The Effect of Alumina and Hydroxyapatite Content on Morphology and Mechanical Properties of Mg Hybrid Composite for Biodegradable Implants Materials
The Effect of Alumina and Hydroxyapatite Content on Morphology and Mechanical Properties of Mg Hybrid Composite for Biodegradable Implants Materials

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Abstract. In biomedical applications, Magnesium (Mg) as a biodegradable implant material becomes one of the most potential candidates for temporary implants and has attracted much people’s attraction. It is because Mg is a light weight, non-toxic and able to degrade in human body. The aim of this research is to investigate the effect of hydroxyapatite(HA) and alumina (Al₂O₃) content on morphology and mechanical properties of Mg hybrid composite for biodegradable implants materials. Several of Al₂O₃ contents (i.e., 0, 5, 10, and 15 wt. %) were introduced in forming the Mg-Zn/HA/Al₂O₃ hybrid composite. The powder mixture of hybrid composite was milled separately in a planetary mill under gas argon atmosphere using a stainless steel container and balls. The powder was milled at 220 rpm for 1 hours and 3% of n-heptane solution was added prior to milling process to avoid the excessive cold welding of the powder. The powder was compacted under 400MPa and sintered with sintering temperature 300°C in a tube furnace for 1hour under the flow of argon. The results show that the sintered compacts were dispersed by uniform Al₂O₃ powder corresponding to white distribution of particles, as shown in the micrograph. As the Al₂O₃ content was increased to 15 wt. %, the mechanical properties such as hardness and compression test was improved.

1. Introduction

Biomedical metals and biodegradable polymers are generally used as implants. However, medical metals such as titanium alloy and stainless steel may result in ‘stress shielding’ of the bone and these permanent implants must to be eliminate by a secondary surgery after curing [1]. Metals such as Mg and its alloys also exhibit a bright expectation as a potential candidate for bio-implants such as orthopedic and craniofacial repair. This is because Mg and its alloys demonstrate a unique characteristic such as can degrade in vivo and have comparable physical properties as natural bones. The mechanical properties of Mg and its alloys such as Young’s Modulus of elasticity (E=41-45GPa) and density (1.74-1.84g/cm³) are recognized to be comparable that of bone (E=15-20GPa and density = 1.8-2.1g/cm³) [2]. There are only small numbers of element that can be tolerated in human body and can also retard biodegradable of Mg alloy including calcium (Ca), manganese (Mn), zinc (Zn) and very small amount
of low toxicity rare earth (RE) elements such as niobium (Nb) and tantalum (Ta). Yang et al. 2014, reported that the addition of Zn mechanically improves the yield strength and ultimate tensile strength of Mg. Zn also provided the lowest hydrogen evolution rate in comparison to Al, Si, Sn and Zr alloying element [3]. Thus addition of Zn into Mg matrix beneficial improves its mechanical properties, corrosion resistance without giving harsh effect to human body [4].

Bioceramics have good osteoconductivity and corrosion resistance but they are brittle and consequently are not suitable used as implant materials alone. Therefore, researchers mix the metals and ceramic forming composites which have the qualities from both metals and ceramics. Hydroxyapatite (HAP) is a biodegradable and bioceramic materials are commonly used in bone replacement application due to its close similarity to bone mineral [5]. Alumina (Al₂O₃) ceramics are known as ‘bioinert’ (although a material should never be considered as totally inert), since no direct bone material interface is created. Al₂O₃ has two main benefits over other materials compared to metals and polymers such as low concentrations and low wear rates of inert wear particles (debris) in the surrounding tissue. The corrosion resistance of Al₂O₃ ceramics is also very high (rate of corrosion 10⁻⁴ mm/y corresponding to a maximum corrosion rate of 1 mm in 10 years) [2].

Therefore, current studies have proved the workableness of it’s used in composite form which encourages the idea to add two reinforcements such as HAP and Al₂O₃ into Mg-Zn biodegradable alloy creating a new hybrid composite, Mg-Zn/HAP/Al₂O₃ hybrid composite.

There were many Mg-Zn based alloys and other metal based composites reinforced by HAP via powder metallurgy method. However, fabrication method of hybrid composite Mg-Zn/HAP/Al₂O₃ is not well discovered and the rightful parameters to fabricate the hybrid composite are yet to be presented. Therefore in the current work, alumina content was investigated on mechanical and microstructure studies of Mg-Zn/HAP/Al₂O₃ composite prepared by powder metallurgy.

2. Experimental study

Different amount of HAP and Al₂O₃ and balanced Mg and Zn powders were mixed in weight proportion. Pure powder were milled to form Mg-Zn/x HAP/x-1 Al₂O₃ (x=0-15 wt. %) composites in a Fritch planetary ball mill, while confined in sealed 250 ml steel containers rotated at 220 rpm for 1 h. The container was loaded with a blended of balls (θ=10, 20mm). The total weight of the powder was about 20g and the ball to powder mass ratio about 1:8.75. n-heptane (3 wt. %) was used as the process control agent to prevent excessive cold welding of powder particles. Then the milled powders were uniaxially cold pressed under 400 MPa for 2 min at room temperature to produce 10 mm diameter of green Mg-Zn/HAP/Al₂O₃ hybrid composite. The sample was sintered at 300°C under argon flow at 10°C/min for both heating and cooling rate for an hour in order to form solid bodies.

3. Results and discussion

The result of compressive strength of hybrid composite can be represented in Figure 1 of Mg/0-15wt. % Al₂O₃. Ultimate compressive strength of 0 wt. % Al₂O₃ was found to be as low as 127.42 MPa compared to 15 wt. % of Al₂O₃ (171.09 MPa) in Mg-Zn/HAP/Al₂O₃ hybrid composite. Thus, when adding Al₂O₃ from 5wt. % to 15wt. % of to the Mg composites, the values was again increased. Mechanical properties of Mg have been extensively investigated by many researches. Varied result have been reported and observed. More or less, these properties are influenced by on how the structures were processed. In addition, sintering temperature, time and pressures of additives and their amount has played major roles in mechanical properties of sintered Mg. The values of compressive strength increased from 0 to 15 wt. % were mainly due to uniform dispersion of Al₂O₃ into Mg matrix. This is due to the hard particles of Al₂O₃ can hinder the mobility of dislocation in the Mg-Zn alloy matrix [5]. Thus, compressive strength is enhanced with higher amount of Al₂O₃. From previous research by
Rahimian et al. 2006, the addition of Al$_2$O$_3$ into Al matrix from 0 to 15 wt. % increased the value of compressive strength however with addition of 20 wt. % Al$_2$O$_3$, the compressive strength value decrease. The decreasing value in compressive strength at 20 wt. % of Al$_2$O$_3$ and above was caused by deterioration and agglomeration of Al$_2$O$_3$ [6]. According to Khalil et al. 2012, addition of 10 wt. % HAP and above can caused agglomeration of HAP particles that lead to degradation of interfacial bonding strength between matrix and reinforcement thus leading to a lower compressive strength [7]. The result with higher HAP content caused the value of compressive strength decrease. It also agreed by Loy et al. 2015, in Mg-Zn/HAP composite finding that the addition of higher HAP content can decrease the value of compressive strength [8]. From this result it can see that the reinforcement constituents are one of the important factors controlling the strength of Mg matrix. Al$_2$O$_3$ particles being brittle and hard lead to dispersion hardening of matrix. These particles acts as second phase in the matrix and resist the movements of dislocations and hence the value of composites.

![Figure 1](image_url) Compressive strength of Mg-Zn/HAP/Al$_2$O$_3$ hybrid composite.

### 3.1 Microhardness Analysis of Sintered Hybrid Composite

As shown in Figure 2, microhardness of hybrid composite of Mg-Zn/HAP/Al$_2$O$_3$ increased from 70.35 HV to 79.85HV when Al$_2$O$_3$ content increased from 0 wt. % to 15 wt. %. The increases in microhardness value of the hybrid composite were mainly attributed to the dispersion effect of Al$_2$O$_3$ within Zn, and HAP into Mg matrix. The harder Al$_2$O$_3$ particles provide sufficient strength to the soft matrices and hence the microhardness values increases due to the dispersion strengthening effect [7]. Based on preview research by Chabri et al. 2013, said the addition of Al$_2$O$_3$ from 5 to 15wt. % into Al/Mg/Cu/Ti matrix increased the hardness values but the addition with 20 and 25 wt. % of Al$_2$O$_3$ caused the hardness values fall gradually due to agglomeration of the Al$_2$O$_3$ particles within the matrices. It is clearly seen that the composite samples dispersed with 15 wt. % of Al$_2$O$_3$ display a maximum hardnness value [8]. The result agreed with Khalil et al. 2015, who found that addition of 10 wt. % of HAP and above gives significant drop in compressive strength and hardness value due to agglomeration of HAP particles. It leads to the degradation of interfacial bonding strength between matrix and reinforcement [5]. In this result, the maximum values of Al$_2$O$_3$ added in Mg composite is 15 wt. % and the results become increased trend without a drop value in hardness when Al$_2$O$_3$ added from 0 wt. % to 15 wt. %. The reason for the increase in the microhardness is probably due to the presence of HAP fragmented at the grain boundary regions. Besides that, the agglomeration of HAP not achieve yet or little occur compared to the previous research said that when added 20 wt. % Al$_2$O$_3$ and above into Mg the agglomeration occur and the result become decrease. Furthermore, with the increase of the content of Al$_2$O$_3$, the microhardness is strictly increased which demonstrates that the fine Al$_2$O$_3$ particles have an effect of strengthening. Al$_2$O$_3$ particles in mixed powder are beneficial to obtaining the smaller powder and can effectively refine grains of composite powders by inhibiting their growth [11].
Figure 2. Microhardness of Mg-Zn/HAP/Al$_2$O$_3$ hybrid composite.

3.2 Microstructure Observation

The effect of alumina particle content on microstructure is depicted in optical micrographs. Figure 3 (a-d) shows the optical micrograph with magnification 5x from 0 to 15 wt. % of Al$_2$O$_3$ dispersed in hybrid composite. From the micrograph, the grey color is Mg matrix while the white color is Al$_2$O$_3$ powder and the dark color is porosity. From the Figure 3 (a-d) shows the presence of Al$_2$O$_3$ becomes increased and more white color presence in 15 wt. % of Al$_2$O$_3$ compared to the others. It reveals that the distributions of Al$_2$O$_3$ particles are well distributed throughout the matrices. The addition of Al$_2$O$_3$ into Mg composite can enhance the compressive strength and hardness values due to dispersion strengthening effect.

Figure 3. Optical Microscope of hybrid composite with magnification 5x (a) 0 wt. % Al$_2$O$_3$ (b) 5 wt. % Al$_2$O$_3$ (c) 10 wt. % Al$_2$O$_3$ and (d) 15 wt. % Al$_2$O$_3$

4 Conclusion
The addition of two reinforcements such as HAP and Al₂O₃ content on Mg-Zn/HAP/ Al₂O₃ hybrid composite increase the values of hardness from 70.35 HV at 0 wt. % of Al₂O₃ to 79.85HV at 15 wt. % of Al₂O₃. Meanwhile for compressive strength the value become increased too from 127.42 MPa to 171.09 MPa. It shows that the addition of two reinforcements can enhance the mechanical properties and for microstructure analysis the Al₂O₃ and HAP content are dispersion well in the matrix of Mg.

5. Acknowledgement

The authors would like to thank to Universiti Sains Malaysia for FRGS Grant No.203/PBAHAN/6071304 and sponsorship scheme of Ministry of Higher Education (Malaysia)

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