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Reseach Paper

Corrosion Resistance of Ternary Zr-Ti-Cu Alloy for Dental Implant Application in Ringer Lactate Solution Contamined with Ulcer Medicine

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Abstract: Implanted material is one of the solutions to overcome damage or the function of human organs. The many needs about implants or biomaterials make researchers continue to conduct various studies. One criterion as an implant material is that having good corrosion resistance so it does not have rejection from the body. This research aims to determine the corrosion behavior of Zr-Ti-Cu implant material in Lactated Ringer's solution. The Zr-Ti-Cu implant material uses a variation of 1% and 3% Cu content synthesized by the melting process using a Single Arc Melting Furnace with an atmospheric environment of argon. The results were characterized using an optical microscope and Vickers test equipment. Corrosion behavior of the Zr-Ti-Cu implant using a potentiostat with the Tafel polarization method in a Ringer's Lactated solution and Ringer's Lactate solution that added with ulcer potion 10 mL. From the results of characterization with optical microscopy and XRD showed phases α-Zr and α-Ti, and intermetallic compounds Zr2Cu and Ti2Cu. Increasing Cu content can increase the hardness value so it has a hardness value between 528-619 HV. The addition of ulcer potion increases the corrosivity level of Ringer's lactate solution. Corrosion resistance increased from 2,140 mpy to 1,571 mpy in Ringer's Lactate solution and from 2,060 mpy to 1,492 mpy in Ringer's Lactate solution with ulcer potion due to the addition of Cu in the alloy.

Keywords: Implant; Corrosion Resistance; Zr-Ti-Cu; Tafel Polarization; Ringer's Lactated solution.

1. Introduction

Biomaterial is any synthetic material that is used to replace or restore function to a body tissue and is continuously or intermittently in contact with body fluids. Exposure to body fluids usually implies that the biomaterial is placed within the interior of the body, and this places several strict restrictionson materials that can be used as a biomaterial. First and foremost, a biomaterial must be biocompatible—it should not elicit an adverse response from the body, and vice versa. Additionally, it should be nontoxic and noncarcinogenic. These requirements eliminate many engineering materials that are available. Next, the biomaterial should possess adequate physical and mechanical properties to serve as augmentation or replacement of body tissues. For practical use, a biomaterial should be amenable to being formed or machined into different shapes, have relatively low cost, and be readily available. One application of biomaterials is to implant devices, such as orthopedic, dental, cardiovascular, etc [1].

Metallic materials are often used to replace structural components of the human body because they surpass plastic or ceramic materials in terms of tensile strength, fatigue strength, and fracture toughness. As such, they are used in medical devices such as artificial joints, dental implants, artificial hearts, bone plates, staples, wires, and stents. They also possess better electro conductivity qualities,

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and hence are used for enclosing electronic devices such as pacemaker electrodes and artificial inner ears [2].

The biological materials like dental implant materials have been well studied and developed. Some conditions should be met for the practical applications of these materials. First of all, implant materials must possess excellent biocompatibility without adverse reactions. In addition, it must have a good combination of excellent corrosion resistance in body fluid, high mechanical strength and fatigue resistance [3][4].

Zirconium is believed to be an ideal alloying element for titanium in biomedical applications. Zr-xTi (or Ti-xZr) alloys exhibit the similar strength and good osseointegration in animal and clinical studies to Ti-6Al-4V alloy [5][6][7][8][9]. In addition to this, Zr-Ti binary alloys present the other advantages, such as low melting point, low magnetic susceptibility, low linear expansion coefficient and less hydrogen absorption compared with cp Ti and Ti alloys [10], which make them become the important candidate materials as permanent prosthesis in dental or orthopedic treatments [11][12]. In the oral environment, the corrosion resistance of the metallic materials is crucial in evaluating their roles as dental implants because the released ions arising from the corrosion of metal or alloy stimulate the growth of the macrophage. The rough surface on the corroded metal also promotes the adhesion of various bacteria and the formation of plaque, which are considered as one of the factors inducing periodontitis and gingivitis [13]. The fatigue failure of dental implant has been reported to be closely related to the corrosion of the metal material [14]. Though zirconium metal offers superior corrosion resistance in acid or alkali solutions, it is susceptible to localized corrosion in the media containing chloride or fluoride. Increasing titanium content reduces the localized corrosion of the Zr-Ti alloys [15][16].

The electrochemical techniques most commonly used for corrosion studies have their own specific advantages for addressing effectively certain aspects of the electrochemical performance of implant materials [17]. The direct current (DC) polarization curves can show the potential region in which the passivity is effectively maintained and the alternative current (AC) impedance method, being a non-destructive electrochemical technique, is particularly useful for monitoring certain electrochemical changes as a function of time. Therefore, the combination of these techniques is often necessary to obtain the most comprehensive information about the corrosion behavior under given circumstance [18].

This investigates was carried out to studied the corrosion behavior of Zr-15Ti alloy with Cu content additions by linear polarization method on Ringer's Lactated Solutions.

2. Research and Methodology

2.1 Materials (Heading two)

The chemical composition of experimental alloys was designed as Zr-15Ti, Zr-15Ti-1Cu, and Zr-15Ti-3Cu with 99,8% purity of Zirconium sponge and also 99,9% purity of Titanium rod and Copper wire. The experimental alloys were prepared and melted by single arc melting furnace with tungsten electrode in the tigettered high-purity argon atmosphere as button ingots. The button ingots were flipped and remelted at least four times to ensure the homogenity of chemical composition and the molten samples were cooled by cooling water in the copper crucible pot. This process resulting cylindrical specimens with a diameter of 15 mm and a thickness of 4 mm. The chemical composition of the Zr-Ti-Cu alloy is shown in Table 1. below.

Table 1. Codefication of Specimen in %Weight.

Specimen (*as cast*)	% Weight		
	Zr	Ti	Cu
Zr-15Ti	85	15	-
Zr-15Ti-1Cu	84	15	1
Zr-15Ti-3Cu	82	15	3

For corrosion test and characterizations, the specimen was prepared by grinding machine to make the surface of samples. To observed the microstructures, samples were mounted and mechanically polished with SiC paper and Cr_2O_3 particles with water and etched with Keller's Reagent. The microstructures were determined by optical microscope (OM). Hardness tested by Vickers micro hardness, and X-Ray Diffraction (XRD) tested to phase identification were permormed at the samples. Corrosion test in a Ringer's Lactated solution and Ringer's Lactate solution that added with ulcer potion 10 mL at room temperature with 10 minutes immersion times used Polarization method accordance to ASTM G59 with Pt support electrode and Ag-AgCl reference electrode. Polarization tested was used scan range -35 to +35 mV with 5 mV/s scan rate and the output were corrosion potential curves, polarization curves and corrosion rates.

The process of data collection is done with the help of software "Gamry Instrument" and "Gamry Electrochrmical Analyst". For final characterization to supported and confirmed tested result, SEM (Scanning Electron Microscophy) - EDS (Energy Dispersive Spectroscophy) to identification microstructure and chemical composition of samples were carried out.

3. Results and Discussion

3.1. Surface Morphology

The surface morphology observation of samples was carried out by camera to learn the differences of surface sample between before and after corrosion. Figure 1-2 shows that there are no important differences of surface samples after corrosion tested.

(a) (b) (c)

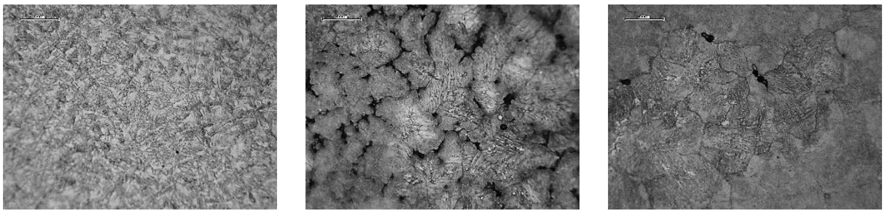
Figure 1. Surface Morphology Before Corrosion Test of (a) Specimen I (Zr-15Ti), (b) Specimen II (Zr-15Ti-1Cu), dan (c) Specimen III (Zr-15Ti-3Cu)

(a) (b) (c)

Figure 2. Surface Morphology After Corrosion Test of (a) Specimen I (Zr-15Ti), (b) Specimen II (Zr-15Ti-1Cu), dan (c) Specimen III (Zr-15Ti-3Cu)

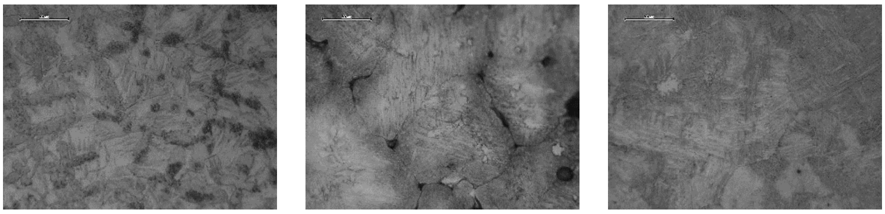
3.2. Microstructure

Based on metallographic examination on Figure 3-4, microstructure obtained in the form of dendritic which shows the results of the casting process. In the microstructure produced α-Zr phase was found as a matrix and α-Ti formed from the grain boundaries and white [19], this is in accordance with the phase diagram of Zr-Ti [20]. The addition of copper (Cu) on a Zr-Ti alloy cause the appearance of such compounds or Zr_2Cu Ti_2Cu based on the phase diagram of Zr-Cu and Ti-Cu phase diagram [20]. Compounds Zr_2Cu and Ti_2Cu gather at the grain boundaries so as to clarify and reinforce the shape of the grain boundaries in the alloy Zr-15Ti-3Cu and are on matrix α-Zr alloys Zr-15Ti-1Cu marked with white spots.



(a) Zr-15Ti (b) Zr-15Ti-1Cu Zr-15Ti-3Cu

Figure 3. The Microstructure with 100μm (200 X) Magnification

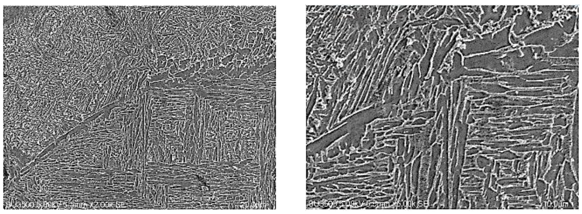


(a) Zr-15Ti (b) Zr-15Ti-1Cu Zr-15Ti-3Cu

Figure 4. The Microstructure with 50μm (500 X) Magnification

3.3. SEM/EDS

Figure 5 shows the result of SEM images captured of Zr-15Ti-3Cu alloy. These image shows that surface structure of Zr-15Ti alloy when it was added by Cu content elements. And the chemical copmpositions identification of Zr-15Ti-3Cu by EDS, determined on Table 2 and Figure 6-7.



(a)2000 X (b)5000 X

Figure 5. SEM Images Captured of Zr-15Ti-3Cu

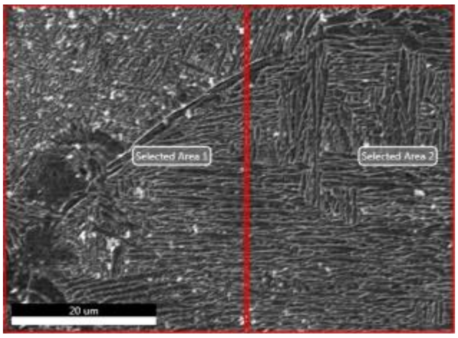
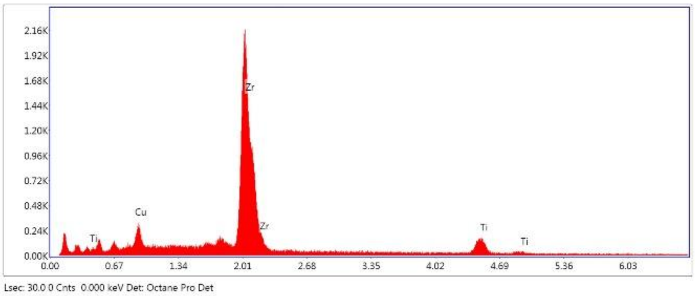
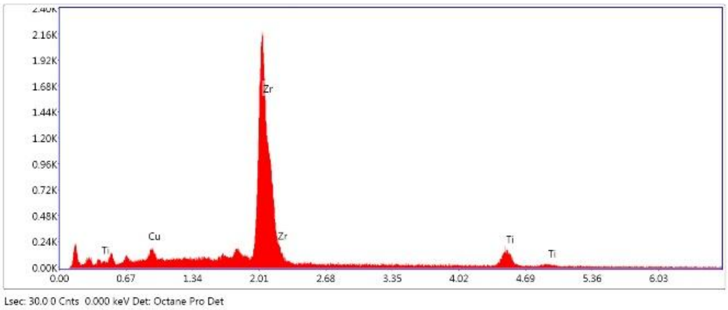


Figure 6. Identification Area of Zr-15Ti-3Cu Alloy by EDS



Selected Area 1



Selected Area 2

Figure 7. Chemical Composition Pattern of Zr-15Ti-3Cu

Table 1. Chemical Composition of Zr-15Ti-3Cu

Element	*Weight%*		
	Rencana Awal	*Area* 1	*Area* 2
CuL	3	4.78	2.52
ZrL	82	79.59	81.92
TiK	15	15.63	15.56

The EDS result data showed that the chemical composition of Zr-15Ti-3Cu were little bit changed from first planned chemical composition. Copper's weight percent of Zr-15Ti alloy has increased from 3 weight percent at first planned, be 4.78 weight percent in area 1 and decreased to 2.52 in area 2, so the Zirconium's weight percent has decreased and increased to balancing it. Titanium's weight percent also little bit increased from 15 weight percent to 15.56 and 15.63 weight percent. It caused by balancing processes for alloying was not exact and make abit friction of chemical composition's plotted on Zr-Ti, Zr-Cu, and Ti-Cu binary diagram to predict the formed of phase or compound but the friction was no far from first planned.

3.4. Hardness and X-Ray Diffraction

Figure 10 shows the Vickers micro hardness tested of as-cast samples. The result showed that Cu content additions were increased the hardness value of Zr-15Ti alloy. The result of X-Ray Diffraction tested for as-cast samples were showed in Figure 11. The result confirmed of metallographic data that the samples has α-Zr phase with highest tetha position, α-Ti phase and intermetallic Zr_2Cu and Ti_2Cu as second phase. But the result also showed that there was another second phase, β-Zr were identificated in Zr-15Ti-3Cu alloy. Thats why the hardness value was increased by Cu content additions, second phase or intermetallic compound and solid solution strengthening [21,22]. There is a β-Zr phase which can be caused by cooling process that is too fast so that the β phase does not have enough time to transform into the α phase.

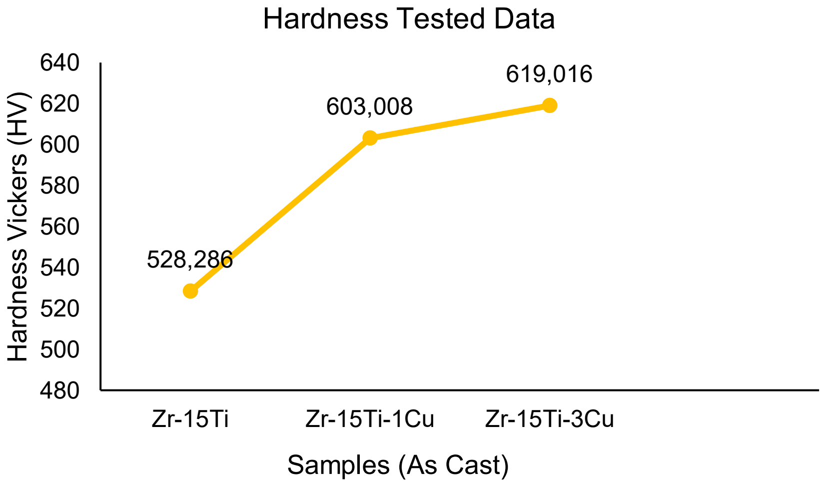


Figure 8. The Value of Vickers Micro Hardness Tested

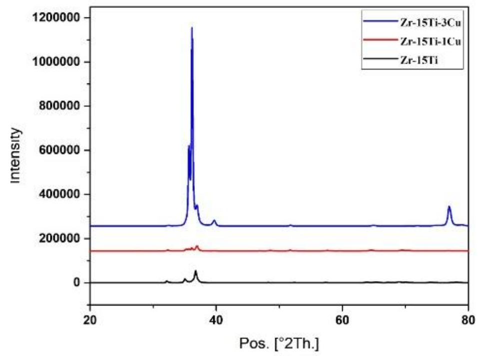


Figure 9. The XRD Profile of Zr-Ti-Cu Alloy

3.5. Solutions Preparation

Table 2. Solutions Data

Data	Solution Composition	
	Simulated Body Fluid Ringer Laktat	*Simulated Body Fluid* Ringer Laktat + Obat Maag
pH Before Corrosion Test	7,80	10,08
pH After Corrosion Test	8,43	10,24
TDS (ppt)	9,13	9,38
Conductivity (mS)	12,84	13,21
Resistivity (Ohm)	79,00	76,00

The solution changes pH because of the ions that break down from the alloy into the solution. Besides, the addition of ulcer potions in the solution causes an increase in pH due to a reaction between Ringer's Lactated solution with Mg $(OH)_2$ and Al $(OH)_3$ in the ulcer drug content, resulting in the formation of strong alkaline NaOH.

The addition of ulcer potions also made the Total Dissolved Solids (TDS) value of the solution increased from 9.13 ppt to 9.38 ppt that indicates an increase in solid particles in the solution. The conductivity value of the solution that has ulcer potion additions were higher than the pure one, while the resistance value was lower. Accorded to these data, the addition of the ulcer potions may increase the corrosivity of Ringer's Lactated solution.

3.6. Corrosion Test

Figure 12-13 showed the potential corrosion of the samples and Figure 14-15 showed the potential curves of the samples. The result showed that the potential corrosion and the potential curves were changed into positive value so the corrosion rate must be decrease.

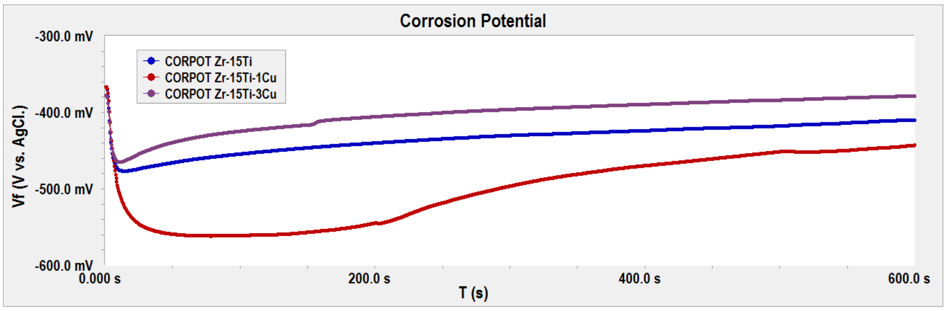


Figure 10. Potential Corrosion in Ringer’s Lactated Solution

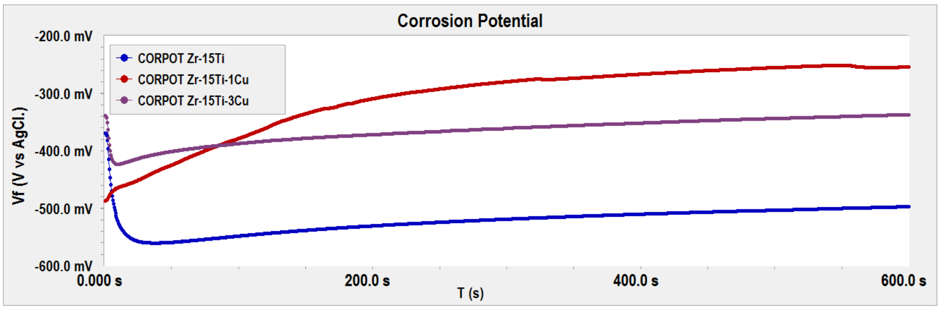


Figure 11. Potential Corrosion in Ringer’s Lactated Solution + Ulcer Potion

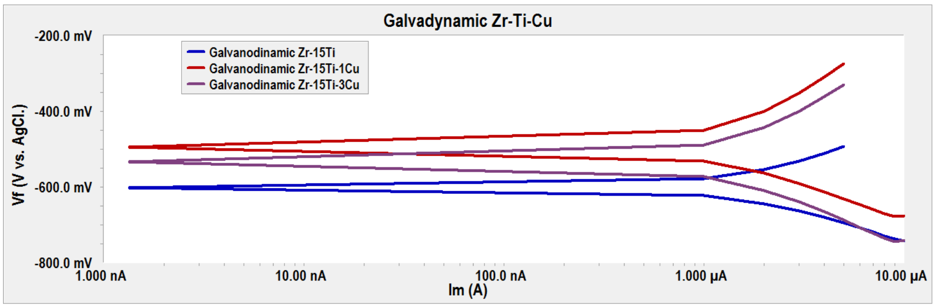


Figure 12. Potential Corrosion in Ringer’s Lactated Solution

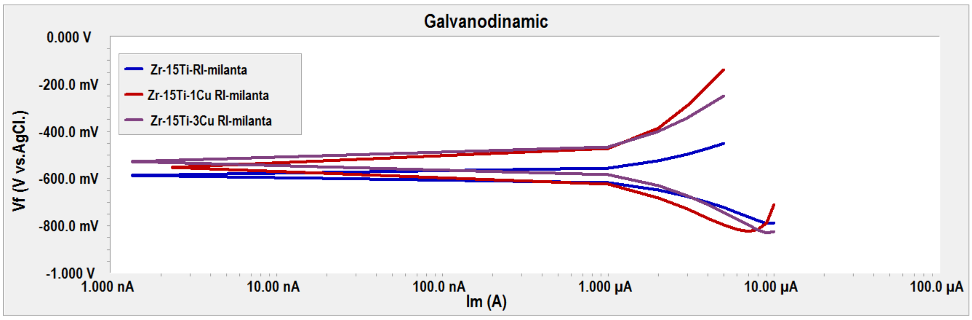
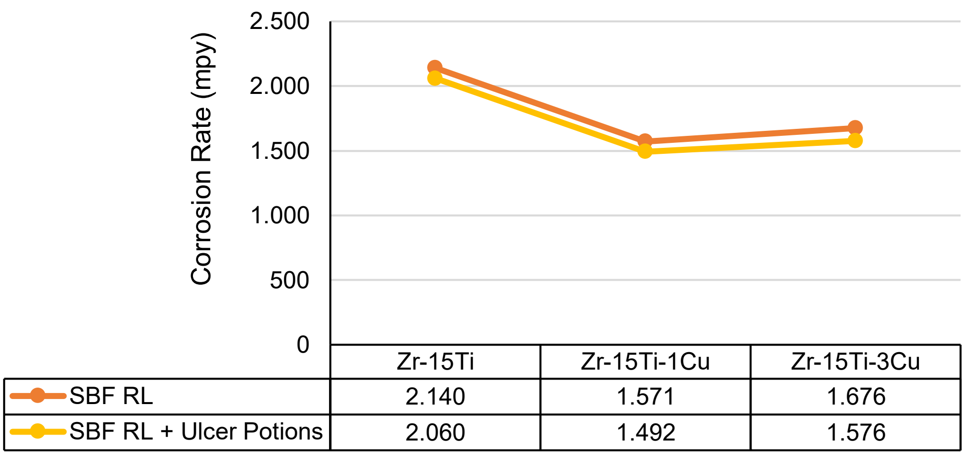


Figure 13. Potential Corrosion in Ringer's Lactated Solution + Ulcer Potion

Table 3. Polarization Data

Samples (As Cast)	Data	Solution Composition	
		Ringer's Lactated Solution	Ringer's Lactated Solution + Ulcer Potion
Zr-15Ti	βA (V/*decade*)	0.2826	0.3366
	βC (V/*decade*)	0.2242	0.3321
	I*corr* (µA)	2.370	2.280
	E*corr* (mV)	-601.0	-586.0
	Corrosion Rate (*mpy*)	2.140	2.060
Zr-15Ti-1Cu	βA (V/*decade*)	0.4665	0.8310
	βC (V/*decade*)	0.2597	0.4447
	I*corr* (µA)	1.740	1.650
	E*corr* (mV)	-494.0	-554.0
	Corrosion Rate (*mpy*)	1.571	1.492
Zr-15Ti-3Cu	βA (V/*decade*)	0.6068	0.5746
	βC (V/*decade*)	0.4319	0.4108
	I*corr* (µA)	1.860	1.750
	E*corr* (mV)	-527.0	-527.0
	Corrosion Rate (*mpy*)	1.676	1.576

Accorded to these data, known that different composition of Cu can make the potential corrosion into positive, so the corrosion rate must be decrease. Figure 11 showed the effect of Cu content additions can decreased corrosion rate of Zr-15Ti alloy. Zr-15Ti alloy has 2.140 mpy on excellent cathegory, Zr-15Ti-1Cu has 1.571 mpy on excellent cathegory and Zr-15Ti-3Cu has 1.676 mpy on excellent cathegory in pure Ringer's Lactated Solution. In a different solution that have higher corrosivity level because addition of ulcer potion on Ringer's Lactated Solution, addition of Cu content still descreased the corrosion rate of Zr-15Ti alloy.



	Zr-15Ti	Zr-15Ti-1Cu	Zr-15Ti-3Cu
SBF RL	2.140	1.571	1.676
SBF RL + Ulcer Potions	2.060	1.492	1.576

Figure 14. Effect of Cu Additions and Solution's Composition of Corrosion Rate Zr-15Ti Alloy

The decreased of corrosion rates by Cu content additions, caused by some content of Zr and Ti were reacted with the environtment and formated passive layer that can protect the surface samples from corrosive environtment. Zr and Ti are more reactive to be oxidized cause the electronegatives value are higher than Cu, so they could make oxide compound as passive layer ZrO_2 and TiO_2[22-24].

4. CONCLUSION

The corrosion behavior of Zr-12Mo alloy with Cu content additions were investigated. And the relations about data by data were disscused. Cu content additions increased the hardness of Zr-15Ti alloy. Zr-15Ti alloy has 528 HV, Zr-15Ti-1Cu 603 HV and Zr-15Ti-3Cu 619 HV. The samples have α-Zr phase with highest tetha position, α-Ti phase and intermetallic Zr_2Cu and Ti_2Cu as second phase. But the result also showed that there was another second phase, β-Zr were identificated in Zr-15Ti-3Cu alloy. Cu content additions decreased the corrosion rate of Zr-15Ti alloy so the corrosion resistance was increased. Zr-15Ti alloy has 2.140 mpy on excellent cathegory, Zr-15Ti-1Cu has 1.571 mpy on excellent cathegory and Zr-15Ti-3Cu has 1.676 mpy on excellent cathegory in pure Ringer's Lactated Solution. In a different solution that have higher corrosivity level because addition of ulcer potion on Ringer's Lactated Solution, addition of Cu content still descreased the corrosion rate of Zr-15Ti alloy.

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