Production of high porosity Zn foams by powder metallurgy method

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Open-cell Zn foams with 74–92% porosity were fabricated by space holder technique, including compacting spherical carbamide granules coated with Zn powders followed by leaching the space holder and sintering. The role of compaction and sintering parameters on pore structure, cell wall integrity and compressive properties of foams was investigated. The results show that compressive yield strength and modulus of elasticity decrease with porosity and a good compatibility with Gibson–Ashby model of cellular solids is discovered. The optimum structure and mechanical properties of Zn foams are achieved by compaction at 300 MPa and sintering for 2 h at 410°C.

Keywords: Metal foam, Powder metallurgy, Space holder, Zinc, Mechanical properties

Introduction

Foams are a class of highly porous materials with a cellular structure that possess a combination of interesting properties such as very low specific weight, high stiffness and high thermal conductivity. Although polymeric foams are the most significant class of foams with extensive applications, metallic foams (MFs) expand the application range of cellular materials because of their excellent physical and mechanical properties, as well as their recyclability compared to polymeric foams. According to the connectivity of cells, MFs can be classified as either closed- or open-cell. Closed-cell MFs possess higher moduli, strength and impact energy absorption capability than their open-cell counterparts, which make them an attractive alternative for structural applications. In contrast, the high surface area of open-cell MFs exploits them in multifunctional structures such as catalysts, battery electrodes, fuel cells, sound absorbers and heat exchangers. Furthermore, in some cases, e.g. filtration, separation, heat or mass exchange, and battery electrodes there is almost no rival for open-cell MFs.

Several methods utilized for production of MFs fall into four broad classes: (i) liquid phase processing (ii) solid state processing (iii) gas/vapour state processing (iv) electro-chemical deposition. Each method can be applied to a small subset of metals to make a cellular metallic structure with a limited range of densities and cell sizes. Among these methods, solid state processing is a versatile method based on powder metallurgy (PM) which offers numerous advantages and has gained a lot of interest in the recent decade. In a well known PM process developed at the Fraunhofer Institute in Bremen (Germany), a MF is fabricated by consolidation of a metal powder with a particulate foaming agent (typically TiH₂) followed by heating near the melting point when the foaming agent releases hydrogen, expanding the material. This process has been successfully used for production of Al, Fe, Sn, Pb and Au foams by choosing appropriate foaming agents and process parameters. The produced foams have closed cells with cell size of 1–5 mm. An alternative PM route for the production of open-cell MFs is based on co-pressing of a metal powder with a leachable powder (space holder) followed by removal of the space holder to leave a porous metallic network. A final sintering step can be applied to further densify the MF skeleton. The use of space holders allows for simple and accurate control of shape, size, fraction and connectivity of pores. The cell size is determined by the space holder particle size, and usually lies in the range 10 μm–10 mm. Ceramics, polymers, salts, or even metals can be used as space holders. Among the various space holder materials mentioned, carbamide (urea) is preferred since it is inexpensive, extensively available as spherical granules and easily leachable by water. The ‘carbamide space holder’ technique was firstly used for fabrication of high-porosity titanium, stainless steel and superalloy parts by Bram et al. and now it has been extended for Al, Mg, Ti alloys and alloyed steels.

Although numerous investigations have been focused on foam manufacturing of various metals, foaming of low melting temperature metals such as Zn has been inadequately noticed. Zn foam has shown promising application potential in filling hollow steel sections, battery electrodes and fuel cells. Chethan et al. have prepared Zn foams by mixing Zn powder with TiH₂ followed by hot pressing and heating above the melting temperature. Kovacik and Simanick have used TiH₂...
or MgH as a foaming agent for the production of Zn or ZnAlCu foams via cold isostatic pressing, hot extrusion and heating. The Zn foams were developed by consolidation of emulsified Zn suspensions by Drillet et al. Recently, microporous Zn foams have been prepared using electrodeposition. However, to the best of our knowledge, there is no report on the production of Zn foams by space holder method. Here, we have fabricated highly porous open-cell Zn foams using ‘carbamide space holder’ technique. The main factors affecting the cell structure and compressive strength were investigated and optimised to achieve the highest porosity with acceptable mechanical properties for specific applications such as battery electrodes or fuel cells.

**Experimental methods**

Commercial purity Zn powder (Sigma Aldrich) with a particle size of less than 10 μm was used as starting material. Narrow size distributions of carbamide particles with various sizes in the range of 0.5–2 mm were achieved by sieving and used as the space former. It should be noted that in order to appropriate coating of the surfaces of carbamide granules by the Zn powders, the size of space former granules should be much larger than that of the metallic powders. The Zn-to-carbamide weight ratios were calculated to obtain porosities ranging from 74 to 92% in the sintered compact. Ethanol was used as a binder for overcoming the difficulty of adhering Zn powders to the carbamide particles and its amount was optimized to ensure powder sticking to the granules while preventing the agglomeration of the granules. Figure 1a shows spherical carbamide granules before and after coating by Zn particles.

The Zn coated carbamide granules were uniaxially compacted under 200, 300 and 400 MPa into cylindrical samples with 20 mm diameter and approximately 16 mm height. Carbamide was leached out from green samples by putting them in cold water for 5 h. After drying at 90°C, sintering was conducted at 320–410°C in a tube furnace under protective argon atmosphere for 2–4 h. A typical image of a fabricated Zn foam is depicted in Fig. 1b.

The porosity of fabricated foams $P_f$ can be estimated by

$$P_f = 1 - \frac{\rho_f}{\rho_s}$$

where $\rho_f$ and $\rho_s$ are the densities of the green foam and fully dense Zn (7.14 g cm$^{-3}$) respectively. The density of the Zn foams, $\rho_f$, was determined by measuring their weight and dimensions.

The structure of the foams for inspection of the cell wall microstructure and cell morphology was studied by an Olympus BX61 optical microscope (OM) and a LEO SUPRA 35VP field emission scanning electron microscope (FE-SEM). For optical microscopy, the foams were mounted in plastic resins and prepared according to the conventional route in metallography procedure.

Mechanical characterisation of the foams was carried out by compression test at room temperature. The traverse cross-head speed of the testing machine was 0.9 mm min$^{-1}$. Before testing, both face surfaces of the samples were ground, polished and lubricated in order to minimize friction between the sample and the cages. The yield strength and modulus of elasticity were determined by 0.2% offset method and from the initial slope of the stress–strain curve respectively.

**Results and discussion**

‘Carbamide space holder’ technique was successfully used for the production of open-cell Zn foams with various porosities up to ~92%. Foams with higher porosities were not achievable because green strength was not sufficient to maintain the foams intact during the ejection from the mould. A typical pore structure of Zn foams is shown in Fig. 2a. The foams are characterized by a homogenous distribution of pores throughout them and a good interconnection of the pores. The cell walls of Zn foams demonstrate a dense microstructure so that the boundaries between the original Zn particles are not visible (Fig. 2b) revealing a complete densification during sintering.

A typical compressive stress–strain curve of Zn foam (Fig. 3) can be demonstrated in three stages:

(i) elastic region
(ii) plastic collapse
(iii) final densification.

The initial stage in the loading curve is the elastic region with approximately linear deformation where yielding occurred. Through the second stage, the pores are compressed and distorted and the stress level is maintained at a relatively constant value until a definite amount of pore collapse, i.e. the extended collapse plateau. Thus, the energy absorption can be observed in this region, which is the most imperitive characteristic of MFs for structural applications. It is pertinent to point out that in metallic foams, brittle or defective cell walls are elastically collapsed just at their strength without strain hardening in the local band, resulting in the discontinuous deformation with stress fluctuation. At the third stage, stress starts to increase considerably...
in view of the fact that the material behaviour changes to a bulk material behaviour under compression. It should be noted that metals with a high specific strength (strength-to-weight ratio) such as Ti (288 kN m kg⁻¹), Al (214 kN m kg⁻¹) and Mg (158 kN m kg⁻¹) are more favourable than Zn (39 kN m kg⁻¹) for structural, load-bearing parts. However, Zn, which is preferred for functional applications such as battery electrodes or fuel cells, should have a minimum threshold compression strength and elastic modulus. Thus, the initial elastic stage is of the utmost importance in Zn foams and we have mostly focused on this region.

3 Representative compressive stress–strain curve of Zn foam with ~92% porosity

4 Compressive stress–strain curves of Zn foams with 74.1, 82.3 and 92.1% porosities

5 Plots of a relative modulus of elasticity versus relative density and b relative compressive yield strength versus relative density³²
Loading curves of Zn foams with 74.1, 82.3 and 92.1% porosity are shown in Fig. 4. Stress fluctuations in all curves were small, which can be attributed to good cell wall integrity and reduced instances of localised cell wall failures. It can be determined from Fig. 4 that a higher foam porosity presents a lower compressive yield strength ($\sigma_f$) and modulus of elasticity ($E_f$) as well as lower stress fluctuation. Figure 5 demonstrates the variations of the normalized modulus of elasticity ($E_f/E_s$) and compressive yield strength ($\sigma_f/\sigma_s$) of the foam with relative density ($\rho_f/\rho_s$), where, $\sigma_s$ and $E_s$ are compressive yield strength and modulus of elasticity of bulk Zn respectively. The data of relative modulus of elasticity as a function of relative density (Fig. 5a) were fitted to the Gibson–Ashby empirical equation for open-cell foams, expressed by

$$\frac{E_f}{E_s} = \left(\frac{\rho_f}{\rho_s}\right)^{2}$$

(2)

As it is clear from Fig. 5a, there was a good agreement between the experimental data and Gibson–Ashby model. A similar relationship has been developed for the normalised yield strength expressed by

$$\frac{\sigma_f}{\sigma_s} = f \left(\frac{\rho_f}{\rho_s}\right)^{3/2}$$

(3)

where $f$ is a density coefficient. By linear fitting the experimental data with equation (3) (Fig. 5b), $f$ value was obtained 1.91. The density coefficient is larger than those reported for pure Ti and Ni alloy foams that can be explained by the formation of denser cell walls in Zn foams, as shown in Fig. 2.

It is well known that compaction pressure has a significant effect on the bonding between metal powder particles formed in the subsequent sintering step. At compaction pressures lower than 200 MPa, the green strength of samples was very low and they were not remained intact during carbamide leach out. On the other hand, increasing the compaction pressure to 400 MPa leaded to severe deformation and even crushing of the carbamide granules, hence the pores became elliptical (Fig. 6a) and some of the cell walls were crushed or cracked (Figs. 6b and c). Owing to
intense friction between the foam and die walls at high compaction pressures, the pores near the outer surfaces were clogged (Fig. 6d). This can noticeably decrease the connection of the pores and thus capability of an open-cell MF. The appropriate compaction pressure was determined to be 300 MPa in that the Zn foams preserved their original shapes with sharp edges without any detrimental damages.

It can be inferred from the compressive stress–strain curves of Zn foams consolidated at various pressures (Fig. 7) that increasing the compaction pressure from 200 to 300 MPa significantly increased the compressive strength and modulus of elasticity, but the improvement in the mechanical properties was not profound by increasing the compaction pressure to 400 MPa. Moreover, at high compaction pressures, stress fluctuations were detected in the plastic deformation region (Fig. 7) which can be attributed to a poor cell wall integrity, as shown in Figs. 6b–d.

Carbamide should be removed from the compacted foams before the sintering stage. While carbamide is extremely soluble in water, it was usually eliminated from Zn foams by water leaching. It has been shown that improper removal of the carbamide promotes the possibility of cracking in the foams during sintering stage.13 Moreover, the remained carbamides decompose during sintering at temperatures higher than about 150°C. Measuring the weight of Zn foams before and after sintering showed a slight decrease in their weight, revealing incomplete dissolution of carbamides during water leaching step. On the other hand, since the weight of Zn foams after sintering was the same as that of Zn powder in compacts, thus the carbamides were completely removed during sintering.

It is documented that selection of an appropriate sintering temperature is imperative in densification and the formation of effective bondings between Zn particles. Both solid-state sintering and liquid phase sintering have been employed for densification of MFs.25 Figure 8 shows SEM images of Zn foams with ~92% porosity sintered at various temperatures. It is evident from Figs. 8a and b that densification of the foams sintered at 320°C (0.86 $T_m$) and 360°C (0.91 $T_m$) were not completed. This can be understood not only from the slight change in spherical morphology of Zn particles, but also from the relative neck-to-powder size ratio, which is obviously lower than 0.3. SEM observation of the inner surfaces of foam cell walls sintered at 410°C (0.99$T_m$) (Fig. 8c) revealed a large number of bondings between Zn particles, i.e. near-complete densification. It is pertinent to point out that since high compaction pressures are not applicable for fabrication of MFs by space holder technique, higher sintering temperatures are required compared to bulk metals to compensate the low driving force for diffusion of atoms.

Inspection of compressive stress-strain curves in Fig. 9 discloses that increasing the sintering temperature from 360 to 410°C had a notable effect on enhancing of compressive strength and modulus of elasticity. Stress...
fluctuation was also decreased at the higher sintering temperature. In fact, partial sintering and the presence of micropores in the foam sintered at a lower temperature obviously deteriorate the mechanical properties by reducing the load bearing cross-sectional area of the pore walls. In spite of the significant role of sintering temperature, it is clear from Fig. 9 that increasing the sintering time from 2 to 4 h at a constant temperature of 410°C had a slight influence on compressive strength and modulus of elasticity. However, the stress fluctuation appeared at prolonged sintering mainly due to the partial oxidation of Zn. Thus, the optimum sintering temperature and time for production of Zn foams was determined 410°C and 2 h respectively.

Conclusions

Open-cell Zn foams with porosities between 74 and 92% have been successfully produced via a powder metallurgy route based on using carbamide as a space holder. The high porosity foams (~92%) exhibited appropriate strength and modulus enough for common applications of open-cell Zn foams such as batteries and fuel cells. The pore morphology and cell structure were controlled by compaction pressure, but the applying of high pressures was limited due to deformation or crushing of the pores. It was shown that Zn foams required higher sintering temperatures compared to Zn bulk bodies so that the highest compressive strength and modulus of elasticity of the foams were achieved at temperatures near to the melting point of Zn (0.997 T\text{m}). Nevertheless, prolonged sintering (>2 h) had not a considerable positive effect on mechanical properties.

References