Improved hardness characteristics of Mg-3Zn-1Cu-0.7Mn alloy composites reinforced with Al\textsubscript{2}O\textsubscript{3} synthesized by powder metallurgy

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Abstract. A novel composite Mg-3Zn-1Cu-0.7Mn reinforced with Al\textsubscript{2}O\textsubscript{3} particulates was synthesized using the powder metallurgy route and extruded at 400°C. The investigation mainly focuses on the influence of Al\textsubscript{2}O\textsubscript{3} on the hardness characteristics of the composites. The results indicate the microhardness of the composite is enormously enhanced by incorporating the Al\textsubscript{2}O\textsubscript{3} particulates to Mg alloy. The homogeneous distribution of the hard ceramic reinforcement particulates and the presence of intermetallic phases such as Cu\textsubscript{5}Zn\textsubscript{8}, MgZnCu, and Al\textsubscript{0.93}Cu\textsubscript{1.07}Mg attributed the improved hardness. It is recognized that the stress-relieving process further improves the hardness of the composites. The extrusion parameters also influence the hardness characteristics of the composites.

1. Introduction
Magnesium (Mg) and Mg-based alloys are extensively utilized in structural applications including aerospace, military, automotive, electrical, and biomedical sectors due to its lightweight, high strength to weight ratio, better machinability, and excellent damping capacity. But its applications are limited at present in the corresponding fields due to the insufficient elastic modulus, strength, and hardness [1, 2]. The mechanical characteristics of the Mg metal can be improved with alloying and heat treatment. The recent studies show that the inclusion of ceramic particles is an efficient method for enhancing the mechanical characteristics of magnesium alloys. In situ composite consists of multiple phases, including the primary and secondary phases. The secondary reinforcing phase is formed inside the metal matrix by specific chemical reactions which is in the form of fine particles and thermally stable in the metal matrix. It is also emerging in thermodynamic agreement at the matrix/reinforcement interface [3, 4]. Thus the Mg alloy based composites fabricated through in-situ methods display excellent mechanical properties.

In the field of lightweight materials, Al matrix composites fabricated through various in-site processes has been drawing attention from researchers for use in industrial utilisation due to its excellent mechanical properties. At the same time, Mg-matrix in situ composites couldn’t find much attraction from researchers. Research studies reveal that Mg -matrix in situ composites can be a potential candidate for both structural applications and biodegradable biomaterials [5, 6]. The literature survey reveals that Silicon Carbide (SiC\textsubscript{p}) are the most preferred reinforcement
among the researchers. The high hardness, wear resistance, elastic modulus, wear resistance, performance at elevated temperatures and low price of the SiC particles cause for the further studies of the composites reinforced with SiC particles [7, 8]. But recently, Al$_2$O$_3$, CNTs, Y$_2$O$_3$, etc. are also emerged as the reinforcements to strengthen the Mg matrix. The pattern of research on the composites is based on the improvement in characteristics by varying the size, weight fraction, morphology and distribution of the reinforcement particles and by altering the fabrication techniques [9–13]. In the last couple of years, several alloys were developed based on Mg-Zn, Mg-Si, Mg-Ni, Mg-Ca, Mg-Sc, and Mg-Cu-Mn [14–17]. Nishiyama et al. fabricated Mg-Cu-Mn alloys through Powder Metallurgy (PM) technique followed by sintering. The properties of the alloys are found to be superior compared to the pure Mg metal. At the same time, Mg-Cu-Mn alloys prepared through simple conventional melting process exhibited better damping properties, even though the tensile strength was reduced [18].

Hot extrusion is a secondary process for improving the mechanical characteristics of the alloys. The microstructure of the alloys is altered during the hot extrusion process. Several new grains are formed, and secondary intermetallic phases are precipitated after the hot extrusion process. The dynamic recrystallization and dynamic precipitation are processes resulting in the abovementioned activities. Gupta et al. have done a lot of work in improving the mechanical properties of the Mg alloys by reinforcing with different reinforcements, particularly Al$_2$O$_3$ [19–22]. The composites based AZ81 reinforced with Al$_2$O$_3$ exhibited superior tensile and compressive characteristics compared to the AZ81 base alloy. The composites strengthened by nano SiC particles by Ferker and Mordike reported improvement in tensile and creep properties [23]. In the present work, a new Mg-3Zn-Cu-0.7Mn based alloys and the alloy-based composites reinforced with Al$_2$O$_3$ particulates are synthesized. The microstructure, metallurgical, and hardness characteristics of the composites are analyzed. The influence of stress-relieving on the hardness characteristics is also investigated here.

2. Experimental procedure
Elemental metal powders of Mg (99.99 wt.% purity, 200 mesh), Zn (99.99 wt.% purity, 200 mesh), Cu (99.99 wt.% purity, 200 mesh) and Mn (99.99 wt.% purity, 200 mesh) are employed for the fabrication of the alloy billet using the PM technique. The ceramic metal powder Al$_2$O$_3$ (99.99 wt.% purity, 200 mesh) is added to the alloy to synthesize the composite. The blend-press-sinter PM technique is used for the fabrication of the alloys and composites. A ball milling machine is exercised for the homogeneous mixing and blending of the metal powders. The ball mill is operated for 24 hours at 100 rpm with a ball feed ration of 3:1. The mixture is compacted utilizing hydraulic power press to form the alloys and composites billet, applying a load of 1500 kg. The sintering of the billets is executed in the Argon atmosphere at a temperature of 400°C for 1 hour. Secondary strengthening of the billets is done with hot extrusion. The billets are hot extruded at 400°C to form rods of small diameter with an extrusion ratio 5.4:1 using an extrusion die with a hydraulic power press at a speed of 0.2 to 0.5 mm/s. The rods thus formed are stress-relieved at 260°C for 15 minutes in the Argon atmosphere in an electronic muffle furnace. The properties of the composite samples are analyzed with two categories, one without the stress-relieving, i.e., as-extruded (represented as E1 and F1) and the other with stress-relieving (designated as E2 and F2). An etchant prepared using 1.5 g picric acid, 25 ml ethanol, 10 ml acetic acid, and 10 ml distilled water is applied for capturing the optical microstructure of the specimens. X-Ray Diffraction (XRD) is used for the detailed phase analysis of the alloys and composites.
3. Results and Discussion

3.1. Microstructural analysis

The microstructural analysis of the samples reveals the morphological changes that happened during the manufacturing process. Figure 1 represents the optical microstructure of the polished, etched composite specimens F1 and F2. According to microstructural analysis, the Al₂O₃ particles are distributed uniformly across the entire microstructure. Minimum pores are observed in the microstructure. It indicates the strong bonding between the alloys matrix and reinforcement phase. The blending parameters used and the higher extrusion ratio employed resulted in uniform distribution of the secondary phases with minimal pores. The limited number of microvoids and the interfacial reaction happened between the primary and secondary phases in the composites caused the extraordinary bonding between the particles [19-21]. The micrographs show equiaxed and well-refined grains. It may be due to the DRX happened following the hot extrusion process. The internal energy stored in the material is dissipated during the hot extrusion at elevated temperature, which causes the formation of DRXed grains. The higher thermal and strain energy provided during the hot extrusion process lead to dynamic precipitation also. Therefore the grains become well refined followed the hot extrusion process through DRX and DP. The number of microvoids and micropores are found to be reduced after the stress-relieving process. The grain refinement took place may be fundamentally due to the ability of Al₂O₃ particles to nucleate Mg grains during the recrystallization process. The pinning effect of Al₂O₃ particulates on Mg grains that caused for restricted grain growth during the recrystallization process. It may also be a reason for the grain refinement.

The research exposes the following facts, (i) homogeneous distribution of reinforcement across the entire microstructure (ii) the bonding between the alloy matrix and the reinforcement phase (iii) minimal porosity of the composites and (iv) the interfacial characteristics of matrix and reinforcement.

3.2. Density and Porosity Results

Table 1 gives the theoretical densities, actual densities, and porosities of the composites fabricated. The experimental density of the stress-relieved composites (F2) is observed to be less than that of the as-extruded composites (F1). It may be due to the limited number of micropores and microvoids after the stress-relieving process. The entrapped gases during the blending process result in the porosity in composites following the PM technique. Since the actual densities and theoretical densities are very close, the porosity values are found to be tiny.
The limited porosity is compatible with the results of the microstructural analysis. The hydrogen in composites also causes the porosity in the composites. The porosity values less than 0.5% indicates the synthesis of the composite was successful, and it is also proved that PM is a proper method for the fabrication of Mg-based composites.

Table 1. Density and porosity of the composite samples at room temperature

| Sl. No. | Material                                      | Theoretical density (g/cm³) | Experimental density (g/cm³) | Porosity (%) |
|---------|-----------------------------------------------|-----------------------------|-------------------------------|--------------|
| 1.      | Mg-3Zn-1Cu-0.7Mn/Al₂O₃ composite (F1)         | 1.834                       | 1.825 ± 0.003                | 0.49 ± 0.006 |
| 2.      | Mg-3Zn-1Cu-0.7Mn/Al₂O₃ composite (F2)         | 1.834                       | 1.829 ± 0.003                | 0.27 ± 0.005 |

3.3. X-ray diffraction studies

The composite specimens in powder form were applied with Cu-Kα radiation of wavelength 1.5406 Å to recognize the different phases associated with the microstructure of the composite fabricated. The scanning speed was set 2°/min with a beam current 30 mA and a voltage of 40 kV. The lattice spacing (d) and the Bragg angles of the phases are compared with related phases of Mg, Al₂O₃, Zinc, Manganese, and Copper. The X-ray diffractograms obtained is shown in Figure 2. From the XRD analysis, it is revealed that the following phases of Mg and Al₂O₃, Cu₅Zn₈, MgZnCu, and Al₀.₉₃Cu₁.₀₇Mg are present as dispersed in the microstructure. The intermetallic phases are found to be in the dispersed form near the grain boundaries of the alloy matrix. The dynamic precipitation occurred due to the hot extrusion process contributed to this much number of phases in the composites, as found in the microstructural analysis.

3.4. Hardness studies

The microhardness of pure Mg, AZ31B, fabricated alloys, and composites are given in Table 2. The maximum microhardness is observed for the stress-relieved composites (F2). The comparison between the alloys and composites are indicated in Figure 3. The microhardness of both the alloys and composites are much improved than pure Mg metal. Multialloying is proved to be a suitable technique to improve the microhardness of the monolithic Mg metal. It is observed that the microhardness of the Mg alloys is further enhanced by reinforcing with Al₂O₃ particulates. Hence it is unveiled that incorporating Al₂O₃ particles to the Mg alloy matrix through powder metallurgy improves the microhardness. Thus PM technique can be used to synthesis Mg composites with superior microhardness.

The influence of Al₂O₃ in improving the microhardness of the Mg composites is remarked here. The primary reason for the improvement is due to the hard ceramic nature of incorporated Al₂O₃ particles. The refined grains attained by the dynamic recrystallization and dynamic precipitation through the hot extrusion process also contributed the improved hardness. Hence
Figure 2. XRD Patterns of as-extruded Mg-3Zn-1Cu-0.7Mn / Al₂O₃ composite (F1) and stress-relieved alloy composite at 260°C (F2) sintered at 400°C

Table 2. Microhardness observed for the alloys and composites

| Sl. No. | Materials                                      | Micro hardness (HV) |
|--------|-----------------------------------------------|---------------------|
| 1.     | Pure Mg                                       | 48 ± 1              |
| 2.     | AZ31B                                         | 63 ± 1              |
| 3.     | Mg-3Zn-1Cu-0.7Mn alloys – as-extruded (E1)    | 74 ± 3              |
| 4.     | Mg-3Zn-1Cu-0.7Mn alloys – Stress-relieved (E2)| 78 ± 2              |
| 5.     | Mg-3Zn-1Cu-0.7Mn /Al₂O₃ composites – as-extruded (F1) | 80 ± 3              |
| 6.     | Mg-3Zn-1Cu-0.7Mn/Al₂O₃ composites – Stress-relieved (F2) | 87 ± 2              |

the influence of the hot extrusion process on the microhardness of the composites is also revealed here. The hard intermetallic phases such as Cu₅Zn₈, MgZnCu, and Al₀.₉₃Cu₁.₀₇Mg found in the XRD analysis also contributed the superior microhardness. These intermetallic phases restrict the deformation of the alloy matrix upon indentation. The limited porosity of the composites, as per the results of porosity analysis, also provided added hardness to the composites compared to pure Mg and the fabricated alloys.

From Figure 3, the potential influence of the stress-relieving process on the hardness of alloys and composites can be recognized. The hardness of the as-extruded composite is reported to be 80.45 HV, which is improved to 87.19 HV after stress-relieving. More than 8% of hardness is achieved through the stress-relieving process. The micropores in the composites are formed due to the entrapment of gases during the blending and mixing process. These entrapped gases create micropores upon the compaction process. Due to the liberation of the trapped gases in the
composites, the size and number of micropores are reduced on stress-relieving. The improvement in microhardness has resulted by the reduced number of micropores and microvoids following the stress-relieving process. The analysis of the optical microstructure validates the minimal amount of micropores in the stress-relieved composites.

4. Conclusion
The fabrication of the composite Mg-3Zn-1Cu-0.7Mn /Al₂O₃ was successful, employing the blend-press-sinter powder metallurgy route accompanied by a hot extrusion process for superior mechanical characteristics. The investigation is mainly focussed on the role of Al₂O₃ particles in improving the microhardness of the Mg alloy matrix composites and the mechanism affiliated with it. The study also examined the influence of the stress-relieving process on the hardness characteristics of the composites. The following parameters are concluded from the research.

(i) Powder metallurgy is proved to be a proper technique for the manufacture of the Mg alloy based composites.

(ii) The grain refinement, followed by dynamic recrystallization achieved through the hot extrusion process enormously, influences the hardness characteristics of the Mg composites.

(iii) The Al₂O₃ particulates incorporated to the Mg alloy enhances the microhardness of the Mg composites due to the homogeneous distribution of the reinforcement of particles over the entire microstructure.

(iv) The presence of hard intermetallic phases such as Cu₅Zn₈, MgZnCu, and Al₀.₉₃Cu₁.₀₇Mg adds improved hardness to the composites.

(v) The stress-relieving process is found to influence the hardness of the composites strongly. The reduced number of micropores and microvoids after the stress-relieving process result in the improved hardness of the composites.

Figure 3. The comparison of microhardness of the alloys and composites fabricated
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