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Development of Lightweight Magnesium/Glass Micro Balloon Syntactic Foams Using Microwave Approach with Superior Thermal and Mechanical Properties

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Abstract: Magnesium matrix syntactic foams (MgMSFs) are emerging lightweight materials with unique capabilities to exhibit remarkable thermal, acoustic, and mechanical properties. In the current study, lightweight glass micro balloon (GMB)-reinforced Mg syntactic foams were synthesized via the powder metallurgy technique using hybrid microwave sintering. The processing employed in the study yielded MgMSFs with refined grain sizes, no secondary phases, and reasonably uniform distributions of hollow reinforcement particles. The developed MgMSFs exhibited densities 8%, 16%, and 26% lower than that of the pure Mg. The coefficient of thermal expansion reduced (up to 20%) while the ignition resistance improved (up to 20 °C) with the amount of GMB in the magnesium matrix. The MgMSFs also exhibited a progressive increase in hardness with the amount of GMB. Although the MgMSFs showed a decrease in the yield strength with the addition of GMB hollow particles, the ultimate compression strength, fracture strain, and energy absorption capabilities increased noticeably. The best ultimate compression strength at 321 MPa, which was ~26% higher than that of the pure Mg, was displayed by the Mg-5GMB composite, while the Mg-20GMB composite showed the best fracture strain and energy absorption capability, which were higher by ~39 and 65%, respectively, when compared to pure Mg. The specific strength of all composites remained superior to that of monolithic magnesium. Particular efforts were made in the present study to interrelate the processing, microstructural features, and properties of MgMSFs.

Keywords: magnesium; glass micro balloon; syntactic foam; powder metallurgy; microwave sintering; mechanical properties



Citation: Padnuru Sripathy, A.; Handjaja, C.; Manakari, V.; Parande, G.; Gupta, M. Development of Lightweight Magnesium/Glass Micro Balloon Syntactic Foams Using Microwave Approach with Superior Thermal and Mechanical Properties. *Metals* **2021**, *11*, 827. <https://doi.org/10.3390/met11050827>

Academic Editor: Thomas Fiedler

Received: 12 April 2021

Accepted: 13 May 2021

Published: 18 May 2021

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1. Introduction

Magnesium (Mg) is considered as an emerging and future lightweight material. The density of Mg is ~1.74 g/cc, which is similar to the density of carbon-fiber composite materials [1,2]. Due to its light weight and higher specific strength, Mg finds applications in aerospace, automotive, military, sports, and electronics industries, as well as building materials [3,4]. However, Mg has a hexagonal close-packed (HCP) crystal structure, which inherently limits the large plastic deformation of the material. Hence, the strengthening of Mg-based materials by work hardening is limited. As a result, solid solution strengthening, precipitation, and particle strengthening have been adopted to effectively enhance the strength of Mg-based materials [5]. Although particle and precipitate strengthening increase the strength of Mg to the desirable level, improving the ductility of Mg-based materials is still a challenge [6–8]. Alloying, laminated metal composites, and Mg matrix syntactic foams are some of the few techniques that can simultaneously enhance the strength and ductility of Mg. Especially, metallic syntactic foams have the capability to exhibit enhanced compressive failure strains, ignition temperatures, damping capacities, high specific strengths, and energy absorption capabilities [9].

Metal matrix syntactic foams (MMSFs) are metal matrix composites that contain hollow particles [10,11]. The hollow reinforcement particles impart porosity to the metal matrix using a closed-cell structure. Unlike open-cell foams, the closed-cell structure enhances the strength of the MMSFs without any compromise in ductility and density [11]. In the past, research works related to MMSFs with various metallic matrices such as steel [12,13], titanium [14], aluminum [15], magnesium [11,16–18], and zinc [19] have been pursued. Similarly, MMSFs have been synthesized with different types of hollow reinforcement particles such as metallic [15], ceramic [20], glass [16] and fly ash cenospheres [17]. Although fly ash cenospheres are inexpensive, engineered hollow particles impart better properties to the matrix compared to fly ash as their structure and properties can be controlled [10].

MgMSFs can be tailored to obtain the desired strength, density, and ductility. For instance, MgMSFs with a density lower than 1.0 g/cc have been achieved [21]. The properties of the MMSFs are influenced by parameters such as the type, composition, and strength of the hollow particles, size, shell wall thickness-to-diameter ratio, amount and distribution of hollow particles, metal matrix, processing techniques, and heat treatments [3,10]. In developing MgMSFs, various processes such as stir casting, disintegrated melt deposition (DMD), pressure infiltration, and powder metallurgy can be utilized. In the stir casting or DMD process, the temperatures are typically more than the melting temperature of the matrix. Due to the lower density of hollow particles, a lower volume addition results in the floating of reinforcements, leading to the nonuniform distribution of the reinforcement in the metal matrix [9]. Apart from this, due to the higher operating temperatures, the reaction between the hollow particles and the matrix results in intermetallics formation [11,21]. Such reactions consume the wall thickness of the hollow particles, thus effectively weakening them. Besides, the intermetallics formed due to chemical reaction might adversely affect the ductility of the developed materials, resulting in early failure of the developed materials [7,8]. Further, high pressures applied during secondary processing such as rolling and extrusion can result in the fracture of hollow particles, compromising the desired density [9].

On the other hand, powder metallurgy (PM) using hybrid microwave sintering is an efficient and versatile processing technique that can be used to develop various materials with a near-net shape. The operating temperatures in PM can be maintained lower than the melting temperatures, thus providing larger control over the formation of intermetallics in the developed materials. However, high compacting pressure during the process might result in the breakage of hollow particles, as well as a higher density [21,22]. Reducing the compacting pressure and/or using hollow particles possessing high crushing strengths can be a potential option in preventing such unintended breakages. As reducing the compacting pressure might lead to low-strength green compacts or billets, engineered hollow particles with high crushing strengths can be a viable option to prevent the fracture of the reinforcement during compacting.

The results of the research work published so far reveal that the MgMSFs exhibit superior specific yield strengths compared to steel, aluminum, or titanium MSFs [10]. Among MgMSFs, there are studies on commercially available Mg alloys AZ91 [17,23], AZ61 [21], ZC63 [24], and ZC alloys [25] as matrices. However, very few publications related to pure Mg-based MSFs with glass micro balloon (GMB) hollow particles are found. Manakari et al. [11,16] developed pure Mg MSFs with GMB hollow particles as the reinforcement using the disintegrated melt deposition technique. The developed materials exhibited superior thermal, mechanical, and tribological properties. Further, the research work showed potential for developing lightweight materials possessing densities lower than 1.5 g/cc using a Mg matrix and hollow GMB reinforcement particles. The authors also reported the formation of Mg_2Si intermetallics due to the reaction between the Mg matrix and GMB during processing. Sankaranarayanan et al. [22] developed MgMSFs with pure Mg as the matrix and hollow fly ash cenosphere as the reinforcement using the PM technique followed by microwave sintering. The author reported the breakage of cenospheres during extrusion, resulting in an increased experimental density of MgMSFs when compared

to the theoretical density. Akinwekomi et al. [21] developed MgMSFs with an AZ61 Mg alloy as the matrix and fly ash reinforcement via PM involving microwave sintering. The authors reported the formation of intermetallics during processing and its adverse effect on the density and mechanical properties of the composite [21,22]. Therefore, pure Mg was chosen as a matrix in this study to avoid processing complexities and additional phase formations that can further deteriorate the properties of the developed MgMSFs.

In the present research work, MgMSFs exhibiting a density lower than 1.5 g/cc with pure Mg as a matrix and GMB hollow particles were developed through PM involving hybrid microwave sintering. The sintering temperature was maintained below the reaction temperature between the reinforcement and matrix. The present work focused on the synthesis and analysis of the microstructure, physical, thermal, and mechanical properties of syntactic foams developed in the present study.

2. Materials and Methods

2.1. Materials

In the current study, the MgMSFs were developed using Mg powder of purity 98.5% as the matrix and hollow spherical glass micro balloons (soda-lime borosilicate glass, iM30K) as reinforcement particles. The main chemical composition of iM30k is SiO_2 , B_2O_3 , CaO , MgO , and Na (salt) [26]. Table 1 lists the raw materials used in the study, including supplier, size, and density. Figure 1 shows the SEM image of hollow GMB particles and their size distribution. The average size of hollow GMB particles was measured to be $16 \pm 6 \mu\text{m}$. The density and the crush strength of the GMB particles are 0.6 g/cc and 193 MPa, respectively, as provided in data sheet by the supplier [27].

Table 1. List of raw materials.

Materials	Supplier	Size (μm)	Density (g/cc)
Magnesium	Merck, Germany	60–300	1.74
Hollow Glass Micro Balloons (iM30K)	3M, Singapore	$16 \pm 6 \mu\text{m}$	~0.6

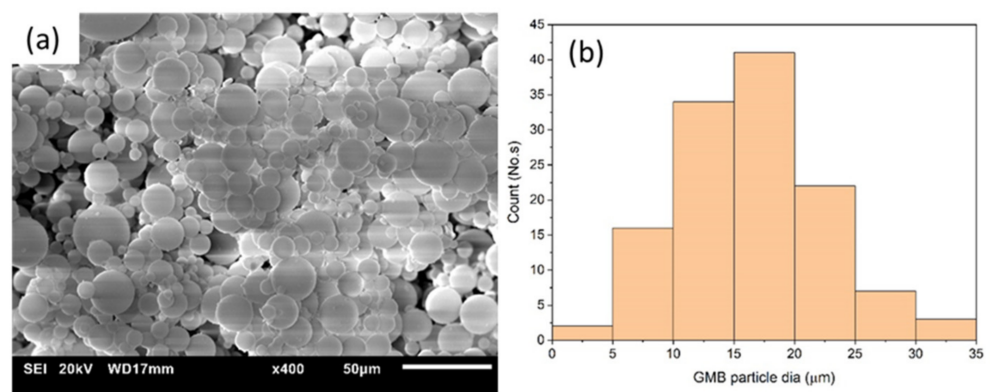


Figure 1. (a) SEM images of hollow GMB particles. (b) Size distribution of hollow GMB particles.

2.2. Methods

2.2.1. Processing

In the present work, the PM technique involving hybrid microwave sintering was utilized to synthesize three different MgMSFs containing 5, 10, and 20 wt.% of GMB hollow particles as the reinforcement, which corresponds to ~13.2, 24.3, and 42 vol.%, respectively. At first, accurately weighed Mg and GMB hollow particles were blended for uniform mixing using planetary ball milling without steel balls for 2 h at 200 rpm. The blended mixture was then uniaxially compacted at 6.9 MPa (1000 psi) for 60 s using a 100 ton press to form billets measuring 35 mm in diameter and 45 mm in height. Further, the compacted billets were heated to 450 °C in a 900 W, 2.45 GHz Sharp microwave oven with

SiC as a microwave susceptor material. Temperature calibration of the sintering setup was performed initially using a sheathed K-type thermocouple in order to determine the appropriate heating duration to reach 450 °C for the sintering of magnesium. The in-situ temperature measurements were conducted by drilling 5 mm diameter holes to depths of 3 and 20 mm for temperature measurements at the surface and in the center of the compacts, respectively. Upon reaching the required temperature, the microwave power was switched off and the billet was allowed to cool to room temperature without any holding time under ambient atmospheric conditions in the absence of an inert protective atmosphere. All the compacted billets were sintered subsequently to the optimized heating duration to reach 450 °C during the microwave sintering process. More details on the microwave setup and the calibration of temperature can be found in earlier publications [28–30]. The sintered billets were soaked at 400 °C for 1 h and then extruded at an extrusion ratio of 20.25:1 and die temperature of 350 °C to form rods of 8 mm in diameter. In addition, pure Mg was also synthesized using a similar technique and process parameters, as a control sample. Overall, samples with four different compositions were synthesized. The samples in the present work are referred to as pure Mg and Mg-XGMB, where X represents the wt.% of GMB in the composition.

2.2.2. Characterization

The grain size of the samples was obtained by etching the polished surfaces using citric acid, and microstructural images of the samples were obtained using a Leica DM2500M metallographic optical microscope equipped with a Leica EC3 digital color camera (Leica Microsystems (SEA) Pte Ltd., Singapore, Singapore). To investigate the secondary phases formed in the samples, X-ray diffraction analysis (XRD) was performed using an automated Shimadzu lab-X XRD-6000 diffractometer (Shimadzu Corporation, Kyoto, Japan). The samples were exposed to Cu K α radiation of wavelength $\lambda = 1.5418\text{\AA}$ with a scan speed of 2°/min and a scanning range of 10 to 80°. Further, a JEOL JSM-6010PLUS/LV scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectrometer (EDS) marketed by JEOL USA Inc., Peabody, MA, USA was utilized to investigate the reinforcement/secondary phase distribution, the presence of secondary phases, and the fracture response of samples.

The experimental density of the samples was measured in accordance with the Archimedes' principle. The samples were weighed in air and distilled water using an A&D ER-182A electronic balance (Bradford, MA, USA) with an accuracy of ± 0.0001 g. The theoretical density was estimated based on the rule of mixture (ROM). The coefficient of thermal expansion (CTE) of the samples was determined by measuring the displacement of the samples as a function of temperature in the range of 50–400 °C using an automated Linseis TMA PT1000 thermo-mechanical analyzer supplied by Gaia Science Pte Ltd., Singapore. A Shimadzu DTG-60H Thermo Gravimetric Analyzer (Kyoto, Japan) was utilized to determine the ignition temperature of the samples. The thermogravimetric analysis (TGA) samples of size $2 \times 2 \times 1$ mm³ were heated from 30 to 750 °C at a heating rate of 10 °C/min in purified air with a flow rate of 50 mL/min to obtain a graph of temperature vs. time. Three replicates were tested of each composition to ensure repeatability, and the average values are reported.

Microhardness measurements were conducted on 5 samples for each composition using a Shimadzu HMV automatic digital microhardness tester machine manufactured by Shimadzu Corporation, Kyoto, Japan. The tests were conducted in compliance with the ASTM test method E384-11e1. In the microhardness test, the load on the polished surface and the dwelling time were 25 gf and 15 s, respectively. To determine the compression properties of the samples, compression testing was performed using an MTS 810 machine supplied by the MTS Systems Corporation, Eden Prairie, MN, USA. The tests were conducted on 5 cylindrical samples of 8 mm in diameter and of 8 mm in height per composition in compliance with the ASTM test method E9-09. The crosshead speed utilized during the compression test was 4×10^{-2} mm/min (strain rate: 10^{-4} /s). The area under the

compressive stress–strain curve was calculated to estimate the energy absorption capability of the materials. The elastic modulus of the Mg MSFs was estimated from dynamic vibration analysis using the resonant frequency and damping analyzer (IMCE, Genk, Belgium), as per ASTM E1876-09. This approach was adopted as the elastic modulus values are more accurate than extracting from the elastic region of static stress–strain curves from the compression testing, especially for porous materials [31]. The machined cylindrical samples of 7 mm in diameter and 60 mm in length were used to measure the elastic modulus of the developed MgMSFs.

3. Results

3.1. Density

The results of the theoretical and experimental densities and thermal properties of the developed MgMSF materials are listed in Table 2. The experimental density of samples was in good agreement with the theoretically estimated density values. The density results suggest that there was no or limited fracture of GMB hollow particles during the material synthesis. Mg-20GMB exhibited a slightly higher experimental density than the estimated density. The addition of GMB hollow particles resulted in the reduction in Mg density by ~8, ~16, and ~26% with the addition of 5, 10, and 20 wt.% of GMB hollow particles, respectively.

Table 2. Results of density and thermal properties of developed MgMSFs.

Materials	Theoretical Density (g/cc)	Experimental Density (g/cc)	CTE ($\times 10^{-6}/K$)	Ignition Temperature ($^{\circ}C$)
Pure Mg	1.74	1.73	26.8	552 $\pm$ 0.6
Mg-5	1.59	1.59 ($\downarrow$ 8%)	24.4 ($\downarrow$ 9%)	563 $\pm$ 1 ($\uparrow$ 2%)
Mg-10	1.46	1.46 ($\downarrow$ 16%)	23.2 ($\downarrow$ 13%)	568 $\pm$ 1.2 ($\uparrow$ 3%)
Mg-20	1.26	1.28 ($\downarrow$ 26%)	21.5 ($\downarrow$ 20%)	572 $\pm$ 1.5 ($\uparrow$ 4%)
AZ61	1.80 [32]	-	26.0 [32]	559 [33]
AM60	1.80 [34]	-	26.0 [34]	525 [33]
ZK40A	1.82 [32,35]	-	26.0 [35]	500 [33]
ZK51A	1.83 [36]	-	26.0 [36]	552 [33]
ZK60A	1.83 [37]	-	26.0 [37]	449 [33]

3.2. Thermal Properties

The coefficient of thermal expansion (CTE) and ignition temperature measurements of the synthesized materials are listed in Table 2. The CTE values of the developed materials reduced with the progressive addition of GMB hollow particles. From the results, the reductions in the CTE in MgMSFs were ~9, ~13, and ~20%, respectively, with the addition of 5, 10, and 20 wt.% GMB hollow particles, showing a linear decreasing trend. The TGA results showed that the ignition temperature of MgMSFs increased with the addition of GMB hollow particles. The addition of 5, 10, and 20 wt.% GMB increased the ignition temperature of Mg by 11, 16, and 20 $^{\circ}C$, respectively.

3.3. Microstructure

Figure 2 shows optical micrographs of the distribution of GMB particles under the extruded condition for developed samples. Figures 3–5 show SEM images of the developed MgMSFs. The figures show the uniform distribution and agglomeration of GMB hollow particles. The magnified images of the agglomerated GMBs reveal the crushing of GMB hollow particles and the presence of cavities in the clustered region (Figures 3–5). Apart from cavities in the clustered region, cavities can also be observed in the Mg matrix, which is highlighted in Figures 3–5. Further, the images also confirm the presence of intact GMB particles in the developed materials. The maximum sizes of intact GMBs in the Mg-5, 10, and 20GMB were 5, 6.5, and 7 μm , respectively.

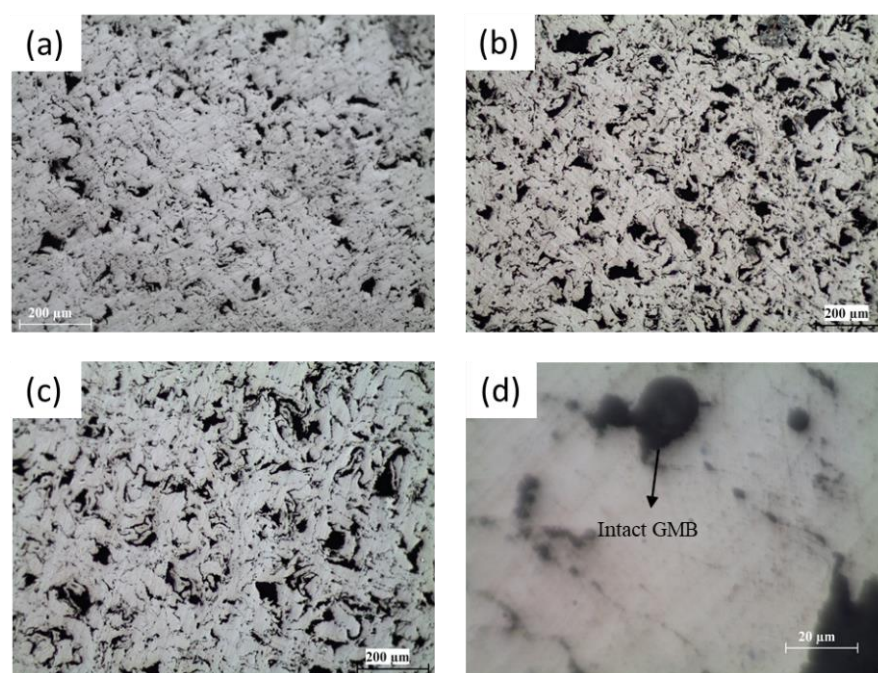


Figure 2. Optical micrographs showing the distribution of GMB particles under the extruded condition for (a) Mg-5GMB, (b) Mg-10GMB, and (c) Mg-20GMB, and (d) magnified view showing the interface between the Mg and GMB particles.

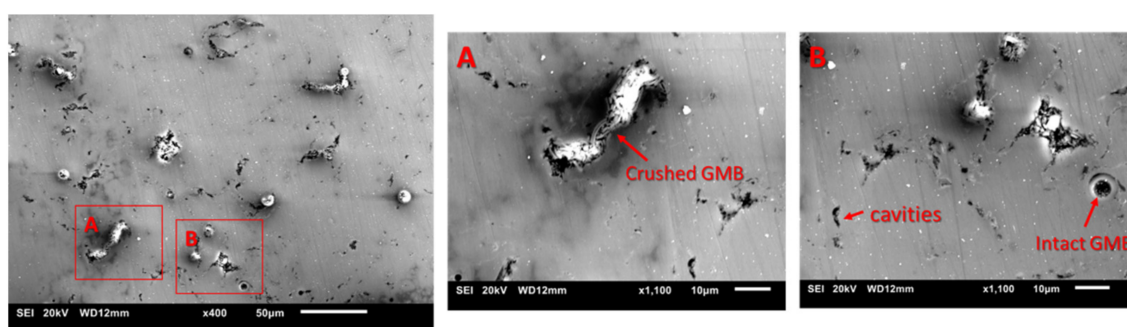


Figure 3. SEM images of Mg-5GMB in various magnifications showing crushed and intact GMBs and cavities. (A) Magnified images showing crushed GMB. (B) Magnified images showing cavities and intact GMB.

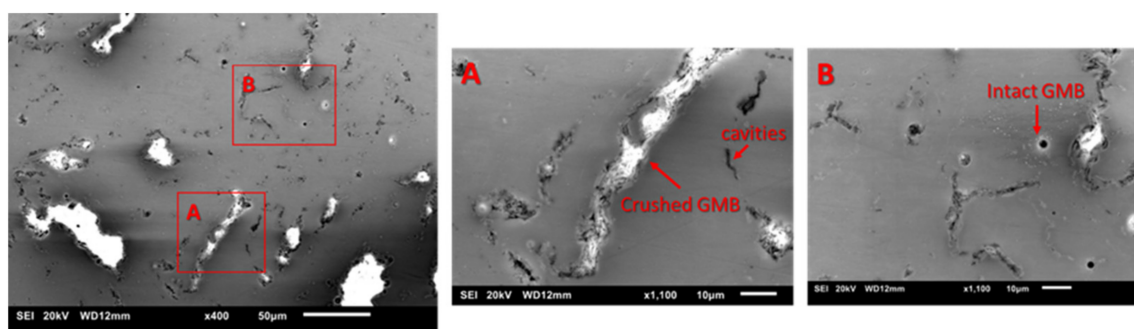


Figure 4. SEM images of Mg-10GMB in various magnifications showing crushed and intact GMBs and cavities. (A) Magnified images showing crushed GMB and cavities. (B) Magnified images showing intact GMB.

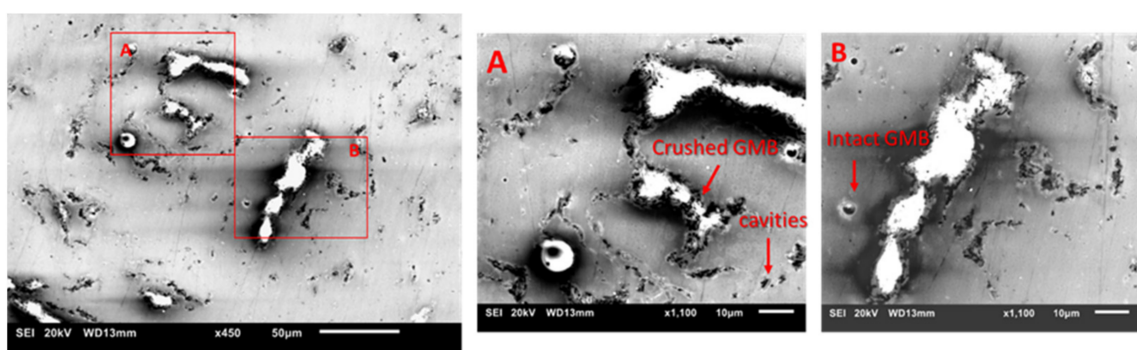


Figure 5. SEM images of Mg-20GMB in various magnifications showing crushed and intact GMBs and cavities. (A) Magnified images showing crushed GMB and cavities. (B) Magnified images showing intact GMB.

3.4. X-ray Diffraction Analysis

Figure 6 shows XRD patterns of the developed materials. The observed XRD patterns of samples Mg-5GMB, Mg-10GMB, and Mg-20GMB matched with the XRD patterns of pure Mg. In addition, the XRD patterns of the Mg-XGMB samples exhibited few peaks matching the SiO_2 peaks, which is the major constituent of GMB hollow particles. Further, the results revealed the absence of other secondary phases, particularly Mg_2Si in the samples.

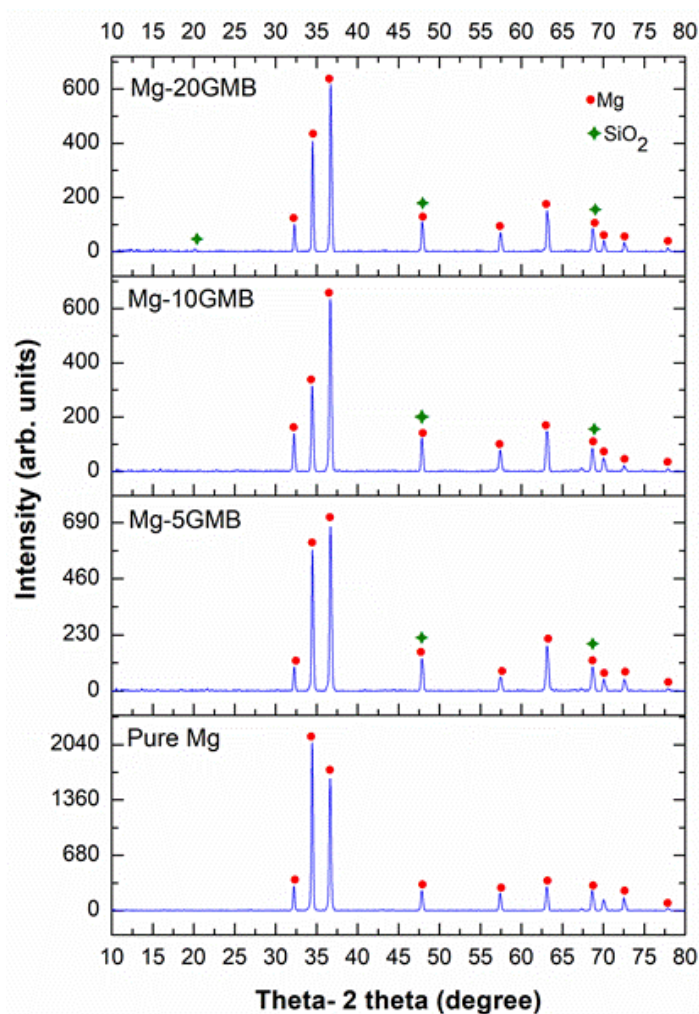


Figure 6. X-ray diffractograms of pure Mg and Mg-GMB syntactic foams.

3.5. Grain Size

The grain size of the developed MgMSFs along the extrusion direction is provided in Table 3. Figure 7 represents the grain size of the developed materials. The results of the grain size measurement showed that the MgMSFs displayed refined grain sizes compared to pure Mg. It was observed that 5, 10, and 20 wt.% of GMB in the Mg matrix resulted in reductions in the grain size by ~36%, ~49%, and ~60%, respectively, when compared to pure Mg.

Table 3. Results of grain size measurement and microhardness studies.

Materials	Grain Size (μm)	Microhardness (Hv)
Pure Mg	47 ± 4	65 ± 1
Mg-5 GMB	30 ± 4 ($\downarrow 36\%$)	76 ± 1 ($\uparrow 17\%$)
Mg-10 GMB	24 ± 2 ($\downarrow 49\%$)	86 ± 1 ($\uparrow 32\%$)
Mg-20 GMB	19 ± 2 ($\downarrow 60\%$)	114 ± 1 ($\uparrow 75\%$)

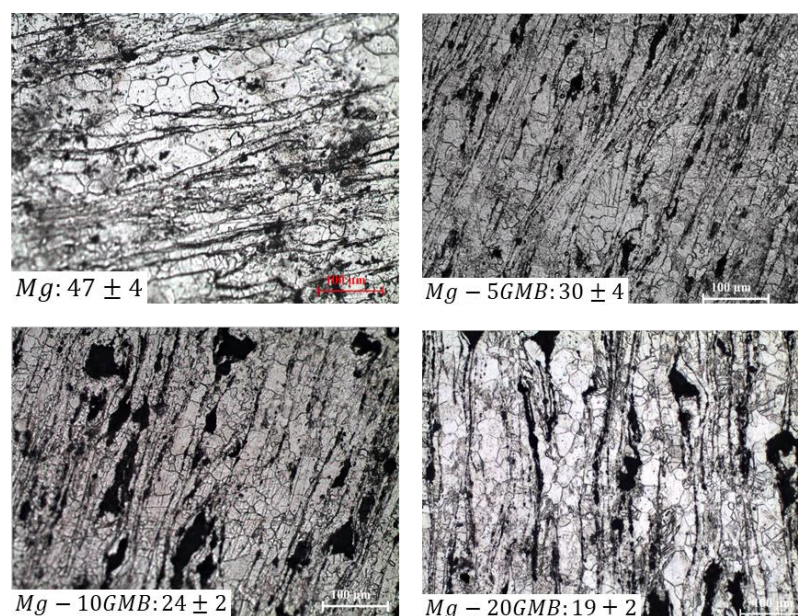


Figure 7. Grain size of developed materials.

3.6. Mechanical Properties

The results of microhardness measurements of the developed MgMSFs are shown in Table 3. The addition of GMB hollow particles to the Mg matrix led to an increase in the hardness of the magnesium matrix. Compared to the hardness of pure Mg, Mg-5GMB and Mg-10GMB samples showed ~17 and ~32% increases in hardness values. The MgMSFs with 20 wt.% of GMB had a maximum microhardness value of 114 Hv, i.e., ~75% improvement compared to pure Mg. Further, the microhardness of the GMB hollow particles in the agglomerated region was measured and was found to be in the range of 158–168 Hv, which was ~2.5 times that of the pure Mg.

Table 4 lists the compressive properties of the developed MgMSFs. Figure 8 shows the compressive stress–strain curves of developed MgMSFs. Figure 9 shows the images of a test sample before and after compression loading. We should note that the initial elastic region of each curve was followed by a region of inelastic deformation until a maximum stress was reached, after which the sample failed. The maximum stress and corresponding strain were considered to be the failure stress or ultimate compressive strength (UCS) and failure strain, respectively. From the compression test results, it can be observed that the 0.2% compressive yield stress (CYS) of developed MgMSFs reduced with the wt.% of GMB in the Mg matrix, while the ultimate compressive stress (UCS) of Mg increased with

the addition of GMB particles. However, the maximum UCS was recorded in Mg-5GMB (321 MPa), and the further addition of GMB resulted in the decrement in UCS but remained higher than that of pure Mg. Similar to 0.2% CYS, the elastic modulus of the developed MgMSFs also decreased with the addition of GMB hollow particles. The fracture strain of developed MgMSFs increased with the addition of GMB in the Mg matrix. The Mg-5GMB and Mg-10GMB showed ~23% increases in the fracture strain compared to pure Mg, whereas Mg-20GMB showed a maximum increase in fracture strain at ~39% when compared to pure Mg.

Table 4. Compressive properties of the samples.

Materials	Density (g/cc)	0.2% CYS (MPa)	UCS (MPa)	Fracture Strain (%)	Elastic Modulus (GPa)	Energy Absorption (MJ/m ³)	Specific Strength (MPa/g/cc)
Pure Mg	1.73	98 ± 2	254 ± 6	15.8 ± 0.5	45.17 ± 0.05	24.8 ± 0.8	147
Mg-5GMB	1.59	91 ± 2 (↓7%)	321 ± 7 (↑26%)	19.5 ± 0.6 (↑23%)	41.96 ± 0.014 (↓7.106%)	38.8 ± 1.3 (↑56%)	202 (↑37%)
Mg-10GMB	1.46	88 ± 1 (↓10%)	287 ± 6 (↑13%)	19.6 ± 0.7 (↑24%)	40.02 ± 0.005 (↓11.40%)	36.3 ± 1.6 (↑46%)	197 (↑34%)
Mg-20GMB	1.28	85 ± 1 (↓13%)	280 ± 4 (↑10%)	22 ± 2 (↑39%)	38.23 ± 0.12 (↓15.36%)	40.8 ± 3.2 (↑65%)	219 (↑49%)
AZ61D [23]	1.87	112 (↑13%)	160 (↓37%)	—	—	—	85 (↓42%)
ZC63 [24]	1.85	206 (↑110%)	293 (↑15%)	—	—	—	158 (↑7%)

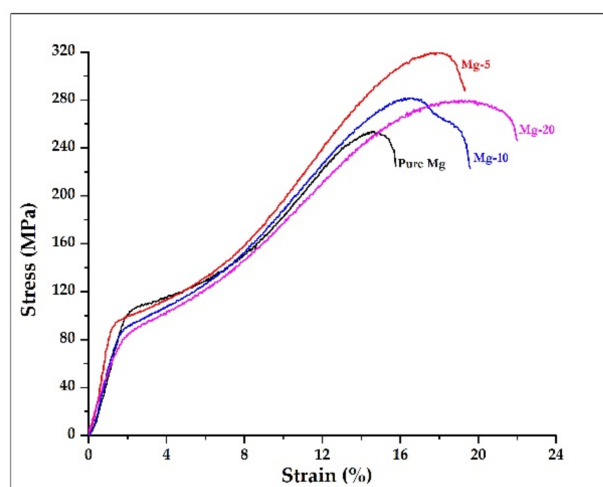


Figure 8. Compressive stress–strain curves of developed MgMSFs.

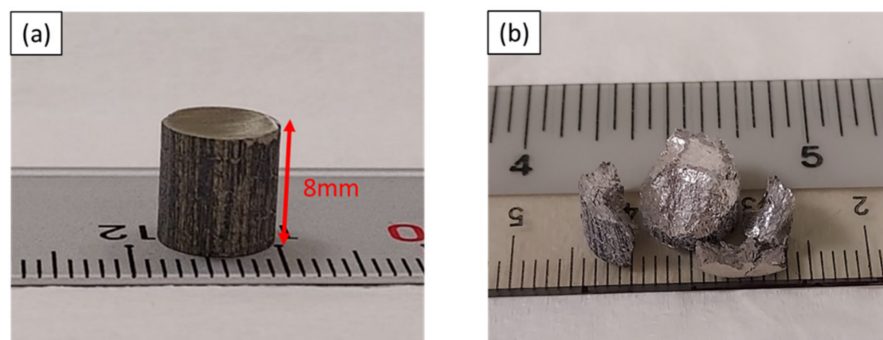


Figure 9. (a) Image of typical compression test samples. (b) Image of a typical sample after compression loading.

The energy absorption capability of developed MgMSFs during compression loading is shown in Table 4. The results revealed that the developed MgMSFs had a higher energy absorbing capability than pure Mg had. The sample with 20 wt.% GMB showed the highest energy absorption of 40.8 MJ/m^3 , which was $\sim 65\%$ greater than that of pure Mg. Although the developed MgMSFs had a lower compressive yield strength, the specific strength (UCS/density) of the developed MgMSFs was significantly higher than that of pure Mg (Table 4). The MgMSF with 20 wt.% of GMB exhibited a $\sim 49\%$ higher specific strength compared to pure Mg. It can also be observed that the developed Mg-20GMB had a specific strength higher than those of commercially available Mg alloys such as AZ61D and ZC63 by ~ 155 [23] and 39% [24], respectively.

3.7. Fractography

The fractography analyses of the post-compressive test samples are shown in Figure 10. Shear bands on the fracture surface were clearly visible in all the samples. The fractography of Mg-20GMB showed internal cracks, as shown by the arrows in Figure 10d, which was not observed in the other samples such as pure Mg, Mg-5GMB, and Mg-10GMB.

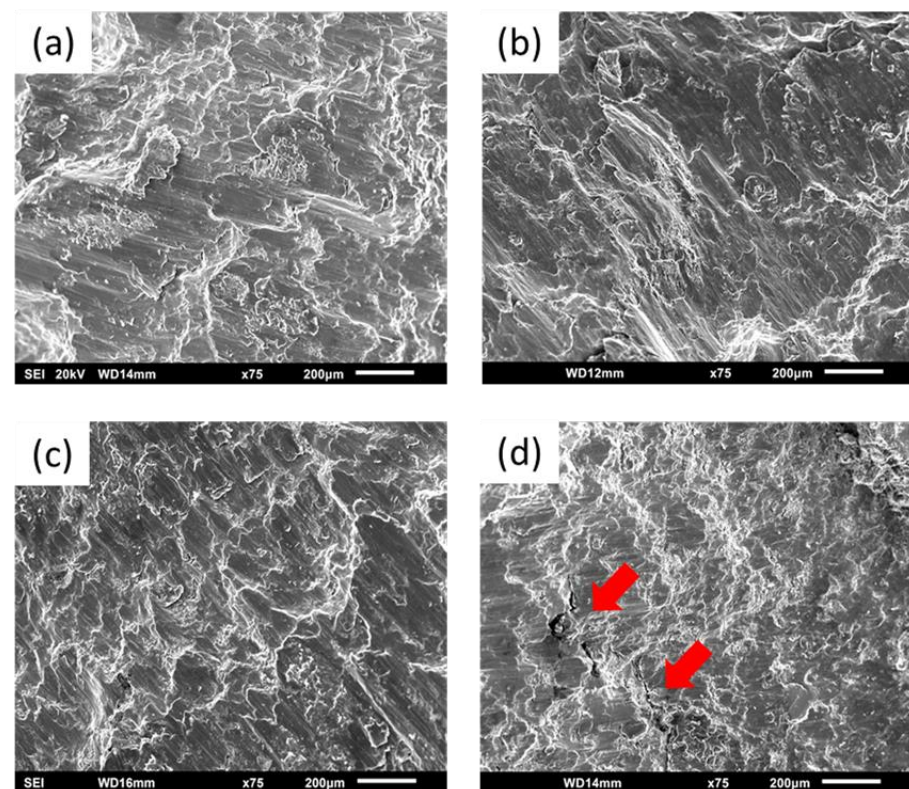


Figure 10. Fractography of (a) pure Mg, (b) Mg-5GMB, (c) Mg-10GMB, and (d) Mg-20GMB with arrows showing internal cracks.

4. Discussion

4.1. Synthesis and Optimization

The reinforcement used in the current study was GMB hollow particles, which consist of SiO_2 as their major constituent. As Mg is a highly reactive matrix at higher temperatures, the chemical reaction between Mg and SiO_2 is inevitable. From the thermodynamic computation, the chemical reaction between Mg and SiO_2 might result in the formation of Mg_2Si and MgO as secondary phases [11]. In such a scenario, secondary Mg_2Si will form by consuming the wall thickness of the GMB particles, resulting in the weakening and fracture of hollow particles, eventually filling up with the Mg matrix. The resulting composition would then be a Mg metal matrix composite (MMC) with particles and

precipitates such as SiO_2 , Mg_2Si , and MgO . This might adversely affect the density of the composite, as densities of Mg_2Si (1.99 g/cc), SiO_2 (2.65 g/cc), and MgO (3.58 g/cc) are all higher than that of the Mg matrix [21]. It might also affect the ductility of the Mg composites [6,7]. Such particles and precipitates can also act as crack initiation sites [8]. To prevent the formation of such detrimental secondary phases, a sintering temperature below the reaction temperatures of Mg and SiO_2 was adopted in this study. Sun et al. [38] studied the formation of intermetallic Mg_2Si in a Mg-Si powder mixture using differential thermal analysis at a different heating rate, and they concluded that the start of reaction $2\text{Mg} + \text{Si} \rightarrow \text{Mg}_2\text{Si}$ begins at 743 K (470 °C).

Further, in order to validate the selected sintering temperature, the billets were also sintered at a temperature of 500 °C. The sintering of the billet at 500 °C resulted in a dimensionally unstable sample owing to the reaction between GMB particles and the Mg matrix, whereas sintering at 450 °C resulted in a dimensionally stable green compact, as seen in Figure 11. A sintering temperature of 500 °C and the rapid heating rates adopted in the microwave sintering process can lead to the formation of Mg_2Si in the elemental matrix, which might have resulted in the deformation and oxidation of the sintered billet, as observed in Figure 11. Based on the results of sintering at 450 and 500 °C and based on the research work of Sun et al. [38], the sintering temperature was maintained at 450 °C to prevent the formation of Mg_2Si in MgMSFs.

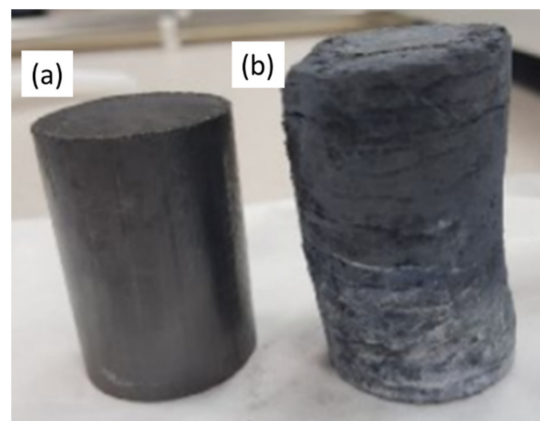


Figure 11. Billets sintered at temperatures of (a) 450 °C and (b) 500 °C.

The XRD analysis results of the samples (Figure 6) also showed no peaks matching Mg_2Si . The XRD analysis showed SiO_2 and pure Mg peaks, which was the chemical composition of the reinforcement and matrix, confirming no secondary phases.

4.2. Physical and Thermal Properties

The theoretical densities for the samples Mg-5GMB, Mg-10GMB, and pure Mg, as estimated based on ROM, were in good agreement with the experimental density. Despite the crushing of the GMB hollow particles, the density measured was similar to the theoretical density. The SEM images of the samples clearly showed the agglomeration of crushed GMB hollow particles with void spaces in them. In addition, they also showed the presence of matrix porosity and intact hollow GMB particles in the samples. The combined effect of matrix porosity, voids in the agglomerated GMB regions, and intact hollow particles might have resulted in experimental densities of the developed materials similar to their theoretical densities.

Both the matrix porosity and crushed GMBs can affect the density of the MgMSFs. Porosity leads to lower densities than the theoretical values, and the crushed GMBs lead to higher densities than the values. From the density measurement results and the microstructural analysis, it is reasonable to believe that most of the GMB particles having a high crush strength of 193 MPa survived at the compaction pressure of 6.9 MPa during the com-

paction stage and began to be crushed during the severe plastic deformation experienced during hot extrusion. The air pores in the GMB particles could be decreased by crushing the hollow particles. The GMBs with a hollow structure were relatively strong, but once crushed, they had a greater decrease in volume, as observed in Figure 3, with the size of intact GMB particles in the range of 5–7 μm . Various models such as the volume method and water absorption method have been suggested by Xue et al. [39] for the estimation of the percentage of crushed hollow particles for syntactic foams synthesized by powder metallurgy. However, in the present study, the crushing of the hollow particles is due to the concurring effect of both compaction and extrusion, and the assumptions made for the suggested models cannot be applied. Work toward validating such models available with the elimination of the secondary process such as extrusion for the synthesis of MgMSFs and developing MgMSFs without the major crushing of the hollow particles is currently under progress.

The coefficient of thermal expansion (CTE) of the Mg-GMB syntactic foams decreased with the increase in the addition of GMB particles (Table 2). This decrease in CTE values with the addition of GMB hollow particles could be attributed to the lower CTE of the GMB hollow particles ($8 \times 10^{-6}/\text{K}$ [16]) and the crushed GMB particles compared to the CTE of pure Mg ($26.8 \times 10^{-6}/\text{K}$). The estimated theoretical CTEs based on the rule of mixture for the Mg-5GMB and Mg-10GMB samples were 24.4×10^{-6} and $22.4 \times 10^{-6}/\text{K}$, which were in good agreement with experimental CTE values. On the other hand, the experimental CTE of the Mg-20GMB sample ($21.5 \times 10^{-6}/\text{K}$) showed a deviation from the theoretical CTE ($19 \times 10^{-6}/\text{K}$) by $\sim 13\%$. The CTE of the syntactic foams depends on the thickness and volume fraction of the hollow particles [40]. Shunmugasamy et al. [40] modified Turner's and Kerner's models to include the thickness and number of hollow particles to predict the CTE of syntactic foams. The modified Turner's and Kerner's models provided results with accuracies of $\pm 15\%$ with respect to the experimental results. In earlier research by Yunk et al. [41], a reduction in the CTE of the epoxy–hollow glass microsphere composite was reported with the addition of GMB particles into epoxy resin. Composites with lower CTEs are generally used in thermal insulation, electronic packaging, PCBs, etc. The composites with lower CTEs show better thermal and dimensional stabilities [11,42], thus reducing the thermal stress at the interfaces, preventing failures [40,41].

The ignition temperature of the Mg-GMB increased with the increase in the addition of GMB hollow particles (Table 2). Ignition is an exothermic oxidation process, and a large amount of heat is generated during the process. Mg is highly susceptible to oxidation at higher temperatures with a Pilling–Bedworth ratio (PBR) of Mg (0.81), suggesting that the formed oxide layers on the surface of Mg are nonprotective. In addition, at the critical ignition temperature, the heat lost to the surroundings is less than the heat generated by the oxidation process, resulting in self-heating and continued oxidation [43]. Aydin et al.'s work [44] on the high-temperature oxidation and ignition of Mg alloys suggested that the oxide layer formation depends on the diffusion kinetics of the ions. When samples are exposed to high temperatures and purified air, Mg reacts with O_2 , forming an MgO outer layer. As Mg^{2+} ions can diffuse faster than O^{2-} across the formed MgO outer layer, the further formation of MgO occurs at the interface of oxide and purified air. In addition, GMBs with Si-O structures have large surface areas and lower densities, and they tend to accumulate near the regressing sample surface without sinking. This can protect the inner matrix by reducing the specific areas of oxidation and, hence, delaying the onset of ignition in Mg/GMB syntactic foams. This results in a SiO_2 -rich layer beneath the MgO layer [11]. With increasing temperatures, the MgO layer breaks away, exposing the SiO_2 layer. The PBR of SiO_2 is 1.89, indicating that the oxide film suppresses oxide diffusivity characteristics [35], increasing the ignition temperature. In addition, the increase in the ignition temperature of the developed Mg-GMB syntactic foams can be attributed to the low thermal conductivity and CTE of the GMB hollow particles. The presence of low thermally conductive particles such as GMBs results in effective shielding of the Mg matrix and prolongs the melting of Mg beneath GMB [43] (p. 330). We should note that the

developed MgMSFs in this study showed better ignition temperatures in comparison with commercial aerospace Mg alloys such as AZ61 (559 °C), AM60 (525 °C), ZK40A (500 °C), ZK51A (552 °C), and ZK60A (499 °C) [33].

4.3. Mechanical Properties

From the microhardness measurement results (Table 3), the hardness of the Mg matrix in samples increased with the progressive addition of GMB particles. The microstructure of MgMSFs showed uniform distributions of agglomerated GMBs (Figures 3 and 4). The measured microhardness of these agglomerated GMBs was in the range of 158–168 Hv, which was ~2.5 times that of the pure Mg. The results suggested that GMB particles of higher microhardness enhanced the hardness of the Mg matrix in samples by resisting the localized deformation of the Mg matrix. Further, the microstructural study of MgMSFs showed grain refinement of the matrix with the progressive addition of the GMB hollow particles. Grain refinement in materials with the addition of nonmetallic particles was also reported by Peroni et al. [45]. Nonmetallic particles—the hollow glass spheres as in this case—are known to restrict grain boundary movement in the metal matrix and, therefore, grain growth during sintering. A high number of small particles are more effective than a few large particles in this respect [45]. The grain refinements in the developed samples might be due to the particle stimulated nucleation (PSN) in the materials. The particle-stimulated nucleation depends on the amount and the size of the reinforcement particles [46,47]. An increase in the number of particles increases the effect of PSN, thereby leading to grain refinement [46,47]. The decrease in the grain size of the developed MgMSFs can activate the Hall–Petch strengthening, resulting in an improved strength and hardness of the developed syntactic foams. As the hardness and strength of the material are interrelated, increases in the hardness values could result in increases in the strength values of the syntactic foams [48].

Figure 8 shows the compressive stress–strain curves of pure Mg, Mg-5GMB, Mg-10GMB, and Mg-20GMB syntactic foams. It can be observed that the compressive stress–strain curves of the syntactic foams showed a similar trend as that of the pure Mg with different 0.2% CYS, UCS, and fracture strain values. Typical compressive stress–strain curves of a syntactic foam were described by Gupta et al. [10] and Gibson [49]. As described by Gupta et al. [10], a typical stress–strain curve of metal matrix syntactic foams has four points. Point 1 is the 0.2% proof stress and point 2 is the maximum stress at the end of the elastic region followed by a drop in strength. Point 3 is the plateau stress and point 4 is the densification strain. The compressive stress–strain curve of the developed samples did not show typical syntactic foam behavior, as explained earlier. The stress–strain curve of the samples (Figure 8) exhibited no drop in stress after the yield point and showed no plateau region. Such characteristics of the stress–strain curve of the developed samples could be explained with the microstructures. The SEM images (Figures 3 and 4) showed an agglomeration of GMB particles and crushing of a large vol.% of the GMB hollow particles in the material, leaving behind a very low vol.% of intact GMB hollow particles. These crushed GMB particles in the Mg matrix acted like particle reinforcements in the matrix, resulting in compressive stress–strain curves similar to pure Mg or metal matrix composites. Manakari et al. [11] suggested that 30 vol.% is the threshold limit for the system to exhibit stress–strain behavior typical of syntactic foams. Although the Mg-20GMB had 42 vol.% of hollow GMB particles by composition, the developed material had a low vol.% of intact GMB hollow particles (Figures 3 and 4).

In addition, the average size of the GMB hollow particles (16 µm) was less than the grain size of the developed materials. Due to the smaller size and low vol.% of intact GMB hollow particles, the collapsing of hollow particles and the load drop after point 2 (maximum stress at the end of the elastic region) were not predominantly reflected in the stress–strain curve. A similar characteristic of the stress–strain curve was observed in MgMSFs developed by Manakari et al. [11] using pure Mg as the matrix and GMB hollow particles (8 and 23 vol.%) of 11 µm in diameter. Similarly, magnesium matrix syntactic foams developed using AZ91 as the matrix and fly ash cenospheres of sizes ranging from

10 to 100 μm as reinforcements by Rohatgi et. al. [17] also showed no drop in stress after the yield point and showed limited or no plateau region. A typical stress–strain curve, as explained in [10], can be predominantly observed in metal MSFs with larger sizes and higher vols.% of hollow particles [20,49,50].

Though the GMB hollow particles were crushed and the samples developed did not represent the typical syntactic foam stress–strain behavior, an increase in the failure strain of MgMSFs was observed with the addition of GMB hollow particles (Table 4). This indicates the collapsing of the leftover intact GMB hollow particles during compressive loading, followed by the further densification of the samples filling the void spaces and cavities in the developed material. The collapsed GMB hollow particles behaved like a particle reinforcement in the matrix, resulting in work hardening. This behavior is typical of the magnesium metal matrix composites [51]. The increase in the UCS of the MgMSFs compared to pure Mg is attributed to the various particle strengthening mechanisms. Among all the developed MgMSFs, Mg-5GMB exhibited a maximum UCS and Mg-20GMB showed a lower UCS compared to Mg-5GMB and Mg-10GMB samples. However, the UCS of Mg-20GMB remained higher than that of pure Mg. In metal matrix composites, strength and ductility balances are generally driven by the load transferring and deformation compatibility between the matrix and reinforcement. While the collapse of GMB assisted in the increase in failure strain value, the UCS diminished due to the embedding of an increased amount of porosity with the addition of 10 and 20 wt.% of GMB particles. This might be due to a decrease in load-bearing capacity of crushed and agglomerated GMB particles. The fractography of Mg-20GMB (Figure 10) showed internal cracks, suggesting a lack of load-bearing capability of the broken GMB particles; thus, a failure of Mg-20GMB samples occurred at lower UCS values. In addition, fracture surfaces were at about 45° with respect to the compression loading direction and shear bands were clearly evident, as observed in Figure 9.

On the other hand, the 0.2% compressive yield strength of the material decreased with the addition of the GMB hollow particles. This downward trend might be due to the lower yield strength of the GMB particles compared to the matrix. It is important to note that the larger vol.% of the hollow GMB particles was crushed during the material processing, and these crushed GMB particles in the matrix influenced the yield strength more than the low vol.% of intact GMB hollow particles. Further, the grain size measurement of samples showed grain refinement with the addition of GMB, suggesting an increase in yield strength as per the Hall–Petch effect. In the current study, the extent of lowered yield strength of the composite by the addition of low-yield-strength GMB particles ($\sim 45\text{ MPa}$ [52]) was higher than the extent of the increase in yield strength of the Hall–Petch effect, resulting in an overall reduction in yield strength. Though the 0.2% CYS and UCS decreased with the addition of GMB particles beyond 5%, the energy absorption capability of the MgMSFs increased with the addition of GMB particles. The increase in the vol.% of GMB in samples increased the embedment of porosity/cavities in the samples. The cavities became crushed during compressive loading, resulting in a higher energy absorption capability of samples. Thus, as the amount of GMB hollow particles increased, it enhanced the energy absorption capability of MgMSFs.

Manakari et al. [9] utilized the ratio of the compressive yield strength of syntactic foams to the matrix versus the density of syntactic foams to understand the impact of the reinforcement on the compression strength of the syntactic foams. Figure 12 shows a similar analysis performed on the developed MgMSFs to understand the impact of the GMB on the Mg matrix. The developed MgMSFs were compared with the Al [50,53–55], Ti [14,56], and Fe [57] MSFs. The results revealed that for the densities of syntactic foams in the range of 1.5–1.2 g/cc, the ratio of the yield strength of syntactic foams to the matrix was 2–5.5 times higher in the developed MgMSFs compared to TiMSFs. Similar to the ratio of the yield strength of syntactic foams to the matrix in the range of 0.8–0.9, the developed materials had a 24–33% lower density compared to Al MSFs, and a 50–68% lower density compared with FeMSFs.

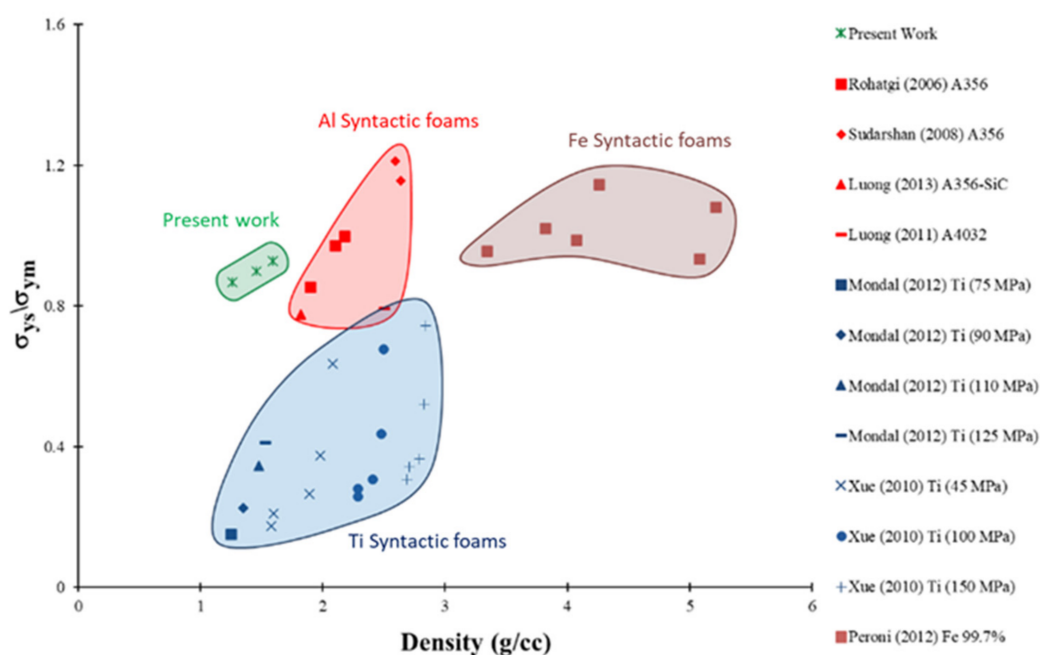


Figure 12. Graph of the ratio of the compressive yield strength of syntactic foam to the matrix versus the density of syntactic foams.

5. Conclusions

Based on the current work, the following conclusions can be drawn:

1. MgMSFs with a GMB hollow particle reinforcement were successfully developed via the powder metallurgy process without any formation of detrimental secondary phases. The results from the XRD and density test showed the suitability of the parameters utilized in developing the Mg-GMB syntactic foams via microwave-assisted powder metallurgy.
2. The coefficient of thermal expansion of the developed MgMSFs decreased (improved thermal stability) and the ignition temperature increased with the addition of GMB hollow particles. Mg-20GMB samples exhibited a CTE ~20% higher than that of pure Mg, and the ignition temperature was 20 °C higher than that of pure Mg.
3. The microhardness of the Mg MSF increased with the increasing addition of GMB hollow particles. Mg-20GMB foams exhibited a microhardness of 114 Hv, which was ~75% higher than that of pure Mg.
4. The ultimate compression strengths of all MgMSFs were higher than that of pure Mg. The Mg-5GMB syntactic composite exhibited the highest UCS of 321 MPa, which was ~26% higher than that of pure Mg.
5. The fracture strain and energy absorption capability of developed the MgMSFs were superior when compared to pure Mg. Mg-20GMB exhibited a fracture strain and energy absorption capability ~39 and ~65% higher than those of pure Mg, respectively.

Author Contributions: Conceptualization, M.G. and V.M.; methodology, M.G., G.P. and V.M.; material synthesis, C.H. and V.M.; experiments, data analysis, and investigation, C.H., A.P.S. and V.M.; writing—original draft preparation, A.P.S.; writing—review and editing, G.P., V.M. and M.G.; supervision, project administration, and funding acquisition, M.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Singapore Ministry of Education Academic Research Funding. The grant number is WBS# R-265-000-684-114.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank Ng Hong Wei, National University of Singapore for his assistance in the CTE and TGA measurements and Juraimi B Madon, National University of Singapore for his assistance in extrusion.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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