

Investigation of Hot-extrusion Effect on Microhardness, Microstructure and Corrosion Behavior of Magnesium-based Bio-composites

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Abstract

Magnesium alloys are a unique choice for orthopedic implants due to their biocompatibility and biodegradability properties. In this article, the impact of hot-extrusion process is investigated on microhardness, microstructure, and corrosion behavior of magnesium/2.5wt% hydroxyapatite (HA) rods as a bio-composite. Hot extrusion process was implemented on the as-cast samples in two different steps resulting two various total extrusion ratios of 5:1 and 20:1. The corrosion susceptibility of the extruded composites was studied by polarization test in simulated body fluid (SBF) as a corrosive environment. According to the results, adding hydroxyapatite reinforcing particles and applying higher extrusion ratios caused grain refinement in the matrix comparing to the pure magnesium. Moreover, while the hardness of the pure magnesium sample decreased slightly after the second extrusion pass, it was enhanced in the composite specimens. Besides, both extrusion ratio and reinforcing particles had direct effects on the corrosion behavior, so that with the presence of HA particles and applying the higher extrusion ratio, the corrosion resistance of the samples was improved.

1. Introduction

Metal matrix composites (MMCs) have recently got increasing demands in different industries due to the possibility of minimizing corrosion rate and their improved mechanical properties such as strength to weight ratio, specific stiffness, and creep resistance [1]. Generally, various methods are used to produce metal matrix composites such as powder metallurgy, stir casting, and squeeze casting methods. Amongst all of them, stir casting can be considered as one of the most cost-effective methods as well as efficient [2].

Bio-composite materials can be adjusted to gain a wide amplitude of mechanical properties as well as the corrosion behavior by selecting the appropriate matrix and reinforcing phases [3].

Previously, in-vivo studies have indicated that magnesium and its alloys are capable components as biodegradable and biocompatible metal implants, although their corrosion rate is not proper enough. Though magnesium alloys are more favorable than pure magnesium to be used as matrix, one of the biocompatibility concerns is that existing alloying elements such as aluminum can cause neurological disorders and diseases such as dementia and Alzheimer [4].

Hydroxyapatite (HA) is the natural bone composition which has a similar chemical and crystallographic structure to bone. It possesses a low solubility in body environment and it is attractive due to its bioactivity which can form a chemical bond with osseous tissue [5–7]. As a result, hydroxyapatite parti-

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cles are a suitable choice to be used as reinforcements in magnesium based composites. Mg/HA composites could increase corrosion resistance, microhardness, and yield stress comparing to as-extruded bulk pure Mg [8]. Furthermore, in order to obtain MMCs with refined structure and improved mechanical properties, thermo-mechanical treatment such as hot-extrusion, hot-rolling, and hot-forging could be implemented on the as-cast materials. Unlike rolling and open-die forging, increasing the applied plastic deformation would not create macro and micro cracks in the material during hot-extrusion process. Moreover, by increasing extrusion ratio, more grain refinement would happen in the matrix and more desirable distribution of the reinforcing particles would be achieved. It could also increase mechanical properties such as hardness [9].

In General, grain refinement can increase corrosion resistance of Mg alloys; however, in some of the magnesium matrix composites, the formation of galvanic corrosion between matrix and reinforcement in the interface is the main problem for reduction of corrosion resistance [10, 11].

In the present article, firstly Mg/HA2.5wt% bio-composite was manufactured by stir casting method. Subsequently, the as-cast pure Mg and Mg/HA bio-composite were hot-extruded (as a bulk metal forming process) using two various extrusion ratios. The aim of this step was to improve both mechanical and microstructural properties and eliminate inevitable porosities of the casting process. Finally, the effect of extrusion ratio was investigated on the grain refinement, microhardness, and corrosion behavior of Mg and Mg/HA bio-composite.

2. Experimental Method

2.1. Preparation of Mg/HA Composites

Pure magnesium (99.93% purity) and hydroxyapatite particles (average particle size: $0.5\mu\text{m}$) were used as starting materials. The chemical composition (wt%) of the as-received pure Mg ingot is shown in Table 1. In this work, HA powder ($\text{Ca}_3(\text{PO})_4(\text{OH})$) was obtained from bovine bone [12]. Fig. 1 indicates the scanning electron microscopy (SEM) image of the hydroxyapatite powder. Stir casting method was applied to fabricate pure Mg and Mg/HA2.5wt% composite samples (with a diameter of 50mm) under argon atmosphere.

Table 1

Chemical composition of the as-received pure-Mg ingot (wt%).

Mg	Al	Cu	Mn	Zn	Sn	Ca
Based	< 0.01	0.001	0.05	< 0.007	< 0.002	0.001

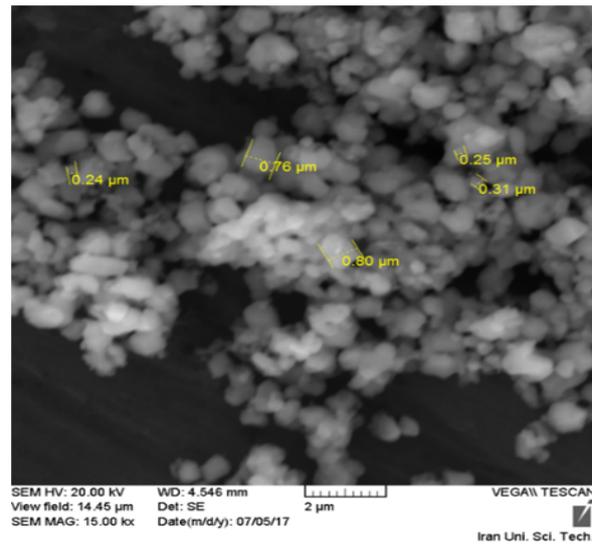


Fig. 1. SEM image of the hydroxyapatite powder.

2.2. Hot Extrusion Process

Hot extrusion process was implemented in two different steps at 350°C . The total extrusion ratio at the end of the first and second steps were 5:1 and 20:1, respectively. Furthermore, the diameters of the samples were approximately 22.3mm and 10mm after two extrusion steps. The extrusion process was carried out using a hydraulic press with a capacity of 75tons at a speed of 5mm/s. In order to achieve 350°C , electric ceramic band heating elements with a heating rate of $8^\circ\text{C}/\text{min}$ were used around the dies. Before starting the extrusion process, the dies and the samples were kept at 350°C up to 1 hour to access a uniform temperature at the whole of the billet specimens. The temperature was monitored and controlled near the extrusion zone using a K-type thermocouple. Fig. 2 shows the schematic equipment of the extrusion process.

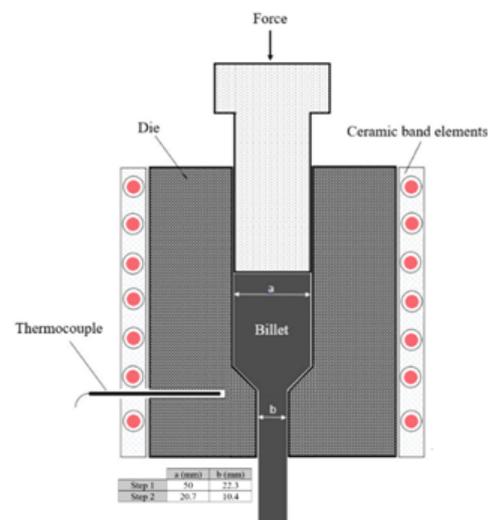


Fig. 2. Schematic view of the equipment of the extrusion process.

2.3. Microstructure and Microhardness

For microstructural evaluation, the samples were grinded, polished, and then etched. The applied etchant was composed of 10mL acetic acid, 70mL ethanol, 4.2g picric acid, and 10mL distilled water with an immersion time of 5-10s. For microhardness tests, 2N force was applied on the grinded samples for 10s as Vickers microhardness method according to ASTM E384. Since it is impossible to obtain a quite uniform distribution of the HA powder in the magnesium matrix, the tests were performed on five different random points through the cross-section of the samples and the average amount have been reported [13].

2.4. Electrochemical Tests

Since magnesium composites could be used as biodegradable orthopedic implants, it is essential to understand their corrosion behavior in the environments similar to human body. For electrochemical tests, first the samples were grinded with sand papers up to 2500 grit. Then, they were cleaned by distilled water and ethanol. The electrochemical tests were carried out at $(37 \pm 0.5)^\circ\text{C}$ s in SBF [14]. For measuring electrochemical data, a three-electrode cell was employed which possessed a Saturated Calomel Electrode (SCE) as a reference, and a platinum electrode as a counter. Additionally, the open circuit potential (EOCP) was determined as a function of time and the polarization curve was recorded at a scanning rate of 1mV/s in the potentiodynamic polarization tests. The volume of the SBF solution which was poured in the electrochemical test chamber was approximately 200mL.

3. Results and Discussion

3.1. Microstructure

The microstructure of the pure Mg and Mg/HA composite samples are shown in Fig. 3 for both extrusion ratios. While the average grain size of the as-cast pure Mg is about $241\mu\text{m}$, it decreases to $38.7\mu\text{m}$ and $18.4\mu\text{m}$ after the first and second steps of the extrusion, respectively. For Mg/HA bio-composite, the grain size is $4.2\mu\text{m}$ at the first step of extrusion, which reduces to $2.0\mu\text{m}$ at the second step.

Hot-extrusion process and presence of HA particles caused grain refinement in the samples. In both pure magnesium and composite samples, grain size decreased approximately 52% between two steps of the extrusion. Moreover, presence of HA caused a reduction of 89% in the both composite samples in comparison to the respective pure magnesium specimens. So, presence of HA particles had greater effect on the grain size.

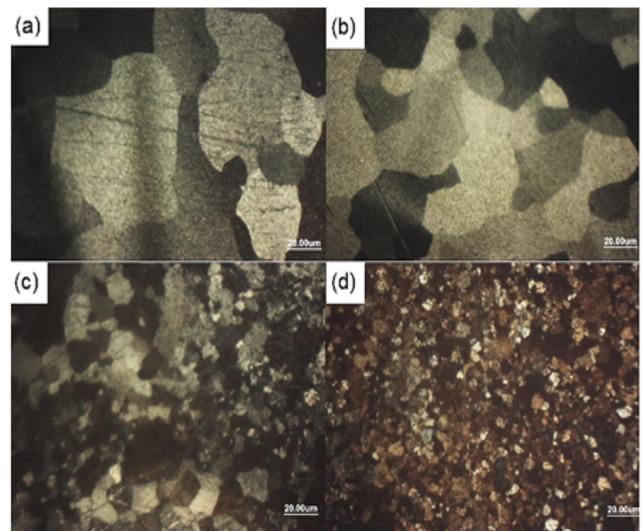


Fig. 3. Microstructure of; a) Pure Mg-step 1, b) Pure Mg-step 2, c) Mg/2.5%HA-step 1, d) Mg/2.5%HA-step 2.

It can be explained that during hot-extrusion process, dynamic recrystallization is the main responsible for grain refinement. On the other hand, reinforcing particles act as barriers to prevent grain growth (pinning effect) during solidification and recrystallization [15]. Furthermore, it was observed that higher extrusion ratio is suitable to break and disperse particle clusters and agglomeration uniformly in magnesium matrix [16].

3.2. Microhardness

Fig. 4 shows Vickers microhardness of the different specimens. According to the results, presence of HA particles has a remarkable effect on the microhardness. Indeed, these particles cause decrease in grain size, increase in dislocation density (due to the mismatch between thermal expansion coefficients and elasticity modulus of the matrix and reinforcing particles), and prevention of dislocations movement and local plastic deformation in the matrix.

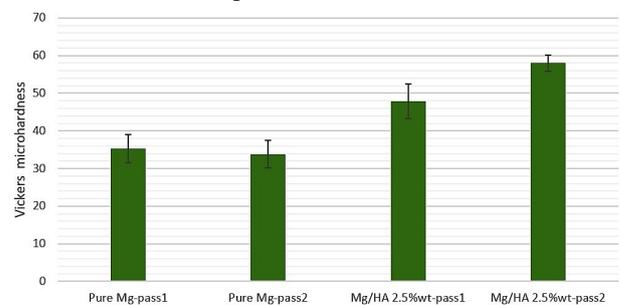


Fig. 4. Micro-hardness of the pure and the composite samples.

Table 2

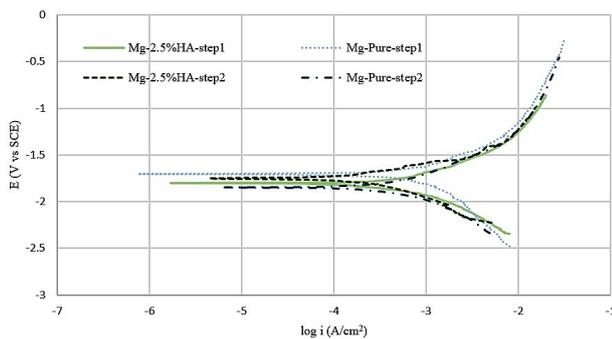
Electrochemical parameters extracted from polarization curve of the pure and the composites samples.

Sample	$E_{corr}(V)$	$i_{corr}(\mu A/cm^2)$	Corrosion rate ($mm\text{y}^{-1}$)
Mg/2.5%HA-step 1	-1.80	-1.80	18.41
pure Mg-step 1	-1.70	1198.53	27.41
Mg/2.5%HA-step 2	-1.76	429.50	9.71
pure Mg-step 2	-1.85	661.83	15.13

Moreover, it is indicated that the second step of the extrusion approximately has no valuable effect on the microhardness of the pure Mg sample, while it increases the microhardness of the biocomposite. The most possible reason could be the effects of preheating at 350°C (before hot-extrusion process) with and without the presence of reinforcing particles. Although extrusion has a special effect on grain refinement and increasing dislocation density, preheating step acts inversely. For pure sample, preheating effect is more considerable and as a result, the hardness decreases slightly. But in the composite, particles cause creation of new dislocations and prevention of grain growth (in preheating step) and more dynamic recrystallization (during extrusion).

3.3. Corrosion Behavior

The potentiodynamic polarization curves of the samples in SBF are displayed in Fig. 5. According to the results, adding HA particle in the magnesium matrix has not changed the general shape of the corrosion graphs significantly. Therefore, it could be concluded that the corrosion mechanism was the same for both pure and composite samples.

**Fig. 5.** Potentiodynamic polarization curves of the pure and the composite samples in SBF.

Electrochemical parameters of the pure and the composites samples are shown in Table 2.

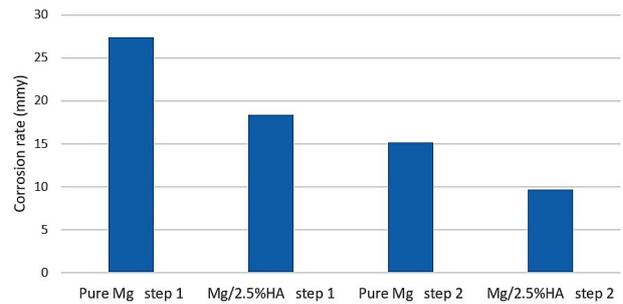
Fig. 6 shows the corrosion rate of the pure and the composite specimens after the first and the second extrusion steps. According to the results, both extrusion process and adding HA particles decrease corrosion rate. This could be due to the smaller grain sizes

after each extrusion step, especially for Mg/2.5%HA composite, which leads to forming a stronger passive layer ($Mg(OH)_2$) on the samples surfaces and increasing the corrosion resistance.

It has been confirmed that the grain refinement increases the resistance of Mg alloys [17]. In magnesium/hydroxyapatite with smaller grain sizes, there are more grain boundaries with more grain boundary defects. Since these defects could act as nucleation sites, creation and growth of the passive layer would be facilitated.

Finally, this protective layer prevents the penetration of the released ion from SBF (OH^-) and diminishes corrosion rate. [18]. Therefore, it can be concluded that applying higher extrusion ratio causes better corrosion resistance in both pure mg and magnesium/hydroxyapatite composite samples.

On the other hand, porosity has been introduced as one of the effective parameters on the corrosion rate. Pitting corrosion occurs in the porous pure magnesium and magnesium/hydroxyapatite composite. Thus, higher extrusion ratios help to decrease the porosities and increase corrosion resistance, consequently.

**Fig. 6.** Corrosion rate of the samples in SBF.

4. Conclusions

In this paper, Mg/HA bio-composite was fabricated using stir casting method and hot-extrusion process. Then, the effect of extrusion ratio and adding HA particles were investigated on microstructure, microhardness, and corrosion behavior. The results showed that extrusion ratio has significant effect on grain refinement of the samples. For pure Mg samples, the first and second extrusion steps decreased the grain size 84%

and 92%, respectively, in comparison to as-cast magnesium. Additionally, the grain size of both composite samples in the first and second steps has decreased about 89%, comparing to the corresponding pure samples. Presence of reinforcing particles and happening of dynamic recrystallization during hot-extrusion process could be the most important reasons for grain refinement. In addition, although the presence of HA particles and applying higher extrusion ratio have a considerable effect on the microhardness of the composite samples, the second step of the extrusion approximately has no valuable effect on the microhardness of pure Mg sample. Potentiodynamic polarization curves showed that corrosion mechanisms of both pure and composite samples are equal in SBF environment. Nevertheless, corrosion resistance of the samples increased by adding reinforcing particles or applying higher extrusion ratio, which could be because of the presence of the smaller grains resulting in faster formation of the passive layer on the samples' surfaces.

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