# Carbonate-Foaming Agents in Aluminum Foams: Advantages and Perspectives

ALI SOLOKI and MOHAMMAD ESMAILIAN

Aluminum foams are commonly produced using hydride foaming agents. Carbonates are inexpensive and more convenient to handle than hydrides. In this review article, the replacement of titanium hydride by carbonate foaming agents in aluminum and aluminum alloys was studied. Carbonate-foaming agents including calcium carbonate, magnesium carbonate, and dolomite were investigated for the production of aluminum and aluminum alloys. The thermal decomposition behavior of the foaming agents was evaluated in conjunction with the cell structure of the aluminum foams produced. From the results, magnesium carbonate and dolomite were selected as suitable foaming agents for aluminum alloys because of lower decomposition temperature than calcium carbonate. It was clarified that dolomite resulted in a fine and homogenous cell structures.

DOI: 10.1007/s11663-014-0262-1

## I. INTRODUCTION

LIGHTWEIGHT metallic foams have alluring potential for different sectors of industrial applications due to the unique combination of low density and novel physical and mechanical properties. In particular, the remarkable absorbing ability of aluminum foams offers significant performance gains for crash protection of vehicle and other applications where effective utilization of impact energy is required. Aluminum foams are also nonflammable, ecologically harmless, and easily recyclable. There are many possible applications for aluminum foams ranging from lightweight construction, sound insulation, and heat insulation to energy absorption applications and lightweight ballistic structures.[1–12]

In general, two processes have been invariably used for Al foaming: (1) the liquid metal route where foaming is accomplished by direct foaming of melt with gas or some foaming agents and (2) the powder metallurgy (PM) route where foaming is affected by foaming a sintered compact.[1] Each production method gives its own characteristic range of densities, cell sizes and shapes. The principle of PM is simple and the process consists of three stages: (1) mixing the metallic powder with foaming agent powder, (2) compacting the powder mixture, and (3) sintering at temperatures slightly above the melting point of aluminum. At these temperatures, the blowing or foaming agents are expected to volatilize and the arising gas forms pores in the metal phase. All three steps are important for the quality of the final production and the properties of the aluminum-foam products.[2]

Foaming agents for aluminum foams can be metal hydrides like (titanium hydride) $TiH_2$ or magnesium hydride ($MgH_2$), carbonates, hydrates, or other volatilizing substances. Among these, $TiH_2$ was mainly applied as blowing agent for both the casting and powder metallurgical procedures of foaming of aluminum.[1] However, $TiH_2$ is expensive and cost reduction can be achieved by replacing expensive $TiH_2$ with alternative inexpensive blowing agents, particularly carbonates such as calcium carbonate ($CaCO_3$), magnesium carbonate ($MgCO_3$), and dolomite $(CaMg)(CO_3)_2$.[3]

As detailed and discussed by Gergely *et al.*, carbonates react with molten aluminum and creating the foaming gas ($CO_2$) and various solid particles (such as CaO, $Al_2O_3$, $Al_4C_3$, and $MgAl_2O_4$), depending on the composition of the aluminum alloy.[4] In contrast to $TiH_2$, in which decomposition leads to the formation of chemically inert hydrogen, the $CO_2$-foaming gas obtained by the decomposition of $CaCO_3$ reacts with melt and results in stabilizing the foam suspension.[3] The results of Gergely *et al.*[4] suggested that, as a result of foaming gas ($CO_2$)/melt reaction, a thin solid reaction layer forms in the early stages of the foaming process causes cell stabilizing, due to the surface tension modification and avoiding cell coarsening and coalescence. In addition, the solid particles obtained by thermal decomposition of carbonates enhance the melt viscosity, further promoting the stabilization of the foam.

Table I summarizes the properties of aluminum foams resulting from titanium hydride and carbonate as foaming agents in different experiments.[3,5–9] In the current study, the comparison of foaming ability between carbonate-foaming agents, $CaCO_3$, $MgCO_3$, and $(CaMg)(CO_3)_2$ for aluminum and aluminum alloys foams were investigated.

---

ALI SOLOKI, Researcher, is with the Department of Metallurgy, Islamic Azad University, Saveh Branch, 1513634714 Saveh, Iran. Contact e-mail: sorentec@yahoo.com MOHAMMAD ESMAILIAN, Professor, is with the Iranian Research Organization for Science and Technology, 3353138646 Tehran, Iran

Manuscript submitted February 23, 2014.

**Table I. Properties of Aluminum and Aluminum Alloy Foams Resulting From Different Foaming Agents**[3,5–9]

| Foaming Agent | Content | Particle Size ($\mu$m) | Matrix | Route | Foaming Temperature (°C) Time (min) | Foam Density (g/cm$^3$) | Foam Porosity (pct) | Foaming Efficiency (pct) |
|---|---|---|---|---|---|---|---|---|
| $TiH_2$ | | | | | | | | |
| Ref. [5] | 0.4 mass pct | 26 | AlSiCu | PM | 856 K (583 °C) | 1.20 | — | — |
| Ref. [6] | 1.5 wt pct | 44 | Al | melting | 3 min at 953 K (680 °C) | 0.625 | 70.03 | |
| $MgCO_3$ | | | | | | | | |
| Ref. [5] | 0.8 mass pct | 11 | AlSiCu | PM | 893 K (620 °C) | 1.05 | — | — |
| $CaCO_3$ | | | | | | | | |
| Ref. [7] | 3 wt pct | 38 | Al | PM | 10 min at 1023 K (750 °C) | 0.42 ± 0.02 | — | 84.4 |
| | 3 wt. pct | 120 | Al | melting | | 0.62 ± 0.03 | — | 77.0 |
| Ref. [8] | 5 wt pct | | $AlSi_9Cu_3$ | thixocasting | 1098 K (825 °C) | 1.13 | — | — |
| Ref. [9] | 10 wt pct | 106 to 150 | Al | PM | 1023 K (750 °C) | 0.65 | — | |
| $(MgCa)(CO_2)_3$ | | | | | | | | |
| Ref. [3] | 3 wt pct | 97 | Al + 5 pct SiC | PM | 10 min at 973 K (700 °C) | 0.5 ± 0.03 | — | 81.5 |
| | 3 wt pct | 76 | Al + 5 pct SiC | melting | | 0.57 ± 0.03 | | 78.9 |
| Ref. [5] | 1.2 mass pct | 3.5 | AlSiCu | PM | 973 K (700 °C) | 1.19 | — | — |
| Ref. [8] | 3 wt pct | | $AlSi_9Cu_3$ | thixocasting | 1098 K (825 °C) | 0.73 | — | — |
| Ref. [6] | 1.5 wt pct | — | Al | melting | 13 min at 923 K (650 °C) | 0.467 | 82.7 | — |

## II. DECOMPOSITION OF VARIOUS FOAMING AGENTS

According to Table II, the decomposition temperature of $TiH_2$ is very low—starting at about 673 K (400 °C) for the untreated hydride—and the solidus–liquidus range of temperature of Al and Al alloys is approximately 833 K to 933 K (560 °C to 660 °C). It is obvious that untreated $TiH_2$ does not match well the melting range of any of the Al alloys applied for foaming. Thermal decomposition of carbonate foaming agents is about 873 K to 1173 K (600 °C to 900 °C) (Figure 1). Because of that, higher foaming temperatures are necessary than with $TiH_2$, particularly when higher foaming efficiency on final foams is required. On the other hand, a higher onset temperature of $CO_2$ evolution from $CaCO_3$, $MgCO_3$ and $(CaMg)(CO_3)_2$ powders enables the incorporation of blowing agent particles into aluminum melt without the need of any special pretreatment to prevent premature gas release. However, thermal decomposition (chemical conversion) of less than 30 pct of the available carbonates in precursor might be sufficient for the production of high porosity (~95 pct) material. Such a partial conversion could be easily achieved by holding the foaming precursors for a short period of time (5 to 10 minutes) to a temperature between 923 K and 1023 K (650 °C and 750 °C).[7]

According to Figure 1, the differential thermal curve of $CaCO_3$ shows an intense broad endothermic reaction starting at about 898 K (625 °C) and ending about 1163 K (890 °C) with a peak at 1113 K (840 °C). The thermal curve for $MgCO_3$ shows a broad, vigorous endothermic reaction that starts about 673 K (400 °C), ends at 963 K (690 °C), and has a peak at 923 K (650 °C). There is also a much smaller endothermic reaction of a much different character immediately following the first. Two endothermic reactions are shown in the $CaMg(CO_3)_2$ curve, both of which are sharper than either $CaCO_3$ or $MgCO_3$. The first starts about 873 K (600 °C) and has a peak at 1053 K (780 °C) and the second has a peak at 1103 K (830 °C) and ends about 1173 K (900 °C).[10]

## III. FOAMING ABILITY COMPARISON BETWEEN $CaCO_3$ AND $(CaMg)(CO_3)_2$ AS FOAMING AGENTS

Haesche *et al.*[8] investigated the influence of $CaCO_3$ and $(CaMg)(CO_3)_2$ as a blowing agent on the foaming capability and cellular structure for $AlMg_{4.5}Mn$ and $AlSi_9Cu_3$ by the thixocasting process. Furthermore, for several specimens 3 wt pct CaO was added for foam stabilization. Three temperatures, 1023 K, 1073 K, and 1098 K (750 °C, 800 °C, and 825 °C), were used as foaming temperatures.

In this study, the results of the expandometer tests for the alloy $AlSi_9Cu_3$ showed that dolomite as a foaming agent leads to a significant increase in expansion when compared with the lime-based variant. Improvements in expansion achieved by using dolomite instead of lime were explicable considering the differences in decomposition of both substances as well as the known stabilization effect of MgO. Energy dispersive X-ray spectroscopy (EDX), is an X-ray technique used to identify the elemental composition or chemical characterization of materials. The assumption that the resulting MgO can act as additional stabilizer was supported by the observation that Mg can be identified by EDX analyses in increased quantities on inner pore surfaces. The best expansion behavior was observed for compositions containing 5 wt pct $(CaMg)(CO_3)_2$ with 3 wt pct CaO. The reason for insufficient expansion in lime would be a lack of blowing gas. Also, the maximum expansions for the alloy $AlSi_9Cu_3$ were clearly higher than those for the alloy

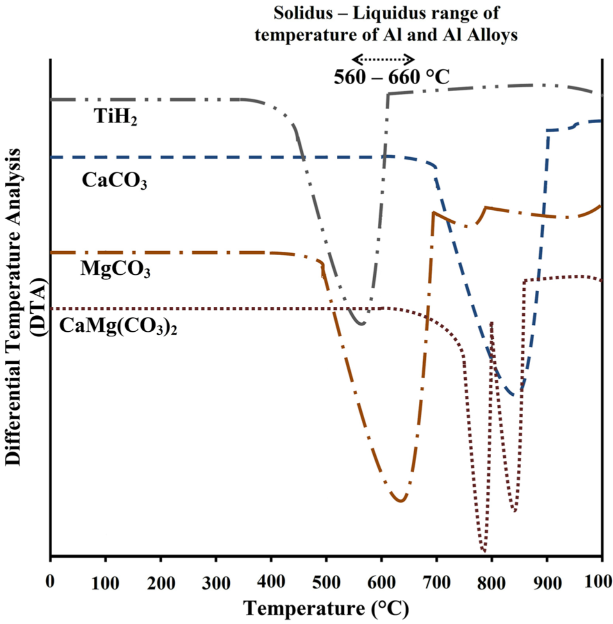


Fig. 1—Differential temperature analysis (DTA) curves of various foaming agents, the solidus–liquidus range of temperature of Al and Al alloys is 833 K to 933 K (560 °C to 660 °C).

**Table II. Decomposition of Foaming Agents [Approximate Solidus–Liquidus Range of Temperature of Al and Al Alloys is 833 K to 933 K (560 °C to 660 °C)]**

| Foaming Agent | Gas | Chemical Reaction | Range of Decomposition Temperature [K (°C)] |
|---|---|---|---|
| $TiH_2$ | $H_2$ | $TiH_2 = Ti + H_2$ | ~673 to 873 (~400 to 600) |
| $MgCO_3$ | $CO_2$ | $MgCO_3 = MgO + CO_2$ | ~773 to 973 (~500 to 700) |
| $CaMg(CO_3)_2$ | $CO_2$ | $CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2$<br>$CaCO_3 = CaO + CO_2$ | ~973 to 1123 (~700 to 850) |
| $CaCO_3$ | $CO_2$ | $CaCO_3 = CaO + CO_2$ | ~ 973 to 1173 (~700 to 900) |

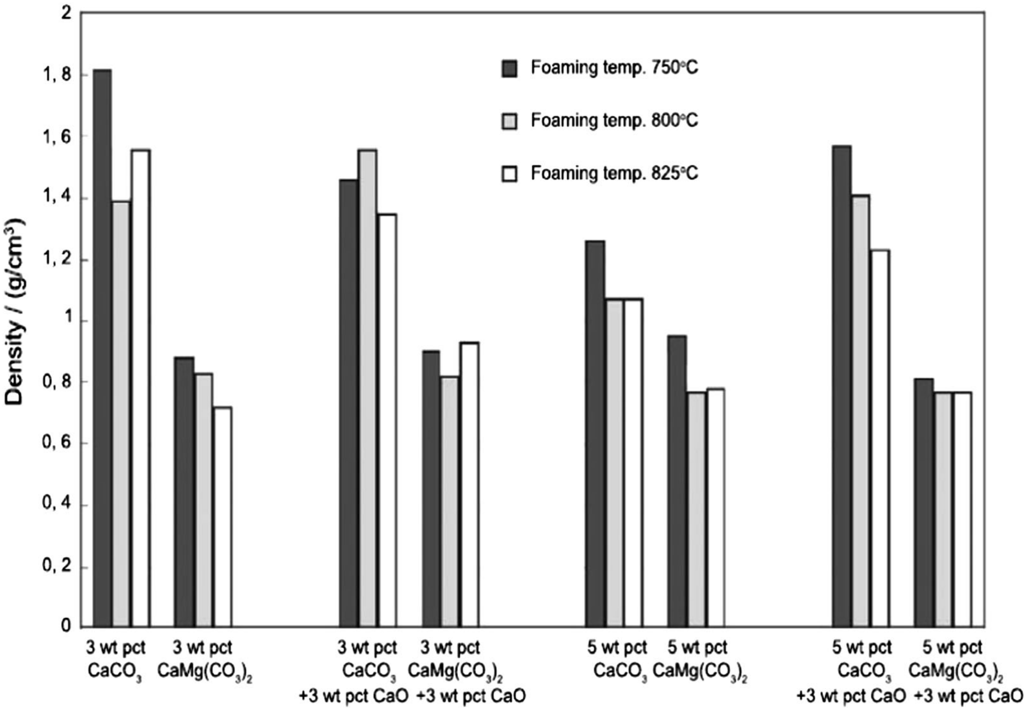
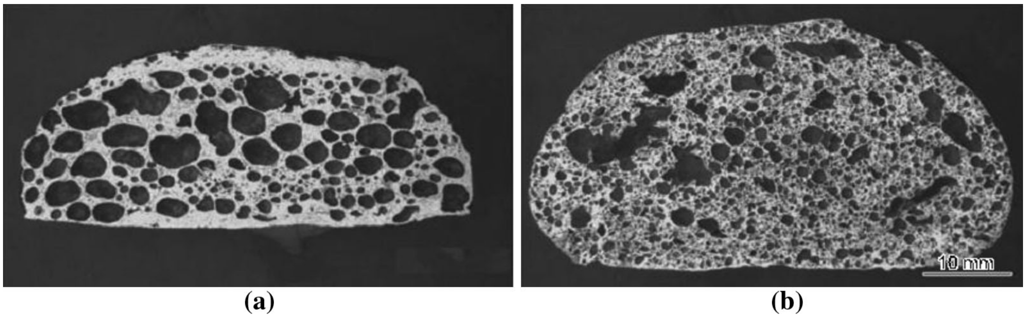


Fig. 2—Densities of free-foaming samples [for Al foams with various amounts of (CaMg)$(CO_3)_2$ and $CaCO_3$. Three specimens. at 1023 K (750 °C), one at 1073 K (800 °C) and 1098 K (825 °C) each].



(a) (b)

Fig. 3—Pore structure of foams with 5 wt pct $CaCO_3$ + 3 wt pct CaO (*a*) and 5 wt pct $CaMg(CO_3)_2$ + 3 wt pct CaO (*b*), matrix $AlSi_9Cu_3$ alloy, foaming temperature 1098 K (825 °C) in both cases[8].

AlMg4.5Mn for all combinations of foaming agents and additives.

The influence of the foaming temperature on density for Al foams containing (CaMg)$(CO_3)_2$ and $CaCO_3$ foaming agents is presented in Figure 2. In any case, increasing the foaming temperature resulted in increasing expansion by up to 22 pct. This level of improvement was reached for the combination of 5 wt pct $CaCO_3$ and 3 wt pct CaO was much lower than (CaMg)$(CO_3)_2$. Because dolomite starts to decompose and develop significant amounts of blowing gas at lower temperatures than lime, the effect of foaming temperature was slightly larger for dolomite.

According to Figure 3, the pore structures were nearly irregular for both dolomite and calcite blowing agents but were dominated by a large number of small pores for dolomite as opposed to lime. This can be explained qualitatively as a result of an increased melt viscosity during foam formation, with the occasional occurrence of individual large pores stemming from the collapse of cell walls as common, negative side effect of this special melt constitution. Furthermore, drainage is practically not visible due to the additional stabilization.

In general, because of deviations in decomposition start temperature and course of reaction of the blowing agents $CaCO_3$ and $CaMg(CO_3)_2$, MgO based stabilization mechanisms, and differences in the amounts of blowing gas released, dolomite as foaming agent had better operation over lime.

However, Kevorkijan *et al.*[3] in two discrete studies investigated the influence of $CaCO_3$ and $(CaMg)(CO_3)_2$ as blowing agents on Al foam properties. In the first study, aluminum foam with $CaCO_3$ as a foaming agent was prepared by two melting and PM routes. In this article, the amount of $CaCO_3$ with three average particle sizes 38 (type A), 72 (B), and 120 (C) $\mu$m, was 3, 5, 7, and 10 wt pct.[6] In other research, aluminum foam with $(CaMg)(CO_3)_2$ as a foaming agent and 5 pct of SiC particles was prepared by two melting and PM routes, and the amount of $(CaMg)(CO_3)_2$ with three average particle sizes 44 (type A), 76 (B), and 97 (C) $\mu$m, was 3, 5, 7, and 10 wt pct. In both studies, under isostatic pressing with an applied pressure (~700 MPa), the precursors prepared by PM possessed closed porosity and densities above 98 pct that of theoretical calculations, whereas as-machined precursors obtained by the melt route had a significant fraction of open porosity and thus were not suitable for foaming to the desired foam densities. However, after additional isostatic pressing, the porosity in these precursors was successfully reduced. Very high precursor densities (>99 pct of theoretical) were achieved only in precursors prepared by the PM route with 3 pct to 7 pct of $CaCO_3$ and $(CaMg)(CO_3)_2$ particles of Type A. With higher particle content and by use of coarser $CaCO_3$ powders of Type B or Type C, this could not be achieved, resulting in a lower foaming efficiency.

General porosity measured in foamable precursors and the apparent densities achieved in aluminum foam samples are inversely proportional. Foamable precursors with lower porosity resulted in foam samples with higher apparent density and lower foaming efficiency. The best results for both blowing agents in these researches are listed in Table III.

According to Table III for both foaming agents, the PM route showed better results than the melting route. Although there was a slight difference between the results of both foaming agents, $CaCO_3$ showed better results than $(CaMg)(CO_3)_2$. These results were inconsistent with research conducted by Haesche *et al.*[8] and shown in Figure 2. According to Figure 2, at all temperatures and amounts of foaming agents, the difference between their results was remarkable. This inconsistency may be due to two reasons. First, in Haesche *et al.*[8] research, all preparations of foam conditions for both blowing agents were identical. Second, in Haesche *et al.*[8] research, the foam matrix was $AlSi_9Cu_3$ and the method of production was the thixocasting process. But in two studies conducted by Kevorkijan *et al.*, the foam matrix was Al and method of production was the PM route.

## IV. FOAMING ABILITY COMPARISON BETWEEN $MgCO_3$ AND $(CaMg)(CO_3)_2$ AS FOAMING AGENTS

Koizumi *et al.*[5] investigated $MgCO_3$ and $(CaMg)(CO_3)_2$ as foaming agents for the production of Al-Si-Cu alloy foams by the PM route. In this study, the average particle size of $MgCO_3$ and $(CaMg)(CO_3)_2$ was 11 and 3.5 $\mu$m, respectively. The melting temperature range of AlSiCu alloy was 793 K to 853 K (520 °C to 580 °C); therefore, it was necessary for the foaming agent to decompose between 793 K and 853 K (520 °C and 580 °C) when using AlSiCu as the matrix. $MgCO_3$ decomposed from 793 K to 993 K (520 °C to 720 °C), and for $(CaMg)(CO_3)_2$, the decomposition stages were 1013 K to 1123 K (740 °C to 850 °C), respectively. The amount of $MgCO_3$ and $(CaMg)(CO_3)_2$ was 0.8 and 1.2 mass pct, respectively.

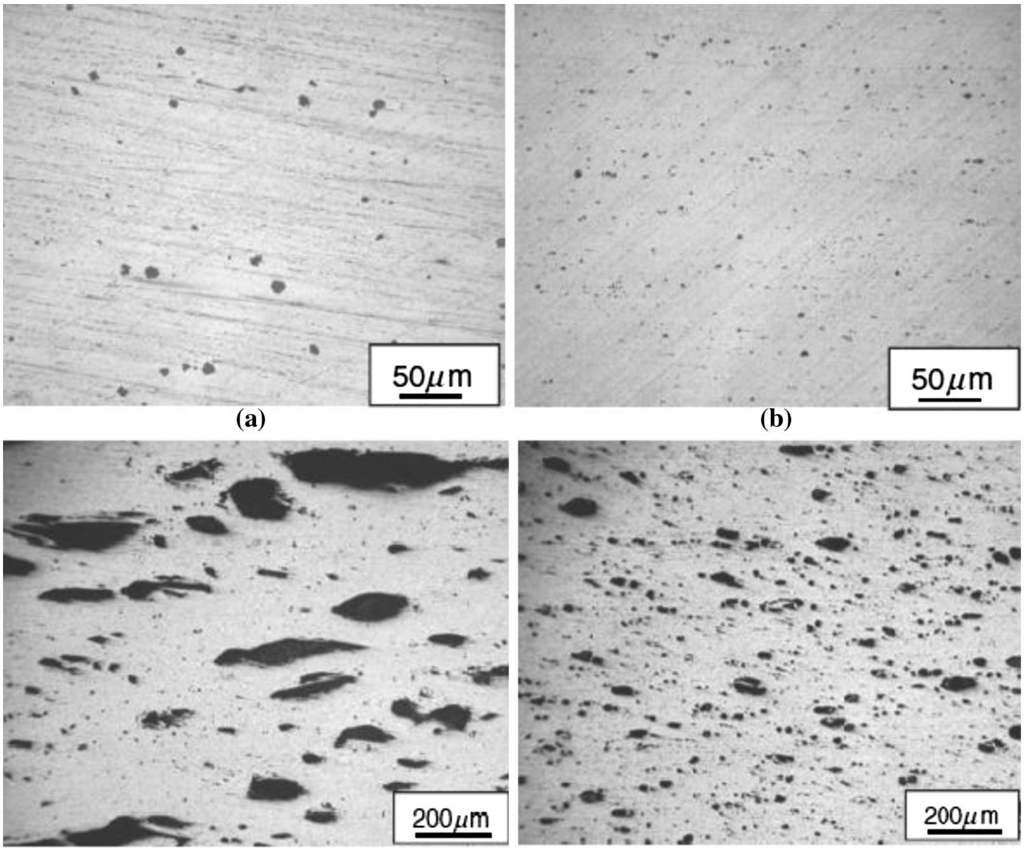
The distribution of the foaming agent in the precursor affects the foam cell structure; therefore, it is important for industrial fabrication. Both $MgCO_3$ and $CaMg(CO_3)_2$ were homogeneously dispersed in the precursor. $MgCO_3$ and $(CaMg)(CO_3)_2$ showed a homogenous cell structure, but the homogeneity of $(CaMg)(CO_3)_2$ was better. $MgCO_3$ expanded to a specific gravity of <1.2 at a lower temperature (620 °C) than $(CaMg)(CO_3)_2$ [973 K (700 °C)]. However, the cell structure of $MgCO_3$ was coarser than that of $(CaMg)(CO_3)_2$ (Figure 4). A smaller radius oxidizing gas was released from $CaMg(CO_3)_2$ (3.3 $\mu$m) than that released from $MgCO_3$ (15.3 $\mu$m), causing the fine and spherical cell structure observed for the $(CaMg)(CO_3)_2$ foam.

## V. FOAMING ABILITY COMPARISON BETWEEN $MgCO_3$ AND $CaCO_3$ AS FOAMING AGENTS

According to Figure 1, the decomposition temperature range of $MgCO_3$ is approximately 773 K to 973 K (500 °C to 700 °C), whereas for $CaCO_3$ this temperature range is approximately 973 K to 1173 K (700 °C to 900 °C). Hence, a higher foaming temperature is required for $CaCo_3$ compared with $MgCO_3$. Using high temperatures are costly and foam stabilization is more demanding as well. However, The results of comparing Figures 3(a) and 4(c) show that $CaCO_3$ as foaming agent results in enhanced foam structure homogeneity and cell size uniformity than $MgCO_3$. On the other hand, the cell morphology in aluminum foams contacting $CaCO_3$ is round and the cell sizes are more uniform.

**Table III. Density, Foaming Efficiency and the Average Pore Size of Aluminum Foams Prepared by PM and Melting Routes[3,7]**

| Rout | Foaming Agent | Weight Percent | Particle Size ($\mu$m) | Density (g/cm$^3$) | Foaming Efficiency (pct) | Average Pore Size (mm) |
|---|---|---|---|---|---|---|
| PM | $CaCO_3$ | 3 | 38 | 0.42 ± 0.02 | 84.4 | 0.8 ± 0.08 |
| | $(CaMg)(CO_3)_2$ | 3 | 97 | 0.50 ± 0.03 | 81.5 | 0.6 ± 0.06 |
| Melting | $CaCO_3$ | 3 | 120 | 0.62 ± 0.03 | 77.0 | 0.9 ± 0.09 |
| | $CaMg(CO_3)_2$ | 3 | 76 | 0.61 ± 0.03 | 77.4 | 0.8 ± 0.08 |



(a) (b) (c) (d)

Fig. 4—Dispersion of foaming agent in precursor: (*a*) $MgCO_3$ and (*b*) $(CaMg)(CO_3)_2$. Microstructures of foams: (*c*) $MgCO_3$ and (*d*) $CaMg(CO_3)_2$.

## VI. CONCLUSIONS

A comparison of foaming ability between $CaCO_3$, $(CaMg)(CO_3)_2$ and $MgCO_3$ as foaming agents was conducted. $MgCO_3$ and $CaMg(CO3)_2$ were selected as suitable foaming agents for aluminum alloys because of lower decomposition temperature than $CaCO_3$. Dolomite $[CaMg(CO3)_2]$ had some advantages as foaming agent in aluminum foams, which are summarized as follows:

1. $CaCO_3$ has a higher thermal decomposition temperature than other foaming agents, significantly above the melting point of pure aluminum and aluminum alloys. A high foaming temperature makes the stabilization of aluminum foams more demanding and costly.
2. The presence of both MgO and CaO in $(CaMg)(CO_3)_2$ results in an improvement in the stabilization of the cell structure of foam.
3. Adequate blowing gas resulting from $(CaMg)(CO_3)_2$, causes an improvement in the expansion behavior of foam.
4. The small radius of oxidizing gas released from $CaMg(CO_3)_2$ causes the fine and spherical cell structure of foam.
5. The low cost of $CaMg(CO_3)_2$ results in cost-effective foaming agent preparation.

## REFERENCES

1. V.C. Srivastava and K.L. Sahoo: *Mater. Sci. Pol.*, 2007, vol. 25, pp. 733–53.
2. I. Paulin, B. Sustarsic, V. Kevorkijan, S.D. Skapin, and M. Jenko: *Mater. Technol.*, 2011, vol. 45, pp. 13–19.
3. V. Kevorkijan, S.D. Skapin, I. Paulin, B. Sustarsic, and M. Jenko: *Mater. Technol.*, 2010, vol. 44, pp. 363–71.
4. V. Gergely, D.C. Curra, and T.W. Clyne: *Compos. Sci. Technol.*, 2003, vol. 63, pp. 2301–10.
5. T. Koizumi, K. Kido, K. Kita, and K. Mikado: *Mater. Trans.*, 2011, vol. 52, pp. 728–33.
6. D.P. Papadopoulos, H. Omar, F. Stergioudi, S.A. Tsipas, and N. Michailidis: *Colloids Surf. A Physicochem. Eng. Asp.*, 2011, vol. 382, pp. 118–23.
7. V. Kevokijan: *MJoM*, 2010, vol. 16, pp. 205–19.
8. M. Haesche, D. Lehmus, J. Weise, M. Wichmann, I. Cristina, and M. Mocelline: *J. Mater. Sci. Technol.*, 2010, vol. 26, pp. 845–50.
9. L.E.G. Cambronero, J.M. Ruiz Roman, F.A. Corpas, and J.M. Ruiz Prieto: *J. Mater. Proc. Technol.*, 2009, vol. 209, pp. 1803–09.
10. F.L. Cuthbert and R.A. Rowland: *Am. Mineral.*, 1947, vol. 32, pp. 111–16.
11. A.V. Byakova, S.V. Gnyloskurenko, A.I. Sirko, Y.V. Milman, and T. Nakamura: *Mater. Trans.*, 2006, vol. 47, pp. 2131–36.
12. C. Umashankar, K. Jha, and K.N. Mahule: *BARC Newsl.*, 2011, vol. 322, pp. 39–43.