Stabilized aluminum foams, unique material for industrial applications

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This paper presents an overview of stabilized aluminum foams (SAF). The main objectives are the evaluation and development of these materials. Metal foams are metal matrix composites (MMC) characterized by: higher specific properties, high capacity vibration damping and sound, mechanical energy absorption etc. The wide range of possible properties can lead to innovative applications, which is a strong driving force for the improvement of metal foam production technologies. Investigated and studied materials are composite of aluminum alloy matrix where the stabilization of the gas bubbles has been done by ceramic particle added. The paper also presents some manufacturing processes of SAF, (such as sheet casting, low pressure casting, precursor technology) and some SAF's characteristic properties. Finally, the various application fields for cellular metals are discussed. They are divided into structural and functional applications and are treated according to their relevance for the different industrial sectors.

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1. Introduction

Metal foams belong to the class of cellular materials which are the basic structural materials of nature. Replacement of the weak natural matrix (e.g. wood) by a stronger metal leads to an improved artificial material. Metal foams can be characterized by three expressions: profitability, safety and noise reduction. By exclusive combination of gas bubbles and metallic materials one can implement an extra increase of the price of a product, new economically important energy absorbing materials increasing safety of the cars and the buildings, noise reduction by sound absorption and vibration damping. The wide range of possible properties can lead to innovative applications [1].

Methods to foam various metals are constantly under development. Currently, aluminum and nickel are the most common metals foamed and are available commercially. It is possible to foam a range of metals and alloys including magnesium, lead, zinc, copper, bronze, titanium and steel, though currently Al foam is attracting the most research attention because of its inherent strength and stiffness to weight properties.

Production of metal foams requires stabilizing particles which can be either nanometer-sized oxide filaments or micrometer-sized particles [1]. The size and type of particles have a pronounced impact on mechanical properties. Whenever micrometer-sized particle are present, the foams are more brittle and cutting is difficult. Sub-micrometer particles should lead to more favorable mechanical properties and less problems with machineability.

Stabilized Aluminum Foam (SAF) is a unique material in which the base material is a metal matrix composite (MMC), composed of metallic alloy base with added ceramic particles. The particles are necessary to

stabilize the foam bubbles, since without the particles the formed bubbles will immediately collapse. The stabilizing particles slow the drainage of the metal in the cell walls and increase the apparent viscosity. Liquid metals are mostly made foamable by Ca additions followed by a thickening period. There is a need for an additive that can be easily admixed to an aluminum alloy melt and makes this melt foamable. Foams were successfully produced using SiC, TiB₂ and TiC particles. Ex-situ characterization of the foams by SEM showed that the particles segregate to the surfaces of the cell walls and lead to almost dense coverage there.

2. Structure and properties of aluminum stabilized foams

2.1 Foam Structure

The term "foam" is usually reserved for dispersion of gas bubbles in a liquid. [2]. The morphology of such a foam can be preserved by letting the liquid solidify thus obtaining what is called "solid foam" (often just called foam or sponge) [3]. The expression "metal foam" [4] strictly valid only for the liquid phase, is often used to describe the solid product thus the liquid counterpart is defined as liquid-metal foam [5].

The term "structure" is used for the description of cellular materials at different levels of observation: the geometric architecture of the solid (skeleton) in the individual cells and their 3D arrangement, the variation of that architecture within a considered sample or part (degree of uniformity), and the microstructure of the solid itself and its surface [4]. Equal size bubbles form a monodisperse foam. The foam is polydisperse if the bubbles show a wide variety in size [6].

We can say that practically foam structure can be in a open cell shape or in a closed one. The open cell metal foams are those that consist of cells connectable to each other through open faces (figure 1). The solid material is contained in cell edges consisting of struts and rods rather than in solid faces. This form of foam is open to fluids passing through and so it is useful as a filtering medium, part of a heat transfer system [6] or cores in sandwich structures.



Fig. 1. Typical open cell metal foam (Gibson L.J. &. Ashby M.F. 1997).

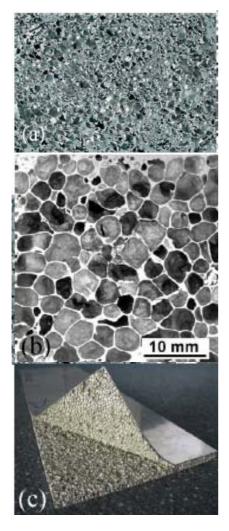


Fig. 2. Example metal foam closed cell structures: [7].

Closed cell metal foams contain non-interconnected cells with solid material faces (Fig. 2). These foams have been investigated for potential uses where the structural properties are desired in combination with one or more of the foam's other properties. The variation in cell size, wall thickness, constituent wall materials, and defects will all affect the mechanical properties of the bulk structure.

The most important feature of foams is the "relative density" [8] that is, the apparent density of the foam, divided by the bulk density of the material from which the foam is made of.

The key parameters of metallic foam stability can be divided into two: the role of the particles and the role of the surface of the cell walls. The particles can be characterized by: their reaction with melt, wetting and distribution in the melt (network formation, clustering and segregation). Aside from the particle concentration, recent investigations showed that the composition of the melts and the materials of the particles also influence the stability. The surface can be characterized by: skin (oxide layer) thickness and the apparent surface tension. Nevertheless, the effect of the blowing gas or the foaming agent to the foam stability is barely investigated so far.

No matter the different processing routes for obtaining metallic foams, the complete foaming process is concerned with foam genesis where the blowing agent decomposes, its evolution and growth of spherical pores, further foaming that leads to thinning of cell wall and thus to change of pore shape from spherical to polygonal and pore coalescence due to surface tension and gravitational forces. The main convict for the destruction of foam is the instability of cell walls under the pressure differences or gravity. As we can see from the third and fourth steps, the death or collapse of foam occurs at the peak of third and start of the fourth step [9]. The strengthening the cell walls can inhibit this phenomenon. This can be accomplished in several ways, e.g., by enhancing the viscosity of melt, using different alloying elements in the melt or employing ex- or in-situ particles that stabilize the wall [10, 11, 12, 13, 14, 15, 16]. Similarly, Koerner et al. [15] discussed the aluminum foam stabilization by the presence of an oxide network. They have also suggested that the effect of the second phase on the stability of foam is due to its wetting characteristics with aluminum liquid. A good wetting (for example, Al/Al₂O₃ contact angle 63° at 1100°C) leads to a decrease in the pressure in particle-free regions of the cell wall which in turn reduces the tendency of liquid drainage and thus cell wall thinning. The ceramic particles are segregated at the cell boundaries, and as the cell grows particles are pushed away. Finally the particles mainly decorate the cell walls leading to its strengthening.

Sometimes, a pre-treatment of the blowing agent also gives better foaming action [17, 18, 19]. A prolonged heating of TiH_2 at different temperatures leads to the formation of an oxide layer on the surface delaying the reaching of decomposition temperature during foaming. Matijasevic and Banhart [18] reported that the delay can be up to 45 s, final expansion of the foam is increased from 4.5 to 5.5 times and a more uniform foam is formed with smoother cell walls and increased roundness of pores.

A high heating rate gives better foaming compared to slow heating [12]. This is attributed to the sufficient time available for the foaming agent to decompose and escape at slow heating rate, and oxidation of a thick oxide layer on the surface as well as inside the precursor material, which inhibits the foaming process by mechanically hindering foam expansion.

Koerner et al. [15] experimented with varying ambient argon pressure on aluminum foaming for different

time periods. It has been concluded from their study that foaming for 600 s at 665°C and at ambient pressure of 1000 mbar does not lead to any drainage. When kept for 1800 s, gas loss was seen only from the top surface of the foam and material redistribution processes induced by the energetically unfavorable cell structures do not take place. A similar experiment at 2800 mbar led to an increase in foam density and decrease in cell size (Fig. 3).

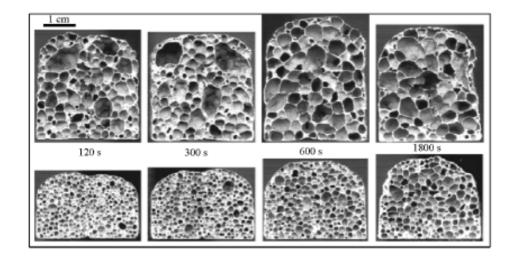


Fig. 3. Foam stability: Cell structure after heating to 665°C and increasing the dwelling time at this temperature before solidification (upper row: 1000 mbar argon; lower row: 2800 mbar argon; precursor material: commercial AlSi10Mg0.5, extruded) [15].

2.2 Structural and mechanical properties

There are several structural parameters of foams describing the cellular architecture of the foams and influencing foams properties: number and size-pore distribution, average size, shape and geometry of the pores, thickness, intersections and defects in the cell-walls and thickness, defects and cracks of the external surface [7, 20, 21].

Progress has been made in understanding the. Although the exact relationship between properties and morphology is not yet sufficiently known, one usually assumes that the properties are improved when all the individual cells of foam have similar size and a spherical shape, defects free, hypothesis not verified experimentally yet. There is no doubt that the density of a metal foam and the matrix alloy properties influence the modulus and strength of the foam and that the real properties are inferior the theoretically expected due to structural defects. This demands a better pore control and reduction in structural defects. Density variation and imperfections yield a large scatter of measured properties, which is detrimental for the metal foams reliability [21]. Wiggled or missing cell-walls reduce strength which causes a reduced deformation energy absorbed under compression [20, 22]. Mechanical studies demonstrate that selective deformation of the weakest region of the foam structure leads to crush-band formation [23]. Cell morphology and

interconnection could also affect thermal and acoustic properties [24]. That's why it is important to produce more regular structures with fewer defects in many ways as possible.

Many literature studies have been undertaken on the mechanical properties of metal foams [7]. Others, have carried out experiments to investigate the behavior of metallic foams under different loading conditions, particularly the properties of metal foams under impact loading. The possibility of controlling the loaddisplacement behavior by an appropriate selection of matrix material, cellular geometry and relative density makes foams an ideal material for energy absorbing structures. Among the several mechanical testing methods available, uniaxial compressive mechanical tests are commonly used to evaluate the compressive behavior and the energy absorbed of these foams. The compression behavior of these Al-alloy foams depends on several parameters such as the Al-alloy composition, the foam morphology (cell size range), the density gradient of samples, the defects of cellular structure (cell walls) and the characteristics of the external surface skin. The elastic modulus, yield and plateau strengths are the most important mechanical properties parameters which are obtained from these curves. The stress-strain curves of closed-cell Al-alloy foams display either plastic or brittle fracture depending on foam fabrication and microstructure [25, 26].

3. Metal foam applications

There are a lot of applications of metallic foams (table 1), but most of them are in the automotive, aircraft and

building industries, in which the SAF manufacturers have the objective to achieve a market penetration that will bring stabilized aluminum foam to where magnesium is today.

Table 1. Some applications	of metal foams. [29]
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Application	Comments	Examples
Light weight structures	Excellent stiffness to weight ratio when loaded in bending	Shipping container, building material, filling in hollow materials against buckling and builders staging
Sandwich cores	Metal foam has low density with good shear and fracture strength	Panel like floor and drop ceiling, aircraft pallet, heavy duty pallet, panel replacing honeycomb, elevator cab and door
Strain isolation (compression)	Metal foams can take up strain mismatch by crushing at controlled pressure	Joining elements
Mechanical damping	The damping capacity of metal foams is larger, by up to a factor of 10, than that of solid metals	Basis of rotating machine or loudspeaker
Biomedical industry	Biocompatibility (titanium or cobalt- chromium alloys)	Prostheses or dental implants
Acoustic absorption	Open cell foams have sound absorbing capacity	Sound barrier for highways, overhead bridge and tunnel, machine casing with improved sound and vibration damping
Acoustic control	Guidance and redirection of the sound waves	Closed cell foams suitable as impedance adaptors for ultrasound sources
Kinetic energy absorbers (compressive)	Exceptional ability to absorb energy at almost constant pressure	Crash attenuator, crash barrier, safety wall of tornado shelter, crash helmet, impact energy absorption parts for cars, lifting and conveying systems
Blast resistance	Excellent energy absorption capability	Amour and gas tank
Storage and transfer of liquids	Cell structure, open structure	Automatic humidity control, self lubricating bearings, porous rolls holding and distributing water or adhesives to surfaces, reducing undesired movements of the liquid in partially filled tanks (anti- sloshing)
Fluid flow control	Many available degrees of "openness" of cellular metals	Flow straighteners in wind tunnels or flow distributors in valves
Artificial wood (with high temperature capability	Metal foams has some wood-like characteristics: light, stiff and ability to be joined with wood screw	Rail car bulkhead, fire door and wall
Filtration and separation	Fine filtration capacity, good particle retention, clean ability, mechanical properties, corrosion resistance and low cost	Filters for cleaning recycled polymer melts, for removing yeast from beer, for contaminated oil, filtration of diesel fumes or water removal in air lines
Heat exchangers/refrigerators	Open-cell foams have large accessible surface area and high cell wall conduction giving exceptional heat transfer ability	Heat sink for processor
Thermal isolation	Thermal conductivities are much lower than those of solid metals, but still much larger than polymer foam	Cooking pot and vessels

Application	Comments	Examples			
Heat shields	Oxidation of cell faces of closed-cell aluminum foams appears to impart exceptional resistance to direct flame	Fireproof wall			
Electrical shielding	Good electrical conduction, mechanical strength and low density make metal foams attractive for shielding	0			
Electrodes and catalyst carriers	High surface/volume ratio allows compact electrodes with high reaction surface area	Long life battery			
Electrode material	Increasing the electrode surface while maintaining the turbulence promotion	Electrochemical reactors, improvement of electro-catalytic processes (electro-oxidation)			
Spargers	Creation of sufficiently small gas bubbles and corrosion, heat or shock resistance	Carbonation of beverages			
Buoyancy	Low density and good corrosion resistance suggest possible flotation application	Ship and boat			
Water purification	Redox reaction between ions and matrix metal of the cellular structure (for instance, electroless reduction of Cr(VI) ions by cast aluminum foams)	Water purifier			
Sporting equipment	Good energy absorption capacity of SAF	Shinbone protectors for football players			
Decoration and arts	Visual appearance or a large volume with a correspondingly low weight	Fancy furniture, clocks, lamps			

4. Manufacturing processes

Metal foams manufacturing processes can be classified in two groups [3]: direct and indirect foaming methods. Direct foaming methods start from a molten metal containing uniformly dispersed ceramic particles to which gas bubbles are injected directly [15] or generated chemically by the decomposition of a blowing agent (e.g. titanium hydride, calcium), or by precipitation of gas dissolved in the melt by controlling temperature and pressure [27]. The indirect foaming methods require the preparation of foamable precursors that are subsequently foamed by heating. The foamable precursor consists of a dense compacted of powders where the blowing agent particles are uniformly distributed into the metallic matrix.

Most commercially available metal foams are based on alloys containing aluminum, nickel, magnesium, lead, copper, titanium, steel and even gold. Among the metal foams, Al-alloys are commercially the most exploited ones due to their low density, high ductility, high thermal conductivity and competitive cost.

Direct foaming methods are currently being commercial exploited in a large-scale. By far the cheapest type of process is melt-route processing (the Alcan/Norsk Hydro process) called Melt Gas Injection – MGI [5]. So, by this method, the Cymat Aluminum Corporation (Canada) manufactures aluminum foams, which are obtained by gas injected directly into a molten metal. Ceramic particles (e.g. silicon carbide, aluminum oxide and magnesium oxide with volume fraction ranges from 10% to 20% and the mean size from 5 to 20 μ m) are used to enhance the viscosity of the melt and to adjust its foaming properties. The ceramic particles trap gas bubbles owing to the favorable interface energy and

serve as stabilizer of the cell walls and delay their coalescence. They also reduce the velocity of the rising bubbles by increasing the viscosity of the melt. The relative density of these foams is within the range 0.05-0.55 g/cm³ and the average cell size 2.5-30 mm. Therefore, the first step requires the preparation of a melt bath containing an aluminum alloy and the needed particles. Then the liquid Metal Matrix Composites (MMC) is foamed in a second step by injecting gas (air, nitrogen or argon) into it, using specially designed rotating propellers or vibrating nozzles, which function is to create very fine gas bubbles in the melt and distribute them uniformly. The floating foam is then continuously pulled of from the surface of the melt with different techniques (for example by means of conveyor belt to obtain sheets). The foam, obtained by MGI, usually presents a gradient in density and pores elongation as a natural consequence of the gravitationally induced drainage and the shearing forces of the conveyor belt that lead to distorted cells in the final product. This obviously has a pronounced effect on the mechanical properties which become anisotropic. The situation could be improved by pulling off the foam vertically [5]. This process is the cheapest of all and allows manufacturing of large volume of foams. Despite this process continuous improvement, the drawing of the foam and the size distribution of the pores are still difficult to control. There is usually necessary to cut the foamed material into the required shape after foaming, operation that can be problematic due the high content of ceramic particles (10-30 vol.%). Hütte Klein-Reichenbach Ges.m.b.H Company (Austria) also produces and commercializes aluminum foams with excellent cell size uniformity, called MetComb. The process used is based on the gas injection method and allows for the production of complex shaped parts by casting the formed foam into the moulds process named MGI-mould process [25].

An alternative way for foaming melts directly is to add a blowing agent to the molten metal. The blowing agent decomposes under the influence of heat and releases gas which then propels the foaming process. Shinko Wire Company has been manufacturing foamed aluminum under the registered trade name "Alporas". This method starts with the addition of 1.5 wt.% calcium metal into the molten aluminum at 680°C, followed by several minutes stirring to adjust viscosity. An increase of viscosity is achieved by the formation of calcium oxides. After the viscosity has reached the desired value, titanium hydride (TiH₂) is added (typically 1.6 wt.%), as a blowing agent by releasing hydrogen (H₂) gas in the hot viscous liquid. The melt starts to expand slowly and gradually fills the foaming vessel. The foaming takes place at constant pressure. After cooling the vessel below the melting point of the alloy, the liquid foam turns into a solid Al foam. After that, the foam block is removed from the mould, it is sliced into flat plates of various thicknesses according to its end use. These foams have uniform pore structure and do not require the addition of ceramic particles, which makes it brittle. However, the method is more expensive than foaming melts by gas injection method requiring more complex processing equipment. The density range of these foams is 0.18-0.24 g/cm³, and the mean cell size is about 4.5 mm

Nowadays, foams manufactured by indirect foaming methods are also in the state of commercial exploitation, but in small-scale by German and Austrian Companies, like Schunk GmbH, Applied Light-weight Materials ALM and Austrian Company Alulight GmbH [17, 18]. Powder Metallurgical (PM) method is one of the commercially exploited indirect methods to produce Alalloy foams. This process consists on the heating of a precursor material which is obtained by hot compaction of a metal alloy (e.g. Al-alloy) with blowing agent powders (e.g. TiH₂), resulting in the foam itself. The metal expands, developing a highly internal porous structure of closed-cells due to the simultaneous occurrence of the melting of the metal and thermal decomposition of the blowing agent with the release of H_2 gas. The liquid foam is then cooled in air. resulting solid foam with closed cells and with a very thin dense skin that improves the mechanical properties of these materials. This process can produce foams with porosities between 75% and 90% [28].

5. Preliminary experiments and results

The injected air causes bubbles to rise to the surface of the melt, forming liquid foam which is stabilized by the presence of solid ceramic particles on the gas liquid interfaces of the cell walls. The stabilized liquid foam is then mechanically conveyed off the surface of the melt and allowed to cool to form a solid slab of aluminum foam. The aluminum foam structure (cell size and cell wall thickness) is controlled by the process variables such as the volume fraction of the solid particles; foaming temperature, airflow rate, and impeller design the foam making process. Unfortunately, no publication has been found in the work on the influence of the process in variables on the cell structure of aluminum foam. In the future we will study and investigate the effect of the concentration of SiC particles on the cell structure and mechanical properties.

The experimental equipment consists of an electric resistance furnace (maximum heating temperature 800°C), which was adapted for insufflations gas (SO₂, N₂, inert gas, etc.) It is also equipped with a wide agitator and a trough acquisition of foam formed (Figure 4).

Has been obtained metal foam by mixing the alloy melt AlMg15 with 10% SiC powder 120 μ m size, at a temperature of 710°C and with SO₂ injection at 1.2 atm pressure. Obtained foam was analyzed macroscopically and microscopically (optical and electronic).

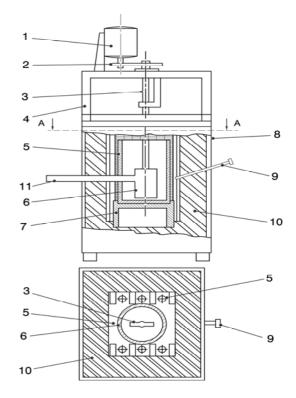


Fig. 4. Electric resistance furnace. 1 – engine,
2 – reducer, 3 – port rod paddle, 4 – metal frame,
5 – crucible, 6 – paddle, 7 - crucible support, 8 – silica bars, 9 – thermocouple, 10 – refractory shield,
11 – collecting gutter foam.

In Fig. 5 is shown the macroscopic image of AlMg15 obtained sample. It is observed that pores have approximately equal sizes and are distributed uniformly on the sample surface.



Fig. 5. Macroscopic image of AlMg15 metal foam.

The quantitative optical microscopic analysis demonstrates relatively uniform dimensional pore sizes between $390 \div 500 \ \mu m$ (figure 6). Analysis were made at X:200/120 and Y:200/120 coordinate. Darker surfaces represent Si from SiC which was added for foam stabilization.

Sr.No	Description	Results	Calibration
			X: 200/120 Y:
		431.718	200/120 Micron
L1	Length	Micron	/Pixel
			X: 200/120 Y:
		496.222	200/120 Micron
L2	Length	Micron	/Pixel
			X: 200/120 Y:
		406.369	200/120 Micron
L3	Length	Micron	/Pixel
			X: 200/120 Y:
		392.092	200/120 Micron
L4	Length	Micron	/Pixel

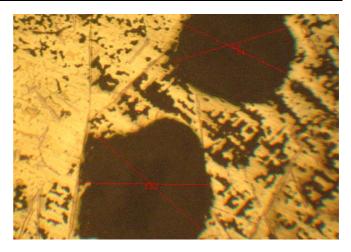


Fig. 6. Size pore measurement by means of quantitative optical microscopy, x200.

Microscopic study of obtained foam (Figure 7) revealed the dimensional uniformity of the formed pores and the fact that they do not communicate. In this figure it can be also observe that the pores are uniform distributed on the foam surface.

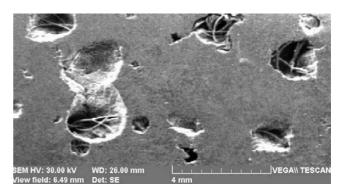


Fig. 7. Electron microscopy of metal foam sample, x100.

Chemical composition of the composite is shown in Table 2 and on EDAX image (figure 8). It makes us believe that foam stability was achieved by depositing of some particles (Al₂O₃, MgO and SiC) on pores walls

Element	AN	series	Net	[wt.%]	[norm.	[norm.	Error in
					wt.%]	at.%]	%
Aluminum	13	K-series	110913	36,3069	45,76441	35,07558	1,849536
Oxygen	8	K-series	23306	28,17555	35,51493	45,90406	3,580796
Magnesium	12	K-series	39495	10,88293	13,7178	11,67166	0,658733
Carbon	6	K-series	2907	2,980624	3,757041	6,468603	0,544201
Silicon	14	K-series	1103	0,665303	0,838606	0,617475	0,065295
Sulfur	16	K-series	726	0,323056	0,407208	0,262613	0,04407
			Sum:	79,33436	100	100	

Table 2. Chemical composition of AlMg15 foam.

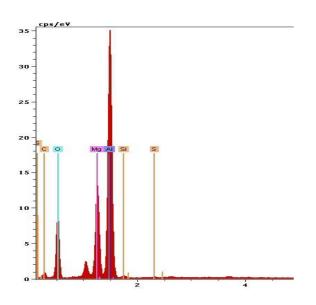


Fig. 8. Electronic microscopic image of AlMg15 foam.

It also has been tried several attempts to obtain stabilized aluminum foam, keeping the same technological parameters and different concentrations of magnesium and silicon carbide.

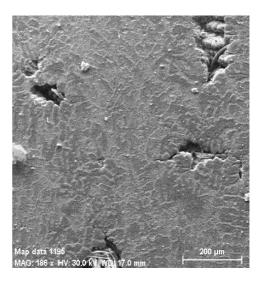


Fig. 9. Electron microscopy of sample (AlMg10).



Fig. 10. Macroscopic image of AlMg10.

Table 3. Chem	ical composition	of AlMg10.
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Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Aluminum	13	K-series	176389	179.7221	83.1032	79.03816	8.439655
Magnesium	12	K-series	26870	9.80956	9.6762	9.120739	1.301259
Oxygen	8	K-series	2190	7.77664	3.806815	6.023802	1.467333
Carbon	6	K-series	1254	4.795549	2.347514	4.948136	1.046168
Silicon	14	K-series	637	1.723273	0.843576	0.760421	0.143538
Copper	29	K-series	333	0.350383	0.171519	0.068334	0.047003
Sulfur	16	K-series	97	0.10455	0.051179	0.040408	0.037578
			Sum:	204.282	100	100	

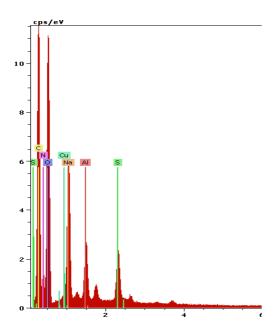


Fig. 11. Electronic microscopic image of sample AlMg10.

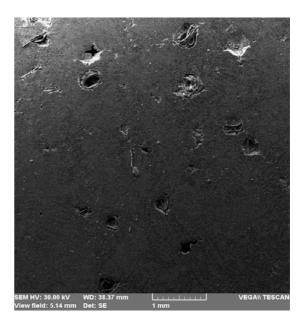


Fig. 12. Electron microscopy of sample (AlMg6), x100.

Table 4. Chemical composition of AlMg6

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	Error in %
Aluminum	13	K-series	182236	78.07581	78.11152	67.76126	3.741066
Oxygen	8	K-series	1778	11.39426	11.39976	16.53978	2.245209
Magnesium	12	K-series	18408	4.365141	4.36821	4.082185	0.400056
Carbon	6	K-series	1449	6.239337	6.242345	12.06442	1.304541
Silicon	14	K-series	1385	1.877259	1.878164	1.552349	0.133711
			Sum:	99.95182	100	100	

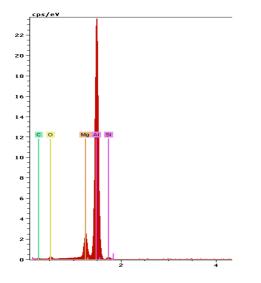


Fig. 13. Electronic microscopic image of sample AlMg6.

As can be seen from the analyses presented, attempts have not had favorable results in terms of getting metal foams.

6. Conclusions

Experiments have shown the viability of the method of obtaining foams and that the foam stability was achieved by depositing of some particles (Al₂O₃, MgO and SiC) on pores walls.

Another reason for applying aluminum stabilized foam achieving are the uniform pore distribution over the entire area and relatively low production costs.

From this study concluded that we need a higher amount of SiC for obtaining foams, and SiC particles must have smaller dimensions, fact that will be studied further.

There are a lot of applications of metallic foams, but most of them are in the automotive, aircraft and building industries, in which the SAF manufacturers have the objective to achieve a market penetration that will bring stabilized aluminum foam to where magnesium is today.

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