EXPERIMENTAL STUDY ON HYBRID MAGNESIUM COMPOSITES FOR HUMAN BONE IMPLANTS

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ABSTRACT

The hybrid Magnesium composite having alloying elements zinc, manganese with the reinforcement of nano TiO_2 and micron level Al_2O_3 was prepared through hot press sintering method. This study is primarily determined the effect of reinforcing multi ceramic particles in the Mg composites for their mechanical and corrosion strength to validate the human bone implants. The scanning electron microscopy and X-ray diffractogram were used to analyze the micro structural variation on the hybrid composites. The microstructural study showed that, many intermetallic phases were formed during the composite preparation process which reduces the porosity and increases density of the composites. The reinforced particles, manufacturing process and after heat treatment or stress reliving process were enhanced the mechanical and corrosion strength of the prepared hybrid composites.

Keywords: Heat treatment, Microstructure, Mg based composite, Al_2O_3 reinforcement, Hybrid composites.

1. INTRODUCTION

The composite formation is defined by adding two or more materials to enhancing the physical, mechanical and chemical properties of the individual materials. Generally researchers were suggested that, the strength of composite material were depends with their reinforcement particles into the base matrix [1]. Recently, composites or their hybridation were used for the engineering field such as aeronautics, sports, soldierly equipment and bio-medical. These applications were requires light weight with high strength and better machinability with damping characteristics. Magnesium and its alloys and composites were possessing these characteristics. A various characteristics of the magnesium could be enhanced by forming alloys and composites through proper selection of alloying elements and particle reinforcements. The after heat treatment process could be further improved these characteristic by forming secondary phases of the elements present in the alloys and composites [2,3,4].

The density of the magnesium alloys are compared to aluminum and titanium alloys, its densities were approximately 35% and 65 % lesser than the respective mentioned alloys [5]. Many researchers suggested that the density ranges of magnesium alloys were lies between 1.74 and 2 gm/ cm^3. This range is similar to the human bone density. Therefore, the magnesium alloys and their composites are useful for biomedical applications [6, 7]. The Magnesium alloys are exhibiting lower young's modulus but the same could be enhanced by the addition of ceramic hard particles as reinforcements in the matrix [8]. The economy and suitability for forming concern of the Mg composites, most of the researchers are concentrates their research work in the field of structural, biodegradable and biomaterials for human body implants [9 - 11].

The Mg based composite studies were mostly concentrated to improve their mechanical characteristics through altering composites metallurgical properties by reinforcements. And, the composite forming techniques such as pressing and extrusion methods also improved their properties [12–14]. Recently researchers were used titanium oxide (TiO_2) as a reinforcing element for preparing Mg composite using powder metallurgy method and proved the incorporation of the same could enhances the strength of the Mg composite than the pure form of Mg [11, 15, 16]. The microstructure alteration could be done through recrystallization of grains and precipitation of the same occurring during hot extrusion process caused the formation of intermetallic phases [15]. Al_2O_3 is one of the reinforced element for the Mg composites which is bio-degradable in nature and the addition of same was enhanced the physical and mechanical characteristics of the Mg composites [17-21]**.**

The bio-medical application requires higher corrosion resistance materials. The corrosion resistance of the pure form of Mg and its alloys were poor due to forming intermetallic second phases at the grain boundaries causing negative polarization with the interior grains thus promoting galvanic corrosion [22- 25]. In-contrast, the addition of Al, Zn, Mn, Sn, Ca were enhanced the corrosion properties of the Mg alloys and composites [26]. However, the requirement of Mg based alloys and composites are yet to be fulfilled in structural and bio-medical applications. Moreover, the superior bio gradable properties of magnesium has received an attraction to the researchers and industrial community to do their reach work with the use of magnesium [27].

The corrosive performance of the magnesium was comparatively low when compared to aluminum and iron metals. The fast degradation of the magnesium implants in human physique is the main shortcoming for the bio-medical applications [28,29]. Therefore, improvement is required for the corrosion issue of magnesium alloy as load bearing biodegradable implants. In fact, the body metabolism and biological mechanism involved the presence of magnesium. Magnesium by nature, it is observed as a biodegradable material and could be degraded in human body fluid. Therefore, magnesium is attracted the researchers to do their research work in the field of biomedical applications using its different forms [30,31].

The fact for the preparation of Mg matrix composites were depended with the selection of suitable reinforcement materials added into the Mg matrix. The selected reinforcement material should have (i) high mechanical strength and (ii) biocompatible and have good corrosion resistance [32, 33]. This work is to prepare and studied the Mg-3Zn-0.5Mn alloy and the reinforcement of nano TiO_2 and Al_2O_3 micro particulates were added hybrid composites. The selected Mg matrix elements and reinforcement elements were biodegradable and are having good mechanical and corrosion strength. The mechanical and corrosion characteristics of the prepared hybrid composites were investigated and the obtained results were discussed.

2. EXPERIMENTAL PROCEDURE

The elements selected to form Mg-alloys were Mg, Zn, and Mn metal powders. These powders were in micron level and the reinforcement material chosen as n-TiO_2 (50 – 100 nm) and μ-Al_2O_3. The alloying metallic elements Zn and Mn powders were added to the Mg-matrix by 3wt% and 0.5 wt%. The reinforcement particle n-TiO_2 was added as 0.1wt%. But, the Al_2O_3 powder added was varied by 1 wt% to 3 wt%. These elements were mixed mechanically at 350 rpm for 1 hour to form a billet of diameter 50mm and the height was 30mm using powder metallurgy technique. A hydraulic power press was used for the compaction process to maintain 690 Mpa pressure.

After forming billets, they were sintered using 400°C temperature. The sintering process was carried out in an argon environment for one hour. The hot extrusion process was carried out to strengthen the billets. This process was carried out at the temperature of 400°C, extrusion ratio of 5.4:1 and speed 0.2 to 0.5 mm/s to form rods of the Mg-alloy and composites. The formed rods were annealed in an electric muffle furnace for relieving their internal stresses. The annealing process was carried out at the temperature of 260°C and which was maintained at 20 minutes in an argon environment. The prepared material were characterized by their as-extruded and after annealing.

The optical microscopy technique (OM) and scanning electron microscopy techniques were used to find their micro structure. The OM machine used was MVHD-1000 AP/MP, Shanghoui Dahens Optics and Fine Mechanics Co. Ltd. For capturing images samples were etched by the etchant which contains picric acid: 1.5 grams, ethanol: 25 ml, acetic acid: 10 ml with 10 ml distilled water. After completing the etching process, the samples were cleaned in distilled water. The corrosion studies were carried out by two methods such as immersion test

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and electrochemical polarization method. The corrosion medium used for the first one was stimulated body fluid (SBF) and rest was aqueous solution which contains 3.5 wt. % NaCl. Because the prepared material is planned to utilize for both structural material and bio-medical applications. The procedure for conducting immersion test is detailed below:

The prepared samples were weighed initially and separately immersed under the SBF solution for 168 Hrs. During this period, the setup was not disturbed. The setup temperature was maintained at 36˚C using incubator. After, 168 Hrs the samples were cleaned by mixed Cro_3 and $AgCrO_4$ solution followed by acetone wash to remove the debris. After wash, the samples were weighed and calculated its corrosion rate using the equation 1[11]. The SBF solution constituents are tabulated in the table 1. (Three trials were taken to found the average value).

$$R = \frac{(W_b - W_a + B)\times 1000}{A\times t} \quad \text{……………………………………………(1)}$$

Where,

R = Rate of corrosion, mg $cm^{-2}day^{-1}$

W_b = Initial weight of the sample (before test (g))

W_a = Final weight of the sample (after test (g))

B = weight loss of blank (g).

A = Sample's surface area (cm^2)

t = exposure time (day)

$$\text{Corrosion rate } (mm.y^{-1}) = \frac{1}{0.274\times\rho} R \quad \text{……………………………………..(2)}$$

ρ = Density of the material

Table 1: SBF solution preparation (source: Judson et. al., (2017)[11])

Sl. No	Materials	Quantity (g/l)
1	NaCl	7.996
2	$NaHCO_3$	0.350
3	KCl	0.224
4	$K_2HPO_4 \cdot 3H_2O$	0.228
5	$MgCl_2 \cdot 6H_2O$	0.305
6	HCl	40 mL/l
7	$CaCl_2$	0.278
8	Na_2SO_4	0.071
9	$(CH_2OH)_3CNH_2$	6.057

The second method is electrochemical analyzing method, which was carried out using electro chemical analyzer CHI-604D, CH Instruments,USA. The analyzer was manufactured with three cell electrode configuration i.e., working electrode is specimen, reference electrode is saturated calomel electrode and platinum metal is as a counter electrode. The corrosion medium used for this study was saline water which contains 3.5 wt. % of NaCl. The scan rate used for this study was 1 mV s^{-1} with the room temperature. The corrosion rate was calculated from tafel electrochemical measurement using the equation (3) [11].

$$\text{Corrosion rate } (mm\ y^{-1}) = \frac{3.28M}{n\rho} i_{corr} \quad \text{……………………………………. (3)}$$

n = Quantity of free electrons involved for corrosion reaction

M= Atomic mass

ρ = Test specimens density

3. RESULTS AND DISCUSSION

3.1 Density and Porosity

The theoretical, actual and relative densities values of the composites were depends with the increasing reinforcement content and its ratio [34,35]. The obtained densities of the fabricated Mg-3Zn-0.5Mn alloys were 1.811g/cm^3 and 1.813 g/cm^3 for before and after heat treatment respectively. The densities variation happened for the fabricated hybrid composites were depicted in the figure 1. The density values of the fabricated alloys and hybrid composites were higher than the pure Mg as 1.74 g/cm^3 at their as-extruded and heat treated conditions. The increasing hybrid composites densities were increases with the increasing Al_2O_3 reinforcements because the added alumina particles were relatively having higher density than the other elements added in the composite matrix. Also, the heat treatment process enhanced the densities of the alloys and composites than its as-extruded condition because during heat treatment, the particles were diffused to fill the pores [36]. The reduction in pores were the main reason for increasing the densities of the hybrid composites.

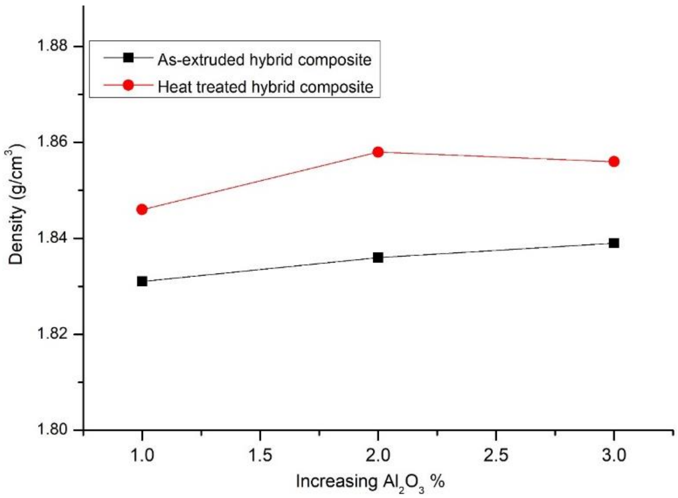


Figure 1: Density variation of hybrid composites

The added 3 wt. % of alumina particles were exhibits lesser density than the 2 wt. % alumina particles at their heat treated condition. This could be due to the agglomeration of the added reinforcement particles. Moreover, when comparing as its as-extruded condition for the mentioned weight percentages, the density variation is not much more. Almost all the conditions of the hybrid composites, the enhancement in density was occurred between the reinforcements weight percentages 1 and 2. It inferred that the higher wt. % of the reinforcements addition in the composites matrix could disturbed the homogeneity of elements distribution in the matrix.

The obtained porosity values of the alloys and hybrid composites after heat treatment conditions were depicted in the figure 2. It's showed that the hybrid composite containing 2% Al_2O_3 with their after heat treatment condition was having minimum porosity value when comparing other fabricated alloys and composites. Moreover, all the prepared hybrid composites with their after heat treatment conditions were exhibits lower porosity than the alloys and pure Mg. As a fact, the porosity of the composites depends with the amount of shrinkage of their volume. The reduction in volume of the materials could be take place during the sintering and hot- extrusion process.

In general, the unwanted gases present in the composites were entrapped during the blending and mixing process. Also, hydrogen evolution process was happened during the sintering process resulted to fill micro pores present inside the composites. When comparing the hybrid composites with 2 and 3 wt. % Al_2O_3 addition, the 3 wt. % Al_2O_3 addition exhibits higher porosity. But it is lesser than the 1 wt. % Al_2O_3 addition. These results inferred that the higher wt. % of Al_2O_3 reinforcements were indulge the porosity characteristics of the composites. This might be the agglomeration of the added reinforcement particles happened during extrusion process.

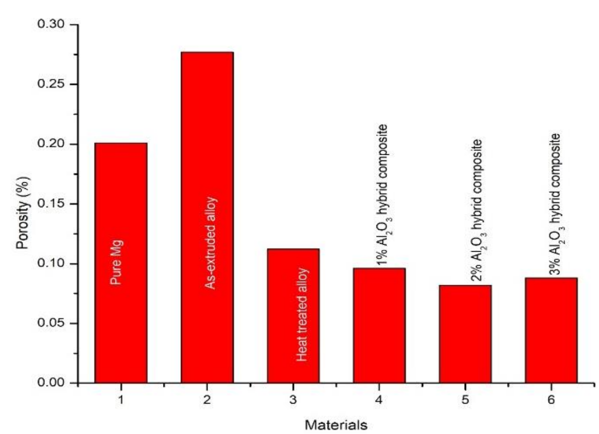


Figure 2: Porosity comparison of prepared alloys and composite materials.

The melting temperature of the Al_2O_3 and TiO_2 particles were higher than the other added elements present in the matrix. The extrusion process disturbed the particles arrangement after sintering causing micro voids and agglomeration of the particles presence. The heat treatment or stress relieving process could rearrange the particles to reduce the micro voids but not completely. This could be due to the melting temperature difference between the reinforcement and alloying elements. The alloying elements recrystallized to rearrange the microstructure of the matrix and fill the micro voids after heat treatment. Moreover, both the alloys and composites showed the porosity values are less than 0.5%. It indicates that composites synthesized through the PM process have produced nearly dense samples.

3.2 Microstructure

The microstructural analysis was carried out on the prepared Al_2O_3 enriched hybrid composites. This analysis was carried out through optical microscope and scanning electron microscope. The resulted images were depicted in figures 3 and 4 respectively. The obtained images were exposed the morphological transformations that happened during the manufacturing process and after heat treatment. From the result of density and porosity, optical and SEM images were took for the 2wt. % Al_2O_3 reinforced hybrid composites for their as-extruded and heat treated conditions and they are mentioned respectively as F1 and F2. The microstructural analysis of the composite samples indicated that the uniform distribution of Al_2O_3 particles over the entire matrix with a limited number of micro pores with their as-extruded and heat treated conditions. Thus, improved the bonding strength of the elements originated between the alloy and reinforcement elements present in the matrix. Even though there was a uniform distribution, certain places clusters of Al_2O_3 particles were also present in the matrix.

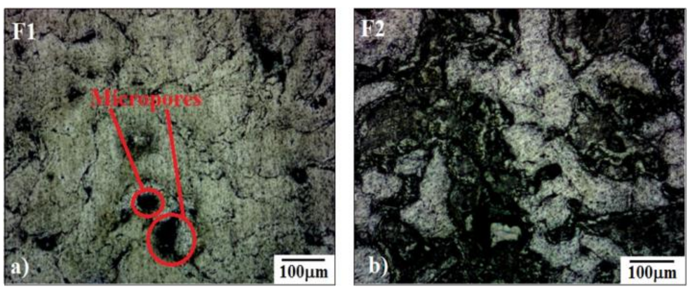


Figure 3: Optical microscope of 2wt. % Al_2O_3 reinforced hybrid composites (a) as-extruded condition (b) heat treaded condition.

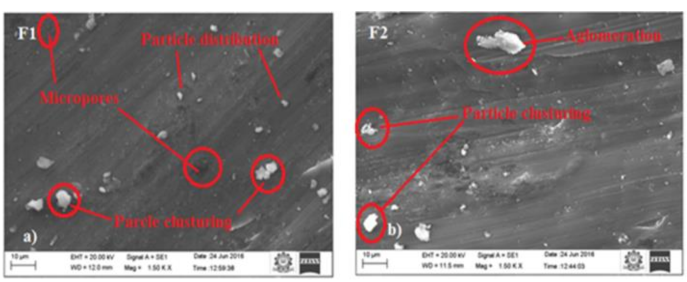


Figure 4: Scanning electron microscope of 2wt. % Al_2O_3 reinforced hybrid composites (a) as-extruded condition (b) heat treaded condition.

The clusters of the reinforced particles present in the matrix were very limited as shown in the figure 4. Thus reduced the porosity and increased the density properties of the hybrid composites. Also, the micro pores and voids were very much lesser as compared to the alloy system shown in the figures 5. The reduction in bores and voids were increases the bonding strength of the composite matrix. Because the interfacial reaction taken place between the matrix elements.

Commonly, the recrystallized elements were capturing reinforced particles during their recrystallization process and if the reinforced particles were having low thermal gradient, both were merged or bonded together. But the reinforced alumina and titanium oxide were having high thermal gradient. Therefore, the outer surfaces were porous and the interior were covered with alloying elements to reduce the porosity. When comparing the optical and scanning electron micrographs of the before and after stress-relieving or heat treatment process carried out on the prepared composites, the after heat treated composites were showed the equiaxed grains formed in their matrix. The sizes of the formed equiaxed grains for the stress-relieved composites were witnessed to be more significant as comparing to the non-treated composites. This could be due to the grain refinement took placed within the matrix by the nucleation of Al_2O_3 particles during recrystallization process. The other reason was the pinning effect of Al_2O_3 particulates on Mg grains that caused restricted grain growth during the recrystallization process.

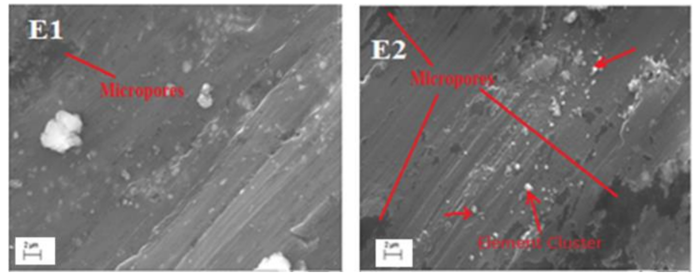


Figure 5: SEM of (a) as-extruded alloy (b) Heat treated alloy.

3.3 Tensile Strength

The tensile strength of the as-extruded and stress relieved Mg-alloys and Al_2O_3 enriched hybrid composites were testing using DAK-UTB9103 computerized mechanical testing machine at room temperature. The movement of the crosshead was maintained at 0.25 mm/min. The obtained tested curves are depicted in the figure 6. From the obtained result showed that the ultimate tensile strength of the pure Mg was 150 MPa which is proved by seetharaman et. al., (2013)[37]. Also the results indicated that the maximum ultimate tensile strength 260 MPa obtained for the Mg alloy and the corresponding fracture strain was 8.3%. The heat treated Al_2O_3 enriched hybrid composites were exhibits lower ultimate tensile strength than the prepared alloy system. But the strain of the hybrid composites were higher than the alloy system and all the tensile properties are superior when compared with that of the pure magnesium metal. The comparison of ultimate tensile strength and strain were depicted in the figures 7 and 8 respectively.

The tensile strength of the fabricated alloy system was exhibited higher strength than the fabricated hybrid composites. When comparing the heat treated heat treated hybrid composites, the 2wt. % Al_2O_3 enriched hybrid composite exhibited higher tensile strength than the other fabricated hybrid composites. This could be due to the obtained well refined grains of the Mg matrices were increases the area of grain boundary and surface integrity between the matrix phase and the reinforcement phases which magnifies the strength of the material. The main parameter that influences the strength of composites was the movement of dislocations. The dislocation movements are stopped or hindered by the ceramic oxide particles, which lead to the accumulation of dislocations and increases the strength of the composites. The dislocation movement heavily influences yield properties.

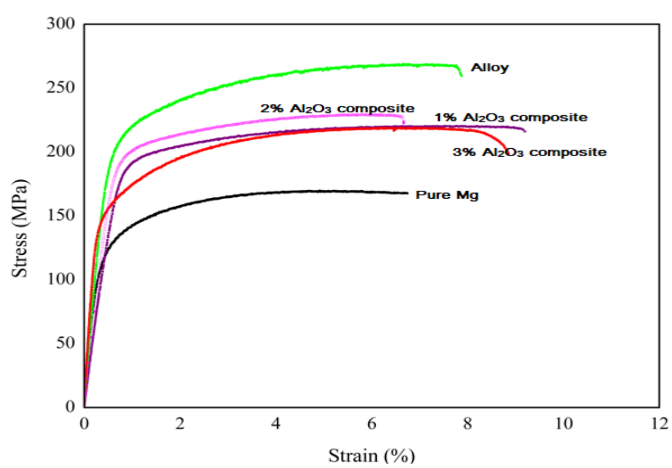


Figure 6: Tensile Strength of the fabricated materials.

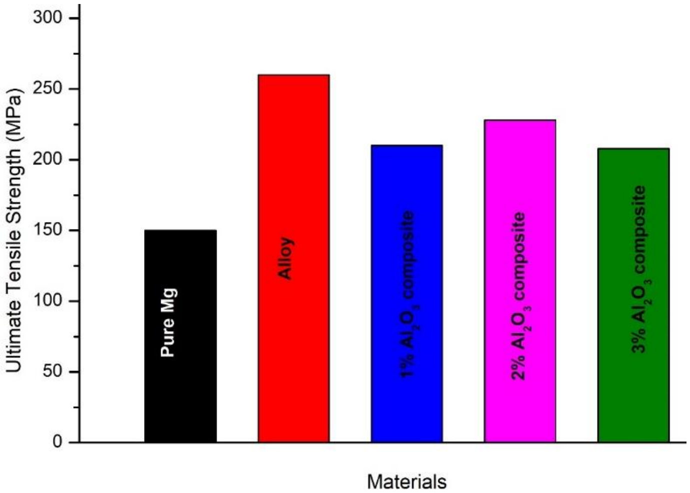


Figure 7: Comparison chart of ultimate tensile strength.

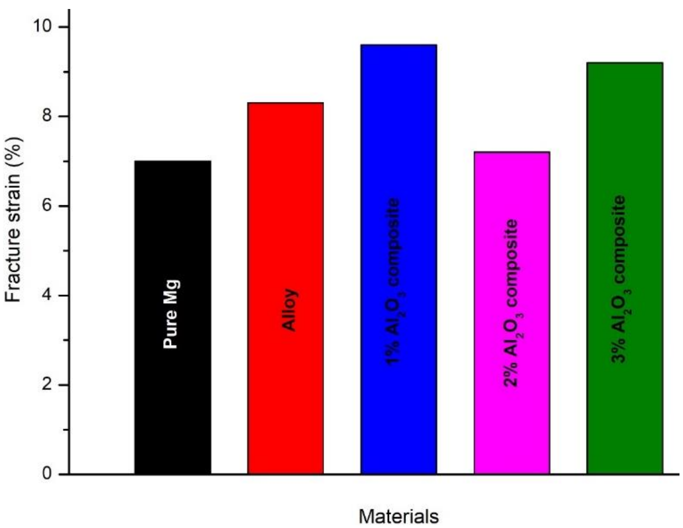


Figure 8: Strain comparison chart for the prepared materials.

The tensile strength of the fabricated alloy system was exhibited higher strength than the fabricated hybrid composites. When comparing the heat treated heat treated hybrid composites, the 2wt. % Al_2O_3 enriched hybrid composite exhibited higher tensile strength than the other fabricated hybrid composites. This could be due to the obtained well refined grains of the Mg matrices were increases the area of grain boundary and surface integrity between the matrix phase and the reinforcement phases which magnifies the strength of the material. The main parameter that influences the strength of composites was the movement of dislocations. The dislocation movements are stopped or hindered by the ceramic oxide particles, which lead to the accumulation of dislocations and increases the strength of the composites. The dislocation movement heavily influences yield properties.

The difference in CTE of the matrix and reinforcement creates thermal stress to induce at elevated temperatures in between the matrix and reinforcement interfaces. The direction of thermal stresses may be in any direction, and it forms multi-glide planes along which the dislocations move. But when the material is loaded, thermal stresses are evolved in multiple directions and builds multiple glide planes. The accumulation of numerous glide planes produced ledges at the grain boundary as shown in the figure 3 and 4, which prevents the free movement of dislocations and increases the strength of the materials.

Here it was noticed that the tensile properties of the Al_2O_3 enriched hybrid composites were somewhat lesser than that of the fabricated alloy. It might be due to the dislocation pile-ups that happened at the grain boundaries. Wu et al., (2010)[38] were agreed the dislocation pile-ups occurred by the accumulation of reinforcements, which is caused by the dispersion of hard oxide particulates at the grain boundary. The thermal stresses between the grains also caused these mass dislocation pile-ups. The cavitation emerged at grain boundaries due to this dislocation pile-ups caused for the reduction in tensile properties of the hybrid composites compared to the alloys.

The fracture strain of the 1% Al_2O_3 and 3% Al_2O_3 reinforced hybrid composites were having higher values than that of the alloy system. In contrast, the 2% Al_2O_3 reinforced hybrid composite could exhibits lower facture strain value than the alloy system. The obtained lower strain value might be due to the dislocation pile-ups mentioned above at the grain boundaries of the composites. The non-homogenous distribution of the reinforcements increases the stress concentration along with the alloy matrix. The reinforcement in the dispersed form across the alloy matrix provides sites for cleavage steps and fractures thus improved the toughness of the composite. The increasing toughness could increases the straining values of the composites. This might be the reason for increasing fracture strain of the 1% Al_2O_3 and 3% Al_2O_3 reinforced hybrid composites.

The fractograms of the hybrid composites after tensile tests were displayed in Figure 9. From the mentioned figure, it was observed that a combination of ductile and brittle fractures had occurred at the fracture surface. The 3wt. % Al_2O_3 addition was comprised a lot of dimples and ridges at the fracture facades thus create a ductile fracture due to increasing toughness of the composites. Therefore, the fracture strain of the mentioned hybrid composite was higher than the 2wt. % Al_2O_3. In contrast, these dimples and ridges were shallower for the 2wt. % Al_2O_3 reinforced hybrid composites.

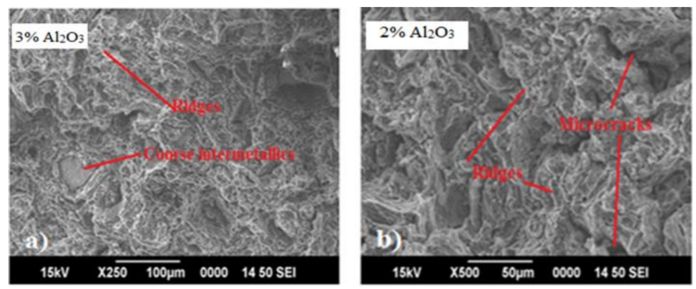
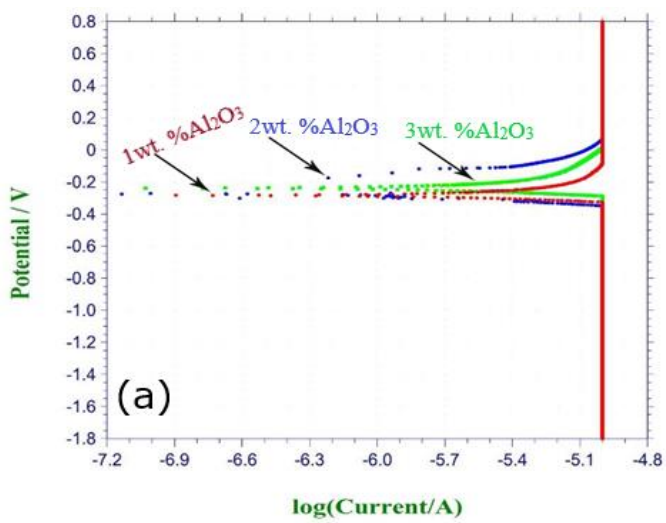


Figure 9: Scanning electron microscope of heat treated hybrid composites (a) 3wt. % Al_2O_3 (b) 2wt. % Al_2O_3.

3.4 Corrosion characteristics

Limited corrosion performance of the magnesium and its alloys are the major bottleneck in widespread usage of the same materials. But it can be enhanced by adding reinforcement to making composites and surface modification technologies [39]. The selected reinforcements n-TiO_2 and Al_2O_3 are having acceptable corrosion performance than the pure magnesium. The electrochemical polarization curves for the hybrid composites were depicted in the figure 10. The Tafel extrapolation method was adopted to find the electrochemical corrosion rate of the materials. The obtained electrochemical corrosion rate and immersion corrosion rate values for the hybrid composites were plotted in the figure 11. When comparing the corrosion rate of the pure Mg was higher than the prepared alloys with their as-extruded and heat treated conditions.



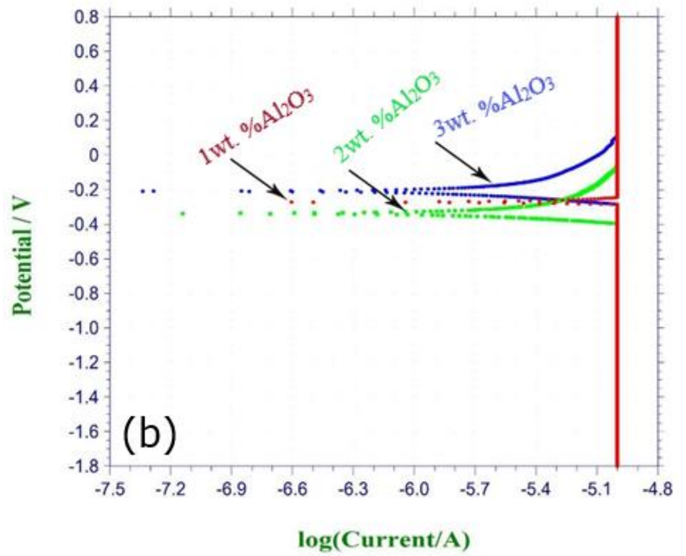


Figure 10: Electrochemical corrosion behavior of hybrid composites (a) As-extruded condition (b) Heat treated condition.

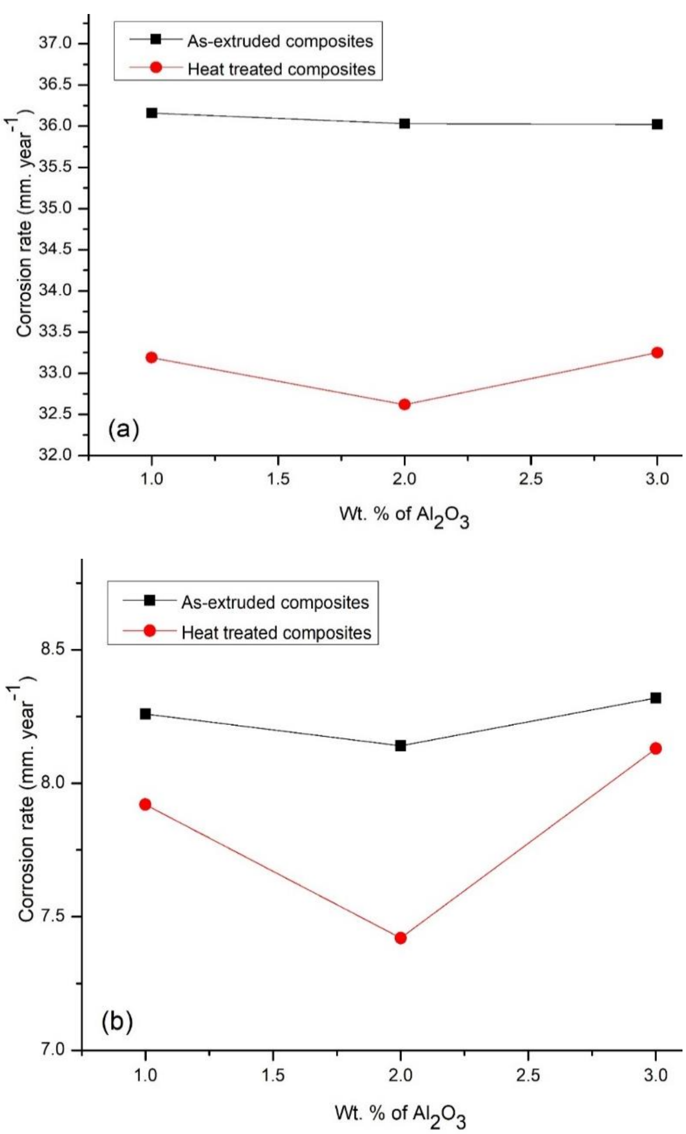


Figure 11: Corrosion rate of hybrid composites (a) Immersion in SBF (b) Tafel exploration method.

Similarly by comparison, all the prepared Al_2O_3 enriched hybrid composites with their as-extruded and heat treated condition were exhibited higher corrosion resistance than the prepared alloy with the mentioned conditions. In-general, the added reinforcement particles were having higher corrosion resistance in SBF and NaCl solution. This character might be influences in the hybrid composites by enhanced the corrosion resistance of the hybrid composites.

From the immersion corrosion test, it was clear that the as-extruded condition of hybrid composites with their varying wt. % of Al_2O_3 hadn't altered the corrosion rates i.e., the corrosion rates of the hybrid composites were more or less as constant. At this condition, the Al_2O_3 reinforced particles corrosion property took a responsibility to maintain the corrosion resistance of the composites as constant as shown in the figure 11 (a). Most of researchers were suggested that the corrosion resistance of the pure Mg is very less compared to other metals. The obtained immersion and electrochemical corrosion test results were proved the same.

The immersion corrosion test also inferred that the corrosion resistance of the prepared hybrid composite with their heat treated condition was behaved differently with their as-extruded condition i.e., the increasing wt. % of Al_2O_3 increases the corrosion resistance. In-contrast, the higher wt. % of Al_2O_3 decreases the corrosion resistance of the hybrid composites as shown in the figure 11 (b). The increasing corrosion resistance was due to the presence of higher corrosion resistance Al_2O_3 particles. But, their higher wt. % say more than 2% creating agglomeration of particles which were forming more galvanic corrosion sites due to the particle's polarity. Thus, increased the corrosion rate of the composite. In the case of heat treated 1 and 2 wt. % of Al_2O_3 particles reinforcement could disturbed the formation of secondary phase MgO film. Thus resist the hydrogen evolution reaction by enhanced the corrosion resistance of the composites [40]. The other fact for the corrosion resistance is the particles pulled out situation which could be higher for the 3wt. % of reinforced particles. The 3wt. % reinforcements were decreases the bonding strength of the composite matrix by their physical contact which resist the formation of secondary phases.

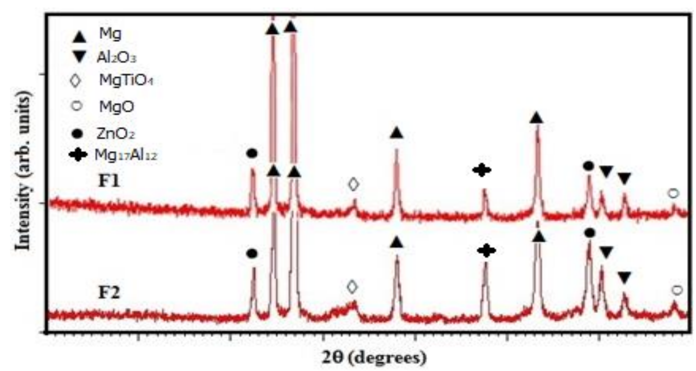


Figure 12: XRD of Al_2O_3 enriched hybrid composite.

The prepared hybrid composite had the combination of various metallic elements. The samples preparation methods were modified the presence of these elements by oxidation and reduction reaction or by recrystallization to form their secondary phases. The presence of these elements and their phases were identified through XRD. The phase detection was carried out on the 2wt. % Al_2O_3 reinforced hybrid composites with their as-extruded condition (F1) and heat treated condition (F2). Because this reinforcement added condition was contributed better result for their density and porosity properties. The obtained XRD were depicted in the figure 12. From the mentioned figure, the Bragg angle (2Θ) and lattice spacing were compared with the standard values of the related phases of Mg, Al_2O_3, TiO_2, zinc, and manganese.

The analysis of the diffractograms indicates that the presence of different intermetallic phases associated with the microstructure of the basic elements used to form the alloy and hybrid composites. The noticed secondary phases were $MgTiO_4$, MgO, ZnO_2, and $Mg_{17}Al_{12}$. This phase identification process was carried out on the crystallized narrow peaks visible in the diffractogram. But variety of partially crystallized peaks were possible to present in the diffractograms. These peaks were not easily find out through this method because these peaks were widen to take more angular space than the intensity. The researchers were suggested that the various non-crystallized secondary phases were present in the composite matrix which were enhances the mechanical and corrosion properties of the composites [41].

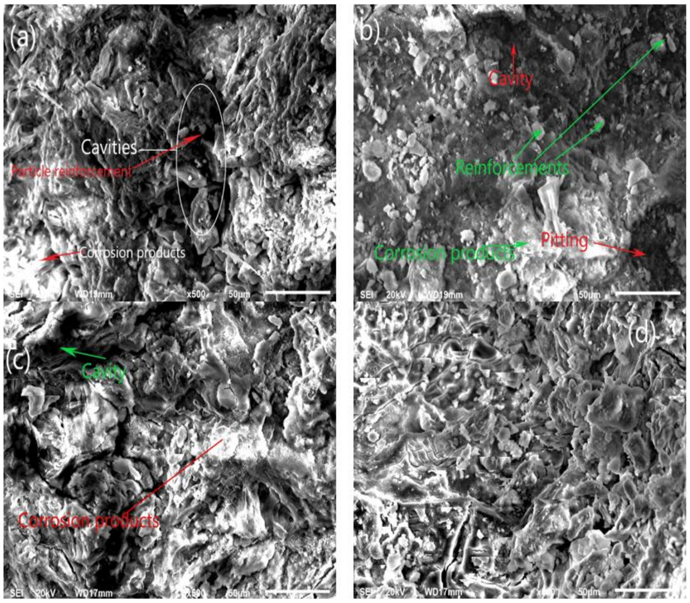


Figure 13: SEM images of hybrid composites after corrosion (a) As-extruded 3wt.% Al_2O_3 (b) Heat treated 3wt.% Al_2O_3 (c) As-extruded 2wt.% Al_2O_3 (d) Heat treated 2wt.% Al_2O_3.

The 3wt. % Al2O3 reinforced hybrid composite having physical contact took place between the reinforcement particles itself by forming agglomeration of reinforcement during extrusion which could create more cavities as shown in the figure 13 (a & b). The formed cavities and micro pore were allowed the corrosion medium could entered in to them. The entered corrosion medium could accelerated the opposite polarity took place between the interior matrix elements and the reinforcement particles due to hydrogen evolution process. Thus reduced the bonding strength (elements interfacing) of the matrix elements with each other and promotes the reinforcement particles pulled out. Therefore, the corrosion rate of the composite was increased. The elements interfacing strength of the lower wt. % of reinforcements were increased by n-TiO_2 particles which were filled the cavities by the action of grain refined caused by heat treatment process as shown in the figure 13 (c & d).

From the XRD pattern as shown in the figure 12, it is clear that the heat treatment process produces secondary phases of the elements present in the matrix which are causing chemical reaction taken place between them. These elements secondary phases were hold the reinforcement particles by grain growth. In which interfacing strength of the composites could increases. The increasing interfacing strength of the composite matrix increases the corrosion resistance of the composites by restricting particle pull out and reduce the number of pores present in the composite matrix. Generally, the pores and cavities were creating galvanic sites to promote galvanic corrosion.

The number of pores were reduces by heat treatment process for the lower wt. % Al_2O_3 particles reinforced composites as shown in the figure 13 (c & d). During corrosion, the magnesium alloys were forming magnesium hydroxide film on the surfaces of Mg matrix which is slightly soluble in aqueous solution thus gives protection to corrosion reaction. The solubility of the protection layer depends with the reaction time and acceleration potential. The formed secondary phases were inert to NaCl solution therefore, they were not to accelerate the corrosion potential causing uniform corrosion and reduce the corrosion rate. But, in the case of cavities formed by particles agglomeration allowed the corrosion medium penetrate deep in to the cavities and stagnant which was promoting pitting corrosion as shown in the figure 13 (b). This could be happened due to the presence of chlorine (Cl) ions in the corrosion medium. The Cl ions destroyed the protective layer of MgO by forming Mg $(OH)_2$ and enhances the hydrogen evolution reaction. Thus promotes the corrosion rates of the composites. When comparing the corrosion rates of the electrochemical corrosion and immersion corrosion, the corrosion rate of the electrochemical corrosion was lesser than the immersion corrosion because the stimulated body fluid in immersion corrosion could absorbed more Mg than the electrochemical corrosion which creating more weight loss. Therefore, the corrosion rate of the immersion corrosion was higher than the electrochemical corrosion.

CONCLUSIONS

This study was concentrated on the effect of n-TiO_2 and µ-Al_2O_3 particles as the reinforcement for the prepared Mg-Zn-Mn alloy based hybrid composites. The impact of the heat treatment process on the prepared composites were also analyzed. Based on the various test results and the subsequent analysis, the following facts were founded.

- The blend-press-sinter PM method was a successful method for the synthesis Mg alloy based composites reinforced with both TiO_2 and Al_2O_3 particulates.
- The homogeneous distribution of the reinforcement particulates was found in the microstructure analysis with minimal porosity. It revealed that, PM method is possible to manufacturing the Mg composites with minimum porosity.
- The prepared hybrid composites enhances the density of the composites than the base alloys due to the presence of high-density ceramic reinforcements. The density and porosity of the fabricated hybrid composites were comparatively higher than that of the prepared Mg base alloy.
- The micro structural study inferred that the uniform distribution of TiO_2 and Al_2O_3 reinforcement was accomplished in prepared hybrid composite before hot extrusion process. The agglomeration of reinforcements could occurred for the higher 3wt. % Al_2O_3 reinforced composites.
- The hot extrusion process was displaced the particles and refined the grains of alloying elements in which, pores and cavities were reduced to gives better mechanical strength.
- The various secondary phases were detected after heat treatment process through XRD.
- The tensile properties of the composites were found to be slightly inferior to the alloys due to the dislocation pile-ups near grain boundaries under tensile loading.
- The corrosion resistance of the hybrid composites were higher than the pure Mg and alloy. And the corrosion resistance of the 3wt. % Al_2O_3 reinforced hybrid composite was lesser than the other prepared hybrid composites for its as-extruded and heat treated condition.
- When comparing immersion and electro chemical corrosion, the corrosion rate of the immersion corrosion was higher than the electrochemical corrosion. This could be due to the absorption of Mg in SBF.

Finally, it was confirmed that the heat treatment process had a strong influence on the mechanical and corrosion properties of the composites because all these properties were enhanced by the heat treatment process.

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