APPLICATION OF CALCIUM CARBONATE FOR FOAMING ALUMINIUM FOAMS

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Abstract

Aluminium foams are materials with a cellular structure that can be achieved in several ways. The most common methods are direct foaming of melt and foaming a compacted Al precursor containing a foaming agent. As a foaming agent, titanium hydride (TiH_2) has the most widespread application and among some other disadvantages has a high price which significantly increases the cost of foam production. In order to reduce the costs, carbonates, such as calcium carbonate ($CaCO_3$) are successfully used as foaming agents. This paper presents the advantages and disadvantages of using TiH_2 and $CaCO_3$ and the recent results of research conducted so far. The decomposition of $CaCO_3$ begins at higher temperatures than TiH_2, which gives a finer foam structure. At the end of the paper, the properties of reinforced metal foams are presented, in which the reinforcement with ceramic particles leads to the improvement of compressive properties with the inevitable reduction of the ductility of the foam itself.

Keywords: *aluminium foam, foaming, calcium carbonate*

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1. INTRODUCTION

Aluminium foams are materials with specific combination of properties due to their cellular structure. Compared to aluminium or aluminium alloys of equal dimensions, aluminium foams have a much lower mass. Their relative density (ρ_{foam}/ρ_{Al}), determined by the degree of porosity, is significantly lower than the density of aluminium. Some of the applications of Al foams are weight reduction of structures, sound and thermal insulation and as parts for impact energy absorption.

The two most common processes for the production of Al foams are foaming of molten aluminium and foaming of a compacted Al precursor containing a foaming agent (powder metallurgy process). The first method can also be divided into two most common techniques: direct injection of gas through the nozzles into a metal melt and injection of a foaming agent which releases gas at higher temperatures.

2. CONVENTIONAL FOAMING AGENTS

In both above mentioned processes for the production of Al foams where foaming agents are used, titanium hydride (TiH_2) is most commonly used, which at higher temperatures decomposes into titanium and hydrogen:

$$TiH_2(s) \rightarrow Ti(s) + H_2(g) \quad (1)$$

However, using TiH_2 also has some drawbacks, and one of the most important is its high cost, which significantly increases production costs. Since the density of TiH_2 (about 3.75 g/cm^3) is significantly higher than the density of aluminium (2.7 g/cm^3), when foaming, TiH_2 and Ti particles are deposited in the lower parts of the foam due to the gravity, resulting in an uneven cell size distribution. One of the disadvantages of using TiH_2 is also the low decomposition temperature into Ti and H_2, which is at about 400 °C for untreated hydride, while in commercial Al alloys the solidus temperature is above 525 °C [1]. In order to obtain a finer and more homogeneous structure of the foam cells, it is necessary for the decomposition of the foaming agent to begin when the Al matrix is already in the molten state [2]. To shift the decomposition temperature of TiH_2 closer to the solidus and liquidus temperatures of Al and its alloys, it is possible to pre-heat the TiH_2 powder or compacted precursor containing TiH_2 to create protective layers of titanium oxide (TiO_2, Ti_3O) which delay the beginning of decomposition [3-5]. Such procedures are successfully applied in practice, but they further increase the cost of production of metal foams. In the process, TiH_2 participates only as a foaming agent and has no role in increasing the stability of Al foam, so it is necessary to use some other particles, such as ceramic, to achieve greater stability of the foam bubbles [1].

In addition to TiH_2, zirconium hydride (ZrH_2) [6], calcium hydride (CaH_2) [7] and magnesium hydride (MgH_2) [8] are also used as hydride-based foaming agents. Also, the use of precursors with complex hydrides ($LiBH_4$, $NaBH_4$, KBH_4 and $LiAlH_4$) and their foaming properties of Al alloys are investigated, and current findings suggest that the use of agents such as lithium-aluminium hydride ($LiAlH_4$) and lithium-boron hydride $LiBH_4$) achieve very similar results as with the use of TiH_2 [9].

3. $CaCO_3$ AS A FOAMING AGENT

An alternative to the expensive TiH_2 is much cheaper calcium carbonate ($CaCO_3$) and some other carbonates such as magnesium carbonate ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) [10]. Unlike TiH_2, where decomposition produces a chemically inert hydrogen that does not increase the stability of Al foam, carbonates, depending on the chemical composition of Al alloy, form solid particles (such as CaO, Al_2O_3, Al_4C_3 or $MgAl_2O_4$) that increase foam stability [10].

Differential thermal analysis (DTA) of various foaming agents determined their characteristic behavior defined by different temperature ranges in which endothermic reactions occur due to their decomposition, which is shown in Figure 1.

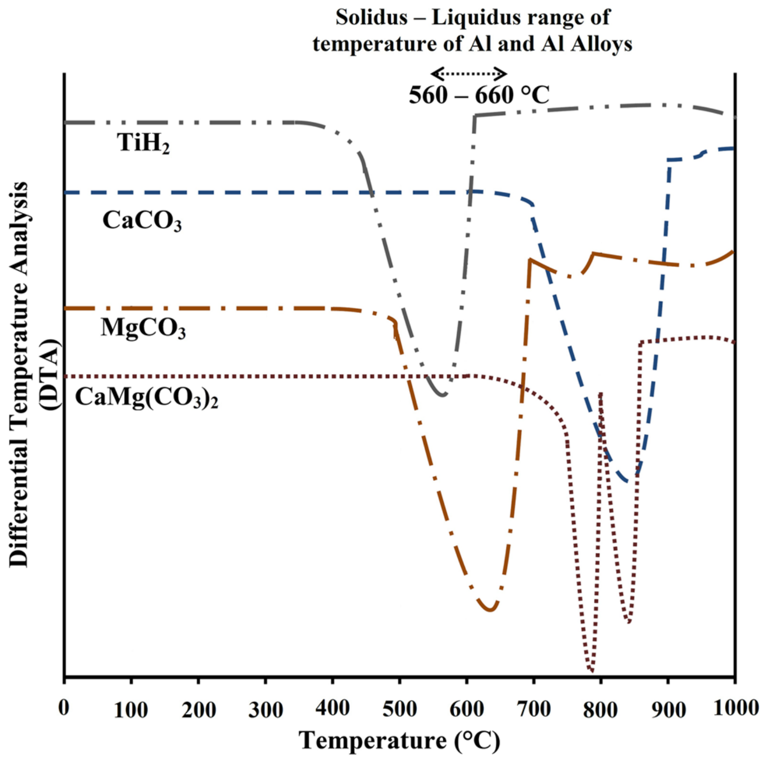

Fig. 1: DTA curves of various foaming agents [10]

Thermogravimetric analysis (TGA) of $CaCO_3$ powder also confirms that its decomposition begins at temperatures around 620 °C and ends at about 850 °C, Figure 2 [11, 12].

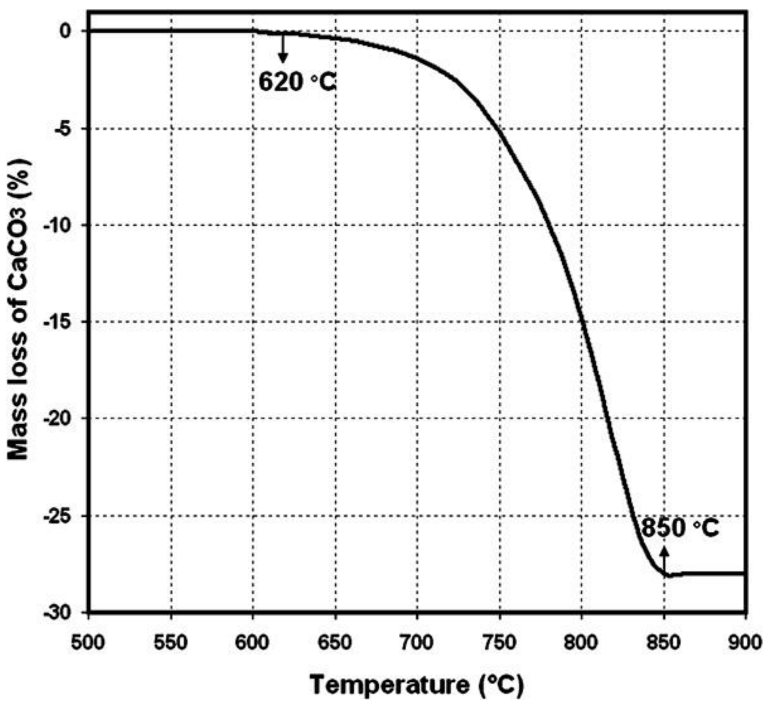

Fig. 2: Thermogravimetric analysis curve of $CaCO_3$ powder [11]

Heating $CaCO_3$ to a temperature above 620 °C decomposes into calcium oxide (CaO) and carbon dioxide (CO_2), according to equation:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad (2)$$

Under normal atmospheric pressure, the decomposition of $CaCO_3$ is thermodynamically favorable only at temperatures above 900 °C, but in real conditions chemical reactions also occur at temperatures below the melting point of Al. In the presence of Al, the chemical reactions that can occur are [12]:

$$2Al(l) + 3CO_2(g) \rightarrow Al_2O_3(s) + 3CO(g) \quad (3)$$

$$8Al(l) + 3CO_2(g) \rightarrow 2Al_2O_3(s) + Al_4C_3(g) \quad (4)$$

$$6Al(l) + 3CO(g) \rightarrow Al_2O_3(s) + Al_4C_3(g) \quad (5)$$

In addition, if Al is alloyed with magnesium (Mg), the following reactions are possible:

$$Mg(l) + CO_2(g) \rightarrow MgO(s) + CO(g) \quad (6)$$

$$2Al(l) + Mg(l) + 4CO_2(g) \rightarrow MgAl_2O_4(s) + 4CO(g) \quad (7)$$

Aluminium oxides, and possibly magnesium, are formed on the inner surfaces of cells and prevent their coarsening and coalescence [12]. Also, if other alloying elements are used, various other compounds may be formed.

As the decomposition temperature of $CaCO_3$ is above the melting point of Al alloys, the metal matrix is already melted during the release of gas, and the viscosity of such a material is not sufficient enough to prevent the escape of gas. To solve this problem, compacted precursors can be preheated before foaming begins. Due to the exposure of the precursor to elevated temperature, the decomposition of $CaCO_3$ begins somewhat earlier and shortens the time to the end of the decomposition [13].

Since TiH_2 releases approximately twice the volume of gas at the same temperature and pressure than $CaCO_3$ [13], it can be concluded that a larger amount of $CaCO_3$ is required to achieve the same degree of foam porosity.

The use of H_2-based foaming agents produces spherical pores, while the use of CO_2-based agents creates more elongated pores [13]. Therefore, the mechanical properties of the foams thus produced differ, and the exploitation requirements should be considered when selecting the type of foaming agent.

When making foams using foaming agents it is necessary to pay attention to the grain size of the agent powder. The larger the $CaCO_3$ powder grains are, the porosity increases but the density, relative density and compressive strength decrease, Figure 3 [14]. It can easily be concluded that higher density leads to higher compressive strength.

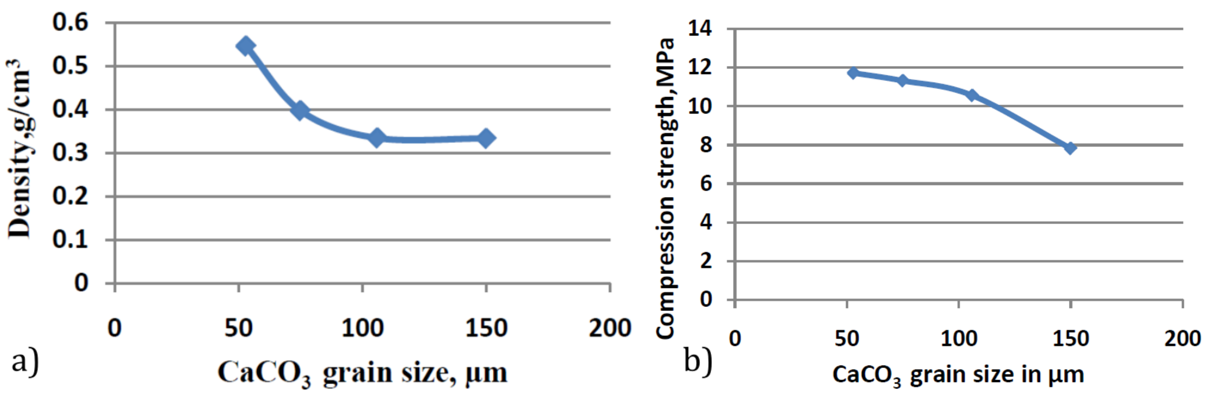

Fig. 3: Influence of $CaCO_3$ grain size on density (a) and compressive strength (b) of Al foams [14]

On the inner surfaces of the foam cell walls foamed with $CaCO_3$, thicker layers of oxides are formed than for the TiH_2 agent, as can be seen from the results of atomic emission spectroscopy (AES), Figure 4 [13]. The reason is that $CaCO_3$ creates a CO_2 atmosphere so that the oxide layer on the surface of the cell wall is easily formed, which improves the stability of the foam. On the other hand, by using TiH_2, a reducing atmosphere is created in the material due to hydrogen and a very thin oxide layer is formed.

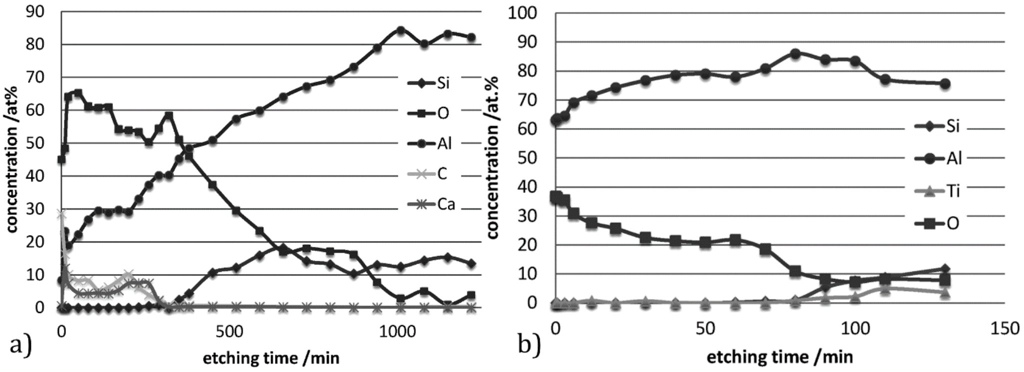

Fig. 4: AES depth profiles of the inner wall surfaces of AlSi12 foam cells foamed with $CaCO_3$ (a) and TiH_2 (b) [13]

Using a melt foaming method, Byakova [15] compared the properties of Al foams with a chemical composition similar to 7075 aluminium alloy using TiH_2 and coated $CaCO_3$ powder as foaming agents. $CaCO_3$ powder was coated with CaF_2 to facilitate its dispersion in the melt. She concluded that the foams in which $CaCO_3$ was used as the foaming agent had a finer cellular structure a lower fraction volume of brittle constituents in the cell walls compared to the foams foamed with TiH_2. Both foams had spherical cells, but those in $CaCO_3$ foams were approximately twice as small ($D \approx 1 - 1.5$ mm) as in TiH_2 foams. In TiH_2 foams, the formation of a brittle intermetallic compound Al_3Ti in the cell walls occured. Due to the finer cellular structure, $CaCO_3$ foams have a more ductile compressive behavior, indicating greater toughness of the cell wall materials in such foams. In the following paper, Byakova et al [16] used both methods, melt foaming and foaming of compacted Al precursor, and here too they came to the same conclusions.

Mirzaei-Solhi et al [17] conducted the melt foaming method using different amounts of $CaCO_3$ foaming agent (0.5 to 2 wt. %) with the addition of Ca (0.5 to 2 wt. %) as a melt viscosity improver. Different stirring speeds, 700, 1400 and 2000 rpm, were used to mix the foaming agents. Although the addition of $CaCO_3$ in larger quantities decreases the density and increases the porosity (Figure 5) due to the greater amount of gas entering the melt, they concluded that the optimal combination of these parameters is 1 wt% $CaCO_3$, 1.5 wt. % Ca and mixing at 1400 rpm / min. With the addition of a larger amount of $CaCO_3$, the structure is no longer uniform due to the formation of larger and more irregular cells. At lower mixing speeds very large cells are formed, while at higher speeds, cracks are induced and propagated in the cell walls.

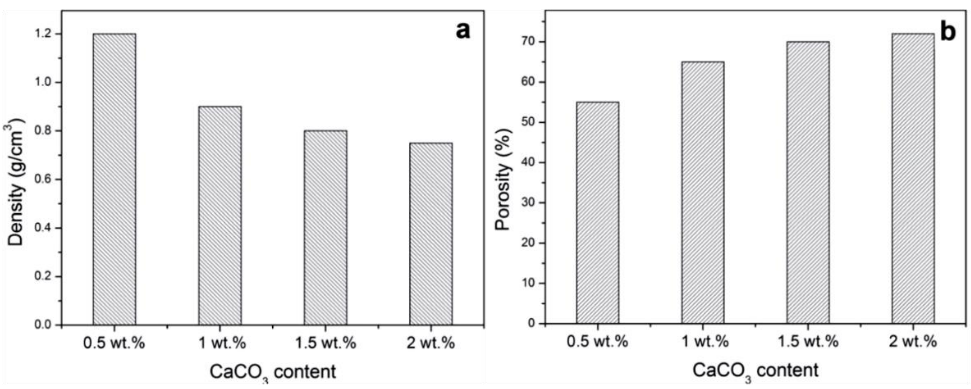

Fig. 5: Influence of $CaCO_3$ content on density (a) and porosity (b) of Al foams [17]

To further increase the viscosity of the melt, which has a positive effect on stabilizing the gas bubbles and creating a more uniform cellular structure, ceramic particles such as aluminium oxide (Al_2O_3) [18-20] and silicon carbide (SiC) [6, 11, 21-23] can be added to the melt or compacted precursor. Figure 6 shows the quasi-static compressive test curves of foams made of 2024Al alloy reinforced with different proportions of SiC particles (0, 5 and 10 wt. %) from which it can be seen that the addition of ceramic particles has a positive effect on the compressive properties. In contrast to the smooth curve in unreinforced foam, in foams reinforced with SiC particles oscillations are visible on the curve, from which it can be concluded that the foam no longer has a plastic behavior, but tends to brittleness. With a larger addition of ceramic particles, the curve is more serrated, i.e. the foam becomes more and more brittle. The reason is that SiC particles alter the mechanism of cell wall deformation. During the compressive loading, particle-reinforced parts of the cell walls cause sudden brittle fractures and the stress also reduces suddenly [6]. Depending on the type and size of the particles, it is necessary to determine their optimal share in the mixture in order to avoid pore coarsening, uneven structure and deterioration of compressive properties.

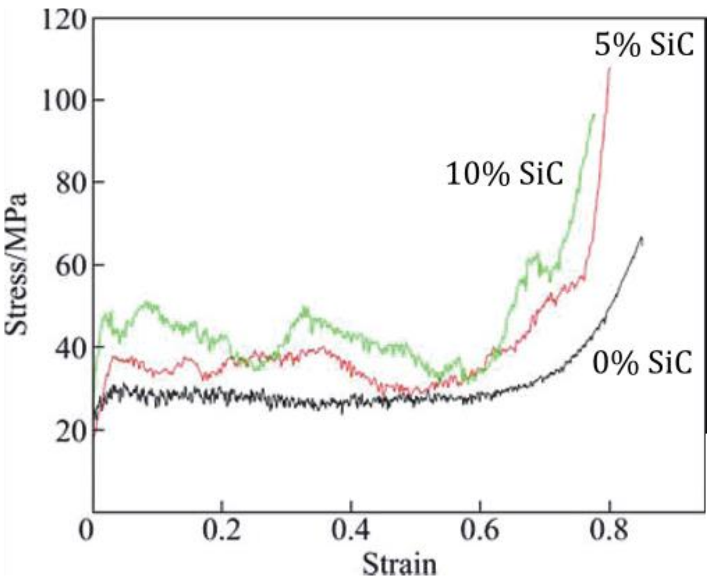

Fig. 6: Quasi-static compressive curves of 2024Al foam with different SiC reinforcement contents [6]

4. CONCLUSION

In the production of Al foams in which foaming agents are used, the most commonly used agent is TiH_2. Today, expensive TiH_2 is successfully being replaced by $CaCO_3$, as indicated by the results of already performed tests. $CaCO_3$ has a higher decomposition temperature compared to TiH_2, it is much cheaper and improves the stability of the foam. Also, when dissolving TiH_2 in an Al melt, intermetallic compounds are formed which negatively affect the properties of the foam. As the amount of released gas when using $CaCO_3$ is less than with TiH_2, it is necessary to use slightly larger amounts of $CaCO_3$ foaming agent to achieve the same degree of porosity.

In the process of production of Al foams, various parameters affect the final obtained properties. Some of these are the grain size of the foaming agent and their proportion, the decomposition temperature and the time needed to complete foaming. Various ceramic particles can be added to the melt itself or to the precursor to increase the viscosity and improve the properties of the foam.

Since the decomposition of $CaCO_3$ into CaO and CO_2 starts at higher temperatures compared to TiH_2, $CaCO_3$ is also more favorable for foaming other metals that have a melting point higher than aluminium.

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