

# SYNTHESIS AND CHARACTERIZATION OF Al FOAMS PRODUCED BY POWDER METALLURGY ROUTE USING DOLOMITE AND TITANIUM HYDRIDE AS A FOAMING AGENTS

## SINTEZA IN KARAKTERIZACIJA ALUMINIJEVIH PEN, NAREJENIH PO POSTOPKU PRAŠNE METALURGIJE Z UPORABO DOLOMITA IN TITANOVEGA HIDRIDA KOT PENILNEGA SREDSTVA

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Production of aluminum foams by the powder-metallurgy process depends on the preparation of pre-cursors. In general, pre-cursors consist of compacted mixture of metallic powder and foaming agent, which is foamed at a pre-determined temperature. Due to high temperature of foaming procedure, the foaming agent decomposes into a solid component that is built into the matrix material, and a gas component that causes foaming of the matrix material. Powder metallurgy is a method for making close-cell foams and it is the best selection, especially for the production of net-shape parts, providing excellent quality of end products. In our research work, powders, precursors and foams, made from different metallic powders (Al 99.7 % purity, AlSi12 alloy) with different foaming agents ( $\text{TiH}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaMg}(\text{CaCO}_3)_2$ ), were examined with different analytical techniques.

Keywords: Al alloys, powder metallurgy,  $\text{CO}_2$  releasing foaming agents, close-cell foams

Aluminijeve pene, narejene po postopku prašne metalurgije, so zelo odvisne od priprave prekurzorjev. Ti so narejeni iz stisnjenih prašnih delcev osnovnega materiala in penilnega sredstva ter penjeni pri določeni temperaturi. Zaradi visokih temperatur penilno sredstvo razpade na trdno snov, ki se vgradi v osnovni material, in plin, ki povzroči penjenje osnovnega materiala. Po postopku prašne metalurgije se izdelujejo aluminijeve pene z zaprto poroznostjo. Ta metoda je najbolj primerna za izdelavo kompleksno oblikovanih končnih oblik izdelkov. Pri našem raziskovalnem delu smo z različnimi analitskimi tehnikami raziskali kovinske prahove (Al, čistote 99,7 %, in zlitine AlSi12) in penilna sredstva ( $\text{TiH}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaMg}(\text{CaCO}_3)_2$ ), prekurzorje ter končne porozne materiale.

Ključne besede: Al-zlitine, prašna metalurgija, penilno sredstvo na osnovi  $\text{CO}_2$ , pene z zaprto poroznostjo

## 1 INTRODUCTION

Production of aluminum foams by the powder-metallurgy process was developed at the Fraunhofer-Institute in Bremen (Germany).<sup>1-4</sup> The production process begins with the mixing of metal powders – elementary metal powders, or alloyed powders or metal powder blends – with a blowing agent, after which the mixture is compacted to yield a dense, semi-finished product (Figure 1).<sup>5,6</sup> The method depends on the preparation of pre-cursors, which in principle can be made by any technique that ensures that the blowing agent is embedded into the metal matrix without any notable residual open porosity. In general, pre-cursors consist of compacted metallic powder that is sintered at a pre-determined temperature. Due to high temperature of sintering, foaming agent decomposes into a solid component that is built into the matrix material, and a gas component that causes foaming of the matrix material.<sup>7</sup> Powder metallurgy is a method for making closed-cell foams and it is the best selection, especially for the

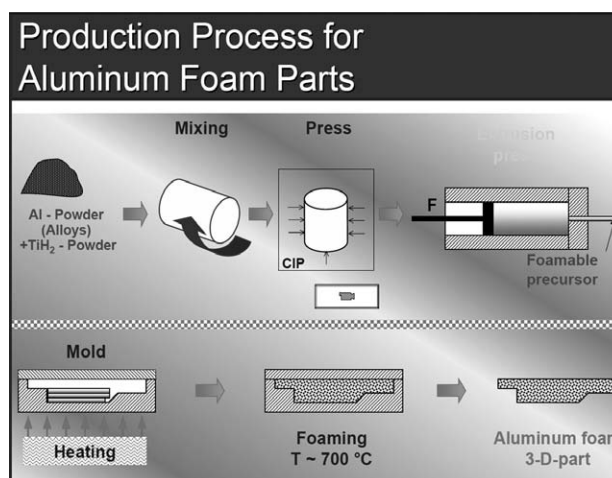


Figure 1: Scheme of aluminium foam preparation by the powder metallurgy route<sup>5</sup>

Slika 1: Shema priprave aluminijevih pen po postopku prašne metalurgije<sup>5</sup>

production of net-shape parts, providing excellent quality of end products.

It is known that aluminium foams are advanced metallic materials that have been known for 30 years but the development of foams has only been intensified in recent 10 years. For making aluminium foams usually  $\text{TiH}_2$  is used as a foaming agent. Moreover,  $\text{TiH}_2$  is a cost driver, amounting to about 10 % of the total costs of powders ( $w(\text{TiH}_2) = 1 \% \approx 1 \text{ €/kg}$ , Al-foams  $\approx 10 \text{ €/kg}$ ).<sup>8-12</sup> Due to high costs of aluminium foam production, industry is looking for a more economical solution to produce aluminium foams, while preserving all the combinations of properties of foams used nowadays.<sup>13,14</sup> In our research a more economical way to prepare foams was sought by using less expensive initial materials, such as natural minerals calcite and dolomite as foaming agents, which proved to be very good substitutions for expensive  $\text{TiH}_2$ .<sup>12,15-19</sup>

To explain the applicability of aluminium foams, comparison in weight reduction when using foams instead of steel construction, while retaining equal mechanical properties, was made. From the literature<sup>20</sup> concerning potential applications of aluminium foams in some constructions the reduction of weight is from 35 % up to 46 %.

Our task was to develop a possible process to prepare aluminium foams cost efficient for wider applications of this unique type of materials in more common final products, not only in high-tech areas.

## 2 EXPERIMENTAL PROCEDURES

Many different analytical techniques were used to achieve the results that would satisfy and justify our research work. The study was systematically planned from the very first literature review and the analysis of the current state of research, to the characterization of the current initial materials and experimental work with the materials, and finally to parameters that were previously used in the production of aluminium foams.<sup>21-23</sup> After mastering the process of preparing aluminium foams by the powder metallurgy route, the second step taken was the selection of new initial materials. Nowadays, technically pure aluminium powder is usually used as a matrix material. Also AlSiMg alloy powders and AlSi powders with smaller amounts of Si can be used. Our intention was to use less expensive materials, and thus powders made of recycled aluminium with a chemical composition close to the Al-Si eutectic with some impurities (named AlSi12 alloy hereafter) were prepared. Furthermore, the most applied foaming agent was substituted with the natural mineral dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ), that needed only to be milled. Those two new initial materials should significantly reduce the production costs of aluminium foams.

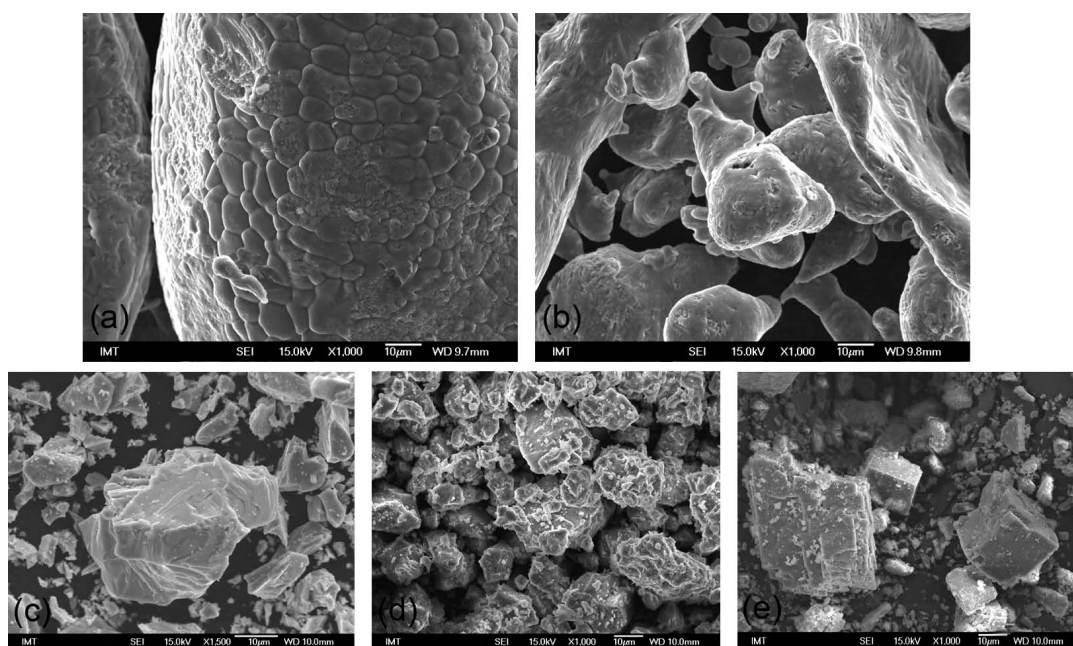
In our study we used two different aluminium powders (pure Al 99.7 % and AlSi12 alloy) and three diffe-

rent foaming agents –  $\text{TiH}_2$ ,  $\text{CaCO}_3$  and  $\text{CaMg}(\text{CO}_3)_2$ , to compare their effects in foaming. Characterization of the used materials was performed by the laser granulometry for particle size distribution. Differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analyses of powders were applied to determine the decomposition temperatures of foaming agents and the melting points of the matrix materials. It was essential to know when the matrix powder began to melt and when adequate viscosity was achieved. Further, SEM/EDS analyses of powder particles (**Figure 2**) were performed. Results showed differences in powder morphology and in the structure of the surface. Also the micro-hardness (by Vickers) of the powder materials was measured.

After knowing all the important characteristics of the initial materials, the compacting of pre-cursors was carefully planned. It was very important to select a method of compacting for the preparation of pre-cursors, since a very high green density was needed to be achieved. The compaction process depended on the properties of the used metallic powder. Aluminium powder was prepared by gas atomization in order to prevent the growth of oxide layer on the surface of powder particles, though the oxide layer decreased the green density of the metallic material. It was also very important to consider the compression properties of the metallic powder in order to achieve the highest possible green density by the optimal compacting effect.

In order to achieve optimal pore sizes, optimal distribution of pores, and required density of aluminium foams, the mixtures of matrix material and foaming agent powders contained various fractions of foaming agents.

The foaming process was checked by observing the pre-cursors in the heating microscope during the process of heating. A small sample of pre-cursor material was put into the furnace within the microscope and heated up to 800 °C at a heating rate of 7 °C/min. Samples began to change their shape and volume at a certain temperature, depending on the matrix material and the type and fraction of foaming agent. Results obtained with the heating microscope enabled to conclude which pre-cursors were adequate for the foaming process and which not. Good combinations of matrix powder and foaming agent were then used for the preparation of pre-cursors for foaming in the lab retort furnace with a section of controlled temperature at the end of retort and a cold section at the beginning of retort. The cold part at the beginning of retort was needed for fast cooling the material which had been foamed. Heating microscope also enabled to observe the collapsing of foams after prolonged foaming times at given temperatures. This resulted in the gas escaping from the bubbles that were formed inside the matrix material. At a certain temperature matrix material achieved good viscosity, which prevented gas from escaping out of the material. Excessive temperatures caused the drop of material



**Figure 2:** SEM images of the powders: a) Al, b) AlSi12, c) TiH<sub>2</sub>, d) CaCO<sub>3</sub>, e) CaMg(CO<sub>3</sub>)<sub>2</sub>

**Slika 2:** SEM-posnetki prahov: a) Al, b) AlSi12, c) TiH<sub>2</sub>, d) CaCO<sub>3</sub>, e) CaMg(CO<sub>3</sub>)<sub>2</sub>

viscosity, and due to pressure in gas bubbles gas escaped and foam collapsed. That was the reason that foams had to be cooled down fast after the desired expansion of material was achieved. Cooling could be achieved either by immersing the foamed product in water or with cold compressed air. In our case, cooling in water was applied.

### 3 RESULTS AND DISCUSSION

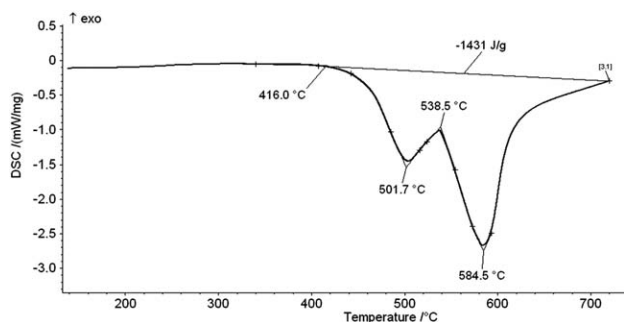
The synthesis of aluminium foams by the powder metallurgy route looks simple at the first glance but it is actually an accurate procedure in the production of net-shape parts, providing excellent quality of end products. The knowledge of the specific product that demands specific quality, in combination with the exact analysis of the case, means that the production of aluminium foams by the powder metallurgy process can be performed for any application.

Firstly, it is very important to compact pre-cursors with very high green densities, though the critical green density is 98.5 %.<sup>24</sup> The selected compacting method depends on the properties of the initial powder material. For softer materials cold double-action pressing is satisfactory, but for harder materials hot extrusion is recommended. Aluminium powder was soft (measured micro-hardness was 22 HV<sub>0.3</sub>) and it was simple to achieve a green density of 99.5 % and even higher with simple double-action cold pressing under a 400 MPa pressing force. On the other hand, AlSi12 powder was harder (measured micro-hardness was 75 HV<sub>0.3</sub>) and it could be less reshaped. Thus, it was impossible to compress the powder enough only with double-action cold pressing.

Even the use of a 1300 MPa pressing force enabled a green density of only 96.5 %, and this was not enough to obtain a pre-cursor that would foam.

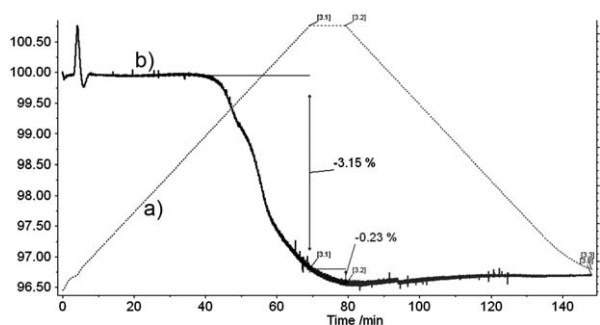
For any other aluminium powder except technically pure Al it was necessary to use hot extrusion to achieve satisfactory green densities. The temperature of extrusion was usually between 350 °C and 450 °C depending on the foaming agent that was used, and the forces of pressing depended on powder mixtures. The critical green density of pre-cursor that should be achieved for material to be able to foam was 98.5 % or higher. In hot extrusion it was important to use temperatures lower than the decomposition temperature of the blowing agent.

The foaming process of individual pre-cursors takes place at various temperatures, depending on the matrix material and the type of foaming agents. For TiH<sub>2</sub> foaming agent a temperature of 30–50 °C above the melting temperature of the matrix material is needed, while temperatures between 750–780 °C are needed for the foaming process when foaming with CaCO<sub>3</sub> or CaMg(CO<sub>3</sub>)<sub>2</sub> powders is applied. TiH<sub>2</sub> decomposes at 450 °C (**Figures 3 and 4**) and the temperature of optimal viscosity of the matrix material is the driving force of optimal foaming. On the other hand, the CO<sub>2</sub> based foaming agents decompose at higher temperatures, 720–750 °C (**Figures 5 and 6**), and the driving force in this case is the initiation of decomposition by pre-heating the material, since foaming takes place at higher temperatures before the viscosity of the matrix material is reduced too much due to prolonged time of heating. However, after foaming at similar temperatures and times, the resulting densities of foams showed that the best pore size, pore distribution and low density were achieved when mass



**Figure 3:** Heating DSC curve for  $\text{TiH}_2$  in Ar atmosphere,  $10\text{ }^\circ\text{C}/\text{min}$  to  $720\text{ }^\circ\text{C}$

**Slika 3:** Segrevalna DSC-krivulja  $\text{TiH}_2$  v argonovi atmosferi pri hitrosti segrevanja  $10\text{ }^\circ\text{C}/\text{min}$  do temperature  $720\text{ }^\circ\text{C}$

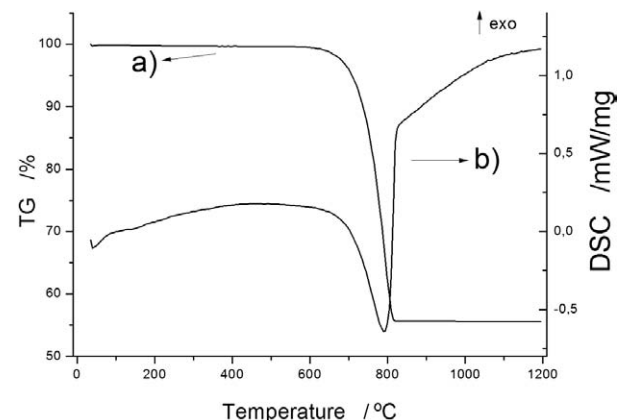


**Figure 4:** TG curve for  $\text{TiH}_2$ , heating up to  $720\text{ }^\circ\text{C}$  and cooling down in the Ar atmosphere,  $10\text{ }^\circ\text{C}/\text{min}$ : a) heating-cooling curve, b) TG curve

**Slika 4:** TG-krivulja za  $\text{TiH}_2$  pri segrevanju do temperature  $720\text{ }^\circ\text{C}$  in ohlajanju v atmosferi argona s hitrostjo  $10\text{ }^\circ\text{C}/\text{min}$ : a) segrevalno-ohlajevalna krivulja, b) TG-krivulja

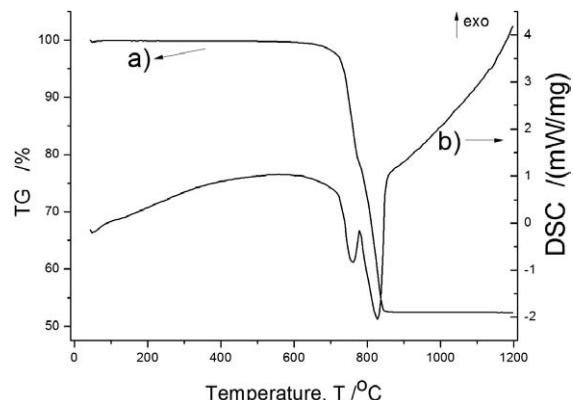
fractions (w) 0.8–1 %  $\text{TiH}_2$ , or 3 %  $\text{CaCO}_3$  or 3 %  $\text{CaMg}(\text{CO}_3)_2$  were applied in the mixtures.

The question is why  $\text{CO}_2$  based foaming agents have not yet been widely used. The answer is given by DSC/TG results where is determine that the agents releasing  $\text{CO}_2$  need higher temperatures for the liberation of gas and the needed temperature is approximately  $100\text{ }^\circ\text{C}$  above the melting point of pure aluminium. In



**Figure 5:** DSC and TG curve for  $\text{CaCO}_3$ : a) TG, b) DSC

**Slika 5:** DSC- in TG-krivulja za  $\text{CaCO}_3$ : a) krivulja TG, b) krivulja DSC



**Figure 6:** DSC and TG curve for  $\text{CaMg}(\text{CO}_3)_2$ : a) TG, b) DSC

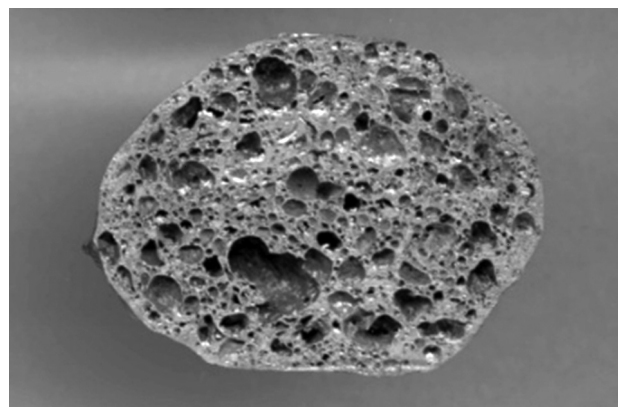
**Slika 6:** DSC- in TG-krivulja za  $\text{CaMg}(\text{CO}_3)_2$ : a) krivulja TG, b) krivulja DSC

such a case, the matrix material is already molten and the viscosity of such a material is not high enough to prevent gas from escaping out of the material. The solution is to pre-heat the pre-cursors before the foaming process begins. When the foaming agents are then exposed to an elevated temperature, the decomposition has been already started and the agent does not need such a long time to decompose completely while the matrix aluminium does not have sufficient time to melt down completely.

In **Figure 7** is a cross-section of Al foam, made of  $\text{AlSi12}$  with  $\text{CaMg}(\text{CO}_3)_2$ , compact with 1200 MPa and pre-heated at approx.  $400\text{ }^\circ\text{C}$  for 15 min.

#### 4 CONCLUSIONS

The use of initial materials similar to recycled aluminium shows that powders made of recycled aluminium or powders made from melted scrub aluminium are a good alternative. Also the substitution of the very expensive  $\text{TiH}_2$  foaming agent with natural and less expensive minerals (dolomite or calcite) is more than welcome for industrial economy.



**Figure 7:** Al foam –  $\text{AlSi12}$  with  $\text{CaMg}(\text{CO}_3)_2$ , foamed for approx. 4 min

**Slika 7:** Al pena –  $\text{AlSi12}$  s  $\text{CaMg}(\text{CO}_3)_2$ , penjeno pribl. 4 min

Compacting forces needed for soft materials, such as technically pure Al, are 400 MPa, while a force of 1200 MPa and higher temperature are needed for harder materials, such as AlSi12 alloy powder. Due to high temperature needed for compacting the powders (AlSi12 and recycling Al), CO<sub>2</sub> gas releasing foaming agents are more sufficient.

It is hoped that less expensive initial materials, more environmentally friendly production processes (milling of natural minerals instead of dissipation production of TiH<sub>2</sub>, using recycled materials instead of pure alloys), and very good achievements of desired properties of final products will lead the industry to the production of aluminium foams by the powder metallurgy route into widely used products in various branches.

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