The Effect of Zr Addition on Microstructures and Hardness Properties of Zn-Zr Alloys for Biodegradable Orthopaedic Implant Applications

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Abstract. The development of Mg and Fe based biomaterials in the past decade has been extensively studied as biodegradable material for medical applications. The development of this material is limited in terms of its suitability for clinical applications. Zn-based alloys began to be an alternative to be studied as a substitute for Mg and Fe based biomaterials. Zn-based alloys have a moderate degradation rate but have low mechanical properties, so other elements need to be added to improve their mechanical properties. In this study, the added element is zirconium (Zr) with a composition variation of 0.5%, 1%, and 2%. The alloying method used was casting with a temperature of 550°C. The results of the microstructure analysis, the addition of Zr to Zn alloys will form precipitates in the side of the grain boundaries and more addition of Zr composition, the smaller grain size formed. The grain size from pure Zn until the addition of 2% Zr in the sequence are 266.40 µm, 20.16 µm, 16.70 µm, and 15.85 µm. The XRD analysis, from the addition of Zr, will form the Zn phase and the intermetallic phase Zn22Zr. The hardness value obtained from pure Zn until 2% Zr in the sequence are 35.162 HV, 41.988 HV, 42.324 HV, 57.112 HV.

1. Introduction
Biomaterial is a material that can interact with biological systems and substitute damaged bone tissue. The use of biomaterials as implant material in Indonesia is increasing along with the increasing cases of fracture that occur in Indonesia [1]. Biomaterials based on the type of material are divided into four, there are metals, polymers, ceramics and composites. Biomaterials that are often used in the medical world are materials with metal materials, such as stainless steel, titanium alloys, and cobalt alloys. The density and modulus of elasticity of non-biodegradable material are higher than bone which can make bones bear heavier loads so that their growth can be inhibited. In addition, these materials also require secondary surgery to prevent the side effects of not being able to decay and toxic in the body [2]. Therefore, we need a biodegradable material where the metal ions can metabolize in the body and not become toxic in the body, particularly in orthopedic implant applications. The kind of biodegradable materials divided into three, there are Mg-based alloy, Fe-based alloy, and Zn-based alloy [3].

The biodegradable material that has been widely researched is Mg-based alloy material. Mg-based alloy materials have the advantage of having mechanical properties similar to bone in the body in terms of yield strength, tensile strength, and elongation. However, this Mg-based alloy material also has the disadvantage of high corrosion levels. Corrosion can result in the formation of hydrogen gas which if
absorbed quickly can cause the effect of gas bubbles in vivo [4,5]. Fe-based biodegradable material was proposed in 2001 for non-rusty stents. This material also has mechanical properties that correspond to bones. But this material has a limitation that is the level of corrosion is too small which requires a long time to disappear. This can cause chronic inflammation, where the inflammatory precipitate can inhibit the completion of the healing process[6].

The development of Mg and Fe-based biomaterials in the past decade has been extensively studied as biodegradable material for medical applications. However, the extensive development of this material system experiences limitations or stagnation in terms of its suitability for clinical applications[7]. In the last three years, Zn-based biomaterials have begun to be proposed to be studied as alternative biodegradable materials besides Mg and Fe. Zinc is one of the essential elements in the body where there are more than 300 enzymes and proteins in the body. When zinc ions are degraded from the implant, they can still integrate into the body's metabolic activities without producing toxic effects [8]. The advantage of other Zn-based alloy biomaterials is the moderate rate of degradation because it has a passive layer of moderate stability and Zn-based alloys are easier to do casting because of their low melting point and low chemical reactivity [9]. However, pure Zn biomaterials still have shortcomings namely the strength and elongation of this material is still low (oUTS ~ 30MPa and ε <0.25%), so it is not enough for medical applications [10].

One way to improve the mechanical properties of pure Zn biomaterial is by adding other alloying elements to Zn-based materials, such as Mg, Al, Cu, Ca, Sr, and Zr. Zirconium (Zr) as an alloying element for Zn-based material has not been widely studied by people. Zr is one element with potential biocompatible and bio neutral elements. Zirconium is also one of the elements that has low systemic toxicity [11]. Based on the Zn-Zr phase diagram, the addition of a small amount of Zr in Zn can form the Zr-rich intermetallic phase (Zn-Zr). The addition of 0.05% wt Zr in pure Zr can increase the strength (UTS) of the alloy to 157 MPa with 22% elongation. The amount of Zr released from Mg-Zn-Zr alloys results in a corrosion rate of 50 µg / day which is still acceptable to the human body [12]. Therefore, with the potential of Zr as a biocompatible element, this study will examine the effect of adding Zr in Zn alloys on the microstructure and hardness properties of the alloy material.

2. Experimental Procedures

2.1. Materials Preparation

The initial stages of the sample making process is doing alloy and mold designs. Materials that use in the Zn-Zr alloy preparation are commercially pure Zinc (99.95 wt%) and Zirconium (powder 99.9 wt%) addition of 0.5%, 1%, and 2% that are melting in the graphite crucible followed by centrifugal casting at 550°C. After that, the Zn-Zr alloy in the form of the melt was poured into a graphite mold with rod-shaped product and cooled at room temperature. Then, homogenized the sample at around 380°C for 8-10 hours. After the sample has been homogenized, then the sample is cutting with a thickness of approximately 5 mm for the sample preparation process. The stages of sample preparation are mounting, grinding, polishing, and etching. The chemical substances that use in sample preparation are resin and hardener for mounting, alumina solution for polishing, and 2 mL of HNO and 98 mL of distilled H2O for etching.

2.2. Microstructure Analysis

The sample for microstructure analysis was ground using sandpaper from 240-2000 grit. After that, the polishing process used a polish machine with alumina solution. Then, the etching process was done using 2 mL of HNO and 98 mL of distilled H2O. The microstructure of Zn-Zr alloys was observed using an Optical Microscope Carl Zeiss Primotech and Scanning Electron Microscope FEI Inspect 50 to determine the shape of the grain, grain size, and intermetallic distribution in the matrix and grain boundaries. Then the X-Ray Diffraction test was done to determine the compound and phases in the sample.
2.3. **Hardness Analysis**

The hardness test was done using BUEHLER micro hardness tester with the applied load of 100 gf. The initial step taken in testing the hardness of Vickers was sample preparation firstly. After sample preparation was finished, then the sample was placed in the area to be tested. After that, the load was set to be used, in this study using a load of 100 gf. Then, the point was found to be carried out as a loading. Once deemed appropriate, then the start button was pressed to start the loading process. Waiting time for the loading process lasts for approximately 10-15 seconds. After loading was complete, then the diagonals formed as a result of loading were measured. After that, the value of the Vickers hardness was calculated.

3. **Result and Discussion**

3.1. **Microstructures**

The results of testing the microstructure of the Zn-Zr alloy can be seen in Figure 1

![Figure 1. Microstructures of (a) pure Zn, (b) Zn-0.5Zr, (c) Zn-1Zr, (d) Zn-2Zr with SEM analysis.](image-url)

In figure 1 (a) it can be seen that the grain size of the pure Zn microstructure test results is quite large and tends to be rough. In figure 1 (b), after adding 0.5% zirconium, a precipitate formation at the periphery is close to the grain boundary. The precipitates were formed due to the casting temperature (550°C) and during the homogenization process (380 °C), zirconium is not dissolved in the Zn matrix. Based on the Zn-Zr binary phase diagram, the precipitate is identified as the Zn$_2$Zr phase [2].

In figure 1 (b) precipitates that are formed still tend to be small and the amount are still less. These precipitates are globular or oval-shaped and the distribution of the precipitates was not evenly distributed and still collects only in some parts of the grain boundary. In figure 1 (c) with the addition of zirconium 1%, the precipitates formed tend to be larger and more numerous. The shape of the precipitate looks sharp and the distribution of the precipitate looks more evenly distributed. In figure 1 (d) with the
addition of 2% Zr, it appears that more precipitates are formed. The shape of the precipitate of this microstructure is that it looks more diverse, there are those in the form of sharp, round, and elongated. The distribution of precipitates is more evenly distributed. It can be concluded that the more zirconium content added in zinc alloys, the more precipitates are formed where the size larger and the distribution of precipitates are more evenly distributed at the edges of grain boundaries.

3.2. Grain Size.
After getting the result of the microstructure of the zirconium content addition variable, then the grain size was calculated. The grain size calculation was done using the Planimetric (Jeffries) method with the help of Fiji ImageJ software application and in accordance with ASTM E112 standards. The results of the grain size calculation can be seen in table 1.

| Sample         | Grain Size (μm) |
|----------------|-----------------|
| Pure Zn        | 266.40          |
| Zn-0.5Zr       | 20.16           |
| Zn-1Zr         | 16.70           |
| Zn-2Zr         | 15.85           |

From Table 1 it can be seen that the more zirconium additions to the Zn-Zr alloys will make the grain size smaller. In other words, the addition of zirconium content in Zn-Zr alloys will reduce the grain size of the alloy. The most significant reduction in grain size occurs from pure Zn to Zn-0.5Zr alloys. The reduction in grain size is caused by the presence of precipitates in the alloy. The presence of precipitates in Zn-Zr alloys will inhibit the process of grain growth, so that nucleation will occur which makes the grain size smaller and more numerous. Reducing the grain size will increase the grain limit per unit volume and will reduce the path free from continuous slips. Small and fine grain size will strengthen the material by blocking the dislocation movement around the grain boundary, where the dislocation movement requires high stress to open or produce a new dislocation on the next item. Alloy with a small and fine grain size will make the strength and hardness of the alloy be increased compared to large and coarse grains. That is because alloys with small and fine grain size have a larger amount of surface in the total grain layer area which will inhibit the movement of dislocations.

3.3. XRD Result
XRD testing conducted in this study aims to determine the phases formed from each alloy. This XRD analysis was carried out using the help of Origin 2018 software. The results of XRD Zn-Zr alloy testing can be seen in Figure 2.

Figure 2 shows the comparison of the XRD test results for the addition of Zr levels in Zn-Zr alloys. The composition of Zr added to Zn-Zr alloy is 0.5% Zr in Zn-0.5Zr alloy, 1% Zr in Zn-1Zr alloy in Zn-1Zr alloy, and 2% Zr in Zn-2Zr alloy. In figure 2 it can be seen that the Zn-0.5Zr alloys have two phases that appear, namely the α Zn phase and the Zn22Zr intermetallic phase. This is consistent with the literature on the Zn-Zr phase diagram, where zirconium at 550°C is not dissolved into the Zn matrix, so at this temperature, the intermetallic phase Zn22Zr is formed. The peak height of the Zn phase is higher compared to the Zn-Zr phase due to the higher Zn concentration compared to Zr, so the Zn phase will be more dominantly formed. The peak of diffraction 2θ in the highest Zn phase is 43.28°. Some of the other 2θ diffraction peaks that occur in the Zn phase are 36.32°, 39.04°, 43.28°, 54.94°, 70.16° and 82.20°.

In the Zn-1Zr and Zn-2Zr alloys, the phases formed are the same as those in the Zn-0.5Zr alloys namely Zn phase and Zn22Zr phase. This is due to the addition of 1% Zr and 2% Zr when casting and homogenizing, the Zr element does not dissolve in the Zn matrix. The difference between Zn-0.5Zr and Zn-1Zr and Zn-2Zr is the height of the peak that occurs. In the Zn-2Zr alloy, the peak of the Zn phase is seen to be lower than the peak of the Zn phase in the Zn-0.5Zr alloy and the Zn-1Zr alloy. The phase
intensity of Zn-2Zr alloys at 43.28° is 21438 a.u, whereas in Zn-0.5Zr and Zn-1Zr alloys are 36267 a.u and 36962 a.u. This happens because of the increasing composition of Zr in the Zn alloy. The intensity of the peak phase Zn will decrease with increasing composition combined.

While the peak height of the Zn$_{22}$Zr phase in the Zn-2Zr alloy looks higher compared to that of the Zn-0.5Zr alloy and Zn-1Zr alloy. This happens because the levels of zirconium in Zn-2Zr alloys are higher than the levels of zirconium in Zn-0.5Zr and Zn-1Zr. Some of the 2θ phase diffraction peaks of Zn$_{22}$Zr that occur in Zn-2Zr alloys are 37.73°, 40.44°, 42.52°, 44.38°, 45.94°, 76.42°.

![Figure 2. XRD result of Zn-Zr alloys.](image)

3.4. Hardness Properties

Hardness testing was done to determine the comparison of the hardness value of each alloy and the comparison of the value of pure bone hardness. The method used for hardness testing in this study is using the Vickers microhardness method. The results of Vickers microhardness testing can be seen in figure 3.

In figure 3, it can be seen that the more zirconium content added in the Zn alloy, the harder the existing value of the alloy will increase. This is because the addition of the Zr element to the Zn alloy will result in smaller and finer grain sizes, the smaller and finer grain size can increase the hardness. The smaller and finer grain size occurs because zirconium does not dissolve in the Zn alloy during the homogenization process. The insoluble zirconium turns into precipitates which will inhibit the growth of grain size so that the grain will undergo nucleation that its size becomes smaller and more numerous.

Meanwhile the addition of other elements to the Zn-based alloy, the value of the resulting hardness tends to be higher than with the addition of Zr. As in the example of research conducted by HF Li, and friends, about the effect of adding Mg, Ca and Sr on Zn-based alloys, the hardness value of the alloys is 78.26 HV for Zn-1Mg alloys, 73HV for Zn-alloys 1Ca, and 61.88 HV for Zn-1Sr alloys [13].

From the results of the study of the addition of other elements to the Zn-based alloy, the value of Zn-Zr alloy hardness is below the value of the addition of other elements [14]. Whereas based on the ASM Metals Handbook, Vol 02 Properties and Selection of Nonferrous Alloys and Special-Purpose Materials, the hardness value of Zn-Zr alloys is between the average hardness values of Zn-based alloys which is between 42-163 HV. From these data, it can be concluded that the value of Zn-Zr alloy hardness is not
too high, possibly suitable for use in biodegradable orthopedic implant applications. This is because if the alloy hardness value is too high it can damage the bone surface due to rubbing against the implant itself.

![Hardness Value graphic of Zn-Zr alloys](image)

**Figure 3.** The hardness value graphic of Zn-Zr alloys.

4. Conclusion
Based on the results of research and analysis of data that has been done, it can be concluded that: adding zirconium content to zinc alloys with 0.5%, 1%, and 2% Zr content, can form precipitates in microstructures. Precipitates that are formed can inhibit the process of grain growth which makes grain size smaller and finer. The smaller and finer grain size makes the strength and hardness values of the alloy larger. The more zirconium content is added to the zinc alloy, the smaller the grain size will be produced. The grain size of pure Zn was 266.40 µm, Zn-0.5Zr was 20.16 µm, Zn-1Zr was 16.70, Zn-2Zr was 15.85 µm. The phases produced in the Zn-Zr alloys from the XRD test are the Zn phase and the Zn,Zr phase. The more zirconium content added to the Zn alloy, the greater the resulting of the hardness value. The value of pure Zn hardness produced was 35.162 HV, Zn-0.5Zr was 41.988 HV, Zn-1Zr was 42.324 HV, and Zn-2Zr was 57.112 HV. Zn-Zr alloy material can be a candidate alloy material suitable for use in biomedical applications because it has a hardness value that is relatively close to the hardness value of the bones (40.38HV)[15], besides that based on the literature Zn alloy material also has a moderate degradation rate[14].

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