

## Preparation of closed-cell Mg foams using SiO<sub>2</sub>-coated CaCO<sub>3</sub> as blowing agent in atmosphere

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**Abstract:** In melt foaming method, the thermal stability and foaming speed of blowing agent significantly affect the pore structure, pore size and porosity of metal foams. To retard the foaming speed and increase thermal stability, Na<sub>2</sub>O-*n*SiO<sub>2</sub> and dilute hydrochloric acid were used to coat SiO<sub>2</sub> passive layer on the surface of CaCO<sub>3</sub> which is the blowing agent of Mg foams. Thermal stability and microstructure of the SiO<sub>2</sub> passive layer were studied by thermo gravimetric analyzer–differential thermal analysis (TGA–DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that the thermal stability of coated CaCO<sub>3</sub> is improved. The SiO<sub>2</sub> layer is amorphous with reticular structure. Contrasting experiments reveal that the coated CaCO<sub>3</sub> can foam placidly. Moreover, large size and homogeneous Mg foams were prepared without protective gas with the ignition-proof by alloying. And the porosity of the Mg foams is 60%–70%.

**Key words:** melt foaming; close-cell Mg foam; foaming agent; SiO<sub>2</sub> coating; CaCO<sub>3</sub>

### 1 Introduction

Metal foam is a class of novel materials with continuous metallic matrix separated by equally distributed gas bubbles. It has many excellent properties, such as high stiffness in conjunction with ultra-low density, low magnetic conductance and good damping performance. Because of these reasons, it can be applied as light structure material or packing medium in the fields of aviation, aerospace, weapon and automobile. And it is also a sort of functional material which can be made into sound barriers, noise reduction metope, etc [1–3].

Recently, researchers have paid more attention to the Mg foams [4]. Because of their lower density as well as higher specific strength and stiffness compared with Al foam, Mg foam may have broader promising applications [5,6]. To date, several methods have been developed to prepare close-cell Mg foam, among which melt foaming process is more cost-effective and has been successfully applied to prepare Al foam [7,8]. In this method, blowing agent is added into the melt to form gas bubbles. Therefore, the thermal stability and wetting

property of the blowing agent is in close relationship with the quality of Mg foams. When Al foam is prepared, the foaming agents (TiH<sub>2</sub>, ZrH<sub>2</sub>, CaCO<sub>3</sub>, etc) are usually processed through heat treatment [9], coating process [10] and tailoring [11] to improve the foaming performance. Because Mg has hydrogen absorbing property, carbonate (CaCO<sub>3</sub> and MgCO<sub>3</sub>) is more appropriate to be the blowing agent of Mg foam. However, the carbonate foams are too intensive, and the Mg melt is extremely easy to oxidize or even ignite due to its active chemical property, so it is difficult to prepare Mg foam with homogeneous pore structure and high porosity by the melt foaming process without protective atmosphere. Ji et al [12] coated SiO<sub>2</sub> layer on the surface of MgCO<sub>3</sub> particles by sol–gel method. The results showed that the decomposition rate of coated MgCO<sub>3</sub> was decreased and the coated MgCO<sub>3</sub> could be taken as foaming agent to prepare foam metals. YANG et al [13] fabricated closed-cell Mg foam using CaCO<sub>3</sub> as blowing agent by the melt foaming method. Homogeneous Mg samples with the porosity of 60.8%–69.8% were fabricated at the temperature of 690–720 °C. Moreover, they proved that the foaming gas was CO during this process. XU et al [4] fabricated close-cell Mg alloy foams with a diameter of

130 mm by the melting foam method, and the porosity of Mg alloy foams is in the range of 60%–90%. They also proved that smaller cell size was beneficial to getting more stable compressive process, and the compressive property increased first and then decreased with the decreasing cell size. However, the gas mixture of CO<sub>2</sub> and SF<sub>6</sub> was applied to prevent the Mg foams from ignition in the above mentioned work, which would decrease the operability and convenience of the experiment. Moreover, the SF<sub>6</sub> has been restricted to use, because it is a potent greenhouse gas (24900 times of CO<sub>2</sub>), which can persist for more than 3200 years in the atmosphere [14]. Because of the environmental impact and tail gas treatment cost of the SF<sub>6</sub>, it is necessary to prepare Mg foams with more environmentally friendly method.

In this work, SiO<sub>2</sub> passive layer was coated on the surface of CaCO<sub>3</sub> to decrease its foaming speed, and the coating effect and mechanism were studied. The ignition-proof of alloying, which depends on the protective oxide films on the surface of Mg melt [15], was applied to prepare Mg foams in order to reduce air pollution. Due to the placid foaming character of coated CaCO<sub>3</sub>, large size and homogeneous Mg foams were prepared without protective gas.

## 2 Experimental

### 2.1 Coating experiment

The CaCO<sub>3</sub> particles were coated by sol–gel method at about 70 °C in water-bath. First, CaCO<sub>3</sub> particles (analytically pure, 23 μm) and Na<sub>2</sub>O·*n*SiO<sub>2</sub> solution (2 mol/L, *n*≈3) were mixed into slurry with a rate of 1 g/mL. Then the mixture was stirred by glass rod, hydrochloric acid (0.15 mol/L) was titrated into the slurry with a speed of 40 mL/h to keep the pH value at about 12. After that, the slurry was held for 2 h to make SiO<sub>2</sub> passive layer precipitate on the surface of the CaCO<sub>3</sub> particles. Subsequently, the slurry was dehydrated to obtain precursor at 200 °C for 2 h. Ahead of the foaming experiments, the precursor was ground and filtrated into proper size. And plentiful experiments showed that the proper size of the coated CaCO<sub>3</sub> was 150–180 μm. Finally, the SiO<sub>2</sub> coated blowing agent of Mg foam was obtained.

### 2.2 Melt foaming method

Mg foam was prepared by the melt foaming process, and the its detailed procedures are as follows.

1) Melting and alloying: A definite quantity of Mg (according to the volume of the crucible) was melted in a crucible at 700 °C. After the molten Mg was heated up to

about 750 °C, calcium (3.0%–5.0%, mass fraction) was added into the Mg melt to ignition-proof.

2) Thickening: SiC particles (3%–5%, 75 μm) were introduced into the melt, and stirred by an impellor with a constant rotation speed of 600 r/min for 5 min to raise the viscosity.

3) Foaming: The blowing agent (CaCO<sub>3</sub> particles, 1%–2%) was dispersed into the thick melt stirred by the impellor with a speed of 900 r/min for 30 s to make the blowing agent distribute homogeneously. And the foaming temperature was 640–660 °C.

4) Holding: After foaming stage, the melt was transferred into a holding furnace immediately, and held at 700–750 °C for 1–3 min to make the bubbles grow up gradually until a cellular structure formed.

5) Cooling: The foam was taken out of the holding furnace, and cooled in the air.

The pore structure of Mg foams was characterized by the porosity *P*, which is calculated by

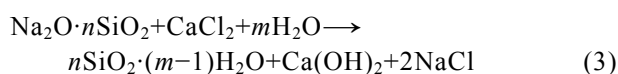
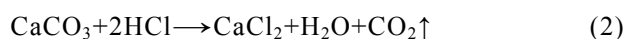
$$P = \left(1 - \frac{m}{\rho \times V}\right) \times 100\% \quad (1)$$

where *m* is the mass of Mg foam, *ρ* is the density of Mg matrix, and *V* is the volume of the Mg foam.

## 3 Results and discussion

### 3.1 Microstructure of passive layer

Heterogeneous nucleation method was used in the coating experiment. pH value of the slurry was kept in a certain range by hydrochloric acid. The hydrated silica (*n*SiO<sub>2</sub>·(*m*–1)H<sub>2</sub>O) could precipitate and condense into a layer of continuous silica gel on the surface of CaCO<sub>3</sub> particles as



The silica gel is unstable and apt to dehydrate, and a passive layer of SiO<sub>2</sub> is formed on the surface of CaCO<sub>3</sub> particle as

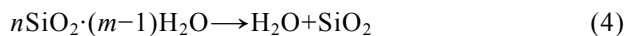
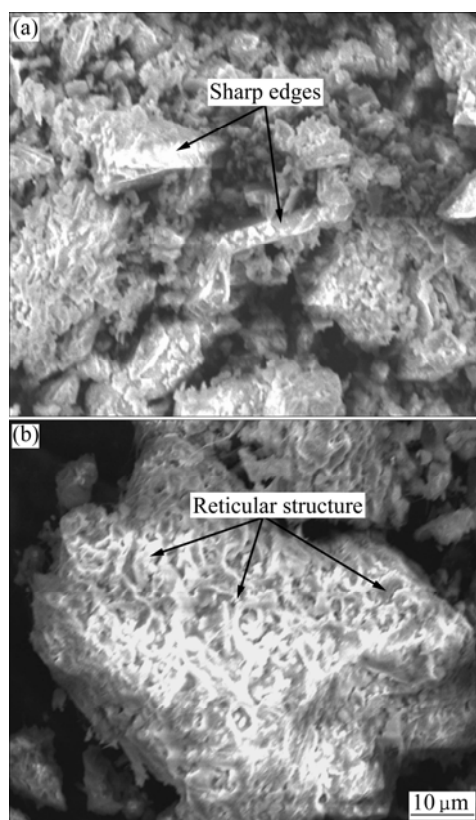


Figure 1 shows the SEM (JEOL JSM–5600LV) images of the uncoated and coated CaCO<sub>3</sub>. The shape of uncoated particles is irregular with sharp edges (Fig. 1(a)). While the coated particles are round with plump edges, and a layer of reticular structure is found on the surface of CaCO<sub>3</sub> particles (Fig. 1(b)). The EDS analysis of the reticular structure shows that the contents of Si and Na are relatively higher, while the content of Ca which is the major element of CaCO<sub>3</sub> is lower. This indicates that the reticular structure is the SiO<sub>2</sub> passive



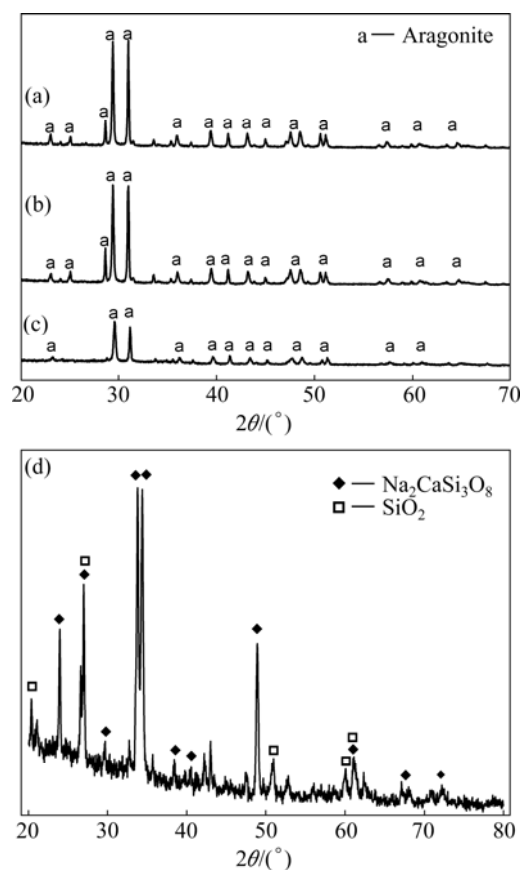
**Fig. 1** SEM images of  $\text{CaCO}_3$  particles: (a) Uncoated  $\text{CaCO}_3$  particles; (b) Coated  $\text{CaCO}_3$  particles

layer, and the reticular morphology is caused by the dehydration of the continuous silica gel layer (Reaction (4)). Besides, the addition of coated  $\text{CaCO}_3$  into the Mg melt is just 1%–2%, and the content of residual NaCl (Reaction (3)) is very tiny (about 0.1%–0.2%), so the impact of residual NaCl added to the closed-cell Mg foams is very little.

### 3.2 XRD results

Figure 2(a) shows XRD (PANalytical, Empyrean) pattern of uncoated  $\text{CaCO}_3$ , and it indicates that the crystal form is aragonite. Figure 2(c) is the XRD pattern of the coated  $\text{CaCO}_3$  after dehydrating at 200 °C for 2 h. Compared to Fig. 2(a), there are no other peaks except those of  $\text{CaCO}_3$  in Fig. 2(c), which reveals that the  $\text{SiO}_2$  in the passive layer is in amorphous state [16] and other substances are scarce and unable to present diffraction peak. Furthermore, the diffraction peaks are less intensive than those of uncoated  $\text{CaCO}_3$  in Fig. 2(a). While the peak intensity in Fig. 2(b) does not change, in which the  $\text{CaCO}_3$  just be dehydrated at 200 °C for 2 h. This phenomenon is caused by the amorphous  $\text{SiO}_2$  layer on the surface of  $\text{CaCO}_3$ , which can reduce the intensity of the diffraction peaks of  $\text{CaCO}_3$ .

In order to confirm whether the passive layer is made of  $\text{SiO}_2$ , the coated  $\text{CaCO}_3$  is roasted at 1000 °C



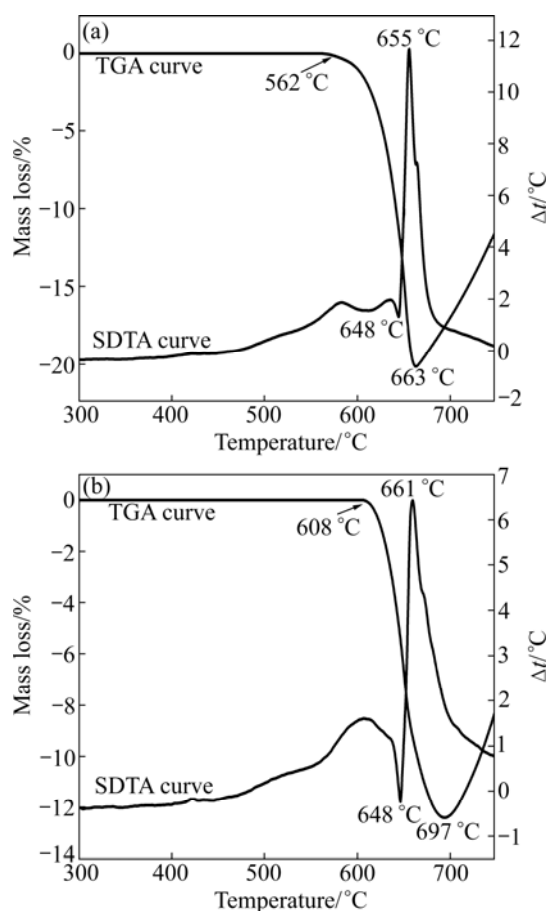
**Fig. 2** XRD patterns of  $\text{CaCO}_3$ : (a) Uncoated  $\text{CaCO}_3$ ; (b) Coated  $\text{CaCO}_3$ , dehydrated for 2 h at 200 °C; (c) Uncoated  $\text{CaCO}_3$ , dehydrated for 2 h at 200 °C; (d) Coated  $\text{CaCO}_3$ , roasted for 0.5 h at 1000 °C

for 0.5 h, and the XRD pattern is shown in Fig. 2(d). There are  $\text{Na}_2\text{CaSi}_3\text{O}_8$  peaks in the XRD pattern. Therefore,  $\text{CaCO}_3$  decomposes into  $\text{CaO}$  completely at 1000 °C, and then reacts with other substance to form  $\text{Na}_2\text{CaSi}_3\text{O}_8$ . And there are  $\text{SiO}_2$  peaks in the pattern as well. Because  $\text{SiO}_2$  can not be formed at 1000 °C by chemical reaction between other substances in the coated particles, it can be confirmed that the passive layer is made up of the amorphous  $\text{SiO}_2$  which can convert to crystalline state from amorphous state at 1000 °C [17]. Moreover, the  $\text{SiO}_2$  passive layer is so stable, and it does not react with other substances even at 1000 °C.

### 3.3 Thermal stability analysis

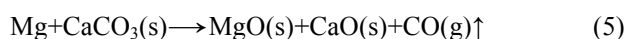
TGA-DTA (METTLER TOLEDO, TGA/SDTA851<sup>o</sup>) was used to investigate the thermal stability of the coated and uncoated  $\text{CaCO}_3$ . To be close to the real foaming experiments, the  $\text{CaCO}_3$  particles were sufficiently mixed with Mg powder with the molar ratio of 1:3. The TGA-DTA experiments were carried out at 300–750 °C with a heating rate of 10 °C/min, and argon was used to protect Mg powder from ignition.

Figure 3(a) shows the TGA-DTA curves of



**Fig. 3** TGA-DTA curves of  $\text{CaCO}_3$ : (a) Uncoated  $\text{CaCO}_3$ ; (b) Coated  $\text{CaCO}_3$

uncoated  $\text{CaCO}_3$  and Mg powder mixture. And the TGA curve reveals that the mixture losses mass at 562–663 °C, which can be explained by the following reaction:



The starting temperature of reaction (5) is over 100 °C lower than the decomposition temperature of  $\text{CaCO}_3$ , corresponding well to the preparation of Mg foams by melt foaming process (foaming temperature is 650–700 °C), so the foaming gas is not  $\text{CO}_2$  but  $\text{CO}$  [13]. In the TGA curve of Fig. 3(b), the starting temperature of the reaction between the coated  $\text{CaCO}_3$  and Mg increases to 608 °C, which reveals that the  $\text{SiO}_2$  passive layer effectively improves thermal stability of  $\text{CaCO}_3$ . Because the experiments are prepared in the air above 650 °C, the redundant  $\text{CO}$  will react into  $\text{CO}_2$  completely. So there is no need to worry about the pollution and poisoning of the  $\text{CO}$ .

In the DTA curve of Fig. 3(a), an endothermic peak appears at 648 °C, corresponding to the melting point of Mg. Subsequently, the exothermic peak appearing at 655 °C corresponds to the Reaction (5). And in Fig. 3(b), the endothermic peak also appears at 648 °C while the exothermic peak temperature of Reaction (5) rises to 661

°C, which further illustrates that the thermal stability of  $\text{CaCO}_3$  has been improved by coating  $\text{SiO}_2$  passive layer. In addition, the exothermic peak in Fig. 3(b) is broader than that in Fig. 3(a), revealing that the reaction speed of  $\text{CaCO}_3$  has been retarded, which is conducive to preparing high porosity and homogeneous Mg foams.

In the TGA curves of Figs. 3(a) and (b), after the samples' mass reduces to the minimum, the mass increases with the rising of temperature instead. This is caused by the oxidation of Mg powder in the mixture. Because Mg is very active at high temperature, the Mg powder is inevitably oxidized although protected by argon. Since the two tests have the same experimental condition, it still can be demonstrated that the coated  $\text{CaCO}_3$  has better thermal stability due to the effect of the  $\text{SiO}_2$  passive layer.

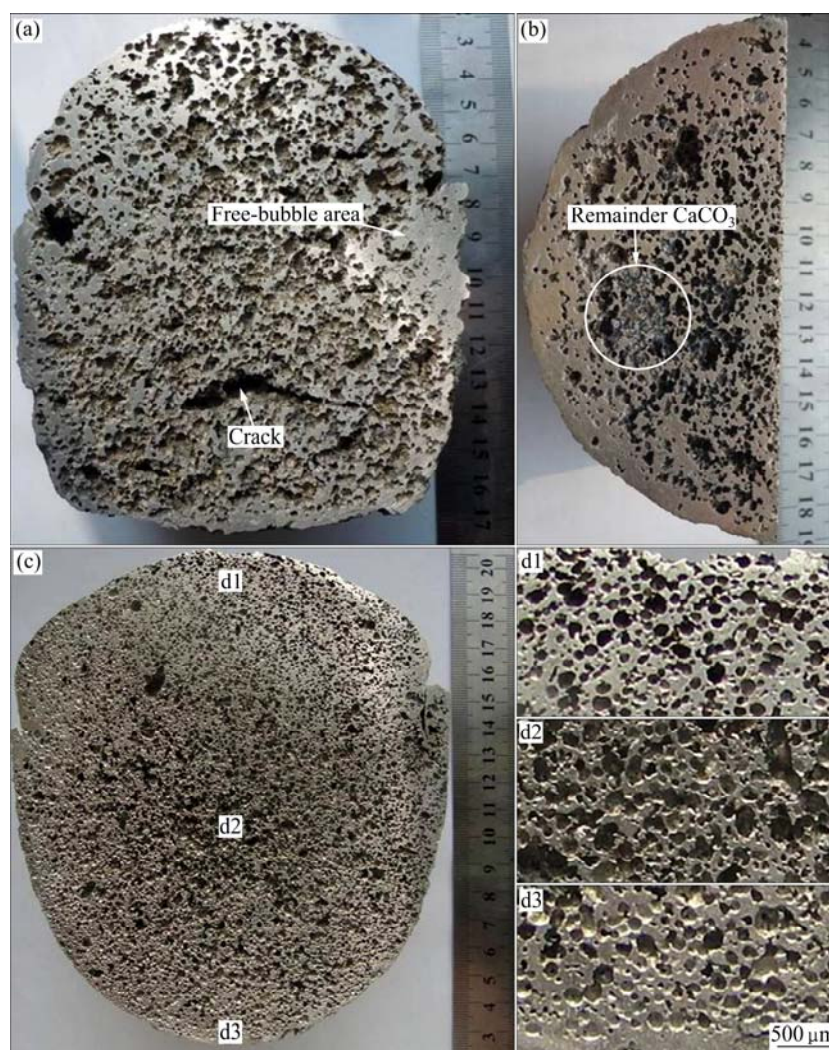
### 3.4 Contrastive experiments

To study the effects of  $\text{SiO}_2$  passive layer, under the same experimental condition, Mg foams were prepared with uncoated and coated  $\text{CaCO}_3$  respectively. Closed-cell Mg foams were prepared without shielding-gas with the ignition-proof by alloying.

Figure 4(a) represents the cross-section of Mg foam sample prepared by uncoated  $\text{CaCO}_3$ . The bubbles distribute unevenly with irregular shape, big crack and free bubble area, and the bubbles diameter varies widely. These defects are caused by the high foaming speed and agglomeration of the uncoated  $\text{CaCO}_3$  particles, which make it hard to scatter the different sizes of gathering  $\text{CaCO}_3$  particles homogeneously in such a short foaming time. In addition, the gathering uncoated  $\text{CaCO}_3$  particles can't foam adequately and form impurities in Mg foams, resulting in inferior mechanical property and worse anti-oxidizability. The impurities can be observed in Fig. 4(b) which shows the longitudinal section of samples in Fig. 4(a).

Figure 4(c) shows the cross-section of the Mg foam sample prepared by coated  $\text{CaCO}_3$ . Obviously, the sample exhibits more homogeneous structure and thinner free-bubble layer (Fig. 4(c)), and its porosity is 60%–70%. During the foaming experiments, the Mg foams grow up gradually. Because of the  $\text{SiO}_2$  passive layer, the thermal stability of  $\text{CaCO}_3$  is improved, there is more time to scatter the  $\text{CaCO}_3$  particles homogeneously by stirring. Furthermore, the size and surface state of the  $\text{CaCO}_3$  particles are changed by coated  $\text{SiO}_2$  passive layer, and the agglomeration of the  $\text{CaCO}_3$  particles is eliminated, which is conducive to dispersing the  $\text{CaCO}_3$  particles evenly by stirring. Because the  $\text{CaCO}_3$  is evenly distributed and completely foamed, no impurities of remainder  $\text{CaCO}_3$  are left in the samples (Figs. 4(d1)–(d3)).



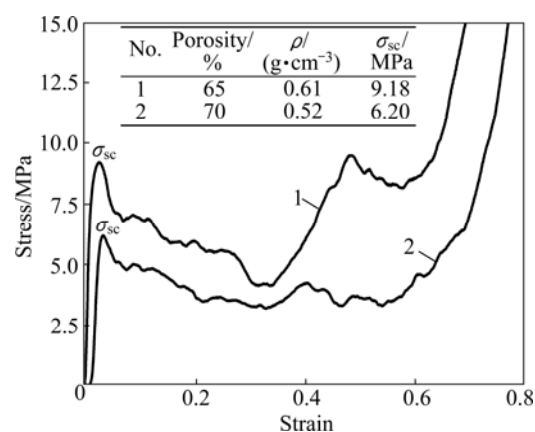


**Fig. 4** Pictures of Mg foam samples: (a) Foaming with uncoated  $\text{CaCO}_3$ , cross-section; (b) Longitudinal section of sample in Fig. 4(a); (c) Foaming with coated  $\text{CaCO}_3$ , cross-section

### 3.5 Compressive characteristics

Compression tests were performed to assess the mechanical properties of the Mg foams foamed with coated  $\text{CaCO}_3$ . The samples were processed into cylinder of  $d18\text{ mm} \times 18\text{ mm}$ , and the tests were carried out at Instron with the quasi-static strain rate of  $10^{-3}\text{ s}^{-1}$ .

Figure 5 presents the stress—strain curves of Mg foams with different density. It is obvious that Mg foams show typical three-states of deformation: linear—elastic deformation, where obvious yield phenomenon present. The second region is collapse region, and the curves show a plateau because the cell edge and the cell wall collapse when the stress is beyond the yield limit. The third region is densification region, where these foams have been compacted gradually and compressive strength increases rapidly with increasing deformation. It is noted that the compressive yield strength of higher porosity Mg foams is relatively lower, because the cell wall of higher porosity Mg foams is thinner.



**Fig. 5** Stress—strain curves of Mg foams foamed with coated  $\text{CaCO}_3$

## 5 Conclusions

1) The uncoated  $\text{CaCO}_3$  particles are in irregular shape with sharp edges, while the coated  $\text{CaCO}_3$  particles

are coated with amorphous  $\text{SiO}_2$  passive layer of reticular morphology.

2) The thermal stability of  $\text{CaCO}_3$  is improved by coating. Comparing to the uncoated  $\text{CaCO}_3$ , the starting reaction temperature between the coated  $\text{CaCO}_3$  and Mg increases by about 40 °C, and the reaction endothermic peak raises to 661 °C from 655 °C.

3) The contrastive experiments reveal that the coated  $\text{CaCO}_3$  has placid foaming speed, and the Mg foams grow up gradually. With the ignition-proof of alloying, large size and homogeneous Mg foams are prepared without shielding-gas.

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# $\text{SiO}_2$ 包覆 $\text{CaCO}_3$ 在无保护气氛下制备闭孔泡沫镁

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**摘 要:** 在熔体发泡法工艺中, 发泡剂的分解速度和浸润性直接影响泡沫金属的孔结构和孔隙率。为减缓泡沫镁发泡剂  $\text{CaCO}_3$  的发泡速度并提高与镁熔体的浸润性, 采用非均匀形核法, 以硅酸钠为原料, 盐酸为酸化剂, 在  $\text{CaCO}_3$  表面包覆  $\text{SiO}_2$  钝化膜。采用 TGA–DTA、XRD、SEM 等方法对包覆后  $\text{CaCO}_3$  的热稳定性和包覆层的微观结构进行分析。结果表明: 包覆后的  $\text{CaCO}_3$  分解温度提高; 包覆层中的  $\text{SiO}_2$  为无定形态; 在  $\text{CaCO}_3$  颗粒表面形成网络状结构。对比实验表明: 包覆后的  $\text{CaCO}_3$  发泡速度平稳。同时, 采用合金化阻燃工艺在无气体保护条件下制备出较大尺寸的泡沫镁试样, 并且试样孔径细小, 孔结构均匀, 孔隙率在 60%–70%。

**关键词:** 熔体发泡法; 闭孔泡沫镁; 发泡剂;  $\text{SiO}_2$  包覆;  $\text{CaCO}_3$

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