

Review article

# Selection of blowing agent for metal foam production: A review

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#### Abstract

Metal foams are cellular solids in which gas is uniformly distributed throughout the metal matrix. One of the cheapest ways of evolving the gas is introducing the blowing agent in parent metal in liquid state. A blowing agent is defined as a material that decomposes under the presence of heat and releases gas which then propels the foaming process. The quality of final foam is influenced by several parameters such as composition, size and volume fraction of the blowing agent used. Different chemicals which can evolve gases such as carbonates and metal hydrides fit into the description of blowing agent. Hydrides during decomposition releases  $H_2$  gas while carbonates release  $CO_2$  or CO gases which are responsible for foaming process. To produce good quality metal foam, the blowing agent must be a compound that does not detriment the foam metallic matrix and must have decomposition temperature closed to the melting point of the metal. This review paper covers the manufacturing processes which uses blowing agent in the formation of metal foam. Furthermore, the paper provides the detail information about the foaming physics, blowing agent's type and selection criteria of blowing agents to produce amorphous metal foam.

# 1. Introduction

With growing interest of researchers in developing noble materials having high strength to weight ratio and finding utility in functional as well as structural applications, many materials have been developed such as composites, honeycomb, metal matrix, metal foam etc. One of the noble material which is catching interest worldwide among researches is metal foam. A metal foam is typically a cellular structure containing pores which are filled by either gas or air. The metal foams consist of uniformly distributed gas pores in a solid metal having the volume fraction ranging from 40% to 98%. The foam morphology consists of a metallic matrix in which single gas inclusions are finely dispersed and totally enclosed by the solid. High stiffness to weight ratio, the low specific weight, the high energy absorption during plastic deformation, good mechanical strength and recyclability are among its major properties which have made them attractive for current and future applications in the automotive and construction industries [1-7].

Mainly foams have three types of structure i.e. open, close and combination of two. Recently a novel structure is developed, which is known as lotus type structure. The open cell structure type consists of interconnected pores, whereas the closed cell structure has sealed pores surrounded by a metallic thin wall and the lotus type has long cylindrical pores aligned in one direction. Lotus type structures are inch forward than other processes by the fact that many gases are soluble in liquid state in comparison to solid state of parent metal resulting in long elongated cylindrical pores [8]. Another category of foam developed which have microsphere arranged in a controlled systematic pattern instead of uniform pores known as syntactic foam. These microspheres are made of glass, polymer, carbon and ceramic or even metal reinforced in metal matrix [9-11]. The morphology of the solid foam is extremely complex and its final properties vary with the type of porosity exhibited.

The production of metal foam can be completed in molten state or powder state of metal. The evolution of pores in the precursor is the classifying criteria of metal foam. The porosity can be generated either by using blowing agent or blowing the air at high pressure inside the melt. Figure 1 shows the production process of metal foam.

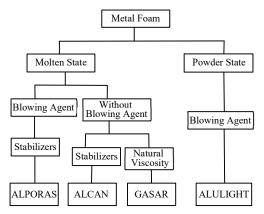


Figure 1. Production process of metal foam.

A blowing agent is a substance which is capable of producing a cellular structure via a foaming process for variety of material that undergo hardening or phase transition. They are typically applied when the blown material is in a liquid stage. Generally, the foaming agents must undergo thermal decomposition and generate gas pressure in the matrix sufficient to overcome atmospheric pressure and cause foaming [12]. Blowing agents preferably decomposes with liberation of gases and care should be taken that these generated gases must be virtually insoluble in the matrix moreover corrosive gases should be avoided from the decomposition products.

Blowing agents have different decomposition temperature. The temperature required for the foaming has to be slightly above the liquids temperature of the used alloy. Generally, hydrides and carbonates are used as blowing agents. The melting behavior and decomposition characteristic of the blowing agent must be coordinated to obtain good quality foam. If the general conditions are met and heating and cooling are properly controlled, the foam with acceptable porosity can be produced. The processes based on blowing agent are melt route and powder metallurgy method. The paper will now focus on the process where blowing agent is used as a key element for producing foam and further physics of foaming for proper growth of metal foam will be elaborated.

#### 1.1 Process based on blowing agent

#### 1.1.1 Powder metallurgy technique

Figure 2 shows the schematic diagram of powder metallurgy technique. This technique uses powder form of parent metal mixed uniformly with blowing agent but the final expansion occurs in liquid state. This mixture is compacted and a semi-finished precursor is obtained. Compaction is obtained by some specific methods like iso-static compression, rod extrusion or powder rolling method [13-17]. Extrusion process is broadly used for compaction process. In this process powder mixture is first precompacted by cold isostatic pressing followed by extrusion to get quality product. Blowing agent should be uniformly distributed in compacted semi-finish product and care has to be taken that no residual porosity is generated. The final step is heat treatment, where it is heated below melting point of mixture. The blowing agent used in the matrix decomposes by the influence of heat and liberate gas, which helps in applying the force on the compressed precursor to form highly porous structure.

This technique was used initially to produce aluminum metal foam. Afterwards it was realized that alloy can offer better properties than pure metal. Now days several metals foam have been developed through this process like tin, zinc, brass, lead, gold and some other metals and alloys by selecting correct blowing agents with appropriate process parameters. Steel foams are also being developed by this technique by using SrCO<sub>3</sub> as blowing agent [18-21].

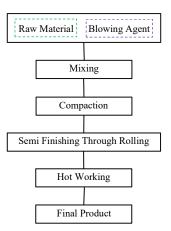


Figure 2. Powder metallurgy process.

#### **1.1.2 Melt route method**

This method is also known as casting method, in which metal or metal alloy is melted in crucible where viscosity enhancer is added at 680°C between 2-3%. The viscosity enhancer generally used are liquid metal matrix composites (MMCs) containing 10-20 vol% particles (typically 10 µm silicon carbide or alumina particles), 5% of 70 Nm SiC, 4 wt% of TiC particles (200-1000 nm). Ca metal between 2-3%. Viscosity enhancer is used to enhance the viscosity which adhere on metal interface and prevent pore coalescence. In most of the cases Ca granules are added as viscosity enhancer at 680°C and stirred up to several min which helps in enhancing the viscosity by a factor upto 5 due to the formation of calcium oxide (CaO), calciumaluminum oxide (CaAl<sub>2</sub>O<sub>4</sub>) or perhaps even Al<sub>4</sub>Ca intermetallics which thicken the liquid metal [22,23]. Viscosity of the melt depends upon stirring time as well as on percentage of viscosity enhancer [1].

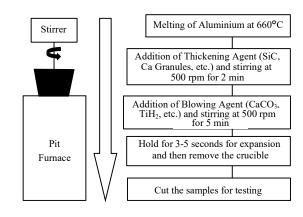


Figure 3. Melt route process for Al metal foam.

Banhart [1] demonstrated that the increasing the percentage of calcium granules and stirring time helped in improving the viscosity of aluminum melt. Figure 3 represents the flow diagram of production of aluminum metal foam. Stirring time, rpm, percentage inclusion of thickening agent and blowing agent and finally the working temperature are the key factors for producing good quality foam. After increasing the viscosity blowing agents are introduced in viscous melt at 680-730°C which is again stirred for few min. At constant pressure due to reaction, molten metal starts expanding slowly and gradually and fills the foaming vessel. After cooling, the solid metal foam is released and cut into desired shape for further processing [24].

Typical stress-strain curve of aluminum metal foam is shown in Figure 4 processed by melt route method. The curve shows three regions elastic, plateau and densification region. Initially the stress changes linearly with respect to strain and this region is known as elastic region. In the plateau region the curve becomes almost flat indicating that the stress becomes almost constant. This occurs due to the pores which initially buckle followed by crushing of cell wall which forms plastic hinges. So the deformation becomes limited and the stress shows the repetitive nature in the process of collapsing and densification. The final region is the densification region where the stress rises sharply and approaches the strength of the bulk aluminum metal [25].

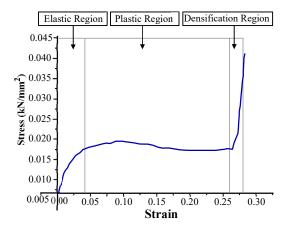


Figure 4. Typical stress strain curve of Al foam prepared through melt route method.

# 2. Physics of foaming process

During the production of metallic foam various steps of foam genesis have to be considered. As soon as the metal softens, the blowing agent expands giving rise to small spherical bubbles. Figure 5 represents the steps of formation of metallic foam. The components of a cell are film (cell wall in the solid state), plateau border and nodes. A film separates two gas bubbles and shows a curvature due to the pressure difference between the two separated bubbles. The intersections of the cell walls are denoted as plateau borders. These are interconnected in a disordered way and form a network whose nodes are junctions of at least four plateau. In 2D, cell walls and plateau borders are represented as lines and intersection of lines, respectively. In order to generate a bubble some value of surface energy is required which is always greater than the thermal energy and can't be minimized. Due to this, foam becomes unstable. During the growth of these bubbles interaction between cells results in change of shape of bubbles from spherical to polygon which places the bubble in metastable stage having minimal surface area and thus final shape of bubble formed is polygon surrounded by liquid layer. This originates plateau border having flat surfaces at middle and curvy at edges. Pressure inside the plateauborders is lower than inside the lamellae and so the liquid tends to flow in towards the plateau-borders, thus these will thicken at the cost of the thickness of the lamellae, which will finally break leading to a coarsening of the foam [26]. This means that the complete event comprises birth, life and death phases and the death phase needs to be avoided. The death of foam occurs at the peak of the third and the start of fourth step. Several factor's influence foam stabilities, including the geometry of plateau border, cell wall thickness, surface adsorption, surface mobility, dilatational viscosity and elasticity [27].

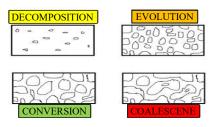


Figure 5. Steps of formation of metallic foam.

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 destabilization caused by perturbation such as thermal fluctuation or surface waves. The stabilizer or thickening agent slows down the different mechanisms of foam ageing: drainage or conversion, coalescence and coarsening. Thickening agent forms a dense mono-layer on a cell wall. Such layers reduce surface tension, increase viscosity, and create electrostatic forces (the so-called disjoining forces) to prevent a foam film from collapsing. So why, it is necessary to add thickening agent for stable formation of bubbles.

The key point is that the foam expansion limits on the ability of a liquid metal film to withstand the stress generated, rather than the gas available for foaming. So, it is clear that stability of foam is a key priority to get quality foam and one of the important factors for stability is cell wall thickness, which depends upon particle diameter, composition of the alloy, foaming temperature and particle material [28]. The larger particles produce thicker and smaller particle produce thinner cell walls [29]. In melt route method the gas evolution is controlled by thermal decomposition of the blowing agent. In order to achieve stable foam through melt route method, proper selection of blowing agent is a crucial factor.

# 3. Blowing agents

In fabrication of quality metal foam through melt route and powder metallurgy method it is necessary to select the proper blowing agent. Main parameters which influence the quality of foams are such as composition, size and volume fraction of particles that have to be added to stabilize the foam; the composition and purity of the gas or foaming agent; the particlesurface interactions; the matrix alloy composition and the thermal processing conditions. The foaming agent must be able to generate a desired amount of gas bubble of desired size.

### 3.1 Hydrides as blowing agents

Metal hydrides are one of the popular blowing agents used for fabricating Al foam.  $TiH_2$  and  $ZrH_2$  are the popular hydrides used for producing Al foam however,  $TiH_2$  is expensive and dangerous to handle. Hydrides, formed as intermetallic compounds are capable to give away large amounts of hydrogen at relatively low temperatures. Chemical reaction of hydrogen with a metal can be written as:

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + Energy$$
 (1)

Table 1. Close cell foams with their properties.

S.N.	Close Cell Foam	Technique	Thickening Agent	Blowing Agent	Porosity %	Mechanical Properties	References
1	2024A1	PM	SiC	CaCO <sub>3</sub>	67-69.1	Yield Strength (31.6-48.2 MPa)	[4]
2	Mg	Melt Route	SiC	SiO <sub>2</sub> -coated CaCO <sub>3</sub>	65-70	Yield Strength (6.2- 9.18 MPa)	[45]
3	Al+Zn	Melt Route	Ca granules	CaCO <sub>3</sub>	75-85	Compressive strength (11.73- 17.77 MPa)	[23]
4	Al	Melt Route	Ca	ZrH <sub>2</sub>	85-95	Energy absorption 1.4 MJm <sup>-3</sup> at 0.6 strain value	[37]
5	Al	Melt Route	copper- coated carbon fibers	TiH <sub>2</sub>	86-89		[38]
6	AlSiCu	PM		(i)2.0 mass% dolomite	75		[42]
				(ii)2.0 mass% dolomite and 1.0 mass% MgCO3	68-78		
7	Fe-based	PM		BaCO <sub>3</sub> SrCO <sub>3</sub> and MgCO <sub>3</sub>			[51]
8	Steel	PM	carbon 2.5 wt%	SrCO <sub>3</sub> and MgCO <sub>3</sub>	46-64	yield strength (95- 320 MPa)	[19]
9	Fe-based	PM	carbon 2.5 wt%	MgCO <sub>3</sub>	40-65	yield strength (30 (par.) – 300 (tverse) MPa)	[20]
10	Fe-based	PM	carbon 2.5 wt%	CaCO <sub>3</sub> and MgCO <sub>3</sub>	53-54	$40 (4.5E-5 s^{-1}) - 95 (16s^{-1})$	[21]
11	AlSi <sub>12</sub>	PM		$\mathrm{TiH}_2$	83-87		[34]
12	Al+Mn	Melt Route	Ca	CaCO <sub>3</sub>	80		[35]
13	Mg alloy	Melt route	Ca	CaCO <sub>3</sub>	55	Yield (16-27 MPa) (Heat treated)	[53]
14	Mg	Melt route		CaCO <sub>3</sub>	53	27.11 MPa	[48]
15	Al +Zn +Mg	Melt route	Ca	CaCO <sub>3</sub>	75-86	Compressive strength (11.7-20.87 MPa)	[25]

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The double-headed arrow indicates that the reaction is reversible and in equilibrium. The energy on the right-hand side of the reaction indicates that energy in the form of heat is released when the metal hydride is formed, and thus, heat must be applied to release hydrogen from the metal hydride phase. The heat is the enthalpy of the reaction and is an indication of the strength of the metal-hydrogen bond in the metal hydride starts to release hydrogen is difficult to determine [30,31]. Hydrides temperature range of decomposition is strongly dependent on several factors such as hydride particle size, amount of initial surface oxidation [32], the atmosphere in which hydrides are heated up [33] and heating rate [34].

Examples of hydrides that have been used as foaming agents are: TiH2, ZrH2 and MgH2. The amount of blowing agent added to the metallic powder to be foamed is usually below 1wt%. Very low contents of metal hydride contain a quantity of hydrogen gas sufficient to create a high degree of porosity [31]. However, volume fraction of blowing agent to be added differs from metal to metal. Kovacik et al. [34] found that for successful foaming TiH<sub>2</sub> required for AlSi<sub>12</sub> alloy was only 0.4% by wt% whereas it was 1 wt% for zinc. Xia et al. [35] prepared closed-cell aluminum metal foams by adding Mn contents in different weight percentage using Ca (2 wt%) as thickening agent and TiH2 (0.8 wt%) as foaming agent with about 80% porosity. XRD pattern showed that TiH<sub>2</sub> appeared in the form TiO<sub>2</sub> in all the specimens due to oxidation between foaming agent and the metal matrix. Linul et al. [36] successfully prepared closedcell aluminum alloy(AlSi10) foam by powder metallurgical (PM) route using 0.4 wt% of TiH<sub>2</sub> as a foaming agent. Wu et al. [37] prepared Al foam by adding ZrH<sub>2</sub> between 0.6-1.4% and Ca 1.5-3% and conclude that the addition of blowing agent should be as much as possible at low temperature. A lot of foaming agent disappears at high temperature during adding process. Al<sub>3</sub>Zr is formed as intermetallic compound in the process which helped in stability of foam. ZrH<sub>2</sub> is suitable for the preparing small aperture with average pore diameter. Sahu [38] prepared closed cell aluminum alloy (AA2014) foam by melt route method using CaH<sub>2</sub>. It is found to be a highly effective foaming agent for aluminum. Kamm [39] checked the suitability of various complex hydrides for foaming Al alloy. AlSi<sub>8</sub>Mg<sub>4</sub> foam was prepared by adding LiBH<sub>4</sub>, NaBH<sub>4</sub>, KBH<sub>4</sub> and LiAlH<sub>4</sub>. LiAlH<sub>4</sub> was found suitable blowing agent which led to foam with a uniform pore structure. It can be used commercially due to its low price. Yang et al. [40] fabricated Cu-Mg metal foam through melt route method by using CaCO<sub>3</sub> as blowing agent. The foam produced are brittle but Mg in the foam helps in increasing the compressive strength. Cao et al. [41] fabricated Al foam by using short copper-coated carbon fibers as a stabilizer and TiH<sub>2</sub> as blowing agent for producing aluminum foam. The stabilizers were located inside cell walls and they were appreciably able to prevent liquid film from rupture. The ability of forming the network structure which is interestingly capable of applying counteract mechanical force to prevent thinning of cell wall makes it an effective stabilizer. The study shows that using 1.7 vol% copper-coated carbon fibers improves the stability of foam significantly.

#### 3.2 Carbonates as blowing agents

Carbonates can be successfully used in place of hydrides as foaming agents. Byakova et al. [42] showed that foaming aluminum alloy with CaCO3 yielded a smaller pore size in comparison to TiH2 and thus a larger stress strain curve was generated before the occurrence of yield at same porosity. Also the plateau stress of Al foam produced by CaCO3 is more stable than foam produced by TiH<sub>2</sub>. Kevorkijan et al. [43] prepared Al foam by adding CaCO<sub>3</sub> replacing TiH<sub>2</sub> successfully. The main reason to replace TiH<sub>2</sub> was its low decomposition temperature, expensive, dangerous to handle, produce high density foam moreover acts only as bowing agent without involving in foam stability. Mg has hydrogen absorbing capacity so CaCO<sub>3</sub> and MgCO<sub>3</sub> is more appropriate blowing agent for producing Mg foam. Xia et al. [44] prepared closed cell Mg alloy foam by adding Ca granules and CaCO<sub>3</sub> powders as thickening agent and blowing agent respectively. CO2 and SF6 were used for protecting the alloy from ignition and oxidizing. Lu [45] fabricated closed-cell Mg alloy (12 wt% Al, 3 wt% Ca) foams by melt route method using MgCO3 as blowing agent. The broken particles (i.e. SiC, Mg<sub>17</sub>Al<sub>12</sub>, Al<sub>12</sub>Ca and Mg<sub>2</sub>Ca) embed in cell edge and cell wall helps in enhancing the strength of foams but make the cell wall brittle. Dong-Hui et al. [46] found that magnesium foam produced by CaCO<sub>3</sub> possessed compressive strength of around 27.11 MPa with 53% porosity. The Mg melt is extremely easy to oxidize or even ignite due to its chemical property so protective atmosphere is required. Ji et al. [47] coated SiO<sub>2</sub> layer on the surface of MgCO3 particles to prepare Mg foam in atmosphere. Same work was done by Lu et al. [48] by coating SiO<sub>2</sub> layer on CaCO<sub>3</sub> to prepare Mg foam in atmosphere. Foams produced using carbonates show marked shrinkage which is not revealed in the case of hydrides. The foam markedly shrank at 1003 K after maximum expansion at 973 K. Koizumi et al. [49] sowed that this difficulty could be successfully removed by using combine dolomite and magnesium carbonate as blowing agent. Kevorkijan et al. [43] represented the disintegration of CaCO<sub>3</sub>:

#### $CaCO_3 = CaO + CO_2$

So thus the gas responsible for foaming process when using  $CaCO_3$  is  $CO_2$ . Additional reactions which occur during  $CaCO_3$  decomposition are

$$2Al (l) + 3CO_2 (g) = Al_2O_3 + 3CO (g)$$
  
 $8Al (l) + 3CO_2 (g) = 2Al_2O_3 + Al_4C_3(s)$ 

#### $6Al(l) + 3CO_2(g) = 2Al_2O_3 + Al_4C_3(s)$

Byakova et al. [42] evaluated that when hydrides were used as blowing agents brittle intermetallic compounds were formed which interfered with the ductility of the material and due to this interference energy absorption capability of the material was reduced. For example, TiH<sub>2</sub> forms Al<sub>3</sub>Ti which is a brittle compound and due to this the energy absorption capability of foams produced by TiH<sub>2</sub> is lower than that of the foams produced by CaCO<sub>3</sub>.Other carbonates which include K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> have been successfully tested in formation of copper and carbon foams. It had been observed that foaming temperature required for Na<sub>2</sub>CO<sub>3</sub> is around 800°C but further carburizing of carbon is required. Bisht and Gangil [25] prepared aluminum metal foam with adding zinc up-to 1wt% by using CaCO3 as blowing agent via melt route method. Addition of Zn at 1wt% shows improved and uniformly distributed pores. Kumar and Pandey [50] prepared LM13 alloy foams via melt route method using pre-treated CaCO3 at 300 °C as blowing agent. The study was conducted for optimizing the various parameters like melt temperature, size and amount of blowing agent and stirring time for producing uniform size foams. It was observed that distribution of blowing agent depends upon viscosity of melt and stirring speed. In their analysis they found 875°C as effective foaming temperature while using 2wt% CaCO<sub>3</sub>. Park et al. [19] prepared steel foam with relative density values ranging between 0.38 and 0.64 by using 0.2 wt% SrCO<sub>3</sub> or MgCO<sub>3</sub> and a carbon content of 2.5 wt%. Paswan *et al.* [51] found that for iron based closed cell foam BaCO<sub>3</sub> is the most promising foaming agent among SrCO<sub>3</sub>, CaCO<sub>3</sub>, and MgCO<sub>3</sub>. For good pore structure 3% BaCO<sub>3</sub> with 2-3% carbon in Fe by foaming at around 1350°C for 3-6 min shows the best expansion.

# 4. Selection criteria of blowing agents

The selection of blowing agents mainly depends upon the following parameters:

#### 4.1 Decomposition temperature

The factors which influence the foam quality are the melting behavior of the alloy system and the decomposition characteristic of the blowing agent. The melting temperature of the metal and the gas decomposition temperature range of the blowing agent have to conform to each other to ensure satisfactory foaming result. Baumgartner *et al.* [31] found that if the blowing agent released gas below the foam matrix melting point, the metal would be expanded in the solid state, which would lead to formation of cracks, leading to considerable consequences for the homogeneity of the foam meso-structure. On the other hand, Zeppelin *et al.* [52] found that if the blowing agent decomposed above the melting point, the viscosity of the melt would be too low for the formation of stable foams. The foaming efficiency of blowing agents is closely related to its hydrogen desorption behavior. In a general way, hydrides that decompose at lower temperatures than the melting point of base metal lose a large fraction of hydrogen well below the foaming onset. In this study they evaluated the foaming efficiency of TiH<sub>2</sub>, ZrH<sub>2</sub> and MgH<sub>2</sub> on zinc foaming. Among them, TiH<sub>2</sub> yielded the best foam expansion results. Its highest desorption rate was the closest to the melting point of zinc (419°C). ZrH<sub>2</sub> and MgH<sub>2</sub> on the other hand, decomposed at lower temperatures and were less effective for foaming. Also Baumgartner et al. [31] found that for AlSi<sub>7</sub> alloy, that when TiH<sub>2</sub> was used as blowing agent the hydrogen evolution was at temperature below the aluminium alloy softening temperature which lead to a local increase in the partial hydrogen pressure causing internal delamination in the plane perpendicular to the pressing direction of the powder preform in contrast to ZnCu<sub>4</sub> alloy where hydrogen evolution begins at temperatures very close to its liquidus temperature resulting in formation of spherical pores, minimizing the surface energy.

#### 4.2 Reactivity of blowing agent with base metal

The blowing agent must not react with the base metal and form intermetallic brittle compounds as they temper the mechanical properties of the foam produced. Byakoval [42] showed that in case of Zn, Al, Mg alloy when TiH<sub>2</sub> was used as blowing agent intermetallic Al<sub>3</sub>Ti was formed which lowered the ductility of cell walls and reduced the toughness of the foam whereas when CaCO<sub>3</sub> was used, a combination of Al and Al<sub>4</sub>Ca was formed which was less brittle and thus did not damage the toughness of the foam. In the case when Mg foam fabricated by melt route method and Mg-Al alloy and Zn-Mg alloy foam by powder metallurgy method [53-55] by using CaCO3 as blowing agent, it was investigated that Mg melt reacts with blowing agent and releases CO gas which help in obtaining good cellular Mg foam material. But in the case when Mg-Al alloy and Zn-Mg alloy foams were prepared, it was observed that CaCO<sub>3</sub>was unable to react with Mg melt directly, and decomposes before the molten point of Mg, which leads in unsuccessful foaming of Mg. But in the case when Mg forms intermetallic compound with Al or Zn and their melting point matches the decomposition temperature range, the foaming becomes successful.

#### 4.3 Particle size of blowing agents

The particle size of blowing agent must be selected according to the intended cell size of the foam and also the particles of the base metal. Kevorkijan *et al.* [43] prepared aluminum foam by using CaCO<sub>3</sub> in different weight percentages of different sizes. While using CaCO<sub>3</sub> in 3 wt%, the obtained result is shown as tabulated form in Table 3.

S.N.	Blowing Agent	Decomposition temperature (K)	References
1	TiH <sub>2</sub>	703	[49]
2	$MgH_2$	553	[49]
3	Mg(OH) <sub>2</sub>	633	[49]
4	4MgCO <sub>3</sub> .Mg(OH) <sub>2</sub> .5H <sub>2</sub> O	Ambient temperature	[49]
5	MgCO <sub>3</sub>	793	[49,50]
6	CaCO <sub>3</sub>	993	[39]
7	SrCO <sub>3</sub>	1563	[18]

Table 2. Decomposition temperature of blowing agents.

Table 3. Result of aluminum foam using 3 wt% CaCO<sub>3</sub>.

CaCO <sub>3</sub>	Density (g·cm <sup>-3</sup> )		Foaming Efficiency %		Average Pores (mm)	
Dia. (µm)	PM Route	Melt Route	PM Route	Melt Route	PM Route	Melt Route
38	$0.42 \pm 0.02$	$0.89{\pm}0.05$	84.4	67.0	$0.8{\pm}0.08$	1.1±0.11
72	$0.46{\pm}0.03$	$0.84{\pm}0.03$	83.0	68.9	$0.5 {\pm} 0.05$	$0.8{\pm}0.08$
120	$0.53{\pm}0.03$	$0.79{\pm}0.04$	80.4	70.7	$0.5 \pm 0.05$	$0.7{\pm}0.07$

From the above table, it can be concluded that in PM route, particle size of foaming agent is responsible for increasing density as well as on the other side responsible for reducing foaming efficiency and pore size. The results obtained in melt route method are quiet opposite than PM route. So increasing the particle size of blowing agent is useful in melt route process while reverse effects are shown in PM technique.

# 5. Performance enhancement of blowing agents

Maijasevic et al. [56] pre-treated TiH<sub>2</sub> under oxidizing condition to shift the decomposition range to higher temperature. Pre-treated TiH<sub>2</sub> powder fit to low melting AlSi<sub>6</sub>Cu<sub>4</sub> alloy. Performance of metal foam can be significantly improved by applying suitable coating agent on blowing agents. Proa-Flores [57] produced aluminum metal foam via powder metallurgy technique by homogeneously coating 96.5 wt% nickel on TiH2 and reduced the initial temperature mismatch by approximately 70°C. The produced foam found to be more homogeneous and reproducible with approximately same pore structures than as-received and passivated TiH2. In this study it was obtained that coated TiH2 with increased particle size influence foam expansion and porosity features and provides more uniform pore distribution and size.

Nakamura *et al.* [58] showed that applying  $CaF_2$  coating on CaCO<sub>3</sub> (blowing agent), low density foams were produced due to wettability enhancement. The coating of CaF<sub>2</sub> helps in reducing the contact angle by 15°, which helped in improving the wettability. In this study aluminum alloy (A356) was prepared by melt route method using conventional TiH<sub>2</sub>, CaCO<sub>3</sub> and CaF<sub>2</sub> coated CaCO<sub>3</sub>. It was clearly revealed that the coated foam exhibited the highest expansion with

smaller pores [56]. Liu *et al.* [59] heat treated SiC (stabilizing agent) to improve the wettability between SiC and Aluminum alloy at 930°C for 6 h. Lu *et al.* [42] found that coating of SiO<sub>2</sub> on CaCO<sub>3</sub> enhanced thermal stability and reduced foaming speed and thus Mg foam expanded gradually with homogeneous structure without shielding gas. In steel foam carbon content had a marked effect on foaming behavior and resulting mechanical properties. For performance enhancement in steel foam carbon must be added between 2-3%.

# 6. Discussion

In the production of close cell metal foams, hydrides and carbonates are used as blowing agents. Carbonates had successfully replaced hydrides due to their superiority in decomposition temperature, low cost, handling issues and expansion properties; moreover, it helped in improving foam stability. But this is not a necessary condition for selecting the blowing agents. A suitable blowing agent's gas decomposition temperature must lie around the melting point of metal as well as the formation of intermetallic compounds should not take place. For the prevention of reactions which leads to formation of intermetallics, coating the blowing agent seems to be a positive approach. So either coated carbonates or coated hydrides, matching the melting point of metals or alloys should be selected for production of close cell metal foam, if not considering the cost and handling issue. In general, TiH2, ZrH2, MgH2 etc. are used in low melting point metals, on the other hand CaCO<sub>3</sub>, SrCO<sub>3</sub>, MgCO<sub>3</sub> etc. are used in high melting point base metals [60]. The other parameters like stirring time. rpm, holding time, particle size of blowing agent, percentage inclusion of thickening agent also play significant role in production of close cell metal foam.

The similar density and uniformity in the size of pores of foam can be obtained by increasing the knowledge about physics of foaming. Due to lack of understanding towards physics of foaming, it needs a proper research in future, which can help in choosing the optimum values of the above mentioned key parameters.

# 7. Conclusion

Blowing agents are used to create gas filled voids in dense metal structure which in turn reduces the density of metal and thus increase its stiffness to weight ratio. Today commonly hydrides and carbonates are being widely used as blowing agents for foam manufacturing. The main gas responsible for foaming process in case of hydrides is hydrogen while in case of carbonates it is mainly CO<sub>2</sub> or CO. Use of suitable coating material on blowing agent helps to improve microstructure and mechanical properties of foam.

The selection criteria of blowing agent depend upon the important given factors as:

(i) Composition of blowing agent and shrinkage resistant ability of blowing agent: The decomposition of blowing agent must take place between the decomposition temperatures of base metal. Release of gas before decomposition of base metal affects foam structure while decomposition of blowing agent at latter stage result in quick release of gas thus making control of process difficult.

(ii) The blowing agent: Blowing agent selected should not form brittle intermetallic compound while reacting with base metal.

(iii) The Blowing agent must have the property to prevent shrinkage of foam at higher temperature.

# References

- J Banhart, "Manufacture, Characterization and Application of Cellular Metals and Metal Foams," *Progress in Materials Science*, vol. 46, no. 6, pp. 559-632, 2001.
- [2] G. J. Davis and S. Zhen, "Metallic foams: their production, properties and applications," *Journal of Materials Science*, vol. 18, pp. 1899-1911, 1983.
- [3] J. Banhart, "Aluminum foams for lighter vehicles," *International Journal of Vehicle Design*, vol. 37, pp. 114-125, 2005.
- [4] J. Banhart, "Aluminum foams: on the road to real applications," *MRS Bulletin*, vol. 28, pp. 290-295, 2003.
- [5] J. Banhart and D. Weaire, "On the road again: Metal foams find favor," *Physics Today*, pp. 37-42, 2002.
- [6] A. Chaturvedi, "Recent developments in the field of metal foam-polymer hybrid materials: A brief overview," *Journal of Metals, Materials* and Minerals, vol. 28, pp. 136-140, 2018.

- [7] A. Chaturvedi, G. Sanyal, S. Chaturvedi, and A. S. Patil, "Compressive properties and imaging analysis of a new metal foam-natural rubber hybrid structure," *Journal of Metals, Materials* and Minerals, vol. 26, pp. 27-30, 2016.
- [8] F. García-Moreno, "Commercial applications of metal foams: their properties and production," *Materials*, vol. 9, pp. 85, 2016.
- [9] K. Myers, P. Cortes, B. Conner, T. Wagner, and B. Hetzel, "Structure property relationship of metal matrix syntactic foams manufactured by a binder jet printing process," *Additive Manufacturing*, vol. 5, pp. 54-59, 2015.
- [10] I. N. Orbulov, "Compressive properties of aluminium matrix syntactic foams," *Material Science and Engineering*, *A*, vol. 555, pp. 52-56, 2012.
- [11] I. N. Orbulov, "Metal matrix syntactic foams produced by pressure infiltration-the effect of infiltration parameters," *Material Science and Engineering*, A, vol. 583 pp 11-19, 2003.
- [12] J. Banhart, "Manufacturing routes for metallic foams," Journal of The Minerals Metals & Materials Society, vol. 52, no. 12, pp. 22-27, 2000.
- [13] A. B. Li, H.-Y. Xu, L. Geng, B.-L. Li, Z.-B. Tan, and W. Ren, "Preparation and characterization of SiC<sub>p</sub>/2024Al composite foams by powder metallurgy," *Transactions of Nonferrous Metals Society of China*, vol. 22, pp. s33-s38, 2012.
- [14] H. Bart-Smith, A. F. Bastawros, D. R. Mumm, A. G. Evans, D. J. Sypeck, and H. N. Wadley, "Compressive deformation and yielding mechanisms in cellular al alloys determined using x-ray tomography and surface strain mapping," *Acta Materialia*, vol. 46, pp 3583-3592, 1998.
- [15] J. Baumeister, "Method for producing porous metal bodies," German Patent DE 4018360, 1990
- [16] J. Baumeister and H. Schrader, "Methods for manufacturing formable metal bodies," U.S. Patent DE 5151246, 1992.
- [17] M. Weber and M. Knuwer, "Metallschäume" In: J. Banhart, editor Proc. Symp. Metallschaume, Bremen, Germany, 6-7 March. Bremen: MIT Press-Verlag, pp. 73, 1997. [in German].
- [18] C. J. Yu, H. Eifert, M. Knuwer, M. Weber, and J. Baumeister, "Investigation for the selection of foaming agents to produce steel foams, Porous and cellular materials for structural applications," *MRS Online Proceedings Library Archive*, vol. 521, pp. 145, 1998.
- [19] C. Park and S. R. Nutt, "PM Synthesis and properties of steel foams," *Material Science* and Engineering, A, vol. 288, pp. 111-118, 2000.
- [20] C. Park and S. R. Nutt, "Anisotropy and strain localization in steel foam," *Material Science* and Engineering A, vol. 299, pp 68-74, 2001.
- [21] C. Park and S. R. Nutt, "Strain rate sensitivity and defects in steel foam," *Material Science and Engineering A*, vol. 323, pp. 358-366, 2002.

- [22] A. E. Simone and L. J. Gibson, "Aluminium foams produced by liquid state processes," *Acta Materialia*, vol. 46, pp. 3109-3123, 1998.
- [23] T. Miyoshi, M. Itoh, S. Akiyama, and A. Kitahara, "Alporas aluminum foam: production process, properties and applications," *Advanced Engineering Materials*, vol. 2, pp. 179, 2000.
- [24] A. Bisht, B. Gangil, and V. K. Patel, "Physicocompression, sliding wear and energy absorption properties of Zn/Mg infiltrated closed cell aluminum foam," *Materials Research Express*, vol. 6, pp. 106583, 2019.
- [25] A. Bisht and B. Gangil, "Structural and physicomechanical characterization of closed-cell aluminum foams with different zinc additions," *Science and Engineering of Composite Materials*, vol. 25, no. 4, pp. 789-795, 2018.
- [26] D. Langevin, "Aqueous foams and foam films stabilised by surfactants. Gravity-free studies," *Comptes Rendus Mecanique*, vol. 345, pp. 47-55, 2017.
- [27] T. Wuebben, S. Odenbach, and J. Banhart, "Investigation of lead foams under microgravity," *Eurofoam*, pp. 98-103, 2000.
- [28] V. Gergely, L. Jones, and T.W. Clyne, "The effect of capillarity-driven melt flow and size of particles in cell faces on metal foam structure evolution," *Title Transactions of JWRI Transactions of JWRI*, vol. 30, pp. 371-376, 2001.
- [29] D. T. Wassan, A. D. Nikolov, L. A. Lobo, K. Koczo, and D. A. Edwards, "Foams, thin films and surface rheological properties," *Progress* in Surface Science, vol. 39, pp. 119-154, 1992.
- [30] N. Babcsan, D. Leitlmeier, and H. P. Degischer, "Foamability of particle reinforced aluminum melt," *Materialwissenchaft and Werkstofftechnik*, vol. 34, pp. 22-29, 2003.
- [31] F. Baumgartner, I. Duarte, and J. Banhart, "Industrialization of powder compact foaming process," *Advanced Engineering Materials*, vol. 2, no. 4, pp 168-174, 2000.
- [32] R. Kennedy, "The effect of TiH<sub>2</sub> heat treatment on gas release and foaming in Al-TiH<sub>2</sub> preforms," *Scripta Materialia*, vol. 47, pp. 763-767, 2002.
- [33] D. Lehmhus and M. Busse, "Potential new matrix alloys for production of PM aluminium foams," *Advanced Engineering Materials*, vol. 6, pp. 391-396, 2004.
- [34] A. Adamčíková and J. Kováčik, "Effect of powder size and foaming agent on aluminium foam expansion," Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, 2008.
- [35] X. Xia, H. Feng, X. Zhang, and W. Zhao, "The compressive properties of closed-cell aluminum foams with different Mn additions," *Materials and Design*, vol. 51, pp. 797-802, 2013.
- [36] E. Linul, L. Marşavina, P. A. Linul, and J. Kovacik, "Cryogenic and high temperature compressive properties of Metal Foam Matrix

Composites," *Composite Structures*, vol. 209, pp. 490-498, 2019.

- [37] D.-W. Li, J. Li, T. Li, T. Sun, X.-M. Zhang, and G.-C. Yao, "Preparation and characterization of aluminum foams with ZrH<sub>2</sub> as foaming agent," *Transactions of Nonferrous Metals Society of China*, vol. 21, pp. 346-352, 2011.
- [38] S. Sahu, D. P. Mondal, J. U. Cho, M. D. Goel, and M. Z. Ansari, "Low-velocity impact characteristics of closed cell AA2014-SiCp composite foam," *Composites, Part B*, vol. 160, pp. 394-401, 2019.
- [39] P. H. Kamm, F. García-Moreno, C. Jiménez, and J. Banhart, "Suitability of various complex hydrides for foaming aluminium alloys," *Journal of Materials Research*; vol. 16, pp. 2436-2443, 2013.
- [40] D. Yang, S. Guo, J. Chen, J. Lu, L. Wang, J. Jiang, and A. Ma, "Fabrication of Cu-Mg alloy foam with close pore structure by gas release reaction powder metallurgical approach," *Journal of Alloys and Compounds*, vol. 766, pp. 851-858, 2018.
- [41] Z.-K. Cao, B. Li, G.-C. Yao, and Y. Wang, "Fabrication of aluminium foam stabilized by copper-coated carbon fibers," *Materials Science* and Engineering, A vol. 486, pp. 350-356, 2008.
- [42] A. V. Byakova, S. V. Gnyloskurenko, and A. I. Sirko, "The role of foaming agent in structure and mechanical performance of Al based foams," *Materials Transactions*, vol. 47, pp. 2131-2136, 2006.
- [43] V. Kevorkijan, "Low cost aluminum foams made by CaCO<sub>3</sub> particulates," *Association of Metallurgical Engineers of Serbia*, vol. 16, no. 3, pp. 205-219, 2010.
- [44] X. Xia, W. Zhao, X. Feng, H. Feng, and Xin Zhang, "Effect of homogenizing heat treatment on the compressive properties of closed-cell Mg alloy foams," *Materials and Design*, vol. 49, pp. 19-24, 2013.
- [45] X. Lu, Z. Zhang, H. Du, H. Luo, Y. Mu, and J. Xu, "Compressive behavior of Mg alloy foams at elevated temperature," *Journal of Alloys and Compounds*, vol. 797, pp. 727-734, 2019.
- [46] D.-H. Yang, Y. Shang-Run, W. Hui, M. Ai-Bin, J. Jing-Hua, C. Jian-Qing, and W. Ding-Lie, "Compressive properties of cellular Mg foams fabricated by melt-foaming method," *Materials Science and Engineering: A*, vol. 527, no. 21-22 pp. 5405-5409, 2010.
- [47] J. Hai-bin, Z. Guo-yin, Y. Guang-chun, and L. Le-tian, "On the silica-coated surface of magnesium carbonate particle," *Journal of Northeastern University: Natural Science*, vol. 30, no. 5, pp. 701-703+707, 2009 (in Chinese).
- [48] L. Guo-qiang, H. Hai, W. Fu-yun, and Z. Xingguo, "Preparation of closed cell Mg foam using SiO<sub>2</sub> coated CaCO<sub>3</sub> as blowing agent in atmoshphere," *Transactions of Nonferrous*

Metals Society of China, vol. 23, pp. 1832-1837, 2013.

- [49] T. Koizumi, K. Kido, K. Kita, K. Mikado, S. Gnyloskurenko, and T. Nakamura, "Method of preventing shrinkage of aluminum foam using carbonates," *Metal*, vol. 2, no. 1, pp. 1-9, 2012.
- [50] S. Kumar and O. P. Pandey, "Study of microstructure and mechanical properties of particulate reinforced aluminum matrix composite foam," in *Advanced composites for Aerospace, Marine and Land applications II*, I. Sano and T. S. Srivatsan, Eds. Switzerland: Springer International, 2016, pp. 245-25.
- [51] D. Paswan, D. Mistry, K. L. Sahoo, and V. C. Srivastava, "Development of iron based closed cell foams by powder forging and rolling," *Journal* of Materials Engineering and Performance, vol. 22, no. 8, pp. 2201-2209, 2013.
- [52] F. Von Zepplin, M. Hirscher, H. Stanzick, and J. Banhart, "Desorption of hydrogen from blowing agents for foaming metals," *Composites Science and Technology*, vol. 63, pp. 2293-2300, 2003.
- [53] D. Yang, B. Hur, and S. Yang, "Study on fabrication and foaming mechanism of Mg foam using CaCO<sub>3</sub> as blowing agent," *Journal* of Alloy and Compounds, vol. 461, pp. 221-227, 2008.
- [54] D. Yang, Z. Hu, W. Chen, J. Lu, J. Chen, H. Wang, and L. Wang, J. Jiang and A. Ma, "Fabrication of Mg-Al alloy foam with close-

cell structure by powder metallurgy approach and its mechanical properties," *Journal of Manufacturing Processes*, vol. 22, pp. 290-296, 2016.

- [55] D. Yang, J. Chen, W. Chen, L. Wang, H. Wang, J. Jiang, A. Ma, "Fabrication of cellular Zn-Mg alloy foam by gas release reaction via powder metallurgical approach," *Journal of Materials Science & Technology*, vol. 33, no. 10, pp. 1141-1146, 2017.
- [56] B. Matijasevic. "Characterisation and optimisation of blowing agent for making improved metal foams," PhD. Thesis, 2006.
- [57] P. M. Proa-Flores, "Aluminium foams fabricated by the PM Route using Nickel-coated Titanium Hydride Powders of Controlled Particle Size," PhD Thesis 2010.
- [58] T. Nakamura, S. V. Gnyloskurenko, K. Sakamoto, A. V. Byakova, and R. Ishikawa, "Development of new foaming agent for metal foam," *Materials Transaction*, vol. 43, no. 5, pp. 1191-1196, 2002.
- [59] S. Yu, Y. Luo, and J. Liu, "Effects of strain rate and SiC particle on the compressive property of SiC<sub>p</sub>/AlSi<sub>9</sub>Mg composite foams," *Materials Science and Engineering A*, vol. 487, pp. 394-399, 2008.
- [60] A. Bisht, V. K. Patel, and B. Gangil, "Future of metal foam materials in automotive industry," in *Automotive Tribology*, Springer Singapore, pp. 51-63, 2019.