Foaming Agents for Powder Metallurgy Production of Aluminum Foam

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Metallic foams are commonly produced using hydride foaming agents. Carbonates are safer to handle than hydrides; however, their use in the powder metallurgy (PM) route to obtaining a fine and homogenous cell structure has not been evaluated. In this study, carbonates and hydroxides were investigated as foaming agents for the production of Al-Si-Cu alloy foams by the PM route. The thermal decomposition behavior of the foaming agents was evaluated in conjunction with the cell structure of the aluminum foams produced. From the results, it was clarified that a foaming agent that began decomposing after the matrix melted is required to obtain a fine and homogenous cell structure. The TiH₂ foam formed under similar conditions was obviously different and had a coarse and rounded cell structure. MgCO₃ and CaMg(CO₃)₂ were selected as suitable foaming agents for the Al-Si-Cu alloy. Once expanded, the CaMg(CO₃)₂ foam had a specific gravity of 1.19 and a homogeneous, fine and spherical cell structure. [doi:10.2320/matertrans.M2010401]

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1. Introduction

Metallic foams have unique properties, such as low density, good energy absorbing capability and low thermal conductivity. Recent research has focused on these foams, and many processes have been proposed for their manufacture. Among these processes, the use of titanium hydride (TiH₂) as a foaming agent is popular in melt processing and powder metallurgy (PM). Alporas foams are produced by a typical melt processing route,¹⁾ in which foams are melted with calcium as a viscosity-enhancing additive and a TiH₂ foaming agent. The Fraunhofer method is a typical PM route²⁾ that involves the hot extrusion of an aluminum matrix powder and a TiH₂ precursor, which is then heated in a closed die to foam for near-net shaping. Compared with the Alporas method, the Fraunhofer method is more expensive and provides a better control of the cell structure and near-net shaping.

TiH₂ is a popular foaming agent because of its decomposition temperature, which is close to the melting temperature of aluminum alloys. However, TiH₂ is expensive and dangerous to handle. Therefore, a cheaper and safer foaming agent is required. Calcium carbonate (CaCO₃), which is a cheap and very stable alternative to TiH₂, has been used as the foaming agent in the melt processing route.³⁾ The use of calcium carbonate in the PM route has not been thoroughly investigated.

In the PM route, the precursor is heated in a metal die. Low temperatures are preferred for this route because of the thermal resistivity of the die material and to reduce the energy requirements of the process. The aluminum alloy Al-Si-Cu has a lower melting temperature than other alloys because the Al-Si and Al-Si-Cu mixtures are eutectic.

In the present study, carbonate and hydroxide were investigated as foaming agents for the Al-Si-Cu alloy by the PM route.

Table 1 Foaming agents.

Foaming agent		Average particle size, d/μm	Gas	Chemical reaction
Titanium hydride	TiH ₂	26	H ₂	TiH ₂ = Ti + H ₂
Magnesium hydroxide	Mg(OH) ₂	7.4	H ₂ O	Mg(OH) ₂ = MgO + H ₂ O
Magnesium carbonate hydroxide	4MgCO ₃ · Mg(OH) ₂ · 5H ₂ O	11	H ₂ O	4MgCO ₃ · Mg(OH) ₂ · 5H ₂ O = 4MgCO ₃ + MgO + 6H ₂ O
			CO ₂	4MgCO ₃ = 4MgO + 4CO ₂
Magnesium carbonate	MgCO ₃	11	CO ₂	MgCO ₃ = MgO + CO ₂
Dolomite	CaMg(CO ₃) ₂	—	CO ₂	CaMg(CO ₃) ₂ = CaCO ₃ + MgO + CO ₂
			CO ₂	CaCO ₃ = CaO + CO ₂
Calcium carbonate	CaCO ₃	13.5	CO ₂	CaCO ₃ = CaO + CO ₂

2. Experimental

Air-atomized AlSiCu powder containing mass fractions of Si(10.8%) and Cu(2.4%), was used to make the precursor. The powder was sieved through a 150 μm mesh before use.

TiH₂, magnesium hydroxide (Mg(OH)₂), magnesium carbonate hydroxide (4MgCO₃ · Mg(OH)₂ · 5H₂O), magnesium carbonate (MgCO₃), dolomite (CaMg(CO₃)₂), and calcium carbonate (CaCO₃) were investigated as foaming agents. Their particle sizes and chemical reactions are given in Table 1. In their reactions, TiH₂ releases hydrogen (H₂), Mg(OH)₂ releases water vapor (H₂O), and 4MgCO₃ · Mg(OH)₂ · 5H₂O releases H₂O and carbon dioxide (CO₂), while MgCO₃, CaMg(CO₃)₂ and CaCO₃ release CO₂.

CaMg(CO₃)₂ is a mineral made of CaCO₃ and MgCO₃, and its composition and purity depend on the area of the mine

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Table 2 Dolomites.

Supplier	Size	Composition (catalog)	Composition (measured, mass%)
Murakashi Lime Industry	3.5 μm (average)	Ca > 20%, Mg > 10%	CaO:70.8, MgO:28.1
Yoshizawa Lime Industry	Coarse	—	CaO:73.7, MgO:23.3
JFE Mineral	<2.36 mm	CaO = 34.5%, MgO = 18.3%	CaO:73.8, MgO:25.0

it was obtained from. The $\text{CaMg}(\text{CO}_3)_2$ samples used in this study were obtained from Murakashi Lime Industry Co., Ltd. (ML), Yoshizawa Lime Industry Co., Ltd. (YL) and JFE Mineral Co., Ltd. (JFE). The data for these samples are shown in Table 2.

The thermogravimetric analysis and differential thermal analysis (TG-DTA) systems obtained from Seiko Instruments Inc. were used to examine the melting of AlSiCu and the thermal decomposition of foaming agents in argon flow. The samples were heated in alumina pans with a heating rate of 10 K/min.

Precursors were formed by hot extrusion at 623 K using a mixture of the AlSiCu powder and foaming agent. The extrusion ratio was 18, and the cross section of each precursor was 5 mm high $\times$ 15 mm wide. The precursors were cut to 30 mm lengths measured with a Type K thermocouple, and they were heated to specific temperatures in a furnace. The formed aluminum foams were cooled in air when expansion started at 843 K. The specific gravity of each foam was measured using the Archimedes principle, and the cell structure of the foams was observed by optical microscopy.

3. Results and Discussion

3.1 Decomposition of foaming agent

The TG-DTA of AlSiCu (Fig. 1) showed that it started melting at 793 K, and melting was complete at 853 K. Consequently, it is necessary for the foaming agent to decompose between 793 and 853 K when using AlSiCu as the matrix. The liquidus temperature of AlSiCu was 80 K lower than that of pure aluminum.

The TG-DTA curves of TiH_2 , $\text{Mg}(\text{OH})_2$, and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ are shown in Fig. 2, and those of MgCO_3 and CaCO_3 are shown in Fig. 3. Starting at 703 K, the mass of TiH_2 decreased with the release of H_2 , and this release was complete at 933 K. The decomposition temperature of TiH_2 is within the melting temperature range of AlSiCu , which indicates that TiH_2 is a suitable foaming agent of AlSiCu . In contrast, neither $\text{Mg}(\text{OH})_2$ nor $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ is an appropriate foaming agent of AlSiCu . Most $\text{Mg}(\text{OH})_2$ decomposes between 633 and 753 K while releasing H_2O , which occurs before AlSiCu begins melting. During the decomposition of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, H_2O is released from ambient temperature to 613 K, and then CO_2 is released by the decomposition of MgCO_3 from 613 to 833 K. Before AlSiCu begins to melt, H_2O and most of the CO_2 are released. MgCO_3 decomposes from 793 to 993 K, which is close to the melting temperature range of AlSiCu . Therefore,

Fig. 1 DTA and TG curves of Al-10.8Si-2.4Cu (mass%).

Fig. 2 DTA and TG curves of foaming agents: (a) TiH_2 , (b) $\text{Mg}(\text{OH})_2$, and (c) $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. Fig. 3 DTA and TG curves of foaming agents: (a) MgCO_3 and (b) CaCO_3 .

MgCO_3 is a suitable foaming agent of AlSiCu . However, CaCO_3 decomposes over 993 K, which indicates that it is not an appropriate foaming agent.

3.2 Decomposition of $\text{CaMg}(\text{CO}_3)_2$

In the SEM images of the $\text{CaMg}(\text{CO}_3)_2$ samples (Fig. 4), the ML- $\text{CaMg}(\text{CO}_3)_2$ sample showed a homogenous particle distribution. However, the YL- and JFE- $\text{CaMg}(\text{CO}_3)_2$ samples showed a heterogeneous particle distribution with coarse particles >0.5 mm in diameter.

In the TG-DTA curves of the $\text{CaMg}(\text{CO}_3)_2$ samples (Fig. 5), two stages of decomposition were observed for YL- $\text{CaMg}(\text{CO}_3)_2$. The first stage began at 713 K and the second stage at 1013 K. The YL- $\text{CaMg}(\text{CO}_3)_2$ sample was slightly

Fig. 4 SEM images of dolomite: (a) Murakashi Lime Industry, (b) Yoshizawa Lime Industry, and (c) JFE Mineral.

wet, and we can assume that the first decomposition stage was the release of H_2O or the decomposition of MgCO_3 . For ML- and JFE- $\text{CaMg}(\text{CO}_3)_2$, the first and second stages began at 773 K and 1013 K, respectively. The two stages of decomposition for $\text{CaMg}(\text{CO}_3)_2$ are shown in Table 1. It has been reported that the number of decomposition stages changes with the type of atmosphere.⁴⁾ For example, in argon, the decomposition could occur in a single continuous stage.

Fig. 5 DTA and TG curves of dolomite: (a) Murakashi Lime Industry, (b) Yoshizawa Lime Industry, and (c) JFE Mineral.

ML- $\text{CaMg}(\text{CO}_3)_2$ was selected because its particles were fine and homogenous, and its decomposition temperature was close to the melting temperature of AlSiCu .

3.3 Evaluation of foaming ability

Precursors were formed with four foaming agents. These were MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$, which were selected because of their suitability for AlSiCu , and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ and TiH_2 , which were selected for comparison.

The distribution of the foaming agent in the precursor is expected to affect the foam cell structure; therefore, it is important for industrial fabrication. Figure 6 shows the SEM images of the foaming agents, and Fig. 7 shows the cross-sectional views of the precursors. The TiH_2 and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ particles were coarse and agglomerated, while the MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$ particles were fine and dispersed. TiH_2 and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ were heterogeneously dispersed in the precursor, while MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$ were homogeneously dispersed.

Figure 8 shows the aluminum foams produced with the four different precursors. After the cooling of the aluminum foams, their specific gravities were measured to range from

Fig. 6 SEM images of foaming agents: (a) TiH_2 , (b) $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, (c) MgCO_3 , and (d) $\text{CaMg}(\text{CO}_3)_2$.

Fig. 7 Dispersion of foaming agent in precursor: (a) TiH_2 , (b) $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, (c) MgCO_3 , and (d) $\text{CaMg}(\text{CO}_3)_2$.

10mm	Cooling temperature	
	843K	$\rho: 1.0 \sim 1.2$
TiH_2 0.4mass%	$\rho: 1.73$	856K, $\rho: 1.20$
$4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ 0.8mass%	$\rho: 1.63$	863K, $\rho: 1.10$
MgCO_3 0.8mass%	$\rho: 1.89$	893K, $\rho: 1.05$
$\text{CaMg}(\text{CO}_3)_2$ 1.2mass%	$\rho: 2.39$	973K, $\rho: 1.19$

Fig. 8 Effect of foaming agent on cell structure.

1.0 to 1.2. The TiH_2 foam had a fine cell structure at 843 K when expansion began, and its cell structure became coarse and rounded at 856 K. The $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ foam expanded to have a specific gravity of <1.2 at 863 K, but its cell structure was broken along the extrusion direction. Both MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$ showed a homogenous cell structure, but the homogeneity of $\text{CaMg}(\text{CO}_3)_2$ was better. MgCO_3 expanded to a specific gravity of <1.2 at a lower temperature than $\text{CaMg}(\text{CO}_3)_2$. However, the cell structure of MgCO_3 was coarser than that of $\text{CaMg}(\text{CO}_3)_2$.

3.4 Effect of foaming agent on cell structure

The different cell structures obtained from the foaming agents (Fig. 8) are determined by various factors, such as the type of gas released and the decomposition temperature. Figure 9 shows the magnified images of the cell structures after the samples were cooled once expansion began at 843 K. At this temperature, the TiH_2 and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ foams had broken cell structures, the MgCO_3 foam appeared flat, and the $\text{CaMg}(\text{CO}_3)_2$ foam had a spherical cell structure.

Fig. 9 Microstructures of various foams: (a) TiH_2 , (b) $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$, (c) MgCO_3 , and (d) $\text{CaMg(CO}_3)_2$.

Fig. 10 Melting rates of AlSiCu and gas decomposition rates of various agents: (a) $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$, (b) Mg(OH)_2 , (c) TiH_2 . Melting rates of (d) AlSiCu , (e) MgCO_3 , (f) $\text{CaMg(CO}_3)_2$, and (g) CaCO_3 .

Figure 10 shows the melting rate of AlSiCu ⁵⁾ and the decomposition rate of the foaming agent. The decomposition rate was calculated from the mass reduction observed by TG-DTA. The decomposition of both TiH_2 and $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$ began at a low temperature. These foaming agents have released over half of their decomposition gas before AlSiCu begins to melt. The released gas breaks the extruded aluminum powder boundary because the solid phase has a higher strength than the solid-liquid phase, and broken cells combine and grow in the extrusion direction. At a high temperature, the TiH_2 foam forms a coarse and rounded cell structure because the cell structures expanded by H_2 are easily combined and deformed to reduce the surface energy of the cell wall.

Table 3 Gas volume and radius at 843 K.

Foaming agent	Average particle size, $d/\mu\text{m}$	Gas mol per 1 mol	Decomposition rate at 843 K	Gas volume at 843 K, v/m^3	Gas radius at 843 K, $r/\mu\text{m}$
TiH_2	26	1	0.82	4.2×10^{-12}	100.2
$4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$	11	10	1	2.3×10^{-13}	38.1
MgCO_3	11	1	0.083	1.5×10^{-14}	15.3
$\text{CaMg(CO}_3)_2$	3.5	2	0.029	1.4×10^{-16}	3.3

The $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$ foam grows as a torn cell structure because the oxidizing gases H_2O and CO_2 are released by $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$ decomposition. This stabilizes the cell wall by oxidation, which prevents the cell from becoming connected and spherical, and leads to the coarse-torn cell structure. To support this, it has been reported that the carbonate foam oxidizes and stabilizes the cell wall.³⁾

MgCO_3 and $\text{CaMg(CO}_3)_2$ have higher decomposition temperatures than TiH_2 and $4\text{MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}$, and <1% of the decomposition gas has been released when AlSiCu starts melting. Most of the decomposition gas is released while AlSiCu melting is well under way, which reduces the flow stress of AlSiCu . These cells do not have torn fibrous aluminum powder boundaries, and their structures could be flat or spherical. Even after expansion, the shape and homogeneity of the cell structure are maintained because of the stability of the cell wall.

To confirm the effect of the released gas volume on the cell structure, the volume and radius of gas released from a particle at 843 K are given in Table 3. The gas volume of one mole (0.0224 m^3) was used as the standard condition. $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ has a large volume because most of the gas has already been released at 843 K. MgCO_3 and $\text{CaMg}(\text{CO}_3)_2$ have small volumes because most of the gas has not been released at 843 K.

The gas released from $\text{CaMg}(\text{CO}_3)_2$ has a smaller radius than that released from MgCO_3 , and the cell structure also depends on the particle size. The smaller radius of the oxidizing gas released from $\text{CaMg}(\text{CO}_3)_2$ presumably contributes to the fine and spherical cell structure observed for the $\text{CaMg}(\text{CO}_3)_2$ foam.

4. Conclusion

A carbonate foaming agent that begins decomposing after the matrix has melted is required for the formation of metal

foams with a fine and homogenous cell structure by the PM route. The TiH_2 foam formed under similar conditions showed markedly different characteristics, and had a coarse and rounded cell structure. MgCO_3 and $\text{ML-CaMg}(\text{CO}_3)_2$ were selected as the suitable foaming agents of AlSiCu . The $\text{CaMg}(\text{CO}_3)_2$ foam had a specific gravity of 1.19 and a homogeneous, fine and spherical cell structure.

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