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A systematic review of processing techniques for cellular metallic foam production

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ABSTRACT

Introduction. The paper presents a comprehensive overview of the manufacturing methods, materials, properties, and challenges associated with cellular metallic foams, primarily focusing on aluminum and titanium-based foams. Cellular metallic foams are gaining interest due to its unique combination of low density, high stiffness, and enhanced energy absorption capabilities. Cellular metallic foam is renowned for its special combinations of physical and mechanical characteristics, containing their increased stiffness, specific strength at high temperatures, light weight, and good energy absorption at relatively low plateau stress. It has extensive uses in the automotive, shipbuilding and space industries. It has high porosity, low relative density and high strength, which increases performance of the product. The aerospace and automotive industries require a material with a high strength-to-weight ratio. **Methods.** To meet this need, many metal foam production methods have been developed, such as melt route method, deposition method and powder metallurgy method. Melt route method is widely used to manufacture metallic foam as compared to other methods. **Results and Discussion.** In the production of aluminum foams, the melt route method is usually used. Titanium hydride (TiH_2) has been a popular foaming agent, but its high decomposition rate and cost limitations have led to the development of alternative foaming agents, such as $CaCO_3$ (calcium carbonate). Titanium foam is often manufactured using the space holder method. This method involves mixing titanium powder with a space holder material, forming a preform, and then sintering to remove the space holder and produce a porous structure as the space holder method allows for precise control over the properties of the foam, including pore size, porosity, and relative density. Results also indicate that porosity in cellular metallic foams can range from 50 % to 95 %, as reported in various journals. Pore structures can include mixed types, open cells, and closed cells, each offering different mechanical and thermal properties. It is also observed from various literature sources that relative density, which is the ratio of the foam's density to the bulk material's density, varies from 0.02 to 0.44 based on the production method used.

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Introduction

In many research papers, cellular materials are called new ones. Initially it was reported by *De Meller* in 1925. His patent proposed foaming of light metals by injection of an inert gas or using a blowing agent, gas-eutectic reaction, etc. These processes require high capital investment and safety equipment because gas release during the foaming processes [1]. Metallic foam can be defined as light weighted material with high stiffness. When blowing agent is added in liquid metal and gases are released, which are trapped after solidification, we get metallic foam, for example, aluminum one. The interest of researchers in developing metallic foams lies in obtaining unique properties such as low specific weight, high gas permeability, high stiffness, low thermal conductivity, electrical insulation properties and high shock-absorbing capacity.

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To obtain these rare properties researchers have tried to create various types of metallic foam from different metals and alloys such as steels, *Cu*, *Al*, *Al-Si*, *Al-Mg*, *Pb*, *Fe*, Ni_3Al, *Mg*, *Zn*, and *Ti*, *Al-Cu*, *MMCs*, metallic glasses etc. Among this variety, aluminium foam has received enormous development in industrial production [2]. Foamed metals are widely used in various industries, such as automotive and aerospace ones due to good mechanical properties and light weight. Aluminum foam has the ability to absorb the shock and vibration due to its closed cell porosity nature. It has good thermal and sound insulation properties. Metallic foam or aluminum foam should be produced using processes that require less capital investment and are the safest.

Methods for producing metallic foam

There is various methods to produce metallic foams, for example, molten metal method, deposition technique, by powder metallurgy which has been mentioned in fig. 1.

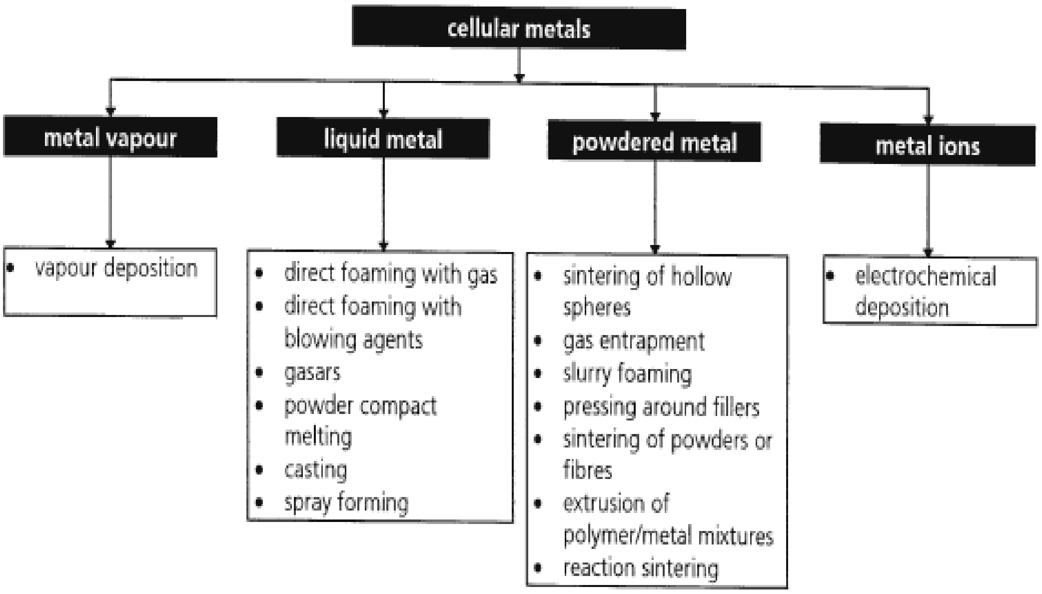

Fig. 1. Metal foam production methods [3]

Production of metal foam from molten metal

This method is commonly used to make metal foam from molten metal due to its cost-effectiveness and simplicity. In this method, the first step is to prepare the molten metal. To obtain a closed cell porous material from molten metal a certain amount of foaming agent or gas injection into the molten material with a stabilizing material (*SiC*, Al_2O_3) is required to increase the viscosity of the molten metal [4].

Solid-gas eutectic solidification. Investment casting method and syntactic foaming using filler material are also used by the researcher are also used by researchers to produce metal foam from molten metal. Selection of method depends on the required porosity, relative density and other factors, as these vary from method to method. Porosity of 80–97 % can be obtained in the metallic foam by the gas injection method, foaming agent method. Porosity of 5–75 % porosity is not very high, but it can be achieved in metal foam through gas-eutectic reaction. This was studied by *Banhart*. The final porosity depends on the processes and controlled parameters such as stirrer's revolutions per minute, stirring time, foaming agent, amount of foaming agent, choice of gases for the injection method, such as argon or neon. To obtain the best result, many researchers have optimized these parameters.

Producing metal foam by injecting gas into molten metal

In this process, metallic foam is produced by injecting suitable gas into the prepared molten metal. The gas injection method is not suitable for easily oxidizable material (*Mg*, *Ti*), but aluminum foam is widely produced in this way, and complex shapes can be easily obtained [5]. This method was developed by *Alcan* international. According to this method, small amount of additives are required to increase the viscosity of the molten metal. Before adding the ceramic powder in the molten metal, preheating is required to increase the wettability between the ceramic particles and the molten metal. The molten metal in the furnace is then injected with inert gas, carbon dioxide, nitrogen, air or any other gas. Gas bubbles rise rapidly through the molten metal due to buoyant force of the molten metal. To stop the flow of gas bubbles inside the molten metal, some additives are added to increase the viscosity of the molten metal. These additives are aluminum oxide, magnesium oxide, silicon carbide. In addition, other parameters such as temperature need to be monitored [6]. It is necessary to continuously create small spherical gas bubbles using a rotating impeller or orifice. *Yuan* and *Li* studied the bubbles' formation stages by using the orifice (**1**) nucleation stage (**2**) growth stages (**3**) detachment stages. Size of the bubbles depends on the wedge angle of orifice (wedge angle of orifice increases bubbles sizes decreases) and cell diameter also depends on the orifice diameter and chamber pressure. The gas flow rate also affects the size of the bubbles. In their opinion, the size of the bubbles increases as the gas flow rate increases [7]. Finer cell size makes the cell spherical, stable and decreases the chance of cell wall defects. Cell size of the metallic foam has not effectively controlled by the static gas injection method. Another method for controlling the pore size in metal was developed by *Ningzhen Wang* and is shown in fig. 2. In that method researcher used dynamic gas injection method. Dynamic gas injection is realized by adjusting the intensity of the vibrator in the range from (0 to 100 %). At 100 % intensity, cells with a diameter of 4 mm are obtained, which is smaller than with static gas injection [8]. In this method, the porosity of the metallic foam can vary from 50 to 90 % [9]. Foam, containing ceramic powder, is difficult to cut due to its hardness. Therefore, to obtain a complex-shaped product from foam metal, one should initially use a special mold. The molten metallic foam is collected from the furnace to be shaped. The production of metal foam by gas injection requires various steps.

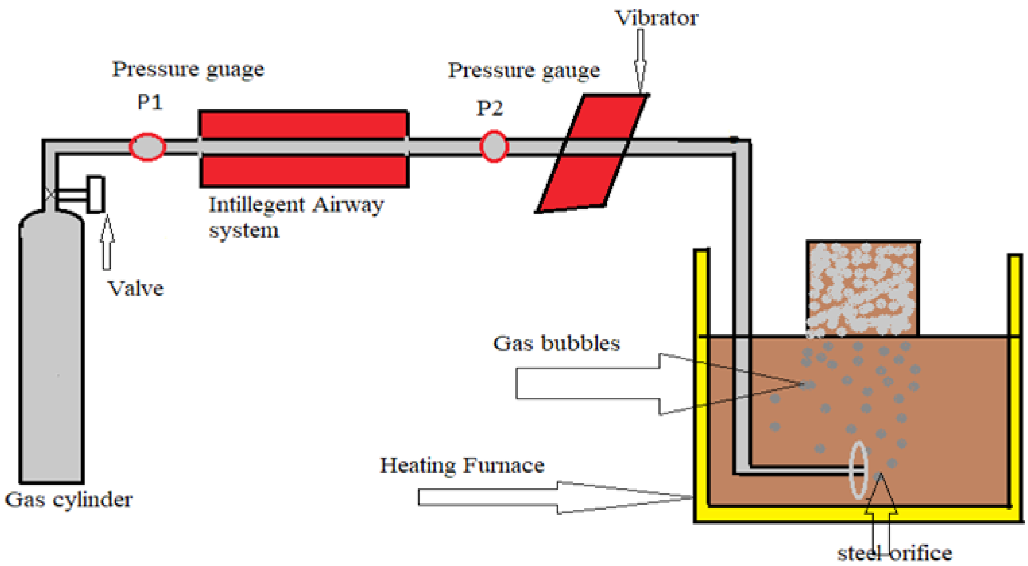

Fig. 2. Melt gas injection method [8]

Producing metal foam by adding the foaming agent into molten metal

According to this method, to produce metal foam, special foaming agents should be added to the molten metal. Foaming agents are titanium hydroxide (TiH_2), calcium carbonate ($CaCO_3$), zirconium hydride (ZrH_2), manganese oxide (MnO_2), dolomite ($CaMg(CO_3)$), magnesium carbonate ($MgCO_3$). Calcium carbonate and titanium hydroxide are most commonly used to produce metallic foam. The decomposition rate of titanium hydroxide is higher than that of calcium carbonate and hence it releases gas easily. To stabilize the molten metal in this case, additives are needed – Al_2O_3, *SiC*. Hence its manufacturing costs increase. To make this processes more economical *M. Hiedari Galeh* has used $CaCO_3$ as foaming agent without the use of stabilizer powder. They take *Al356* aluminum alloy for making the metallic foam. The aluminum alloy is heated above its melting point. After the aluminum melts (~700 °C), $CaCO_3$ is added to the melt and the decomposition of the foam agent begins and as a result of decomposition gas (CO_2) is released. $CaCO_3$ should be mixed uniformly with the help of stirrer. Here controlled parameters are speed of rotation of the stirrer, amount of foaming agents, stirring time, temperature, gas bubbles rise speed and melt viscosity. Stirrer casting setup is shown in fig. 3. These parameters affect the cell size, relative density, porosity of the metallic foam. Pore size and its distribution affect the strength, sound insulation, and thermal properties, etc. By controlling the size of the bubbles formed during the formation of gas inside the melt, the researcher controls the pore size and their distribution [10]. By adding additives into the molten metal, which increase viscosity, stabilize the cell walls and prevent the bursting of bubbles, the correct foam structure is created [11]. Porosity and pore size are controlled by holding time and amount of $CaCO_3$. As the calcium carbonate content increases, the pore size increases, which negatively affects the cell size, porosity, and relative density. It means cell size, porosity and relative density decreased, increasing in the amount it is sure to there is in increment in porosity level but simultaneously reduction takes place in the pore size [12]. Compressive properties of metallic foam depend on the porosity, cell size and relative density. Relative density and cell homogeneity are factors affecting the strength of the metallic foam. Compressive strength and energy absorption capacity increase with increasing cell size. Both of these properties deteriorate as the amount of $CaCO_3$ in the molten metal increases. The porosity of foam metal depends on the foaming temperature, because it affects density; the compressive strength of foam metal depends on it to a lesser extent, but strongly depends on the stirring time [13].

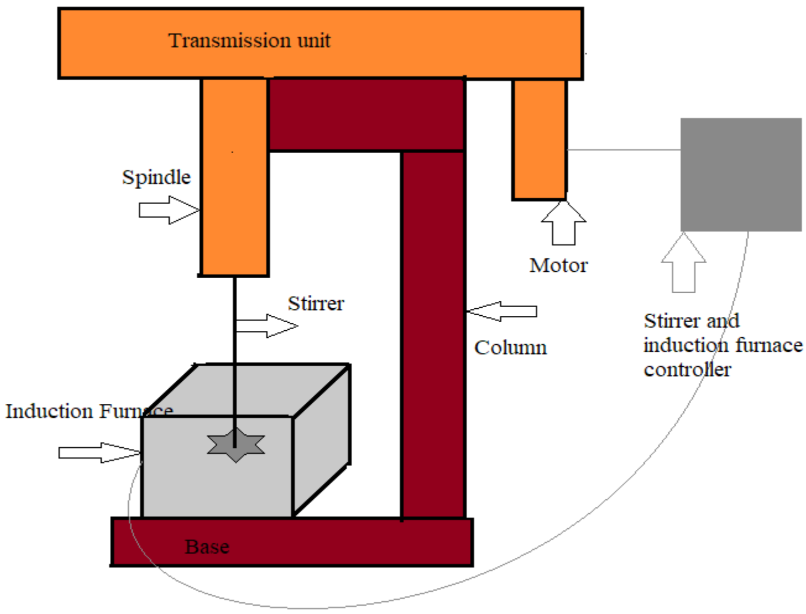

Fig. 3. Stirrer casting setup [12]

Two metallic alloys are manufactured by the two different methods: stir casting and inflation; both have the same compressive strength, but less porosity is obtained in case of implementing stir casting method as compared to infiltration one. Metal foam produced by infiltration is used to obtain higher strain rates. The strain rate will be high in the case of high porosity; high porosity is achieved by adding a large amount of foaming agent to the metal – 10 % or 15 % [14]. Researchers are trying to optimize the various parameters to achieve the best mechanical properties and surface structure, pore size, relative density, etc. *C.C Yang* assumed that that there is no need to control the rate of decomposition, since it is important to control the dissolution of the foaming gas in the molten metal and it should be directly proportional to each other. If this does not happen, the foam structure will be unstable. The efficiency of foaming molten metal with hydrogen gas is 17 %. Therefore, it is necessary to use a foaming agent in an appropriate amount, since excess gas can escape from the molten metal [15]. Compared to the *GI* method, less closed porosity and more micropores in the cell walls are obtained. In this case, aluminum foam is produced both by foaming and by gas injection methods [16].

Solid-Gas Eutectic Reaction Method

This method is also known as *GASAR*. It was developed by the Ukrainian scientist *Shapovalov V.* in 1993. Its advantages over the powder metallurgy processes and foaming method are: no losses of raw materials, no chemical treatment, ease of control of pore size and orientation, and, in addition, compared to other processes, it is cost-effective [17]. The metal is melted in an autoclave under high pressure, which allows large amounts of hydrogen to be introduced into it. After reducing the temperature and pressure, the alloy is in "liquid + gas" state; upon subsequent cooling below the eutectic temperature, the liquid crystallizes and a "solid + gas" is obtained. The formation of bubbles occurs due to the release of hydrogen during the solidification of the metal due to the decrease in solubility of hydrogen gas when the solidification of the liquid metal begins under controlled gas pressure.

In this method, axial or radial pore orientation can be achieved by controlling the heat dissipation direction. Porosity, pore size, morphology, pore orientation can be easily controlled during the solidification. These things are controlled by gas pressure, solidification rate, pouring temperature, total solidification gas pressure, solidification cooling rate, and solidification cooling direction. Among these controllable parameters, gas pressure plays important role in deciding the pore size in the metallic foam. The researcher implemented two conditions: 1) only pure hydrogen gas was used. In this case, a decrease in porosity occurred with an increase in gas partial pressure (P_{air}); 2) the total gas pressure (P_{total}) remained constant, while the porosity increased with increasing partial pressure of hydrogen gas (P_H) [18]. An increase in solidification pressure has a negative effect on the pore size – its diameter decreases. The pore diameter varies from 10 μm to 10 mm, and the porosity ranges from 5 to 75 %. Due to the fact that the material contains small and large pores, the distribution is uneven [19].

Producing metal foam by investment casting method

Investment casting is also used to produce metallic foams. In this case, no foaming agents are required; instead, open-cell polymer foam is used. Usually, polyurethane is used to fabricate a model. Polyurethane is a linear covalently bonded polymer with relatively long, flexible, soft chain segments joined at the ends. Open cells are filled with the heat resistant resin, such as plaster slurry, a mixture of mullite and calcium carbonate, which is dissolved in water after the polymer foam model is filled with plaster slurry and left to dry. Plaster slurry act as space holder in the polymer foam. During subsequent heating, the polymer foam burns out, leaving a porous cavity in the mold [20, 21]. Further molten metal is poured into the mold cavity under pressure to fill all areas of the mold. The mold is additionally vacuumed. After crystallization of the melt, the mold is irrigated with water; the plaster is soaked and washed off. The porosity in the metallic foam obtained in this way ranges from 80 to 97 %, and the pore size varies from 4 to 0.5 mm [22, 23]. The mechanical properties of metal foam produced by modified investment casting are higher than those of reticulated foam; the permissible compressive load is significantly higher than that of reticulated metallic foam [24]. Various chemical compositions, high compressive strength with high strain hardening are possible. Mechanical properties are improved by struts [25]. *Alfredo* suggested that the external cell size is greater than 0.05 mm, so the resulting foam should be less defective. He used logistic regression to optimize the process parameters and obtain the best aluminum foam [26].

Producing metal foam by deposition technique

The technology of solid phase deposition is similar to the technology of investment casting. In both cases, neither foaming agents nor gas injection into the molten metal are required. The polymer foam is electroplated with dissolved metal ions, and then the polymer foam is replaced with molten metal. Galvanic deposition on polymer foam requires some electrical conductivity of the initial polymer foam. To make polymer foam electrically conductive, a thin conductive layer is applied to its surface using electrolytic deposition. This process is suitable for a limited number of materials. The low deposition rate and non-uniform pattern of deposition are the reason for the low mechanical properties of the resulting material. For this reason, another method uses chemical vapor deposition to produce metal foam [23].

Producing metal foam by powder metallurgy

Powder metallurgy processes also used to manufacture the metallic foam. In this case, instead of molten metal, metal powder is used and other processes are involved. These include: *Fraunhofer* process, gas entrapment, foaming of slurries.

Metal powder used to produce the metallic foam whereas we have seen that molten metal has been used in the above technique. In this several other techniques are used to manufacture the metal foam. These techniques are Fraunhofer processes, Gas entrapment method, Foaming of slurries. Molten route method is commonly used method and more popular one, but it also dominates in terms of quality. Sandwich panels can be manufactured using this method. All methods are characterized by three stages: mixing the metal powder with a foaming agent or space holder, compacting the metal powder to provide shape and strength, and sintering the compact shape at its recrystallization temperature.

Fraunhofer processes

This method is not as popular as the melt route one. Advantages of the *Fraunhofer* method over the melt route method/processes are: the ability to produce a product of complex shape and size, as well as better control of the porous structure. Metallic foam manufacturing begins with mixing metal powder with the suitable foaming agent. The preparation of the metal powder makes the *Fraunhofer* method expensive, and its storage requires certain conditions. When mixing metal powder and foaming, it is necessary to achieve its uniform distribution. The resulting mixture is compacted by pressing. The compaction process can be realized by hot isostatic pressing, hot compaction, extrusion and powder mixture rolling. The choice of compaction method depends on the desired final shape. The material should be compacted before plastic deformation of the powder particles begins. Compacted metal powder contains small pores and cracks, which can hinder foaming processes [27]. Heat treatment is carried out at a temperature below the temperature of the metal powder melting point. When choosing a foaming agent, it is important to ensure that its melting point is lower than the melting point of the metal powder. During heat treatment, the foaming agent, which is uniformly distributed throughout the melt, decomposes. The released gas forces the source material to expand, forming a highly porous structure. In a semi-solid metal, expansion occurs quickly, but the bubbles collapse, so rapid cooling is required to fix the foam structure.

The stability of aluminum alloy foam can be improved by adding Mg to the powder mixture. After the Mg addition, Al_2O_3 particles at the interface are more fully incorporated into the cell walls [28].

The controlled process parameters are: the foaming agent content, temperature and heating rates. These are common in the production of metal foam. Further, the percentage of porosity and relative density required will depend on the process parameter. TiH_2 is the most popular foaming agent because its melting point is close to that of aluminum alloy. Titanium hydride is expensive and dangerous to handle due to the risk of fire due to the release of hydrogen gas during the decomposition of TiH_2, so another foaming agent, calcium carbonate, was proposed [29].

The characteristics of $CaCO_3$ and TiH_2 as foaming agents were determined. It was found that metal foam using $CaCO_3$ has a finer and more homogeneous pocellre structure [30]. $CaCO_3$ is used as a foaming agent in the production of foams from magnesium alloys. However, it is impossible to produce foam metal with adequate structure using only Mg and $CaCO_3$ alone, because $CaCO_3$ may decompose to release CO_2 before Mg melts, which will lead to two consequences: the starting material may crack and a reaction may occur between the released CO_2 and Mg. Therefore, it is necessary to reduce the melting temperature of the starting material by adding Al and Zn so that $CaCO_3$ reacts with molten Mg and cracking of the material does not occur [31].

Cylinder-shaped metal foam is manufactured by hot powder extrusion (press machine) and foaming, which attempts to determine the relative density and deformation energy of the foam. Aluminum alloy powder with a foaming agent is heated above its melting point in a foaming mold and a relative density of 0.22 is obtained. The density of metal foam decreases as the molding speed increases [32]. Aluminum foam manufactured by this method has a homogeneous cell structure and a relative density 20 % less than solid aluminum, while the relative density of steel foam is 40 % less than solid steel. This porosity helps during deformation, that is, it absorbs mechanical energy by collapsing the cell pores [33].

Gas entrapment

This concept was developed by *Martine*. The process is rarely used because of the complex processing involved. The mixture of base material is enclosed in a shell, the air is replaced with α-stabilizing gas, such as argon, and it is sealed. The filled shell is then placed in a gasostat and subjected to hot isostatic compression, thereby achieving a density of 95 %. At the next stage, the semi-finished product is rolled and, at the final stage, heated in a furnace. Since the shell is sealed, the argon contained in the space between the powder particles begins to expand and further consolidate the particles of the base metal from the inside, forming partitions of the future foam. The porosity of the powder obtained in this way reaches 50 %, and the pore diameter varies from 6 to 10 μm. Low porosity and various cell size are significant disadvantages of this method [34].

Space holder method

In powder metallurgy, space holder method gives maximum control over the shape, pore size, porosity distribution. In this method metal powder is mixed with space holder material along with binder, which provides strength to green powder during compaction. Mixing time can range from 1 to 4 hours; actually it depends on how long it takes to mix to a homogeneous state. It is necessary to ensure that the metal powder is mixed until homogeneous, otherwise the cell size and percentage of porosity will be less. It is necessary to select a space holder in such a way that it can easily evaporate during sintering (1), not react with the metal (2), is easy to process (3), and there should be no residue left after processing. To manufacture aluminum foam, sintering in an electric furnace and plasma-spark sintering are used, and for the production of copper foam, carbonate-free sintering is used [35]. In biomedical implants, space holder residues in metal foam are a serious problem. Therefore, sodium chloride is widely used as a space holder in the manufacture of titanium biomedical implants, since it is easily removed when dissolved in water. According to literature data, the maximum porosity in steel foam is 60%. *D.P. Mondal* tried to increase the porosity of stainless steel foam to 80 % using ammonium bicarbonate as a space holder. Pore size, porosity and relative density depend significantly on the sintering temperature; at 1,100 °C the cell size is the same as the size of the space holder particles, if sintering occurs at a higher temperature than this, the pore walls will become permeable, and hence the porosity can be reduced. Other space holders (carbide, sodium chloride, tapioca starch, magnesium) were used to produce open-cell titanium foam [36]. *Nidhi Jha* used *NaCl* powder as a space holder with a particle size seven times larger than the particle size of titanium powder, this ensured that the titanium powder would be completely dispersed around the *NaCl* powder, making it possible to obtain uniform porosity throughout the titanium foam. The thickness of the cell wall increased as the amount of titanium in the powder mixture increased. Cell size and porosity varied depending on *NaCl* size and the ratio of components in the mixture [37]. The researcher identified some parameters that affect the cell pore size, porosity and strength, etc. These parameters were the mixture composition, sintering temperature and pressing pressure. The small pore size, its uniform distribution and spherical shape give metal foam better mechanical properties. However, it is difficult to control these parameters during processing [38]. Aluminum fractions affect the relative density and compressive strength. Mechanical properties can be improved by increasing the ratio of cell wall thickness to cell wall length by reducing the cell size. The density of the foam can also be controlled by the amount of *NaCl*. *Sazegaran* studied the effect of the chromium amount on the density of unsintered and sintered products. When chromium was added to the original powder, the product density initially decreased, but after adding additional chromium amount, the density of the unsintered and sintered material increased [39–40].

Various method and its relative density and porosity

Various methods have been developed to manufacture the metallic foam. Different methods achieve different percentage level of porosity and different pore structure, such as open porous and closed porous. Table bellow discusses the various methods, indicating porosity and pore structure, as well as challenges.

Porosity, pore structure and challenges of different metallic foam

S.no	Method	Material	Foaming agent/ gas/space holder	Challenges	Pore structure	Porosity %	Relative density	Ref. No.
1	Gas injection method	*A356*	Compressed air, Carbon dioxide, Nitrogen, H_2, Argon	Fine size bubbles formation, for its uniformly distribution and it is not suitable for oxidizing material	Closed cell structure	50 to 80	0.02 to 0.2	[5–8]
2	Foaming method	All grade of aluminium	TiH_2, $CaCO_3$, $MgCO_3$, $Mg(OH)_2$, $CaMg(CO_3)_2$, $(4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O)$	Bubbles entrapment. to increase the viscosity of molten some are added.	Closed cell structure	60 to 86	0.12 to 0.44	[10–16]
3	Solid gas eutectic reaction	*Ag*, *Cu*, *Al*, nickel, Chromium	Hydrogen gas supplied at 50 atm pressure.	It is restricted to the hydrogen gas.	Closed and open cell structure	5 to 75	0.12	[17,18]
4	*Fraunhofer* processes	*Al* (spherical) powder, *Ti*, Brass	TiH_2, $CaCO_3$	Material should have high affinity towards other material	Closed and open cell structure	75 to 95	0.22	[27–34]
5	Gas entrapment	Titanium powder	Argan gas	Complicated set up required	Closed and open cell structure	50	0.16 to 0.22	[34]
6	Space holder method	Stainless steel, mostly used for titanium	*NaCl*, Urea, tapioca starch	Selection of space holder, which easily removed	both	80	0.22 to 0.3	[35–38]

Conclusion

Due to its' mechanical and thermal properties, metallic foams can be widely used in the aerospace and automotive industries. Many methods have been developed to manufacture metal foam, but the most popular is the melt route method.

Aluminium alloy is mainly used to manufacture a metallic foam by melt route method. TiH_2 is commonly used for foaming, but due to its high decomposition rate and cost, another foaming agent, $CaCO_3$, has been proposed. This foaming agent is most suitable for aluminium alloys because it does not require any stabilizer. It is possible to develop another new foaming agent that does not require a stabilizer.

The melt route method is not widely used in the production of stainless steel foam because the melting point of stainless steel is quite high.

In powder metallurgy, space holder method is used to manufacture the biomedical implants and engineering equipment. Typically, titanium foam is made by space holder method. The advantage of this method is that pore size, porosity and relative density can be controlled by the size, shape and volume fraction of the space holder. Other foams are also manufactured using this method. This method is not limited to titanium metal only.

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Conflicts of Interest

The authors declare no conflict of interest.