The Microstructural and Bioactivity Behavior of Magnesium Alloy Filled with Bioglass For Biomedical Application

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**Abstract.** Magnesium alloy have known as degradable implant material due to biodegradable properties. However, by developed Mg alloy matrix composites containing a bioceramic will produced more biodegradable and does not need second surgical to remove the implants in body. Powder metallurgy route was used to fabricate the AZ91/BG composite by mixing, compacting and sintering. Mg alloy (AZ91) was reinforced with 0, 3, 6, and 9 wt% of bioglass (BG) before compact and sintered at 400°C for 2 hours. The Vickers hardness, scanning electron microscope, and x-ray diffraction are used to investigate the effect of BG particles addition on the mechanical properties and microstructure of the composite AZ91/BG. Bioactivity behaviour was studied by immersion test of AZ91/BG composite into phosphate buffered saline (PBS) solution for 72 hours. The results showed that as the addition of BG increases from 3 to 9 wt%, the hardness of AZ91/BG decrease from 43.3HV to 27.9HV. The result also showed the formation of protective layers or apatite layer on the surface of AZ91/BG composite after immersed in PBS solution for 72 hours. Phase analysis by XRD shows the presence of peak Ca₁₀(OH)₂(PO₄)₆ as the BG increased from 3 to 9 wt%. As a conclusion, AZ91/3BG shows the optimum composite for biomedical application based on its properties and bioactivity behaviour.

1 **Introduction**

Magnesium (Mg) is the lightest common structural metal with a density of 1.74 g/cm³, in its solid state. The mechanical and physical properties of Mg are relevant to design of lightweight components and structures [1]. AZ91 is one of Mg alloy that consist of Al and Zn as major alloying elements. Composition of the alloy is 9 % Al and 1 % Zn was used to gives better properties than pure Mg. AZ91 has good corrosion resistance, low cost and good strength and cast ability [2]. The alloys results in a considerable improvement in the mechanical properties. Bioglass (BG) is a type of glasses and originated from family of bioactive glass group which have high bioactivity. BG is a family of bioactive glasses.
composed of silicon dioxide, natrium oxide, calcium oxide, and phosphorous pentoxide. The most familiar properties for BG is that they tied to bone with no fibrous tissue at the interface [3]. They also shows fast surface reaction which cause to fast tissue bonding, by developing a layer called apatite layer. However, BG has a minimum degradability and its bioactivity still needs to be improved. Therefore, by fabricate magnesium-matrix composites containing a bioceramic phase will produce more biodegradable yet bioactive material than BG itself for biomedical applications.

In this project, the effect of different addition of BG to Mg alloy will be focus in term of the mechanical properties, microstructure and also bioactivity behaviour of AZ91/BG composites for biomedical application. Powder metallurgy method will be used to fabricate AZ91 with 0 wt%, 3 wt%, 6 wt% and 9 wt% of BG to determine the optimum weight percent of BG addition to Mg alloy for biomedical application.

2 Materials and Method

The alloy powders ratio is calculated according to the composition of Mg alloys (AZ91), with 90 wt% Mg, 9 wt% Al and 1 wt% Zn. These alloy powders were mixed with four different additional amounts of BG powders which are 0 wt%, 3 wt%, 6 wt% and 9 wt% respectively by processing in a roll mill with 113 rpm for 1 hour. Then, they were cold compacted by using hydraulic press into pellet specimen at 443.5 MPa followed by sintered at 400°C for 2 hours using tube furnace.

After sintering, the samples of AZ91/BG were grinding on a series of SiC papers, followed by polishing on the soft napped cloth. Digital Vickers hardness tester was used to test the hardness of samples under a load 0.1 kgf. Then, these samples were observed by scanning electron microscope (SEM), equipped with energy dispersive x-ray spectrometer (EDS) for element identification followed by x-ray diffraction (XRD) analysis.

The immersion tests for all samples were carried out in a phosphate buffered saline (PBS) solution according to the standard BS ISO 23317:2007 [4] in order to evaluate the bioactivity behaviour of the AZ91/BG composites. Bioactivity test was conducted for each sample in water bath for 72 hours to determine the bioactivity behavior of the specimen. Vickers hardness test, SEM observation and XRD analysis were performed again for AZ91/BG composites after bioactivity test.

3 Results and Discussion

Fig. 1. shows the results for hardness of AZ91/BG samples before and after bioactivity test. The hardness value for sample AZ91/0BG is decrease from 35.8 HV to 28.7 HV. Meanwhile, the next sample which had been added with 3 wt% of BG give the highest value of hardness which is 43.3 HV before bioactivity test and fell to 32.3 HV after bioactivity test. The lowest hardness value before and after bioactivity test is sample AZ91/9BG with only 27.9 HV and 16.1 HV respectively. Hence, the higher the additional of BG into the composite, the lower the hardness value recorded. The reduction of hardness is due to the agglomeration of the BG particles so that the reinforcement effect from reinforcing particles cannot be delivered [5].
Fig. 1. Hardness of samples before and after bioactivity test.

Fig. 2. shows the SEM micrographs for sample AZ91/0BG, AZ91/3BG and AZ91/9BG after sintering. Fig. 2. (a) shows the least pores with EDS analysis indicates the only phase of Mg, Al, and Zn respectively existed. Sample AZ91/3BG in Fig. 2. (b) have more pores which can be related with its EDS analysis of BG particles revealed the presence of silicon (Si), natrium (Na), calcium (Ca), phosphorus (P) and oxygen (O). Meanwhile, in Fig. 2. (c) shows micrographs of AZ91/9BG with EDS analysis proved the existence of higher count of Ca, Si, Na, and O among the others because it contents the highest amount of BG.

Fig. 2. SEM of (a) AZ91/0BG, (b) AZ91/3BG and (c) AZ91/9BG composites after sintering.
According to Fig. 2., matrix of AZ91 reveals very good bonding and adhered well between Al, and Zn grains. However, the bond between AZ91 and BG showed viscous flow of matrix when in contact with BG. This happened due to the heat treatment coming from sintering process where Mg reacts with gases trapped in the pores [6]. As the composite is made up from combination of metal and ceramic, there are no inter-particles reactions compare to the others that invented from metal which developed inter-particles necking between powder particle due to the diffusion process of metallic particles [7].

Fig. 3. shows the results for XRD for AZ91/BG composites after sintering. Sample AZ91/0BG in Fig. 3. (a) is only presence peak of Mg, Al and Zn according to their weight percent. Next sample is added with 3 wt% of BG in Fig. 3. (b) shows a new peak indicates SiO$_2$ at 45°. For sample AZ91/6BG in Fig. 3. (c), peak of phase SiO$_2$ become higher at 9°, 18° and 45° due to its additional of BG particles. Meanwhile, peak at 9°, 18°, 29°, 30°, 45° and 66° for sample AZ91/9BG in Fig. 3. (d) presence more peak of SiO$_2$ among the others as it contains the highest amount of BG. According to Fig. 3., randomly it can be observed that there is a presence of new peaks as the amount of BG particles increase. Bioglass (BG) is found as minor phases in case of these composites. The presence of SiO$_2$ is representing of BG due to the amorphous structure of BG. Thus, it proved that the increase amount of BG in the composites from 3 to 9 wt% of BG, the more presence of phase SiO$_2$. 
Fig. 4. SEM of (a) AZ91/0BG, (b) AZ91/3BG and (c) AZ91/9BG composites after bioactivity test.

Bioactivity test was running by immersed all the samples in PBS solution for 72 hours. Fig. 4. shows the SEM micrographs for AZ91/BG composites after bioactivity test. Microstructures in Fig. 4. (a-c) shows a white precipitate which known as apatite layer on the surface of a sample after bioactivity test. The apatite layer shape like a cauliflower as they presence a lot. It can be observed that the distribution of apatite layer increases with the increasing amount of BG. Fig. 4. (b) presented 3 wt% BG shows more growth of apatite layer and little count at phase of Ca in energy dispersive spectroscopy (EDS) analysis compares to sample in Fig. 4. (a) AZ91/0BG. Meanwhile, Fig. 4. (c) with 9 wt% of BG shows the apatite layer fully covered the sample surface and the EDS analysis shows the highest peak of phase Ca.

The growth of apatite formation increase as the amount of BG increases may be due to several reasons. First, this may be contributed from the reducing rate of corrosion as the composite material decremented the amount of direct contact with PBS solution. This is due to the reinforcement can allowed the precipitation of a passive layer on the surface. Besides that, large amount of Mg ion released during corrosion of AZ91/0BG sample will possibly inactivated the formation of apatite [8], resulting in less amount of apatite formation around the AZ91/0BG. Thus, the increasing amount of apatite formation on AZ91/9BG due to least of Mg ion and operating of BG particle release as nucleation sites for apatite formation on the sample surface, which can enhance to generate the growth of new bone tissues [9].
Fig. 5 shows XRD analysis that revealed the peaks for Mg and Mg(OH)₂. For apatite, Ca₁₀(PO₄)₆(OH)₂ (Fig. 5b-d), the peak could still be observed but difficult in monitoring. AZ91/9BG shows peaks for Mg and Mg(OH)₂ but not with the same as AZ91/0BG due to its highest content of BG. Meanwhile, there are more presence of peak Ca₁₀(PO₄)₆(OH)₂ for apatite can be observed at 32°, 34°, and 45°. As the samples are immersed in the PBS solution, normally the main corrosion products are magnesium phosphates and Mg(OH)₂. These will invite high concentration of chloride ions to transform Mg(OH)₂ into more soluble MgCl₂. Thus, decomposition of Mg(OH)₂ will decrease the protected area, which may lead to promoting further dissolution of substrate. Ion OH⁻ that generated during Mg dissolution can increase the degradation rate of Mg.

4 Conclusions

As a conclusion, AZ91/BG has been fabricated by powder metallurgy method with the different amount of BG which is 3 to 9 wt%. BG is uniformly tabulated in the AZ91 matrix and it was agglomerated at the grain boundaries as the content of BG increased. Vickers hardness before and after bioactivity test of AZ91/3BG successfully recorded as the highest hardness value with 43.3 HV and 32.3 HV. SEM observation of all sample shows that there are no inter-particles reactions compare to the others that consist of metal which developed inter-particles necking between powder particle due to diffusion process of metallic particles. The increase amount of BG, the more peak presence of phase SiO₂ representing of BG due to the amorphous structure according to XRD analysis. As a conclusion, AZ91/3BG showed the best metal matrix composite which very favourable for biomaterial applications due to the highest hardness, and the formation of apatite layer on the AZ91/BG surface shows the mark of bioactivity.

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