The Fabrication of Zn-Zr Alloy through Centrifugal Casting and Box Furnace Method for Implant Application

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Abstract. Recently, zinc (Zn) is extensively observed as biomaterial or biodegradable implant for medical application. A biomaterial is any substance that has been engineered to interact with biological systems for a medical purpose. Zn is chosen because it has moderate degradation compared to Mg and Fe. Unfortunately, Zn has limitation on its mechanical properties that still low. The Alloying element is needed to improve the mechanical properties of Zn. Alloying element, such as zirconium (Zr) can improve the mechanical properties of Zn. In this study the addition of Zr with the composition variations of 0%, 0.5%, 1%, and 2% were used. Two kinds of alloying method used are centrifugal casting and box furnace with a temperature of 550°C. The aims of this study are to know the effect of each fabrication method to the mechanical properties and the result of Zn-Zr alloy microstructures. The results show that the microstructure of the alloy from centrifugal casting is more homogenous than the box furnace method. The mechanical properties of centrifugal casting are also higher than the box furnace method. The hardness value obtained from centrifugal casting of 0, 0.5, 1, 1.5 and 2% of Zr are 35.162 HV, 41.988 HV, 42.324 HV, 57.112 HV, respectively.

1. Introduction

The number of traffic accidents in Indonesia has been increased. This traffic accident becomes the main reason of some bone fracture chases in Indonesia. It is noted that 50 percents of bone fracture chases are caused by the traffic accident. Not only the traffic accidents, another accident such as the work accident also contributed to the number of bone fracture chases [1]. To overcome these bone fracture chases, doctors are using implant for the replacement of bone structure, while the injured bone is still in the healing process. The implant materials are commonly made of stainless steel and titanium alloy [2].

Stainless steel and titanium alloy has broadly used as implant materials [3]. These materials are chosen to be implant material because of their excellent corrosion resistance in the biological environment. The combination has an exception degree of biocompatibility which it shares with only a handful of other materials. The stainless steel and titanium alloy are good mechanical properties to be used as implant material [4]. However, these types of materials are not biodegradable, makes them need to be extracted after the healing process. This implant extraction process or second operation makes the healing process not effective because of the longer recovery time, even when the bones injure are fully-healed.

So that, to overcome this conventional implant problem, researchers are developing biodegradable implant made of biodegradable materials or metals such as Iron, Magnesium and Zinc alloy[5]. Biodegradable metals, also known as bioresorbable or bioabsorbable metals, are compatible with human tissues and degrade to nontoxic by-products through oxidation and dissolution of the metal [6]. Degradation rate of the metals takes the important role to the biodegradable implant. The degradation rate
of these metals has been extensively studied. Zinc has moderate degradation rate compared to the iron and magnesium alloy [7,8]. This characteristic makes zinc a promising material for biodegradable implant.

Unfortunately, the mechanical properties of zinc are still lower than the bones. It is noted that the ultimate tensile strength of zinc about 30 MPa, while the bone’s strength about 150 MPa [9]. This property is not enough for implant application. Addition of alloying element into the zinc can improve the ultimate tensile strength of zinc. For example, addition of 3wt% copper into zinc can improve the mechanical properties of zinc up to 257 MPa, with 47% of elongation and 0.372 μA/cm² of degradation rate. However, the overdose of copper content inside the human body can cause some neurodegenerative diseases such as Alzheimer, Menkes, and Wilson [10].

Therefore, another alloying element, zirconium is used in this research. Zirconium as alloying element for zinc is still rarely observed by the researchers. Zirconium is a biocompatible and bioneutral element. The Zirconium also has low systemic toxicity. Based on the Zn-Zr phase diagram, with a little addition of zirconium into zinc can form Zn-rich intermetallic phase (Zn$_{22}$Zr). The number of dissolved zirconium inside Mg-Zn-Zr alloy is 50 μg/day and is still allowable in human body [11-13]. These potentials make zirconium a promising alloying element to improve zinc mechanical properties for implant application.

2. Experimental Method

This research is started with the making of samples through the centrifugal and box furnace casting. The pure zinc and zirconium materials were obtained from Alfa Aesar. The zinc was mixed with the zirconium with variation of zirconium of 0.5, 1.0, 1.5, and 2.0 wt%. Each variable was heated at 550 °C for 15 minutes and poured into the mold until solidified for the box furnace casted samples. The molten metal that will be casted through centrifugal casting method was rotated in the mold with speed of 500 rpm using Neutrodyn Easity machine as shown in Figure 1. The casted samples then homogenized at 380 °C and followed by the quenching process using medium water to make homogeneous grain size.

![Figure 1. The centrifugal casting machine.](image)

Then, the homogenized samples are prepared for the Vickers hardness test and SEM-EDS examination. The samples are cut for easier handling during the preparation process. The samples are grinded by using sand paper with grit number of 240, 320, 600, 800, 1000, 1200 and 2000. Then, followed by the polishing process used polishing machine and alumina paste to get fine surface. The polished samples etched with the mixture of 2 ml of HNO$_3$ and 98 ml of H$_2$O then examined under the Vickers hardness test and SEM-EDS.
3. Results and Discussion

3.1. Microstructure

After the addition of zirconium into the zinc, it is found that the microstructure of zinc has changed. The SEM examination in Figure 2 using secondary electron shows that after the addition of zirconium there is formation of some particles. These particles are intermetallic phase which is formed after the addition of zirconium.

![Figure 2. The microstructure of zinc; a) pure zinc, b) zinc with zirconium addition.](image)

Figure 3 shows the differences of microstructures resulted from two different processes, the centrifugal casting and box furnace casting. It is found that the centrifugal casting gives more homogeneous microstructure than the box furnace casting method. The intermetallic particles are well-distributed all around the zinc matrix. This condition happened because of the centrifugal force in centrifugal casting that makes the intermetallic particles well-distributed.

![Figure 3. The microstructures of (a-d) box furnace casted and (e-h) centrifugal casted alloy.](image)

The centrifugal casting is also cleaner than the box furnace casting, it has a closed process thus there is no time for the molten metal to interact with the environment. There is no white region in the centrifugal casted sample’s microstructure, but some white regions inside the box furnace casted sample’s microstructure is found. These white regions are the oxide that is formed when the casting process was done by the box furnace method. 

\[ 2 \text{ Zn} + \text{O}_2 \rightarrow 2 \text{ ZnO} \]  

(1)
In contrast with the centrifugal casting, the box furnace casting method is an open process, which molten metal can interact with the atmosphere and then the molten zinc reacted with oxygen, formed oxides as the equation 1.

3.2. Vickers Hardness
The addition of zirconium into zinc can improve the hardness of zinc. It is found that the hardness increased with the increment of zirconium content inside zinc. The optimum strength is reached by the addition of 2 wt% zirconium with Vickers hardness number of 57 VHN (Figure 4).

![Figure 4](image-url)

**Figure 4.** The Vickers hardness number of centrifugal casted and box furnace casted alloy.

The increment of hardness is caused by the existence of intermetallic particles. These particles have good adhesion with the zinc matrix, thus in can hinder the dislocations movement and strengthen the material. The addition of zirconium also makes the grain size of the alloy is finer. Finer grain size can strengthen the material because the number of grain boundaries that can hinder the dislocations movement also increase. The addition of zirconium inside the zinc made the material becomes stronger.

3.3. Energy Dispersive Spectroscopy (EDS)
The energy dispersive spectroscopy is used to investigate the composition inside some particles that are formed after the alloying process. Figure 5 shows the EDS result of Zn-2Zr which is made through centrifugal casting.
Figure 5. The EDS spectroscopy of centrifugal casted Zn-2Zr alloy.

The EDS spectroscopy of centrifugal casted alloy confirmed that the particles are formed after the addition of zirconium. The spectroscopy shows only zinc and zirconium inside the particles. This indicates that the particles formed are Zn$_{22}$Zr. The solubility of zirconium inside zinc is very limited, so the addition of zirconium inside zinc will lead to the formation of intermetallic phases [13].
Figure 6 shows the spectroscopy of box furnace casted Zn-2Zr alloy. The spectroscopy of box furnace casting shows the existence of oxygen inside the alloy. This result indicates the formation of oxides with the box furnace method. As mentioned before, the box furnace method is an open process. This process let the molten zinc reacted with oxygen and formed oxides.

4. Conclusions
The fabrication of Zn-Zr alloy has been done successfully. The microstructure of zinc changed after the addition of zirconium with the formation of intermetallic phases. These intermetallic phases or particles are formed because the solubility of zirconium inside zinc is very low. Thus, the addition of zirconium inside zinc will lead to the formation of intermetallic phases. The addition of zirconium also gives finer grain size compared than the zinc without any addition of
zirconium. The addition of zirconium can improve the hardness of zinc. The optimum hardness is reached by the centrifugal casted alloy with addition of 2 percent zirconium with Vickers hardness number of 57 VHN.

The centrifugal casting method gives more homogenous microstructure of Zn-Zr alloy. The intermetallic phases that are formed in this process are well-distributed due to the centrifugal force. The alloy from this process also gives higher Vickers hardness number than the box furnace casting because the intermetallic phases that act as reinforcement and grain refinement are well-distributed, thus it can strengthen the material. The EDS spectroscopy also shows that the centrifugal casting is cleaner than the box furnace casting. There is no oxygen spectroscopy inside centrifugal casted alloy, this is indicating there is no oxides formed with this process.

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