The Effect of Zirconium Addition on Corrosion Behavior of Zn-Zr Alloys as Biodegradable Orthopedic Implant Application

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Abstract. In this work, corrosion behaviour of zinc-based alloys with addition of 0.5%, 1%, and 2% of zirconium for biodegradable material as orthopaedic implant were investigated. The potentiodynamic polarization method is carried out to determine the corrosion resistance and corrosion rate of each composition in order to observe the effect of zirconium addition in a Kokubo simulated body fluid solution. The result showed that the addition of 0.5% and 1% of zirconium would decrease the corrosion rate of Zn-xZr alloys corresponding to 0.079 mm/year and 0.116 mm/year whereas the 2% addition would increase the rate to 0.188 mm/year due to the formation of Zr-rich precipitates inside the alloys. The passivation zone on the polarization curve showed the formation of the protected thin layer on the surface of the alloys which caused the corrosion rate to decrease, therefore confirmed the degradable ability of the Zn-xZr alloys. In general, the corrosion rates of Zn-xZr alloys were higher than Fe-based alloys and lower than Mg-based alloys. Moreover, the corrosion rates were much lower than the maximum rate of 0.4 mm/year for biodegradable implants so Zn-xZr alloys were suitable as biodegradable material implant for orthopaedic application.

1. Introduction
Biomaterials are defined as a substance that has been engineered to take a form to replace or assist part of an organ or tissue in living things and will be in direct contact with it [1]. In the body, biomaterials will interact with their supported organs or tissues so they must have good biocompatibility. In the medical world, biomaterials are widely used as orthopaedic, cardiovascular, ophthalmic, dental implants, wound healing, and drug delivery system. Orthopaedic implants are medical devices used to replace or assist the healing process of bones, or to replace articulating surfaces of a joints [2]. The main function of orthopaedic implants such as joint prostheses, plates, and screws is to provide strength and stability, directs the process of bone or joint growth by interacting directly with the damaged tissue [3].

Based on World Health Organization data, it is estimated that there will be an increase in the need for orthopaedic implants for the next few years. Based on research conducted by the World Health Organization, there is an increase in world average life expectancy between 2000 and 2016 that was 5.5 years to 72 years (74.2 for women and 69.8 for men), the fastest increase since the 1960s. In 2019, the average age of the world's life expectancy is 72.5 years. With the increasing of life expectancy, people worldwide will live longer. In 2050, the world population above 60 years is estimated to reach 2 billion people, of which 80% come from low and middle income countries. As the world’s population is getting older, there will be an increase in musculoskeletal diseases, such as osteoporosis.
and osteoarthritis as well as an increase in demands for orthopaedic implants. Therefore, the development of biomaterial implant will greatly influence the application of these orthopaedic implants.

These days, biomaterials used as orthopaedic implants are still dominated by non-degradable metals, such as stainless steel, titanium alloys, and Co-Cr alloys. Biodegradable materials are begun to develop rapidly following disadvantages of the non-degradable metals, such as inflammatory reactions [4], the required of second surgery for removal of the implant [5], bone degradation [6], and so on. Meanwhile, biodegradable material does not require further surgery because it will dissolved in the recipient body. Therefore, essential metals in the body are needed to be developed as biodegradable material. Until now, only three alloys have been developed as biodegradable material, namely Mg-alloys, Fe-alloys, and Zn-alloys.

Magnesium is the first material developed as a biodegradable material and has been used commercially as an orthopaedic implant. Magnesium is harmless to the body and plays a role in several biological functions of the body, such as enzyme reactions, digestive functions and nerves, metabolism, synthetic proteins, and the immune system [7]. Magnesium has mechanical properties that are similar to the mechanical properties of human bones [8]. However, pure magnesium has a high rate of degradation and can produce hydrogen gas which can harm the tissue around the implantation sites [9][10].

Iron is the second metal in development as a biodegradable material which has reached in vivo stage development in animals. Iron is one of the essential elements for oxygen transfer into body tissues and an important component in many types of enzymes [8]. Iron alloys have good mechanical properties so they are suitable for orthopaedic implants. However, iron alloys have very low degradation rates and require a long time for dissolving into the body. Thus, they can produce similar side effects to permanent non-degradable implants [11][12].

Zinc is the third metal developed as biodegradable material. In human body, zinc is the second most transition metal element after iron that present in all organs, tissues, and secretions of body fluids with the most amount found in muscles and skeleton (86%), skin (6%), liver (5%), brain (1.5%), and other tissues that are evenly distributed. As one of the essential elements in the body, zinc has various roles in human biological functions, specifically to support the immune system, enzyme synthesis, wound healing and protein formation, and bone formation [13][14]. Zinc is known to have a degradation rate between magnesium alloys and iron alloys. With a lower degradation rate, zinc alloys will produce less hydrogen gas which are expected to be able to dissolve in accordance with bone healing time (approximately 6 months) [15]. In addition, zinc alloys are also easier to be manufactured than magnesium alloys. However, zinc has relatively low mechanical properties, so the combination with other alloy elements is needed.

Zirconium is one of the transition metal elements that has been widely used in the biomaterial world, especially for dental implants and alloying element in magnesium based biodegradable material. Inside the body, zirconium has no crucial role in biological functions. Moreover, zirconium shows no toxic effects on body tissues. The addition of zirconium is known to be able to improve the mechanical properties of magnesium alloys through the mechanism of precipitate strengthening [16]. In this study, we will further investigate the effect of zirconium addition on the corrosion behavior of zinc alloys.

2. Materials and experimental details

2.1. Material preparation

Zn-xZr alloys with different content of Zr (0.5, 1, and 2 wt.%) as well as the pure Zn reference sample were prepared by melting high purity Zn (99.99%) and high purity Zr (99.99%) ingots using a graphite crucible under air atmosphere. The melts were stirred and kept for one hour in 550°C to ensure that zirconium are completely dissolved, and then poured into graphite mold and cooled at room temperature. The melted alloys then homogenized at the temperature of 380°C for 8 to 10 hours. After that, the samples were prepared for the microstructure analysis by cutting it for 5 mm in thickness. The surface of the alloys were mounted, grinded, polished and etched with 2 ml HNO₃ and 98 ml distilled
water to prepare for surface analyzing using an optical microscope Carl Zeiss Primotech and scanning electron microscope FEI inspect 50 to determine the shape of the grain and intermetallic distribution of the alloys.

2.2. Electrochemical measurements
In this study, the corrosion properties of Zn-xZr alloys would be measured in a simulated body fluid using potentiodynamic polarization tests on Autolab (PGSTAT-302N) with a standard set-up of three electrodes. The three electrodes used in the tests were platinum plate as counter electrode, silver silver chloride (SSC) as reference electrode, and the alloys as the working electrodes. Before the tests, the Open Circuit Potentials (OCP) of the specimens would be monitored for 3600 s. The OCP was measured to see whether the alloys would be stable inside the fluids. The tests were recorded at scanning rate of 1 mV/s, starting from -250 mV to +500 mV at the temperature of 37°C in simulated body fluid. From the tests, the corrosion rate would be calculated based on ASTM G102-89.

3. Results and discussion

3.1. Microstructure of Zn-xZr alloys
Fig. 1 shows the surface of the samples after potentiodynamic polarization test while Fig. 2 shows the microstructures of the alloys under scanning electron microscope. The characterization of the microstructures shows the addition of the higher value of zirconium that led to the formation of the interconnected networks of intermetallic compounds. Consequently, the formation of these intermetallic compounds would increase the corrosion rates, although it also displaced the corrosion potentials of the Zn-xZr alloys to more noble values.

![Image](image_url)

**Figure 1.** Visual inspection of (a) Zn-0.5Zr, (b) Zn-1Zr, (c) Zn-2Zr after potentiodynamic polarization test.

3.2. Corrosion behaviour of the Zn-xZr alloys
The potentiodynamic polarization curves of the Zn alloys are shown in Fig.3. The corresponding electrochemical performance parameters are listed in Table 1. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are -0.875 V vs SSC in saturated KCl and 9.88 μA/cm² for pure zinc, -0.965 V and 5.29 μA/cm² for Zn-0.5Zr, -0.984 V and 7.73 μA/cm² for Zn-1Zr, and -0.893 V and 12.50 μA/cm² for Zn-2Zr, respectively. The corrosion potentials of zinc alloys are lower than that of pure zinc which suggest that the Zn-xZr alloys are more prone to corrosion than pure zinc. Meanwhile, with the exception of Zn-2Zr, the current density of the Zn-xZr alloys are also relatively lower than the pure zinc. The corrosion current density would be used to determine the corrosion rate of the alloys. The corrosion rate (V_{corr}) was calculated based on ASTM G102 in which pure zinc will corrode with the rate of 0.148 mm/year, 0.079 mm/year for Zn-0.5Zr, 0.116 mm/year for Zn-1Zr, and 0.188 mm/year for Zn-2Zr, respectively. The reduction of alloy corrosion rate can be linked to the refinement of the
microstructures caused by the addition of zirconium. It has been studied that the smaller grain size creates more grain boundaries and, also reduces the corrosion rates of the alloys. On the other hand, the addition of zirconium beyond the previously mentioned value led to a deterioration of the corrosion behaviour of the Zn-2Zr alloy with a higher current density, which indicates that Zn-2Zr has the lowest corrosion resistance between the zinc alloys examined in this study.

![Microstructures of Zn-0.5Zr, Zn-1Zr, Zn-2Zr](image)

**Figure 2.** Microstructures of (a) Zn-0.5Zr, (b) Zn-1Zr, (c) Zn-2Zr with SEM analysis.

During anodic polarization, a passive film is formed on the surface and provide a protective barrier that keeps the corrosion current at low level. Figure 3 shows that passive films were formed in the alloy which indicated by the passivation potential (E_{pp}) and passivation current density (i_{pp}) in the polarization curve. Passivation potential and passivation current density are the point in which the passivation zone started to form on the surface of each alloy. On the other hand, the end of the passivation zone is signed by the breakdown potential (E_{b}). This is the potential in which the passive film breaks to the surface of alloys. The details of the breakdown potentials are also shown in Table 1. As shown in Fig. 3, Zn-1Zr would be the first to form the passivation zone, followed by Zn-0.5Zr, Zn-2Zr, and lastly the pure zinc. On the other side, the breakdown potential of pure zinc is higher than that of Zn-0.5Zr and Zn-1Zr alloys, suggesting that the two alloys are more sensitive to local corrosion by destroying the protective layers whilst Zn-2Zr is more likely to avoid the local corrosion due to passivation phenomena. The formation of the passivation zone also shows the resistancy of the alloys to corrode where Zn-2Zr shows the highest resistance among the alloys with its high E_{pp} and E_{b}.

As biomaterial, it is required for an orthopedic implant to hold 95% of its area during to the first six weeks of implantation. It is needed to ensure that the material used as the orthopedic implant will not degrade completely before the healing process of the bone which usually takes six to 12 weeks is finished. If the material in used breaks down too fast, the sudden lost of bone support will disrupt the healing process and may impair the formation of the bone as well. Therefore, it is studied that the maximum corrosion rate allowed for biomaterial used for implant is 0.4 mm/year[17]. For that reason, the alloys studied here will be suitable to use as biodegradable implant. However, Zn-0.5Zr will not be effective because its corrosion rate is even lower than that of pure iron. On the other hand, Zn-2Zr will be a better choice with its higher corrosion rate. In comparison, Zn-1Zr has a slightly lower corrosion rate than Zn-2Zr, but it also has low corrosion resistance which is proven by its low OCP and the short range of potentials in which the passivation zone is formed. Therefore, in practice, Zn-1Zr will corrode faster than Zn-2Zr as shown in Fig. 1 where Zn-1Zr has the more blackened area than the Zn-2Zr alloys.
Figure 3. Polarization curve of Zn-xZr alloys with pure zinc as reference.

Table 1. Value measured from potentiodynamic polarization tests of Zn-xZr alloys and pure Zn.

| Alloys | Ecorr(V<sub>vsSSC</sub>)<sup>a</sup> | icorr(μA/cm<sup>2</sup>)<sup>b</sup> | CR (mm/y)<sup>c</sup> | E<sub>pp</sub> (V<sub>vsSSC</sub>)<sup>d</sup> | ipass (μA/cm<sup>2</sup>)<sup>e</sup> | E<sub>b</sub> (V<sub>vsSSC</sub>)<sup>f</sup> |
|--------|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Zn     | -0.875                        | 9.88            | 0.148           | -0.84841        | 27.40           | -0.71241        |
| Zn-0.5Zr | -0.965                       | 5.29            | 0.079           | -0.86951        | 8.55            | -0.80451        |
| Zn-1Zr  | -0.984                       | 7.73            | 0.11            | -0.95145        | 46.79           | -0.82045        |
| Zn-2Zr  | -0.893                       | 12.50           | 0.188           | -0.86788        | 25.53           | -0.71088        |

<sup>a</sup> Corrosion potential  
<sup>b</sup> Corrosion current density  
<sup>c</sup> Corrosion rate  
<sup>d</sup> Potential in which the passivation zone starts to form  
<sup>e</sup> Current density in which the passivation zone starts to form  
<sup>f</sup> Breakdown potential

4. Conclusions

Based on the research, it can be concluded that the addition of zirconium will decrease the corrosion rate of Zn-xZr alloys until a certain value of zirconium where the intermetallic compounds will be formed and increase the corrosion rate of the alloys. The formation of passivation zone shows that the protected layer covering the surface of Zn-xZr alloys will also play a part to their biodegradable capability. In general, Zn-xZr alloys are suitable to be used as biodegradable implant for orthopedic application with Zn-2Zr as the most effective alloy among others.

Acknowledgment

The authors would like to thank the Direktorat Riset dan Pengabdian Masyarakat Universitas Indonesia (DRPM- UI) for the financial support under the grant of Hibah PITTA UI 2018 No. 2535/UN2.R3.1/HKP.05.00/2018.
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