

Fabrication of Mg Alloy Foam via Melting Foaming Method Using CaCO₃ as Blowing Agent

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CaCO₃를 이용한 발포 마그네슘 합금의 제조

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Abstract

For the first time AZ91 (MgAl9Zn1) and AM60 (MgAl6) Mg alloy foams with homogeneous pore structures were prepared successfully via melting foaming method by using CaCO₃ powder as blowing agent. The possible foaming mechanisms and pore structures of these Mg alloy foams were discussed and investigated. The results show that Mg alloy melt can affect CaCO₃ decomposition behavior and AZ91 Mg alloy is relative easy to be foamed into metal foam with high porosity and big pore size.

초 록 : CaCO₃를 발포제로 사용하여 균일한 기공구조를 가지는 AZ91과 AM60 마그네슘 합금의 발포 금속을 주조법을 통하여 제조하였다. 발포 금속의 제조가 가능한 이유와 발포 마그네슘 합금의 기공구조가 연구를 통하여 논의되었다. 마그네슘 합금의 용탕은 CaCO₃의 분해 거동에 영향을 미친다. 제조된 AZ91 마그네슘 합금의 발포 금속은 높은 기공률과 큰 기공의 크기를 가졌으며, 발포 금속들 중에서 상대적으로 쉽게 발포되는 것으로 판단된다.

Key words: Mg alloy foam, Blowing agent, CaCO₃ powder, Pore structure.

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1. Introduction

Metal foam is a class of attractive materials, which exhibits unique combinations of physical, mechanical, thermal, electrical and acoustic properties[1]. In particular, it is light and good at absorbing energy, which is drawing much attention in automotive, locomotive and aerospace applications from the view point of environmental preservation. Al and Al alloy foams have been developed successfully and have been employed in the new generation of crash boxes[1,2]. Mg alloy foams are definitely expected to be particularly advantageous due to low density of their metal matrix, which is approximately two thirds that of aluminum and good mechanical properties.

Up to now, several preparation processes have been developed to fabricate the Mg alloy foam with closed pore structure: powder metallurgical (PM) method[1], solid-state foaming method[3], high pressure casting method[4], vacuum foaming

method[5] and GASAR method to make lotus type Mg foam [6]. But investigations have shown that Mg foams fabricated by these methods are relative expensive. Therefore it is necessary to develop a cost-effective and easily controllable manufacturing process to prepare the Mg alloy foam.

Melting foaming process, containing addition of TiH₂, to a melt, is one of cost-effective methods to make the metal foam and it has been applied successfully to fabricate Al foams[1]. But surprisingly, few studies have been carried out on Mg alloy foam fabrication by using melt foaming method successfully. In this paper, melt foaming method was applied to prepare the AZ91 (MgAl9Zn1) and AM60 (MgAl6) Mg alloy foams with homogeneous pore structures successfully by using CaCO₃ powder as blowing agent. Then the decomposition properties of blowing agent, CaCO₃, in the melt, bubble stabilization mechanisms in Mg alloy melt and pore structures of Mg alloy foam were discussed.

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2. Experimental

2.1 Materials

Commercial AZ91 (Al: 8.5~9.5 wt%, Zn: 0.45~0.9 wt%, Mn: 0.15~0.40 wt%, Si: <0.20 wt%, Cu: <0.08 wt%, Ni: <0.01 wt%, Mg: Bal.) and AM60 ingots (Al: 5.6~6.4 wt%, Zn: <0.20 wt%, Mn: 0.26~0.50 wt%, Si: <0.05 wt%, Cu: <0.008 wt%, Ni: <0.001 wt%, Mg: Bal.) were used to prepare the Mg alloy foams in this work.

Both CaCO_3 powder (purity >99.8 wt%) and TiH_2 powder (purity >99.2%) were chosen as blowing agent to prepare the Mg alloy foam. The particle mean sizes of CaCO_3 and TiH_2 powders are about 5 and 40 μm respectively according to the particle size distribution analysis (Laser Particle Sizer, Analysette 22, Germany).

2.2 Mg alloy foams preparation procedure

The Fabrication apparatus used for making Mg alloy foam mainly consists of a resistance furnace, crucible, a stirring paddle driven by a motor which can provide various revolution speed and a gas system to supply the protecting gas. The preparation procedure of magnesium alloy foam involves the following steps: *Melting*: The Mg alloy (~1 kg) is melted in a crucible at a fixed temperature. *Thickening*: Ca particle (2 wt%, purity >99.9 wt%) is introduced into the melt by the impeller with a constant revolution speed of 400 rpm for 10 minutes to raise the melt viscosity. *Stirring*: CaCO_3 powder (2 wt%) is dispersed into the melt with the impeller revolution speed of 800 rpm, leading to the melt being foamed gradually. This time interval is defined as stirring foaming stage whose duration is defined as stirring time, t_s . In this study, the t_s is set as 30 s. TiH_2 powder is also used as blowing agent to foam Mg alloy melt for comparison purpose. *Holding*: After stirring foaming stage, the melt is held in the furnace to let bubbles in the melt continuously grow until a certain cellular structure is formed. This time interval is defined as holding foaming stage whose duration is defined as holding time, t_h . In this study, the t_h is set as 20 s. The summation of t_s and t_h is defined as the total foaming time, t , and the temperature during the total foaming time is defined as foaming temperature. *Cooling*: The crucible is removed from the furnace and the melt, which has been foamed, is allowed solidify by air blowing. The whole fabrication process was operated under the mixture gas atmosphere of CO_2 and SF_6 (volume ratio: 6:1) to prevent the Mg alloy melt from ignition.

3. Results and discussion

3.1 Mg alloy foams prepared by different blowing agents

There have been reported that both TiH_2 and CaCO_3 can be

used as blowing agents to fabricate Al alloy foam successfully [1,7,8]. The melting points of Al alloy and Mg alloy are quite similar, so these two agents are also possible candidates used for making Mg alloy foam.

But Fig. 1(a)~(c) shows the Mg alloy foams prepared by using TiH_2 have very coarse pore structures while Fig. 1(d)~(e) shows the Mg alloy foams prepared by using CaCO_3 as blowing agent have homogeneous pore structures. Although the difference of pore stabilization mechanisms by using these two blowing agents is needed more investigations, there are two possible reasons to explain the difference. One is that, for AZ91 case, after adding 2 wt% Ca, although the viscosity of AZ91 melt is at same level as that of thickened Al melt, which is about 10~14 cp[9,10], the surface tension of AZ91 melt, which is about $0.45 \text{ N}\cdot\text{cm}^{-1}$ [10], is so low compared with thickened Al melt, which is about $600 \text{ N}\cdot\text{cm}^{-1}$ [10] that bubbles likely can not stay stable in the Mg alloy melt if TiH_2 is used as blowing agent; On the other hand, the blowing gas released by CaCO_3 decomposition in the melt can react with Mg alloy melt to form more solid particles, which will be discussed in section 3.2, and it is these solid particles that can slow down the cell wall rupture process and hence inhibit cell coarsening while H_2 released by decomposition of TiH_2 does not have these effects.

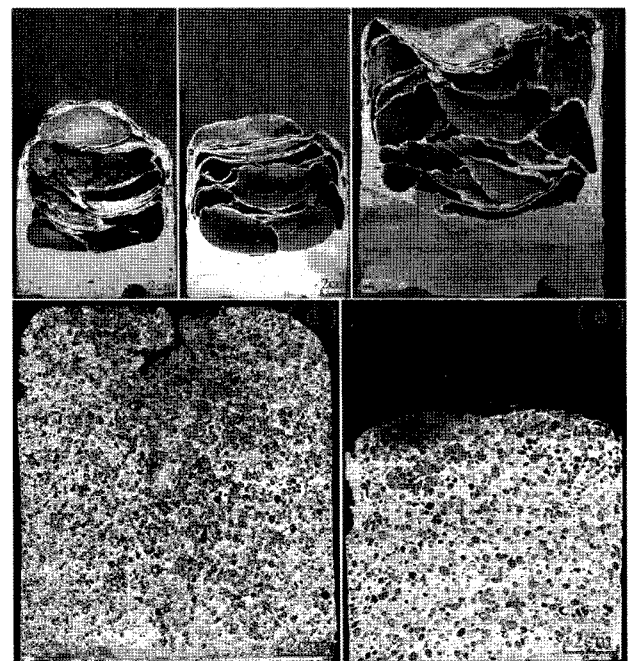


Fig. 1. Mg alloy foams prepared by different blowing agents. (a)~(c): AZ91 foams using TiH_2 as blowing agent. The foaming temperature of (a) is 700°C , (b) is 670°C and (c) is 650°C . Both the Ca and the TiH_2 addition are 2 wt%. (d) and (e) are the AZ91 foam, AM60 foam respectively using CaCO_3 as blowing agent. The foaming temperature of (d) is 690°C , (e) is 750°C . Both the Ca and CaCO_3 addition of (d) and (e) are 2 wt%.

3.2 Gas evolution kinetics of CaCO₃ and reaction thermodynamics

The blowing agent decomposition behavior is in close relationship with the Mg alloy melt foaming process. Proper gas releasing rate of blowing agent is critical to foam the Mg alloy melt with good cellular structure.

Fig. 2 is the mass loss curves of CaCO₃ powder as the function of time at different fixed temperatures in air flow, which shows that the decomposition quantity of CaCO₃ is less than 1 wt% in the temperature range from 650°C to 750°C in 50 s, indicating that the gas amount released from CaCO₃ decomposition is not high enough to foam Mg alloy melt effectively in 50 s, so the Mg alloy melt should influence the gas release rate of carbonate deeply. In addition, Fig. 1 suggests that there is a cell wall stabilizing mechanism operating in the carbonate-foamed melts, slowing down the cell wall rupture process and hence inhibiting cell coarsening. All possible reactions and associated thermodynamic data[11] (assuming 1atm pressure of the gas involved) are shown below.

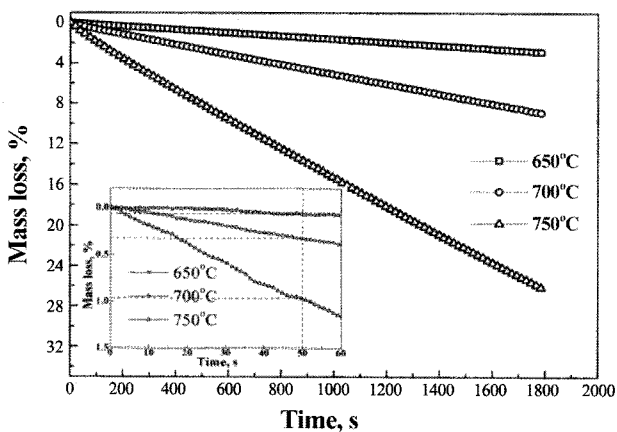
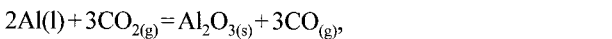
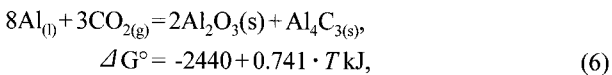
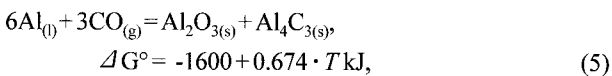
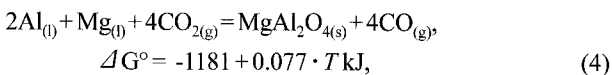
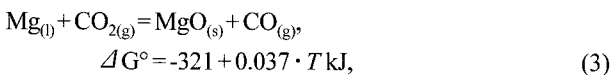
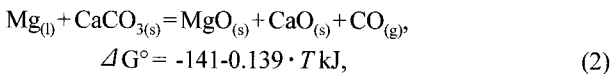
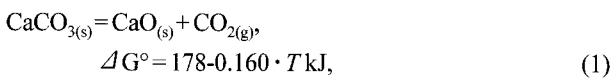


Fig. 2. Thermogravimetry curves of CaCO₃ powder (The initial part is enlarged in the left small figure). The experiments were carried out in air atmosphere.

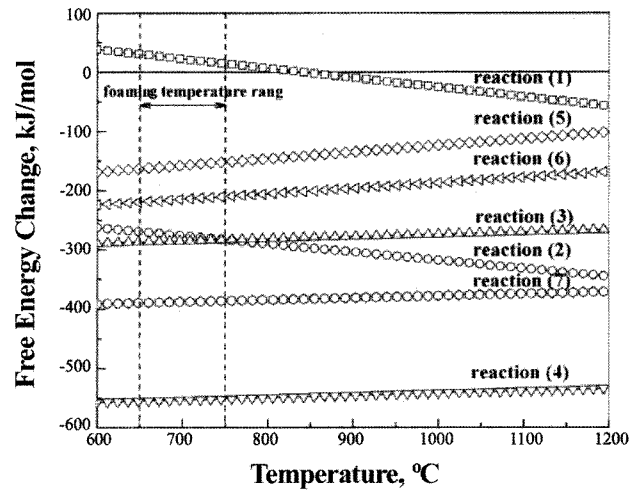


Fig. 3. Free energy changes as a function of temperature for various possible reactions between Mg alloy melt and a foaming gas. The values of relative free energy change are normalized for 1 mol of aluminum/magnesium.

$$\Delta G^\circ = -840 + 0.066 \cdot T \text{ kJ}, \quad (7)$$

Fig. 3 is the free energies of reactions (1)-(7) as a function of temperature, which indicates that reactions (2)-(7) are all thermodynamically favorable over the temperature range of melt foaming, and the Mg alloy melt likely react with CaCO₃ to produce gas (Fig. 3 reaction (2)). In addition, the CaCO₃ powder is so fine (5 μm) that the melt-solid interface is high for the reaction (2) happening possibly. This is a reasonable gas source that makes Mg alloy foam be foamed in 50 s. Further more, there is another reasonable assumption, which is that Mg alloy melt likely possesses catalytic ability on CaCO₃ decomposition, but it is needed further investigations. Reactions (3)-(7) indicate that the blowing gas can react with melt to produce solid particles, which leads to increasing the viscosity of melt higher and higher during the foaming process and high melt viscosity is advantageous to inhibit cell coarsening and rupture.

3.3 Pore structures of Mg alloy foam

Porosity, pore number and pore size are three important parameters used to describe the metal foam pore structures. In this study, porosity of Mg alloy foam, which refers to the volume fraction of all pores in a metal foam, is calculated from the weight *W* and volume *V* of a sample using the equation expressed as Pr (porosity) = $(V \cdot W / \rho) / V \times 100\%$, where ρ is the matrix's density. Mean pore size and pore number are obtained by analyzing corresponding section images of Mg alloy foams. According to Deless law[12], the plane pore structures can be used to reflect the bulk pore structures if the macroscopic structure is homogeneous.

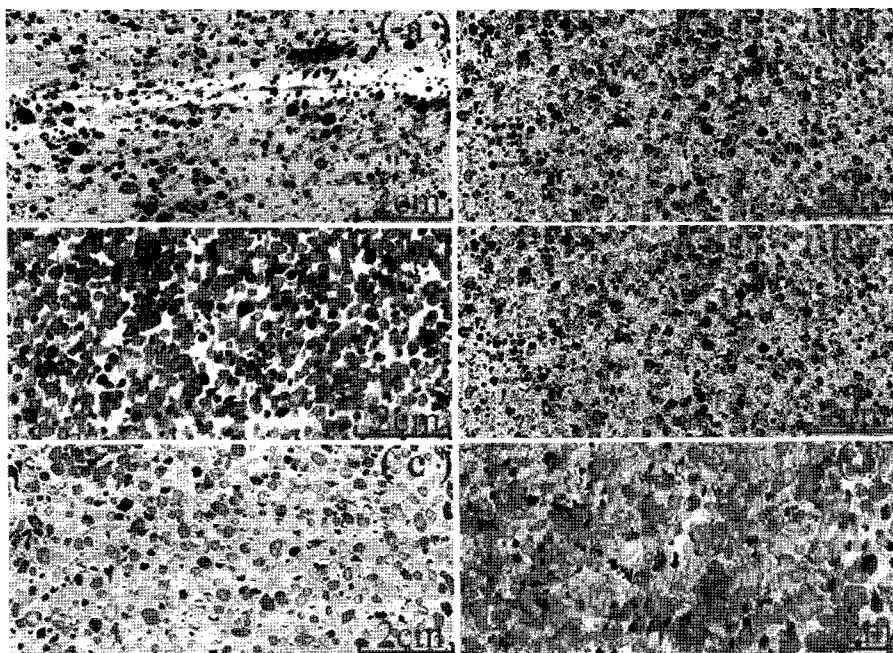


Fig. 4. Section images of Mg alloy foams. (a)~(c): AM60 foams; (d)~(f): AZ91 foams. The foaming temperature of (a) and (d) is 690°C, (b) and (e) is 720°C, (c) and (f) is 750°C. Both the Ca and the CaCO₃ addition of (a)~(f) are 2 wt%.

The section images of AZ91 and AM60 foams prepared at different foaming temperature are shown in Fig. 4. After analyzing corresponding section images of Mg alloy foams, the relationship between porosity, pore number and mean pore size of AZ91, AM60 foams and foaming temperature can be obtained (see Fig. 5), which clearly shows that (1) the porosities of both AZ91 and AM60 foams increase with the foaming temperature rising, but AZ91 can be foamed into the metal

foam with higher porosity than AM60 is under the same foaming temperature (Fig. 5(a)); (2) the pore number decreases greatly for AZ91 foam prepared at higher foaming temperature while pore number of AM60 foam does not change very much with increasing the foaming temperature (Fig. 5(b)); (3) the mean pore size of AZ91 foam increase greatly from about 1.9 mm at foaming temperature of 690°C to 4.2 mm at the foaming temperature of 750°C while the pore size of AM60 foam does not change much, which is around 2.0 mm in the foaming temperature range from 690°C to 750°C (Fig. 5(c)). Summarily, the formability and foaming results of AZ91 and AM 60 is different. AZ91 can be relatively easily foamed into metal foam with high porosity and big pore size.

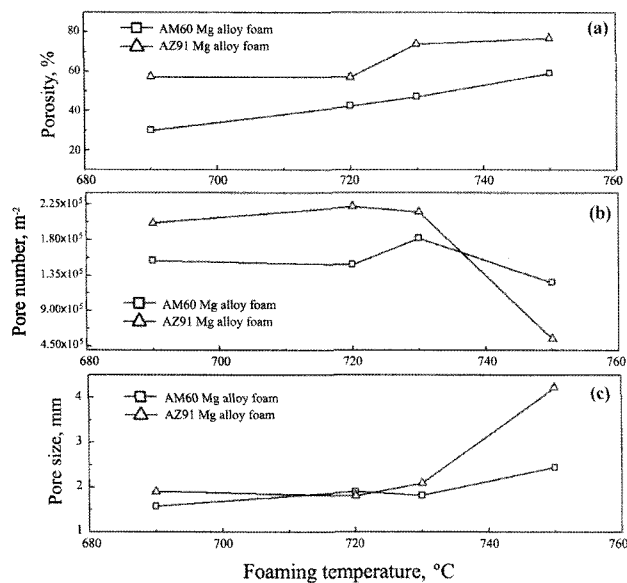


Fig. 5. The variation in porosity, pore number and mean pore size of Mg alloy foams as a function of foaming temperature.

4. Conclusions

In summary, we have succeeded in developing AZ91 and AM60 Mg alloy foams with homogenous pore structures by using melting foaming method with CaCO₃ powder as blowing agent. The Mg alloy melt can influence CaCO₃ powder decomposition behavior, which is favorable to foam the Mg alloy melt. The reactions between blowing gas, CO₂/CO, and Mg alloy melt can produce the solid particles, which lead to make Mg alloy foam with good pore structures. AZ91 Mg alloy is relative easier to be made into corresponding foam with higher porosity and bigger pore size than AM60 Mg alloy is.

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