Appl. Phys. A (2015) 119:533–538
DOI 10.1007/s00339-015-8985-7

Applied Physics A
Materials Science & Processing

Influence of calcium addition and stirring on the cellular structure and foaming behavior of molten zinc

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Received: 15 October 2014 / Accepted: 8 January 2015 / Published online: 23 January 2015

Abstract In this paper, the influence of calcium addition and melt stirring on the structure and foaming behavior of molten zinc was investigated. In this regard, zinc foam was produced by Alporas method (in which foam alloy melts and titanium hydride is used as a blowing agent). Optical microscopy and scanning electron microscopy were used to investigate the phase distribution and structure in the foams. Results showed that addition of calcium increased foamability and foam efficiency of the molten zinc. In contrast, stirring had no significant effect on the foaming behavior of the melt. Microstructural examinations indicated that improving the foaming behavior of molten zinc was attributed to the formation of $CaZn_{13}$ intermetallic phase and ZnO particles in the foam structure, which increased viscosity and reduced drainage rate.

1 Introduction

Metal foams with a cellular structure are a new class of materials. In the past two decades, they have attracted strong industrial and scientific attention due to interesting combination of their physical and mechanical properties, such as high stiffness in conjunction with very low specific weight or high gas permeability and high thermal conductivity [1–3]. Aluminum, magnesium and zinc alloys are mainly suitable for foaming due to their relatively low melting points and favorable liquid properties. Among these metals, zinc alloys are inexpensive and versatile. They also have higher viscosities than molten aluminum. Besides, zinc foam has shown promising potential application in filling hollow steel sections to improve their stiffness [4, 5]. However, most of the works on metallic foams have focused on aluminum and magnesium alloys, and only a few studies have been carried out on zinc alloys as metallic foams [6, 7].

There are many ways to manufacture cellular metallic materials which include solid-state foaming method [8], powder metallurgy method [9], vacuum foaming method [10], high-pressure casting method [11] and melt foaming method [12]. In the melt foaming process, increasing the stability of the melt via controlling viscosity is necessary, since proper viscosity can prevent escaping and coalescing of gas bubbles. Furthermore, proper viscosity leads to regular and homogeneous cell structure in terms of size and dispersion [13].

From literature, stabilization of aluminum foams has been conducted either by addition of ceramic particles to produce composite foams or by addition of metallic calcium to the melt and stirring the mixture in order to increase the viscosity. In relation to zinc alloys, addition of ceramic particles to the melt to increase the melt viscosity and foam stability has been reported before [7, 13, 14], but addition of metallic calcium and control of the melt viscosity, which has been studied for aluminum [15, 16], have not been reported for zinc alloys. Therefore, the aim of this paper is fabrication of zinc foam using Alporas method. Furthermore, the effects of calcium addition and melt stirring on the foaming behavior of the molten zinc are also investigated.

2 Experimental procedure

The materials used in the present work were commercially pure zinc (Zn purity >99.9 wt%), calcium granules

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(Ca purity >98.5 wt%) as a viscosity modifier of the molten zinc and titanium hydride powder (TiH_2 >98.0 wt%, with 44 μm in diameter) as a blowing agent.

This study was based on experimental procedure involving a number of steps; step (1): Zinc was melted in a graphite crucible under the temperature of 450 °C in ambient atmosphere. Step (2): To modify the viscosity of molten zinc, calcium in 0, 0.5, 1.0 and 1.5 wt% was added to the melt and stirred to completely dissolve. In order to study the effect of stirring on the foaming behavior of molten zinc, this step was performed again, and this time after dissolution of added calcium, the melts with different amounts of calcium were stirred at 600 rpm for 10 min. Step (3): 1 wt% titanium hydride as a blowing agent was added to the molten zinc and dispersed after stirring at 1,000 rpm. Step (4): The crucible was held in a furnace in the temperature of 450–500 °C to allow the blowing agent to be completely decomposed. Step (5): Finally, the crucible was removed from the furnace. The melt was directionally solidified in water from the bottom of the crucible to obtain the foamed zinc. The microstructure of the foams was characterized by both optical and scanning electron microscope (SEM).

3 Results and discussion

3.1 Influence of calcium addition

Figure 1 illustrates macro- and microstructure of solidified Zn-1 wt% Ca without blowing agent. As can be seen in Fig. 1a, two distinct zones can be distinguished: a highly thickened zone at the top and non-thickened zone at the bottom of sample. The viscosity measurements using a high-temperature falling ball viscometer [17] show that the viscosity of the non-thickened zone was severely lower than that of thickened zone. Results of microstructural examination (Fig. 1a, b) and XRD analysis show that the higher viscosity of the upper zone is attributed to the formation of $CaZn_{13}$ intermetallic particles with 5–30 μm in diameter. Generally, in the dissolution of a solid metal with high melting point in a liquid metal, intermetallic phases that are richer in molten metal are created [18, 19]. In this case, after addition of calcium to the molten zinc and stirring for the appropriate duration, the added calcium is completely dissolved and $CaZn_{13}$ particles are produced. These particles have tendency to flow up and form the thickened zone at the top due to the lower density than molten zinc. It should be noted that the density of molten zinc is 6.57 g/cm^3, [20] and the density of $CaZn_{13}$ intermetallic phase at room temperature is 6.55 g/cm^3 [21]. It is noteworthy that the further addition of calcium leads to the increase in thickness of the thickened zone. In fact, calcium acts as a thickening agent and increases the viscosity of the melt.

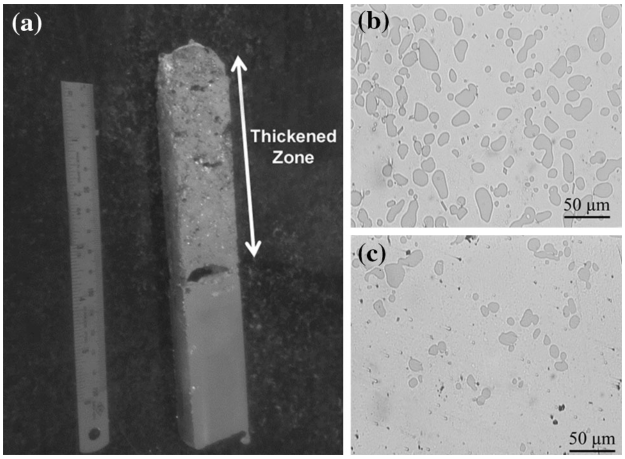

Fig. 1 Structure of solidified Zn-1 wt% Ca obtained without the addition of blowing agent: **a** macrostructure, **b** microstructure of thickened zone and **c** non-thickened zone

3.2 Influence of melt stirring

Figure 2 shows formation and inhomogeneous dispersion of ZnO oxide particles in the structure of pure zinc and Zn-1 wt% Ca after stirring at 600 rpm for 10 min. In fact, stirring not only accelerates the oxide formation, but also breaks and disperses these oxides to individual fine-size oxide particles. These particles by interactions with each other and the melt reduce the fluidity of the melt. Viscosity measurement reveals that the pure zinc viscosity increases from 4.18 to 6.12 cP after stirring at 600 rpm for 10 min. Thus, the role of oxide particles is similar to the $CaZn_{13}$ intermetallic phase.

As can be seen in this figure, oxide particles are also formed in the presence of calcium but in the lower amount. The quantification of oxide particles obtained by Image-Pro Plus image analysis software indicated that the average percentages of oxide particles in pure zinc and Zn-1 wt% Ca are 15 and 10 %, respectively. With addition of calcium to the molten zinc, it reacts with zinc and forms an intermetallic phase [22]. Hence, calcium is not free to dissolve in the melt and react with atmosphere without constraint. Therefore, added calcium cannot affect the protective film on the melt surface and raise the oxidation rate, while in the case of molten aluminum due to the presence of calcium with high oxygen affinity and the reaction of calcium with atmosphere, the compact aluminum oxide film on the surface of the melt is destructed, which leads to an increase in the melt oxidation rate [15, 16]. On the other hand, addition of calcium increases the viscosity of molten zinc. So reduction in the turbulent flow during stirring leads to a decrease in oxidation rate. For these reasons, the amount of oxide inclusions has been reduced.

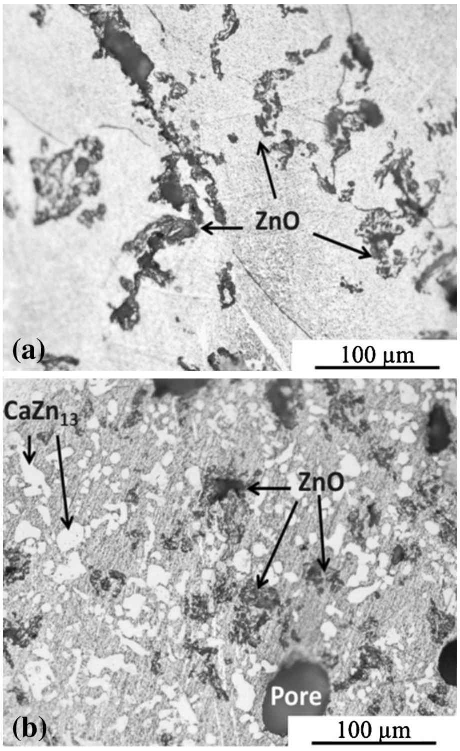

Fig. 2 Dispersion of oxide particles in the structure of: **a** pure zinc and **b** Zn-1 wt% Ca after stirring at 600 rpm for 10 min

3.3 Macrostructure of zinc foam

Figure 3 shows the macrostructure of fabricated foams with different amount of calcium. It is clear that with increase in calcium content, the thickness of the bubble-free zone decreases. This is because during the admixing of blowing agents due to buoyancy force, TiH_2 powders move to the melt surface and scatter. However, with addition of calcium and formation of a thickened zone on the surface, the blowing agent is trapped under the thickened zone. Consequently, it can interpenetrate homogenously in both zones during stirring step. It should be said that in melt foaming process using blowing agents, usually a portion of the melt is not foamed and a thick layer of metal or bubble-free zone forms at the bottom of the sample. Formation of this zone can be attributed to the obvious gravity-driven drainage during the foaming process [23, 24].

3.4 Evaluation of foaming behavior

The main parameters which are used to describe the foaming behavior are foamability and foaming efficiency.

Foamability is the ability of the system to be foamed, and it can be estimated by measuring the foam volume immediately after preparation. Since the density of metal foams is a significant parameter, changes in the density of foam can be defined as foamability. Therefore, foamability can be defined as Eq. (1):

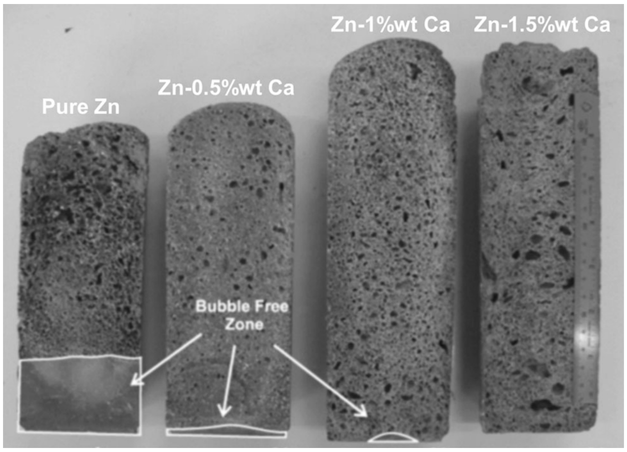

Fig. 3 Macrostructures of fabricated foams using different calcium content

$$F(\%) = \frac{\rho_s - \rho_f}{\rho_f} \times 100 \tag{1}$$

where ρ_f and ρ_s are the densities of the foam and the alloy, respectively.

Foaming efficiency can be calculated by considering the amount of remaining liquid in the bubble-free zone according to the Eq. (2) [25]:

$$\eta(\%) = \frac{m_f - m_z}{m_f} \times 100 \tag{2}$$

where m_f is the mass of total zinc foam, and m_z is the mass of bubble-free zone.

To study the effect of calcium addition on the foaming behavior of molten zinc, the foaming parameters for fabricated foams are given in Table 1. It is clear that with addition of Ca up to 1 wt%, foamability increases and density decreases, while addition of 1.5 wt% Ca leads to a reduction in foamability and an increment in foam density. This behavior implies that the extra amount of calcium suppresses the formation and growth of the bubbles which leads to the non-uniformity of the sample. As mentioned earlier with increasing calcium content, the thickness of the bubble-free zone decreases which means that the foaming efficiency increases (see Table 1).

To expose the effect of stirring on the foaming behavior of the molten zinc, after addition and dissolution of calcium in molten zinc, the melts were stirred at 600 rpm for 10 min. The foaming parameters for fabricated foams in this condition are listed in Table 2. It is evident that although stirring increases the foamability and foaming efficiency of pure zinc and Zn-0.5 wt% Ca, but has no effect on the foaming behavior of the Zn-1 wt% Ca. In

Table 1 Density, foamability and foam efficiency of fabricated foams (without stirring for 10 min after calcium addition)

Calcium conten (wt%)	Density (g/cm^3)	Foamability (%)	Foam efficiency (%)
0	2.288	212.063	78.512
0.5	1.813	293.822	Almost 100
1.0	1.507	373.789	Almost 100
1.5	1.565	356.230	100

addition, in the case of Zn-1.5 wt% Ca, stirring leads to a decrease in both the foamability and foaming efficiency.

Figure 4 shows random distribution of $CaZn_{13}$ particles in the plateau border and film between two bubbles which confirm that improvement in the foaming behavior is due to the increase in the viscosity. By formation of particles in the melt, the fluidity of the melt reduces due to the particle–particle and particle–melt interactions [26]. In fact, the existing particles slow down the drainage with creation of obstacles in the drainage path or modify the flow direction consecutively, and lead to the hindrance of downward movement. It is noteworthy that the $CaZn_{13}$ particles due to in situ production are thermodynamically stable and also have a strong interfacial bonding and good wettability with matrix [27, 28].

In the presence of calcium, the stability of bubbles is mainly improved by formation of $CaZn_{13}$ particles, while in pure zinc as shown in Fig. 5, oxide particles which are produced during stirring have a complementary role in improving the foamability. In fact, oxide particles are proper sites for porosity nucleation which improve the foamability of the melt [29]. As pointed out before, with addition of calcium up to 1.5 wt%, the foamability decreases. It should be mentioned that the reduction in foamability is related to the high-volume fraction of $CaZn_{13}$ intermetallic phase and formation of oxide particles during stirring in the melt.

An interesting point of this study is that contrary to pure aluminum, pure zinc is capable to be foamed without addition of additives or viscosity modifier. This is because the viscosity of the molten zinc (3.85–4.15 cP) is higher than that of molten aluminum (1.33 cP) at their melting points [30]. Besides, the surface tension of molten zinc is lower than that of molten aluminum. From the literature, surface tension of molten zinc and molten aluminum is 789 and 1,070 mJ/m^2, respectively [31]. As pointed out that earlier, higher viscosity could retard the drainage and escape of bubbles toward the surface of the melt and improves foamability of the melt. In contrast, lower surface tension decreases the pressure difference (i.e., ΔP in Eq. 3) which creates due to the curvature between gas–liquid films interface (r) and the surface tension (γ) [32]. The pressure difference and gravity cause the liquid to be expelled until the films become unstable. On the other hand, foams are thermodynamically unstable; therefore, by decreasing surface tension, the free energy of coalescence ($\Delta G = -2\gamma$) becomes less negative [33].

Table 2 Density, foamability and foam efficiency of fabricated foams (with stirring for 10 min after calcium addition)

Calcium content (wt%)	Density (g/cm^3)	Foamability (%)	Foam efficiency (%)
0	1.673	326.778	90.859
0.5	1.558	358.280	Almost 100
1.0	1.489	379.517	Almost 100
1.5	1.714	316.569	100

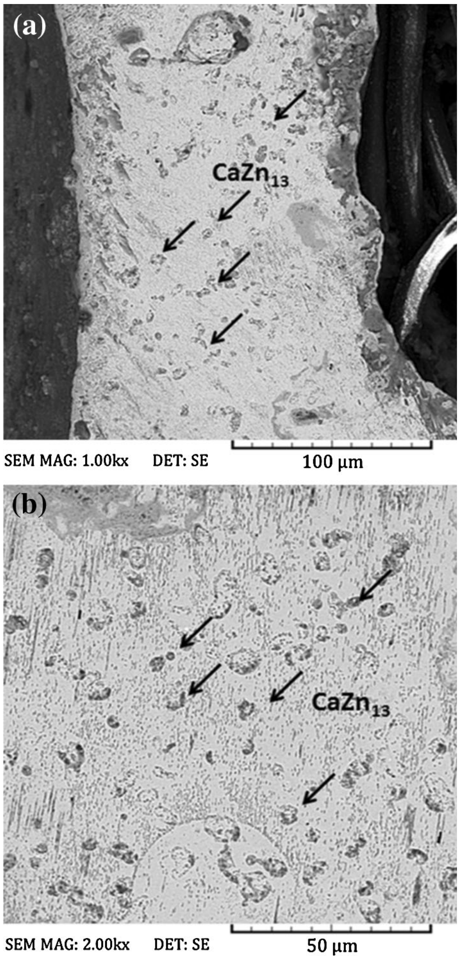

Fig. 4 Distribution of $CaZn_{13}$ particles: **a** film between two bubbles and **b** plateau in Zn-1 wt% Ca

$$\Delta P = \frac{2\gamma}{r} \tag{3}$$

It might be imagined that the foamability of pure zinc is due to the formation of $TiZn_{16}$ particles as a result of

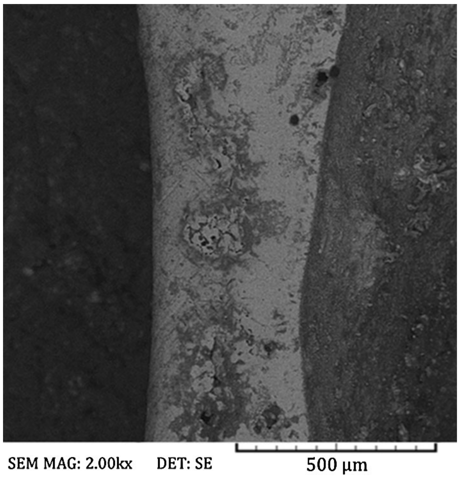

Fig. 5 SEM micrograph of the film between bubbles and distribution of ZnO particles in pure zinc after stirring at 600 rpm for 10 min

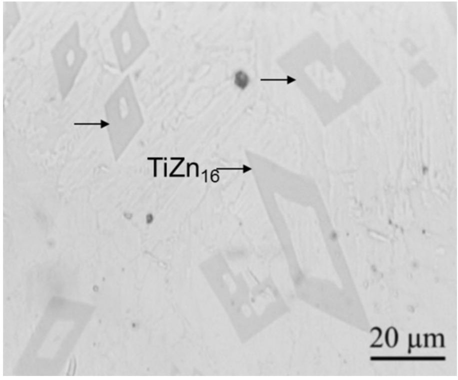

Fig. 6 Optical micrograph shows morphology and size of $TiZn_{16}$ particles as a result of decomposition of TiH_2 and reaction of titanium with molten zinc

decomposition of TiH_2 and reaction of titanium with molten zinc. Figure 6 indicates the morphology and size of these particles after addition of TiH_2 to the pure molten zinc without stirring the melt. However, as is shown in Fig. 7, there is no sign of these particles in the plateau border or in the film between two bubbles, and they are probably accumulated in the bubble-free zone. It is remarkable that in particle-stabilized foams, the film thickness is always greater than the particle diameter [34]. In this case, the minimum thickness of the film is approximately 12 µm, whereas the $TiZn_{16}$ particle diameters are bigger than the minimum film thickness (see Fig. 6). Therefore, it is clear that these particles are not involved in foaming process.

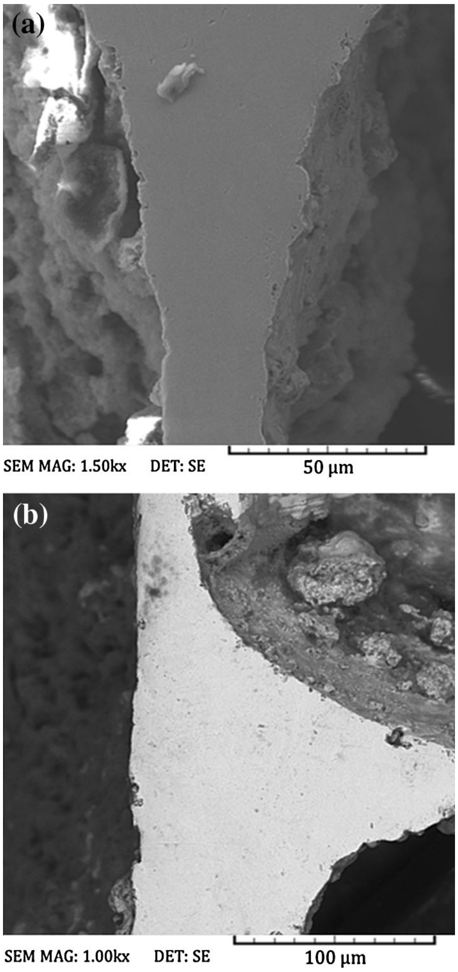

Fig. 7 SEM micrographs of **a** the film between bubbles and **b** the plateau in pure zinc without stirring 10 min

4 Conclusions

In this paper, fabrication of zinc foam using Alporas process was investigated. In this regard, the effects of calcium addition and stirring on the foaming behavior of molten Zn were studied. Results are as follows:

- Addition of calcium to the molten zinc leads to the formation of $CaZn_{13}$ particles. These particles increase the viscosity of the melt and improve foaming behavior.
- Stirring of molten zinc leads to formation of oxide particles in the foam structure. These particles by interactions with each other and the melt reduce the fluidity of the melt.
- Pure zinc can be foamed without addition of additives or viscosity modifier. This behavior can be ascribed to the high viscosity and lower surface tension of the molten zinc.

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