dispute.

Foamable liquid metals always contain some kind of solid inclusions, either micrometre-sized particles or nanometre thick oxide films that are located inside and/or on the surfaces of the cells. In the former case the particles are added to the melt at some stage of the processing route, while in the latter the oxide films usually enter the material as a side product of powder production which creates thin oxide films on each powder particle.

Metal foams of "Cymat", "Formgrip" and "Metcomb" type (see Sec. II) show analogy with some nowadays investigated "dirty water" foam systems, where particles stabilise aqueous foams.

To produce stable liquid-metal foam by blowing gas into a metallic melt a minimum amount of solid particles is necessary [36]. The first schematic stability map giving limits for the volume content and particle size required for metal foam creation was published by I. Jin [9]. This map was interpreted by Kaptay [37] on the basis of theoretical

considerations. Several foam stability theories exist in the literature. Gergely et al. [38] state that viscosity increases with particle content and reducing the temperature close to the melting point slows down the vertical motion of liquid. Ip et al. suggests that solid particles lead to flatter curvatures [36] around the Plateau borders which reduces suction of metal from the cell wall into the border. Kaptay pointed out that the wetting angle has to be in a certain range and particles stabilise the gas/liquid-bubble interface [39]. Particle addition to liquid-aluminum alloy can significantly decrease the apparent surface tension of the liquid-metal dispersions [40]. An additional stabilisation effect of the oxide skin on the inner surface of the liquid cell walls which is formed via reaction of the liquid metal with the oxidising blowing gas (shown in Fig. 1 for a foam after solidification) was justified by Babcsan et al. [40, 41] and Leitlmeier et al. [10].
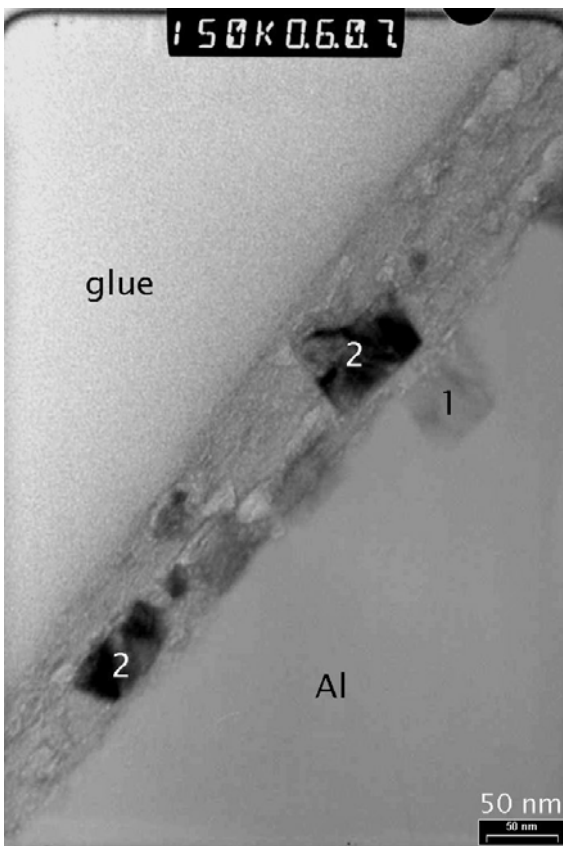
Fig. 1. Oxide skin on "Cymat" foam cell consisting of 1: primary oxide and 2: secondary oxide particles. It confirms the observation that the high temperature surface films are duplex. The amorphous oxide film first formed can be transformed into secondary crystals inside the oxide layer or primary crystals can nucleate below the amorphous layer.

For foams created from powder compacts Arnold et al. stated that solid oxide networks are responsible for foam stability [42]. Wübben et al. used micro-gravity experiments to show that the primary action of the solid stabilising component is to prevent films from coalescing while their influence on viscosity must be less important [43].

The distribution of particles and the forces acting between them are well known in aqueous suspensions. The transparency and the low melting point facilitate doing colloid chemistry in water. In high temperature systems such as metallic dispersions until now only post-solidification metallographic methods were available. In such studies one has to take into account that solidification might change the distribution, e.g. by the pushing effect or particle engulfment of a solidification front. We hope that new methods based, e.g., on synchrotron radiation experiments, could help establishing a new discipline called *high temperature colloid chemistry* which would then help to understand the stability of liquid metal foams in further detail.

Particles can agglomerate on the surface of rising bubbles during liquid-metal foam production in a similar way as in flotation. Leitlmeier et al. measured the volume fraction of particles in foam by the travelling distance for bubbles in the melt given by the distance from the injector to the metal surface. Below a critical travelling distance no stable foam could be produced [10]. Ip et al. suggested that complete coverage of the bubble surface by particles is not required to attain stable liquid-metal foam and assumed a minimum surface coverage of 50% [36]. Babcsan et al. measured the surface coverage of "Metcomb" foams. The maximum coverage of Al_2O_3 and SiC particles was found to be 45% using nitrogen as a foaming gas. This value drastically decreased by applying oxidising foaming gases [41].

It is thought that films of metallic melt cannot be stretched to the extent of aqueous films. Metallic melt films and liquid-metal cell walls usually rupture below a critical thickness ranging from about 40 to 100 μm [44] for foams made from powder compacts and similar values for foams produced by gas injection [40]. In the latter case it could be shown that the cell wall thickness depends on: a) the particle diameter [38] – larger particles produce thicker, smaller particle thinner cells walls –, and b) the composition of the alloy [40], c) the particle material [40], and d) the foaming temperature [40].

3.2.1. Influence of particle size

Our recent investigations on "Formgrip" foams by x-ray radioscopy show the effect of particle size. Precursors containing two types of SiC particles were foamed under equal conditions and observed in-situ. It was found that bubble coalescence was much more pronounced for the precursor containing the coarse particles (see Fig. 2 and Fig 3).
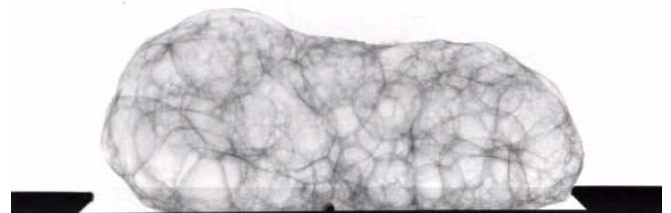

Fig. 2. Liquid-Al foam stabilised with 13 μm SiC particles produced from "Formgrip" precursors containing AlSi9Cu3 + 10 vol.% SiC and 0.5 wt% TiH$_2$ as blowing agent, real-time x-ray radioscopy picture was obtained using a synchrotron beam.

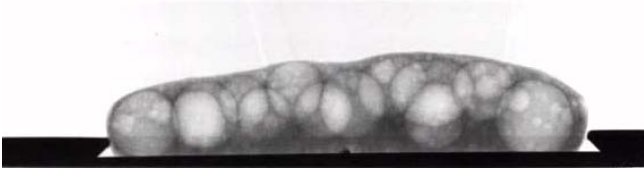Fig. 3. Same as Fig. 2 but for 70 μm SiC particles.

Fig. 5. Same as Fig. 4 but for 70 μm SiC particles.

Ex-situ SEM analysis of solid cell walls in the solidified foam showed a dense coverage with particles for 13 μm size (Fig. 4). While these 13 μm particles segregated on the surface only a small amount of the 70 μm particles can be found on the surface (Fig. 5). The final cell wall thickness also varied with the particle size: 13 μm particles produced cell walls about 85-100 μm thick whereas 70 μm particles increased the cell wall thickness up to 300 μm. The cross-sections of the cell walls of these two foams shown in Fig. 6 and Fig. 7 confirm this picture.

For the sake of completeness it has to be noted that the foam with 13 μm particles was made of commercial Duralcan MMC while the raw material of the foam with 70 μm particles was manufactured by another company. Therefore, except for the difference in size other properties may also play a role.

Fig. 6. Cell wall cross-section of metal foam produced from "Formgrip" precursor containing 13 μm SiC particles, SEM picture.

Fig. 4. Top view SEM image of a cell wall in a foam prepared from "Formgrip" material containing 10 vol.% 13 μm SiC particles.
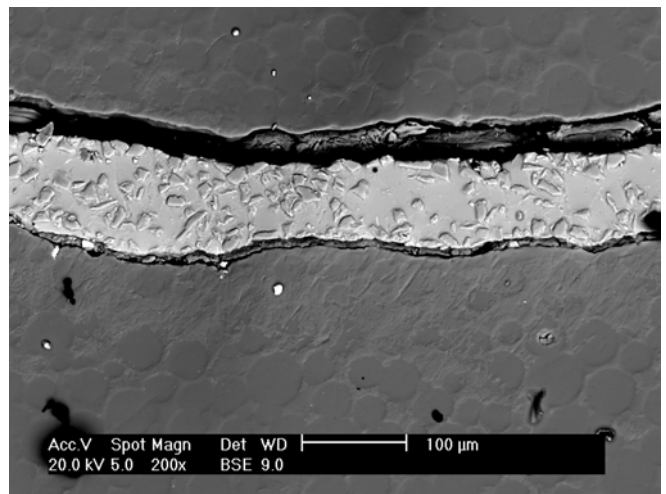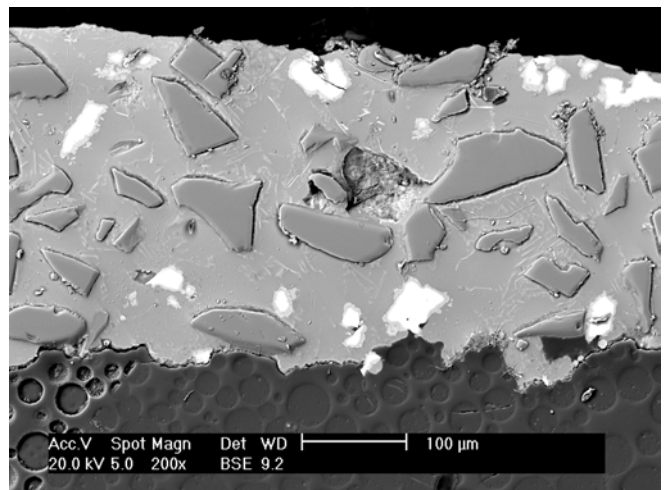

Fig. 7. Same as Fig. 6 for 70 μm SiC particles.

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3.2.2. Influence of volume fraction

What remains to be explained is why it is necessary to use a much higher volume fraction of inclusions for obtaining a stable foam in the melt route, e.g. by bubbling gas through a melt, than in the route based on melting powder compacts.

Powder compacts used for foaming contain thin oxide films which previously covered the surface of the metallic powder particles. After extrusion of the powder mixtures to compacts these thin oxide films are converted to broken oxide filaments with a size between 4 and 100 nm with an average of ~20 nm [45]. These oxides are homogeneously distributed in the precursor. Melting and stirring a molten precursor (without the presence of a blowing agent) will lead to agglomeration of the oxide films [42]. Weigand reported that for good foam generation from powder compacts at least 0.2 wt.% aluminium oxide was necessary to obtain good foamability [46]. Lead foam was found much more stable if the oxygen content was 0.16 wt.% rather than 0.06 wt.% in another sample with poor foamability [43].

Leitlmeier et al. reported that in aluminium foams generated by bubbling gas through melts at least 10 vol.% SiC particles of 9 μm size are necessary to stabilise the foam at 727 °C. The minimum volume fraction required in the melt decreased when the immersion depth was increased [10]. Ip et al. determined a minimum of 8 vol.% for foamability in an aluminium alloy melt containing 10-15 μm SiC particles. This minimum concentration rises to 10 vol.% when the temperature of the melt is elevated from 735 to 775 °C. In both cases the immersion depth of the injector was 3 cm [36]. Babcsán et al. determined that a minimum of 5 vol.% of 11 μm Al_2O_3 particles are necessary in an aluminium melt to produce stable foam at 700 °C with 18 mm immersion depth [40]. Early work of Jin et al. confirms these results [9].

The stabilisation mechanism for "Alporas" foams (see Sec. 2.1.2.) has not yet been discussed in the literature. To be able to compare the stabilisation of "Alporas" with that of the foams already treated a commercial "Alporas" foam sample was polished and etched with 0.5 vol.% HF water solution. Our SEM and EDX examination (Fig. 8) showed deeply etched valleys (2,5) with high oxygen content and secondary phases attached to line-shaped pores with higher Ca and/or Ti content (1,3) than the matrix (4). These line-shaped pores - most probably oxide bifilms [47] - form networks [48] decorated with secondary phases. We suspect that these decorated bifilms could play a crucial role in the stabilisation of "Alporas"-type metal foams. The size and volume fraction of these inclusions is estimated to below 1 μm and 1 vol.%.
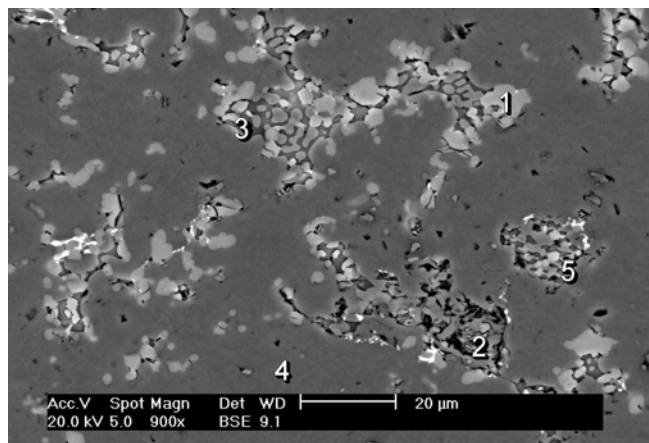

Fig. 8. Oxide bifilm networks decorated with secondary phases in an etched cross section of "Alporas" foam cell, SEM picture.

The investigations mentioned above give clear evidence that a lower volume fraction of inclusions is necessary in the powder compact foaming route (using oxide films) than in the melt foaming process (adding particles). From the viewpoint of stabilisation these two processes could be brought closer to each other by using a lower fraction of smaller (nanometre-sized) particles in the melt route. Submicrometre-sized particles are difficult to mix with an aluminium melt. In-situ gas reaction synthesis of stabilising particles was reported recently [49] and might be a way to produce smaller particle sizes. As a side effect more easily machinable metal foam products would result.

Our speculative volume fraction size diagram shows a possible relationship between the parameters describing particle stabilisation (Fig. 9).
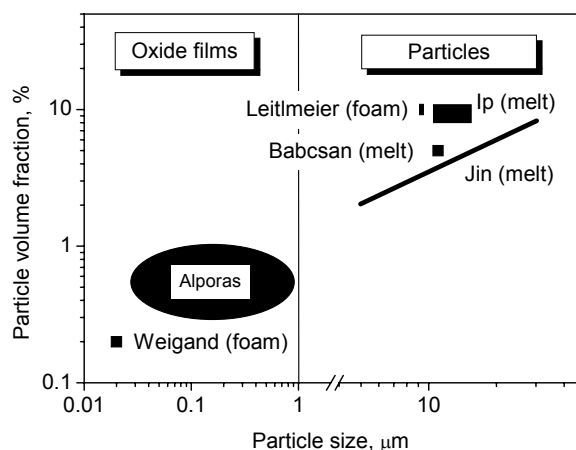

Fig. 9. Speculative stability diagramme for metal foams relating particle volume fraction and particle size. Data given by various authors measured in the foam or in the melt are included.

3.2.3. Particle composition

The stabilisation effect also depends on the chemical composition of particles. Al_2O_3, SiC and MgO particles increase stability of liquid aluminium foam made by gas

injection. Foaming of pure Al powder compacts could be stabilised with TiB_2, Al_2O_3, and SiC in this order [50].

It is common believe that the composition of the particles determines the stabilising effect through the contact angle with the melt [39, 51, 52]. To make a trial a particle type was selected having a contact angle out of the preferable contact angle range (60-90°). TiB_2 was chosen, as its contact angle is 98° at 900°C in pure Al [53]. The aluminium (AlSi10 +15wt.% TiB_2 particle of 3-6 μm size) foam was created by gas injection into the melt at 700°C. It was found that TiB_2 is not an effective stabiliser for this particular aluminium foam. Only irregular bubble remnants could be produced as it is shown in Fig. 10. TiB_2 particles fall out from the bubble surfaces leaving a significant amount of powder on the surface of the melt. Particles can be extracted from the melt only if they are non-wetted by the melt indicating that that TiB_2 is non-wetting. Therefore, selecting stabilising particles by exploiting tabulated data for contact angles is one successful strategy.
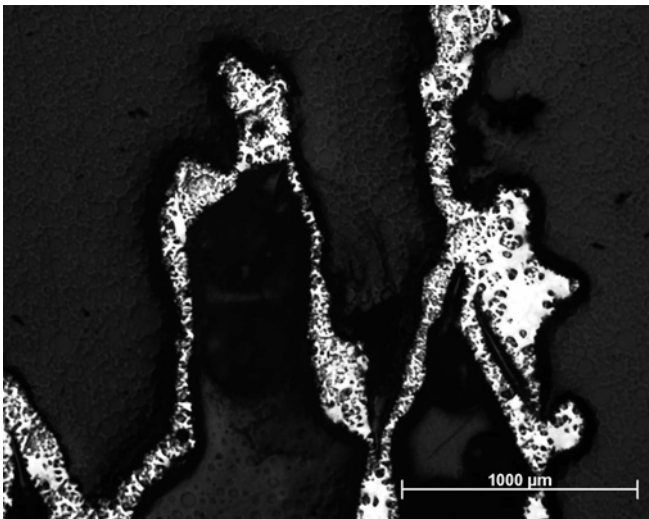

Fig. 10. Irregular metallic bubble remnants produced when foaming aluminium alloy reinforced with TiB_2 particles. A cross section of the remnants is shown with optical microscopy.

There is strong evidence that not only the chemical particle composition but also other particle properties govern their behaviour in a metal film. Such factors can be *particle shape* – round or angular –, *surface morphology* – smooth or rough –, or the occurrence of *reaction layers* [54, 55] on the surface of stabilising particles.

3.2.4. Influence of reaction layers on particles

Foaming of MMC melts based on AlSi0.8Mg0.8 +10 vol.% Al_2O_3 (Duralcan) by gas injection produced thicker cell walls (Fig. 11) and more clustering of particles than a modified MMC with a higher Si/Mg ratio (Fig. 12). SEM, EDX and XRD analysis of the particles in the fractured cell walls revealed that a spinel (Al_2MgO_4) layer forms on the alumina particles if the Si/Mg ratio is low (Fig. 13). If more Si is present, spinel layers did not form (Fig. 14) leading to thinner cell walls and inhibiting cluster formation.

We also showed that SiC looses its ability to stabilise a melt after overheating. XRD analysis showed the formation of Al_4C_3 in the melt at high temperature [56, 57]. The carbide formation on the surface of stabilising particles can modify the contact angle of the particle putting it outside the preferred region.
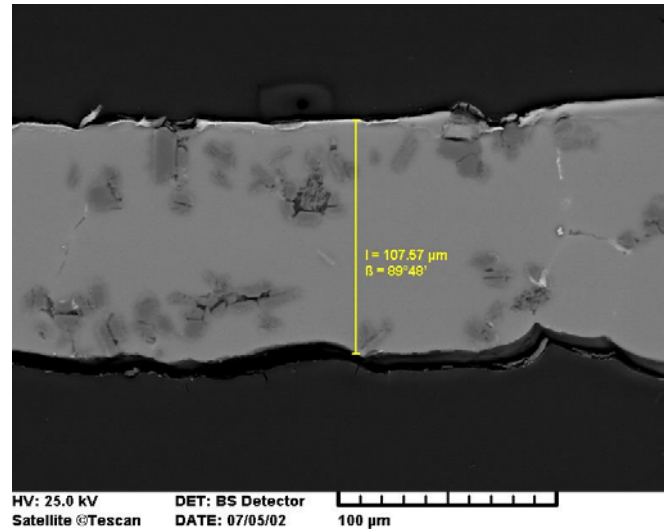

Fig. 11. Clustering of spinel coated Al_2O_3 particles in aluminium foam with low Si/Mg ratio, cell wall cross-section, SEM picture.
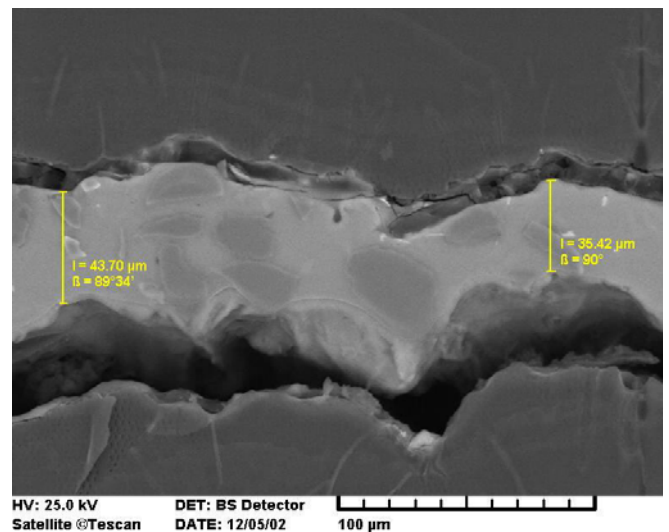

Fig. 12. Single spinel free Al_2O_3 particles in aluminium foam with high Si/Mg ratio, cell wall cross-section, SEM picture.
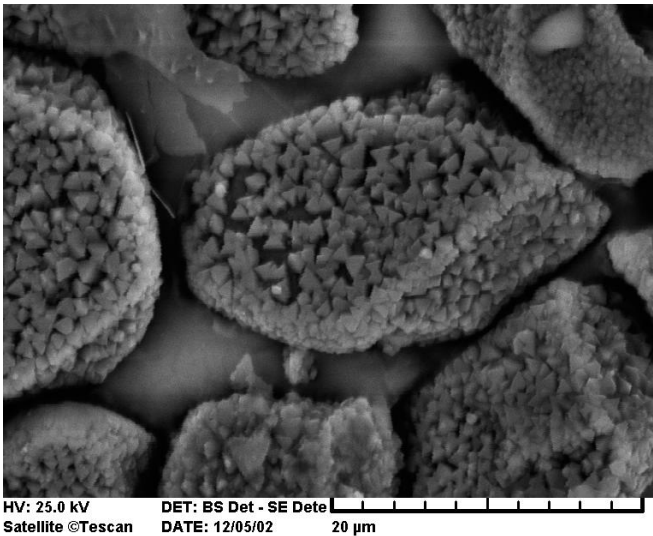
HV: 25.0 kV DET: BS Det - SE Dete
Satellite ©Tescan DATE: 12/05/02 20 µm

Fig. 13. Spinel crystals on the surface of an Al_2O_3 particle in Al foam with low Si/Mg ratio, SEM picture.

HV: 25.0 kV DET: SE Detector
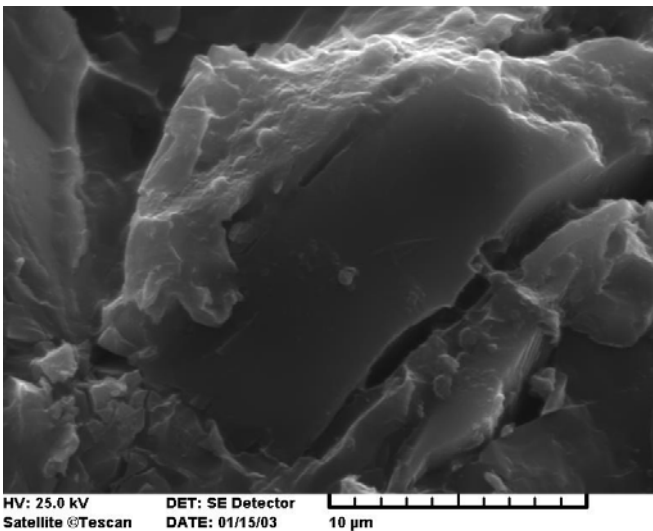Satellite ©Tescan DATE: 01/15/03 10 µm

Fig. 14. Same as Fig. 13, but high Si/Mg ratio. No spinel is visible.

3.2.5. Influence of foaming gas

Stability was found to depend strongly not only on particle properties but also on the foaming gas used. If the gas is hydrogen as it is usually in powder compact foaming when TiH_2 is used as blowing agent, the liquid foam films rupture frequently and the excess liquid generated in such bursts drains out to the bottom.

When foaming melts by injecting gases the gas composition can be varied. It was shown on cross sections of monodisperse aluminium foam samples which were first generated and then held isothermally for 0, 10 and 100 min that use of an oxidising gas practically eliminates drainage and coalescence phenomena even for the longest holding time [41].

4. CONCLUSIONS

The key parameters governing metallic foam stability can be divided into two groups: the role of solid inclusions (particles and/or thin non-metallic films) and the role of the surface skin formation. The role of the surface skin have already been investigated in the literature for metal foams produced by gas injection.

In our paper the effect of *solid inclusions* on foam stability is considered. We can conclude that solid inclusions are influencing foam stability through their wetting behaviour and their distribution in the melt (network formation, clustering or segregation). Beside the particle concentration and size, recent investigations showed that the compositions of both the metallic melts and the stabilising particles influence stability. It is believed that the temperature and the composition of the melt act through the formation of additional surface layers on the particles.

Differences and similarities of foam stabilisation in aqueous and metallic foams are summarised in Table I.

TABLE I. Comparison of foam stabilisation in aqueous and metallic foams.

	Aqueous foams	Metallic foams
Differences	Surface-active agent: *molecules* Additional stabilisation: structural force	Surface-active agent: *particles* (60-90° contact angle) Additional stabilisation: solid (oxide) skin and networks of inclusions
Similarities	• Surface-active agents are required, both molecules and particles decreasing the surface tension adding elastic behaviour to the liquid films. • To slow down drainage, a high viscosity (bulk and surface) is important. • Surface viscosity can be increased by oxide skin (metallic) or suitable surface-active molecules (aqueous) on the cell wall.	

5. CHALLENGES

A more profound understanding of some of the phenomena in metallic foam formation could be obtained by carrying out experiments on:
- wet liquid-metal foams,
- particle tracing in liquid-metal foam column,
- forced drainage experiments in liquid-metal foams,
- stabilisation of liquid-metal foams with nano-sized particles.

This might lead to new or more advanced metal foam product, such as
- metal foam with controlled pore morphology,
- machinable metal foams by using the cheaper melt route and nano-sized stabilisation particles.

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