Fabrication, microstructure and compressive behavior of ZC63 Mg–microballoon foam composites

A. Daoud a,*, M.T. Abou El-khair a, M. Abdel-Aziz a, P. Rohatgi b

a Composites Materials Laboratory, Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87, Helwan, Cairo, Egypt
b Composites Materials Department, CEAS, University of Wisconsin, Milwaukee, WI, USA

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Abstract

ZC63 Mg alloy-fly ash microballoon foam composites were fabricated by melt stir technique with the use of fluxes. The influence of various processing parameters such as melt temperature, type and dimensions of the stirrer, pouring temperature and mould type on distribution of the fly ash microballoons in the Mg matrix alloys was presented. Density measurements of the composites revealed that the addition of fly ash microballoons significantly reduced the density of the composites. As the volume fraction of microballoons increased, the density of the composites decreased. Composites in the as-cast condition exhibited smaller dendrite arm spacing/cell size compared to unreinforced ZC63 Mg alloy. The average dendrite arm spacing/cell size of the composites was about 10 µm compared to 100 µm of the unreinforced magnesium alloy. The microstructure of the composites demonstrated even distribution of the microballoon in the Mg alloy matrix and there was no sign of fly ash cluster or residual porosity. Also, it was observed that there were some fly ash microballoons filled with Mg matrix alloy. SEM micrographs showed those fly ash microballoons, eutectic phase and other intermetallic compounds segregated at the magnesium cell boundaries. Examination of the composite interface indicated that the eutectic and other intermetallic compounds phases were able to heterogeneously nucleate on the fly ash microballoons. SEM, XRDA and EDXA of the composites showed clear evidence of reaction product at fly ash/matrix interface. On the basis of XRDA and EDXA, composition, structure and thermodynamic analysis, the main interfacial phase between the fly ash and ZC63 Mg alloy was identified as MgO. The compressive properties of the foam composites were characterized. The foam composites produced in the present work demonstrated typical behavior of an elastic-plastic foam material in compression. They had an initial linear elastic region, followed by a long region of deformation at a relatively flat stress level. The composites containing microballoons up to 20 vol% significantly revealed higher energy absorption in comparison to the solid ZC63 matrix alloy or the composite containing 25 vol% microballoons.

Keywords: A. ZC63 Mg; A. Fly ash; A. Microballoons; A. Foam; A. Composites

1. Introduction

Recently, metal foams, as new functional materials, are extensively researched and developed [1]. Because of their characteristics of porous structure, metallic nature and low density, they possess a lot of excellent functional properties, such as vibration reduction, sound absorption, fire proofing and good permeability [2,3]. The mechanical properties of the metal foams can be engineered to meet the demands of a wide range of applications by altering the size, shape, and volume fraction of cells [4].

In the closed cell metal foams the cellular structure is typically disordered due to wavy distortions of the cell walls, cell wall thickness variation, and non-uniform shape and size of the cells [5,6]. These lead to anisotropic properties, making it difficult to predict the foam’s performance characteristics. These non-uniformities can be overcome through producing foam composites by incorporating preformed microballoons which have uniform cell size and...
wall thickness. Also, the microballoons can be arranged into a dense arrangement of repeatable cell structure.

The foam composites can be made by incorporating carbon, glass, and alumina microballoons into metallic matrices [7–10]. Since the microballoons have lower density than the matrix, the density of the foam composite is significantly reduced by incorporating microballoons in the matrix. Such an approach permits the design of ultra-light and stiff components. These materials have excellent thermal insulation properties due to the fact that ceramic microballoons are commonly used to make such composites and these microballoons have a lower thermal conductivity as compared to that of a metallic matrix. The thermal expansion coefficient of these foams is much lower than that of the matrix material. Foam composites are attractive materials for energy absorbing applications and are likely to possess unique properties such as high energy damping capacity [11]. Moreover, foam composites have advantages in uniformity, isotropy, and mechanical properties that allow for consistency in engineering design applications.

In the last few years, considerable development has occurred in the potential use of cast metal matrix composites for many applications. However, cost still remains a major barrier in the wide spread use of metal matrix composite components in industry. One of the options to decrease the cost of the metal matrix composites is to decrease the cost of reinforcements or use low cost reinforcements. One of the opportunities to reduce the cost of composites is to use fly ash microballoons a by-product coal-fired power plants as a reinforcements in metal matrix composites. Currently, huge quantities of coal combustion by-products are generated world wide. Many of the fly ash particles are solid (precipitator ash) and some of them are hollow referred to as microballoons with very low densities. The fly ash microballoons are spherical in shape and sphericity is close to 100%. The fly ash microballoons have true density of 0.4–0.6 g/cm³ similar to expensive microballoons of glass, carbon and ceramics, providing an opportunity of producing low-density composites. Therefore, fly ash microballoons are extremely attractive materials because of their relatively lower prices and interesting physical and mechanical properties [12,13].

Magnesium alloys are raising more interest for the industrial applications due to their relatively low density, good damping capacity, castability and machinability [14–16]. Magnesium matrix based composites satisfy the demands for low density, good mechanical properties, high wear resistance and low thermal expansion, and have great potential in automotive, high performance defense and aerospace applications. In spite of that only a few studies have been reported for magnesium matrix composites compared with aluminum matrix composites.

The interfacial microstructure between the matrix and reinforcement plays an important role in determining the properties of the composites, especially for magnesium matrix composites, due to the high reactivity of Mg. The nature of the interface of Mg alloys based composites depends on a variety of factors, such as: the composition of the Mg matrix alloy; the composition and the nature of the surface of the reinforcement; the fabrication techniques; and the thermal treatment conditions applied to the composites [17,18].

Accordingly, the present paper reports on the use of stir casting process for the fabrication of ZC63 Mg reinforced with different volume fraction (10, 20 and 25 vol%) of fly ash microballoons with the use of flux. The aim of the present investigation was to characterize the cast foam composite microstructure and study the interfacial microstructure in the composite, with particular emphasis on the phase identification of the reaction products and the formation mechanism of the reaction products. The compressive properties of the foam composites, including yield stress, plateau stress and strain, and compressive strength were measured.

2. Experimental procedure

ZC63 Mg alloy-fly ash microballoon composites were processed by melt stir technique. The melting was carried out using a resistance heating furnace. Crucible with a capacity to hold 2 kg of Mg was used for melting Mg and subsequent processing of composites. The main chemical constitutes of fly ash microballoons in wt% is SiO₂ 61%, Al₂O₃ 25%, Fe₂O₃ 5%, MgO 1.6% and TiO₂ 1%. Based on the chemical compositions of Mg-6% Zn-3% Cu and 0.5% Mn (alloy ZC63), commercially pure Mg, Zn, Cu and Mn were selected to prepare the matrix alloy. The desired volume fraction of fly ash microballoons with 100 µm average size and density of 0.6 g/cm³ was added manually into the vortex formed by stirring on the surface of melt. The density of the composites was determined using Archimedes’ method, with ethanol as the suspending medium. A precision research balance (resolution 0.00001 g) was used throughout. The theoretical density value of the composite was calculated using rule of mixture: \[ \rho_c = \rho_p + \rho_m (1-V_p) \]

where \( \rho_c \) = density of the composite, \( \rho_p \) = density of the fly ash microballoons, \( \rho_m \) = density of the matrix, and \( V_p \) = volume fraction of the fly ash microballoons.

Optical microscopy was used to reveal the microstructural features and the distribution of the fly ash microballoons. Compositional spot analyses were performed in and around the microballoons using an energy dispersive X-ray analysis (EDXA) facility in the SEM. X-ray diffraction analysis (XRDA) was carried out to identify the phases in the matrix alloy and composite.

Compressive testing of the foam composites was conducted at room temperature using samples having a height of 20 mm and diameter of 10 mm. The specimens were compressed in a computer controlled Schematzue/UHF Tester at the crosshead speed of 0.5 mm/min. To evaluate the compressive properties of the foam composites, the yield stress, plateau stress and compressive strength were measured. After compression testing, fractured specimens were examined by SEM. The microstructural damage...
associated with the deformation was examined on longitudi-
dinal polished surface through the fracture.

3. Results and discussion

3.1. Foam composites preparation

The composites were processed by melt stir technique. The procedures employed for the fabrication of composites were as follows. About 1 kg of magnesium and alloying elements were placed and melted in the crucible. During melting, the Mg melt was covered with flux. This was done to minimize contact between the atmospheric oxygen and Mg metal and, therefore, prevent oxidation and burning of magnesium metal. Melt temperature is an important process parameter. An optimum temperature of the melt is the ideal for fly ash microballoons dispersion. Higher melt temperatures result in severe erosion of the stirrer, excessive chemical attack of the fly ash microballoons by the melt, gas pick up and oxidation and burning of magnesium metal. On the other hand, too low melt temperatures invariably lead to difficulty in fly ash microballoons dispersion. The temperature was monitored and controlled closely and care was taken to maintain the melt temperature around 700 °C. At this temperature, the Mg alloy was melted with very little oxidation. Before stirring, the temperature of the molten Mg alloy was further lowered to 650 °C and then the flux was removed. This was quickly followed by stirring the melt by rotating impeller. During this period, very little burning was observed on the surface of the melt. The melt was stirred with the surface of the molten Mg metal being protected by nitrogen gas. The stirrer was positioned just below the surface of the melt. Then the fly ash microballoons were added manually to the vortex formed on the surface at a rate of approximately 30 g/min and a stirring speed of 700 rpm. The stirrer type, dimensions and position play an important role in the suspension of the fly ash microballoons in the melt. Total suspension of the fly ash microballoons is necessary for obtaining a good dispersion. The type and dimensions of the stirrer depend on the melt pool height to diameter ratio. In this work, the melt pool height to diameter ratio was about unity. Hence, three-blade stirrer was found effective. The stirrer was designed to move close to the wall of the crucible in order to induce a high shear and create a vortex for dispersion of the fly ash microballoons in the melt. Many of the attempts to prepare these composites by stirring melts at low speeds (200–500 rpm) were unsuccessful. The stirring speed was insufficient and the vortex was very shallow. At higher stirring speed (700 rpm), the vortex formed (for the dimensions of the crucible used in the present investigation) was sufficiently deep and the extent of agitation was adequate to provide shearing action and ensure total suspension of the fly ash microballoons in the melt. The pouring temperature of the liquid composite has a major effect on the distribution of the fly ash microballoons in the cast composite. As the pouring temperature was increased, the time allowed for the fly ash microballoons to float up prior to solidification increased. Hence, with the increase in the pouring temperature, there was the possibility that the fly ash microballoons floated in the cast ingot. As the temperature was decreased, the viscosity of the melt increased. Hence, it made difficult for the melt to be poured. Therefore, the pouring temperature was set at 50 °C above the Mg alloy liquidus temperature (685 °C). Prior to pouring, the melt was carefully skimmed. The thermal gradient setup in the mold and the cooling rate of a casting depend upon the mold material. Materials with greater capacity for heat extraction exhibit steeper thermal gradients and faster heat dissipation. Therefore, the composite slurry was cast into cast iron mold to obtain uniform microballoon distribution in the matrix and a fine microstructure owing to the relatively fast cooling rate obtained in metallic mold. The mould was heated to a temperature of 200 °C before pouring to prevent chilling effect on the mold surface and, therefore, get a good surface quality of the cast composite. The liquid composite was poured into a preheated cast iron rectangular mould of 30 × 40 mm and 300 mm height dusted with sulfur powder to minimize oxidation. The material loss incurred by this method was less than 5 wt%.

3.2. Density

The average density measured for the ZC63 alloy and composites is presented in Table 1. It can be noted that the addition of fly ash microballoon significantly reduces the density of the composites. As the volume fraction of microballoons increases, the density of the composites decreases. From Table 1, it can be seen that there is about 0.1% porosity in the unreinforced alloy. However, the measured density of the composites is higher than the calculated. This is attributed to the filling of some fly ash microballoons with Mg matrix alloy. The infiltration of Mg alloy into the inner hollow space of the fly ash microballoon is undesirable because it increases the density of the Mg–microballoon composite.

3.3. Microstructure

Visual inspection of machined surface of the cast Mg–fly ash composite showed uniform distribution of fly ash microballoons throughout the casting. Casting defects were not noticed on the casting surface. The microstructures of the reinforced and unreinforced materials in as-cast condition are shown in Fig. 1. The microstructure of unreinforced material in Fig. 1a consists of α-Mg and Mg(Zn,Cu)2 eutectic phase, Cu₉Zn₈ and CuMnZn at the interdendritic regions as can be seen in XRDA, Fig. 2a. Fig. 1 b–e shows the microstructure of the ZC63 Mg–fly ash microballoon composites. The microstructure exhibits round dark fly ash microballoons with an average microballoons size of 100 μm dispersed in the Mg alloy matrix of light phase. The microstructure demonstrates even
distribution of the microballoons in the Mg alloy matrix and there is no sign of fly ash cluster or residual porosity. It can be observed that there are some microballoons filled with Mg matrix alloy. From the microstructure of the ZC63 alloy and its composites in Fig. 1, it can be noted that ZC63 exhibits typical dendritic structure where ZC63-fly ash composites show cellular dendritic structure, Fig. 1f. It is possible that the presence of reinforcement change the morphology of the growing interface from dendrite in Mg alloy into cellular-dendrite interface in Mg-fly ash composite. Similar change in morphology of interfaces during solidification of Al based composites has been reported [19,20] and this has been attributed to changes in temperature gradient and or convection in the melt during solidification. From Fig. 1 it can be seen that there is a marked difference in the dendrite arm spacing (DAS)/cell size of

Table 1
Average density of ZC63 matrix alloy and foam composites

<table>
<thead>
<tr>
<th>Alloy</th>
<th>ZC63</th>
<th>ZC63-10 vol% fly ash</th>
<th>ZC63-20 vol% fly ash</th>
<th>ZC63-25 vol% fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured density (g/cm³)</td>
<td>1.85</td>
<td>1.8</td>
<td>1.68</td>
<td>1.57</td>
</tr>
<tr>
<td>Theoretical density (g/cm³)</td>
<td>1.87</td>
<td>1.73</td>
<td>1.6</td>
<td>1.54</td>
</tr>
<tr>
<td>Relative density (ρ_foam/ρ_matrix)</td>
<td>1</td>
<td>0.97</td>
<td>0.9</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Fig. 1. Optical microstructure of ZC63 Mg alloy matrix and composites (a–d) and magnified view showing the interface between the ZC63 Mg alloy and microballoon (e, f).
composite compared to ZC63. DAS/cell size of all the composites prepared in the present work is much smaller than that of the unreinforced ZC63. The average dendrite arm spacing/cell size of the composites was about 10 μm compared to 100 μm of the unreinforced magnesium alloy.

It is noted that the fly ash microballoons, eutectic phases and other intermetallic compounds are rejected to the cell boundaries of the magnesium matrix. This suggests that during solidification process of magnesium based composite, fly ash microballoons were pushed by the primary magnesium phase into the last freezing regions, then entrapped in this area. On the other hand, during the cooling process of magnesium melt, the solutes such as Cu, Zn, Mn were also rejected into the lasting freezing magnesium melt due to their low solid solubility in magnesium. Then the solutes rich magnesium melt resulted in the eutectic reaction. This made the fly ash microballoons and eutectic phases mixed and segregated at the magnesium cell boundaries. It is normally expected that the surfaces of ceramic microballoons suspended in solidifying melts would be favorable sites for heterogeneous nucleation. However, the solidification microstructures of magnesium composite show that primary magnesium phases can not heterogeneously nucleate at the microballoon surfaces and push the microballoons as they grow until they impinge on neighboring dendrites and entrap the microballoons in the cell boundaries. It is well known that the thermal properties mismatch between the reinforcement and the matrix melt is one of the most important factors for the heterogeneous nucleation of primary phase. The thermal conductivity and heat diffusivity of fly ash microballoons are less than those of magnesium melt [21]. Thermal diffusivity represents a measure of the disappearance of temperature gradient within the material. Hence, if the temperature of fly ash microballoons in magnesium melt is equal to that of the surrounding magnesium melt before composite casting, then during the cooling process the temperature of fly ash microballoons will be somewhat higher than that of the surrounding magnesium melt. The hotter fly ash microballoons would heat up the surrounding magnesium melt, and thus delay the solidification process of the surrounding melt. In addition, the latent heat of fusion released during solidification of the matrix will reduce the cooling rate of the fly ash microballoons, resulting in temperature gradients such that the fly ash microballoons and the melt in their vicinity will continue to be hotter than the melt away from the fly ash microballoons. In such a case, it is very difficult for primary magnesium phase to nucleate at the fly ash microballoon surfaces. From the above, it can be concluded that the refinement effect of fly ash microballoons is attributed mainly to the restricted growth of primary Mg crystals by the fly ash microballoons.

From Fig. 3a and b, it can be seen the eutectic phase and other intermetallic compounds at the surface of the fly ash microballoon. This suggests that eutectic phase and other intermetallic compounds could nucleate on the fly ash microballoon surface. This process of nucleation results in a partial modification of the eutectic phase, Fig. 3c and d. These observation can be explained by the thermal lag model previously proposed: the growth of the α-Mg nuclei at a distance away from the microballoons leads to enrichment of solutes in the remaining melt. The α-Mg solidification front progresses between the microballoons and this results in the liquid in contact with the microballoons to be the last one to solidify at the microballoons. Therefore, eutectic phase and other intermetallic compounds solidify at the fly ash microballoon surface.

3.4. Interfacial reaction

The interfacial microstructure between the Mg alloy matrix and reinforcement plays an important role in the properties of the composites based on Mg alloys due to the high reactivity of Mg. Since the interfacial characteristics are influenced by many factors, there is a large range of possible interface conditions in Mg-fly ash composites. Figs. 1e and f and 3a and b show micrographs of interface between fly ash microballoons and ZC63 matrix alloy. It can be seen that the interfacial phases are continuously and evenly distributed at the fly ash /matrix interface, growing from the fly ash microballoon surface into Mg matrix. The thickness of the phase is about 10 μm. Fig. 4a and b shows the EDXA spectra for matrix and fly ash/matrix interface, respectively. The Mg, Zn and Cu peaks from matrix and Mg, Zn, Cu, Al, Si and O peaks from fly ash/matrix interface can be noted from the EDXA results. The ZC63-fly ash composite system can be
considered as an Mg–Al–Si–O system, the possible reaction products that can form at the interface of ZC63-fly ash composite are MgAl₂O₄, Mg₂Si, and MgO, etc. Because the Mg–O, Al–O, Cu–O and Si–O bonds are significantly stronger than the Al–Mg and Mg–Si bonds [22], oxide phases should form in preference to other possible compounds, such as Mg₂Si and Mg–Al, until all of the available oxygen is consumed. Among the possible oxides, the formation free energy for MgO is lower than that of MgAl₂O₄, CuO or CuAl₂O₄ [23]. The study on thermodynamic stability of Al–Mg oxides in Al–Mg alloys [24] shows the formation of MgAl₂O₄ and MgO are competitive processes, with preferential MgO formation for high Mg content (more than 7%). These thermodynamic considerations show that the most stable oxide in Mg based composite is MgO. On the basis of composition, structure, thermodynamic analysis and the XRDA and EDXA, the main interfacial phase between the fly ash and ZC63 Mg alloy could be identified as MgO. The presence of Cu at fly ash /matrix interface (Fig. 4b) could be explained by the formation of cupric aluminate (CuAl₂O₄) at the microballoon surface. But, the formation of CuAl₂O₄ at fly ash/matrix interface may be hindered by the Mg that preferentially reacts with O to form MgO.

3.5. Compressive properties

The compression stress–strain behavior of the ZC63 matrix alloy and foam composites is illustrated in Fig. 5. The composite samples containing 10 and 20 vol% microballoons exhibit typical behavior of an elastic-plastic foam material in compression [25]. They have an initial linear elastic region, followed by a long region of deformation at a relatively flat stress level. On the other hand, solid ZC63 matrix alloy and composite containing 25 vol% microballoons do not exhibit the same behavior. Table 2 presents the compressive properties of the investigated materials. Generally speaking, the compressive properties of the foam composites are lower than that of the matrix alloy.

Usually, the composite strength is increased by the presence of solid particles dispersed in matrix material. This is attributed to: the transfer of stress from the matrix to the reinforcements, the difference in texture between the composite matrix and the matrix material without reinforcement, the reduction in composite grain size, and the generation of a high dislocation density in the matrix as a result of the difference in thermal expansion between the metal matrix and the reinforcement [26–28]. Load transfer is the major mechanism affecting the strength of the composite; the other mechanisms are very small. However, the present work shows that the compressive strength values of the composite are lower than those obtained from the unreinforced alloy. This can be attributed to the fact that microballoons have strength lower than the matrix strength.

In metal matrix composites, when the Young’s modulus of the particles present in the matrix is higher than that of the metallic matrix alloy, the composite is expected to have a higher modulus than that of unreinforced alloy. However, when microballoons having lower Young’s modulus than that of the metallic matrix alloy are present (like in
the present work), the composite is expected to have a lower modulus than that of the matrix alloy as can be seen in Table 2.

From Fig. 5, it can be noted that at approximately strain of 10% and 15%, the foam composites of 10 and 20 vol% microballoons, respectively, approach densification as the microballoons are completely collapsed. The average plateau stress is about 200 MPa for composite sample containing 10 vol% microballoons and 260 MPa for composite sample containing 20 vol% microballoons. It should be mentioned that for cushions or impact mitigation, the plateau stress is important design factor because it represents the onset of the mechanical instability of foam composites. It can be observed from Fig. 5 that higher plateau stress can be obtained by increasing volume fraction of microballoons in the matrix up to 20%. Also, it can be noted from Fig. 5 that a larger plateau strain range is likely to be attained by increasing volume fraction of microballoons in the matrix up to 20%.

Generally, the modulus of elasticity for composites containing microballoons or foam materials is expressed in terms of the relative densities of the composite and matrix, as shown in Eq. (1) [29,30]

$$E_{\text{foam}} = E_{\text{matrix}} \left( \frac{\rho_{\text{foam}}}{\rho_{\text{matrix}}} \right)^2$$  \hspace{1cm} (1)

where $E_{\text{foam}}$ and $E_{\text{matrix}}$ are the modulus of the composite and the matrix, respectively, and $\rho_{\text{foam}}$ and $\rho_{\text{matrix}}$ are the densities of the composite and the matrix, respectively. The measured and theoretically calculated modulus values of the composites are given in Fig. 6. It can be seen that the predicted values are in good agreement with experimental results. However, the measured modulus value of the foam composite containing high microballoons volume fraction (25 vol%) is slightly higher than the predicted. This is due to the presence of the fly ash microballoons which increases the modulus of foam composite materials in comparison to conventional foam materials [30]. It is expected that the composite containing ceramic microballoons exhibits a higher modulus than that of foam materials having only pores without ceramic microballoons.

Attempts to predict the compression yield strength of the foam composites with models developed for foam materials, e.g.

$$\sigma_{\text{foam}} = 0.3 \sigma_{\text{matrix}} \left( \frac{\rho_{\text{foam}}}{\rho_{\text{matrix}}} \right)^{1.5}$$  \hspace{1cm} (2)

where $\sigma_{\text{foam}}$ and $\sigma_{\text{matrix}}$ yield strength of the foam composite and matrix alloy, respectively [29], lead to significant underestimation of compression yield strength of the foam composites since these models do not take into account the strengthening effect of the ceramic microballoons. It has been noted that composites containing microballoons (like in the present work) have a higher compression yield strength compared to other foam materials reported in the literature [31,32]. As can be seen from Eq. (2), compression strength of foam is primarily related to density of foam; for syntactic foams of the type made in the present study a term related to the properties of the wall material of the microballoons may need to be included.

The energy absorption capacity is defined as the energy necessary to deform a given specimen to a specific strain. So the absorption energy per unit volume for a sample can be evaluated by integrating the area under the stress-strain curve [30]. The energy absorbed values per unit volume of the foam composites at different strains are shown in Fig. 7. It can be noted that as the compressive behavior departs from the linear elastic region, the energy absorption of the composites increases dramatically compared to matrix alloy, Fig. 5. The composites containing microballoons up to 20 vol% significantly reveal higher energy absorption in comparison to the solid ZC63 matrix alloy.

![Fig. 4. EDXA of the ZC63 alloy (a) and interface (b), see Fig. 1(e).](image-url)
or composite containing 25 vol% microballoons. The energy absorbed at strain of 10% is 19.17 MJ/m$^3$ for ZC63-10 vol% microballoons and 18.65 MJ/m$^3$ for ZC63-20 vol% microballoons, and the energy absorbed for ZC63-20 vol% microballoons at strain of 14% is 30.1 MJ/m$^3$. Table 3 presents comparison between the specific energy absorption and density of the foam composites produced in the present work and other foam materials. The energy absorption values of the foam composites are significantly higher than those for closed cell aluminum alloys foams [33], and higher than those reported for syntactic foams fabricated by liquid metal infiltration of aluminum and 7075 Al aluminum into preforms of hollow ceramic microspheres at strain of 10% [25]. Also, they are higher at strain of 10% than that for steel foams synthesized by powder metallurgy and comparable to energy absorption values of the steel foam at strain of 20% [34]. These steel foam composites also display superior mechanical properties compared to conventional aluminum alloys. Table 2 shows the compressive properties of the ZC63 matrix alloy and foam composites containing 10, 20, 25 vol% microballoons.

Table 2

<table>
<thead>
<tr>
<th>Sample (%)</th>
<th>Modulus (GPa)</th>
<th>Yield strength (MPa)</th>
<th>Ultimate strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.5</td>
<td>206</td>
<td>293</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
<td>156</td>
<td>239</td>
</tr>
<tr>
<td>20</td>
<td>11.77</td>
<td>157</td>
<td>348</td>
</tr>
<tr>
<td>25</td>
<td>11.5</td>
<td>208</td>
<td>270</td>
</tr>
</tbody>
</table>

Fig. 6. Comparison between measured and predicted modulus of the foam composites.
foams have lower relative density \(q_{rel} = 0.4\) than Mg based foam composites studied, but greater absolute density \(3.8 \text{ g/cm}^3\).

In foam materials, a number of mechanisms contribute to energy absorption [35,36]. Some are related to the elastic, plastic or brittle deformation cell walls; others to the friction between the collapsed cell walls and the creation of surface. The relevant mechanisms for a particular foam depend on the behavior of the cell wall material (plastic or brittle) and structure of cells (open or closed) [32]. For the present foam composites, the energy is absorbed largely through the fracture of microballoons walls followed by the collapse of microballoons and Mg matrix surrounding it. The continued compression will cause the cavity to be filled by the collapsing walls of the microballoons and surrounding materials, leading to the structural densification.

The foam composite containing microballoons can be evaluated in terms of bending and axial stiffness. Maximum value of modulus to density \(E/q^2\) for axial stiffness can result in minimizing the mass of a beam of a given bending stiffness. Fig. 8 shows the variation of \(E/q^2\) for the composites with the volume fraction of the microballoons. It can be seen that increasing the microballoons volume fraction up to 25 vol% leads to increasing the \(E/q^2\) value. The maximum value of \(E/q^2\) is 4700 MPa cm\(^6\) g\(^-2\) for the composites containing 25 vol% microballoons.

### 3.6. Fractography

Generally, the possible failure mechanisms of the foam composites containing microballoons are microballoon cracking, microballoon matrix debonding and microballoon agglomerate decohesion. The latter two mechanisms are of secondary importance when the microballoon are well distributed and strongly bonded in the matrix as in the present work. The present foam composites show homogenous distribution of the microballoons because the microballoons tend to be separate and not large agglomerates due to the small contact area between the microballoons, Fig. 1 b–d.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Density (g/cm(^3))</th>
<th>Relative density</th>
<th>Specific energy absorption (MJ/m(^3))</th>
<th>Strain%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZC63-10 vol% microballoons</td>
<td>1.83</td>
<td>0.97</td>
<td>19.17</td>
<td>10</td>
<td>Present work</td>
</tr>
<tr>
<td>ZC63-20 vol% microballoons</td>
<td>1.68</td>
<td>0.9</td>
<td>18.65</td>
<td>10</td>
<td>Present work</td>
</tr>
<tr>
<td>Al foam</td>
<td>0.57</td>
<td>0.21</td>
<td>4.3</td>
<td>75</td>
<td>[33]</td>
</tr>
<tr>
<td>Al 4Cu foam</td>
<td>0.54</td>
<td>0.2</td>
<td>4.6</td>
<td>10</td>
<td>[34]</td>
</tr>
<tr>
<td>Al 12Si0.6Mg foam</td>
<td>0.60</td>
<td>0.23</td>
<td>6.4</td>
<td>65</td>
<td>[33]</td>
</tr>
<tr>
<td>Al 1Mg0.6Si foam</td>
<td>0.57</td>
<td>0.21</td>
<td>4.3</td>
<td>75</td>
<td>[33]</td>
</tr>
<tr>
<td>Al-microspheres foam composite</td>
<td>1.4</td>
<td>0.52</td>
<td>8.5</td>
<td>10</td>
<td>[33]</td>
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<tr>
<td>7075 Al-microspheres foam composite</td>
<td>1.66</td>
<td>0.59</td>
<td>15.6</td>
<td>10</td>
<td>[33]</td>
</tr>
<tr>
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<td>3.8</td>
<td>0.46</td>
<td>8.5</td>
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<td>[34]</td>
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<td>0.46</td>
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<tr>
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<td>0.46</td>
<td>60</td>
<td>50</td>
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</tbody>
</table>

Fig. 7. The energy absorbed per unit volume at different strains % for the foam composites.
Thus, it is microballoon cracking that has a major influence on the compressive strength of foam composite materials. Therefore, in the present foam composite, it is believed that the damage occurred first by microballoons fracture because the interface between fly ash microballoons and Mg is relatively strong.

In summary, the fracture mode of the foams is first the fracture of microballoons followed by the collapse of the Mg matrix surrounding it, leading to the structural densification, Fig. 9.

The smaller microballoons are much less likely to fracture at a given applied stress than the larger ones. This could be seen in the fracture surfaces of the composites (Fig. 9). This means that the probability of the microballoons cracking increases with increasing its size (the average microballoon size used in the present work is relatively large (100 μm)).

As shown in Fig. 5, the composites containing microballoons show a linear elastic region at relatively low stresses followed by a plateau, representing fracture of microballoons and then increase in stress, representing densification of foam. Since the plateau stress or strain is associated with the collapse of microballoons, the continued compression will cause the cavity to be filled by the collapsing walls of the microballoons and surrounding materials. Fracture surface of the composite in Fig. 9 shows fragments of

![SEM of the composites fracture surface](image_a)
![Optical micrographs of longitudinal sections](image_b)
![Microballoons Fragments](image_c)

Fig. 9. SEM of the composites fracture surface (a, b) and optical micrographs of longitudinal sections beneath the fracture surface (c) after compression showing microballoons fracture and fragments.
microballoons in the ZC63 matrix alloy. This means that many microballoons were completely crushed under compressive stress. The crushing process of the microballoons enhances the energy absorption capabilities of the composites. As shown in Fig. 5, when we considering the foam composites containing up to 20% vol microballoons, the range of strain corresponding to plateau stress increases and the overall plateau stress increases with increasing the volume fraction of the microballoons in the matrix up to 20%.

Finally, the present foam composites containing microballoons exhibit the same behavior of conventional foams in compression where they initially deform in a linear-elastic manner, then reaches a plateau of deformation, and finally exhibit a region of densification as the cell walls crush together, Fig. 9. Microstructural variations within each conventional metal foam specimen lead to a larger scatter in the mechanical properties data. The scatter in the measured properties seems to be related to various factors including the variations in size and shape of cells, the nonuniform distribution of cells, and the defects present in cell walls. It has been reported that metal foams with uniform cell size and shape have higher yield strength than specimens with nonuniform cells [37,38]. In the present foam composites, the microballoons act as cells, which absorb energy when crushed. Cell morphology and distribution can be controlled in the composites containing microballoons. A narrow range of microballoon size will provide more uniform cell morphology than that formed by foaming agents in the melt in foam materials. Therefore, the present foam composites can provide uniform distribution and uniform size of cells, and uniform cell walls in the matrix. On the other hand, when foaming agents are used to generate pores in the melt, obtaining uniform distribution of cells and uniform cell walls is not easy to control. Moreover, the cell size in conventional foams is much larger (millimeter in size) than the cell size (100 μm) obtained by the present foam composites.

The preparation of syntactic Mg based foams by stir casting technique, which is simple and inexpensive method, may open up the possibility of producing foam materials with other microballoons, not just fly ash, in foundries. The present experimental results demonstrate that the foam composites have higher densities than conventional foams, but they have the advantages of high compressive strength and modulus, and energy-absorbing capabilities which make them useful in applications such as energy-absorbing applications, packaging, armor, or automotive bumpers [31]. Also, their closed-cell geometry is attractive for mechanical and insulating properties.

4. Conclusions

1. ZC63 Mg alloy–microballoon foam composites are successfully fabricated by melt stir technique with the use of fluxes. 2. The addition of fly ash microballoon significantly reduces the density of the composites. As the volume fraction of microballoon microballoons increases, the density of the composites decreases.

3. Composites in the as-cast condition exhibits smaller dendrite arm spacing/cell size compared to unreinforced ZC63 Mg alloy. The morphology of the growing interface changes from dendrite in Mg alloy into cellular-dendrite interface in Mg-fly ash composite.

4. The microstructure of the composites demonstrates even distribution of the microballoon in the Mg alloy matrix and there is no sign of fly ash cluster or residual porosity.

5. The fly ash microballoons, eutectic phase and other intermetallic compounds mix and segregate at the magnesium cell boundaries. The eutectic and other intermetallic compounds phases are able to heterogeneously nucleate on the fly ash microballoons.

6. The fly ash reacts with the ZC63 Mg alloy to form reaction product at fly ash/matrix interface. The main interfacial phase between the fly ash and ZC63 Mg alloy is MgO.

7. The foam composites produced in the present work demonstrate typical behavior of an elastic–plastic foam material in compression. They have an initial linear elastic region, followed by a long region of deformation at a relatively flat stress level.

8. The composites containing microballoons up to 20 vol% significantly reveal higher energy absorption in comparison to the solid ZC63 matrix alloy or the composite containing 25 vol% microballoons.

References


