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Annealing Effect on Improving the Mechanical Properties of Zirconium Based Biomaterials with the Addition of Yttrium Elements for Bone Plate Application

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Abstract: To improve the mechanical properties of biomaterials with zirconium-based alloys, especially on ductility, an annealing process was carried out. The process was carried out at a temperature of 800 oC and holding time for 3 hours in a vacuum chamber which was flowed by high purity argon gas. The composition of the alloy used in this study was Zr6Mo4TixY (x= 0, 1 and 3 %wt). Microstructure observations were carried out using microscope optic and Scanning Electron Microscopy (SEM) and mechanical properties observation using tensile testing. In this study, micro-sized specimens were used and followed the ASTM E8-04 standard with a surface roughness of 1µm. The results showed an increase in the tensile strength value after annealing process and decrease the modulus elasticity. In addition, the grain boundaries of the alloy are getting smaller, this shows the effect of annealing on changes in the properties of the material.

Keywords: Biomaterials, Zirconium Based, Mechanical Properties, Annealing, Micro Specimens.

Abstrak: *Untuk meningkatkan sifat mekanik biomaterial berbasis paduan zirkonium, khususnya pada aspek keuletan, telah dilakukan proses anil (annealing). Proses ini dilakukan pada suhu 800 °C dengan waktu tahan selama 3 jam di dalam ruang vakum yang dialiri gas argon murni. Komposisi paduan yang digunakan dalam penelitian ini adalah Zr6Mo4TixY dengan variasi x = 0, 1, dan 3 % berat. Pengamatan mikrostruktur dilakukan menggunakan mikroskop optik dan Scanning Electron Microscopy (SEM), sedangkan pengujian sifat mekanik dilakukan melalui uji tarik. Dalam penelitian ini digunakan spesimen berukuran mikro sesuai dengan standar ASTM E8-04 dengan kekasaran permukaan 1 µm. Hasil penelitian menunjukkan adanya peningkatan nilai kekuatan tarik setelah proses anil, serta penurunan nilai modulus elastisitas. Selain itu, batas butir dari paduan menjadi lebih halus, yang menunjukkan adanya pengaruh proses anil terhadap perubahan sifat material.*

Kata kunci: *Biomaterial, Paduan Zirkonium, Sifat Mekanik, Anil, Spesimen Mikro.*

INTRODUCTION

Biomaterials can be classified into 3 groups according to their intended use, namely: biocompatible, bioinert and biotolerant [1], [2]. In recent years, metallic substances have been chosen as biomaterials, especially for orthopedic implants, rather than ceramic or polymeric substance because of their exceptional mechanical properties under load. At present, the biomaterials circulating in the market are Fe-based (Fe-18Cr-14Ni- 2.5Mo, Fe-11Mn-17Cr-3Mo) [3], Co-based (Co-28Cr-6Mo, 40Co-20Cr-16Fe-15Ni-7Mo) [4] and Ti-based (Ti-6Al-4V, T1-13Nb-13Zr) [5].

Zr-based alloys are potential to be developed into one of biomaterials. Zr is a metal that has good mechanical characteristics, is non-toxic and has good biocompatibility properties [6]. Zr presents advanced mechanical strength, substantial fracture toughness, and great malleability to serve as a constructural material in alloys. Another advantage of zirconium is that not affected by magnetic fields, so it does not interfere in the process of medical treatment that requires MRI (Magnetic Resonance Imaging) [7]–[10].

Several Zr-based alloys have been previously researched and developed such as: Zr-12Nb-4Sn [11], Zr-4Mo-4Sn [10], Zr-Mo-Ti [12], Zr-Nb-Ti [13], Zr-Mo -Sn [10], Zr-Al-Cu-Ni-Y [14], Zr-Ti-Cu-Al-Y [15], Zr-Sn [16], [17], and Zr-Nb [18], [19]. However, Zr alloys with the addition of yttrium have not been explored extensively. Yttrium is evident to be adequate to boost the corrosion resistance of Zr–Ti-Cu-Al [15], Zr- Al-Ni-Cu [14] alloys. Adding yttrium to Zr alloys can also decrease porosity, high density, and high flexural force, improve compressive strength as well as are appropriate for biomedical applications especially bone plate. This has prompted researchers to produce zirconium-based biomaterial alloys with the addition of yttrium and combined with molybdenum and titanium.

In this study, the annealing effect on the improvement of the mechanical properties of Zr-Mo-Ti-Y alloy biomaterials has been examined. The effect of changes in alloy grain on increasing tensile strength properties was observed to obtain a comprehensive analysis of the effect of the annealing process. This research has significance to produce biomaterials that have mechanical properties close to human bone in order to minimize differences in properties that can cause uncomfortable effects on biomaterial users.

METHODS

Sample Preparation

Zr–6Mo–4Ti–xY alloy ingots with x=0, 1, and 3 %wt were made using an vacuum arc melting furnace with the stoichiometric calculation method. All elements in the alloy use materials with a purity of 99.99%. The smelting process was repeated 5 times with high purity argon gas flowing to obtain a homogeneous alloy and free from oxides. The smelting is carried out within 120 seconds with a current setting of 150 A and a voltage of 230 V. Furthermore, the diameter and width of the resulting ingot were 30 mm and 8 mm respectively.

Annealing Process

The annealing process aims to diffuse the atoms of the elements contained in the alloy into the matrix so that the solubility becomes homogeneous. In addition, this process aims to eliminate residual stresses and segregation of smelted products. The annealing process uses a vacuum tube furnace in an inert condition fed by UHP argon gas at a temperature of 800 ^{o}C with a holding time of 3 hours and then cooled with air media.

Microstructure and mechanical characteristics

Microstructure observations were conducted using an optical microscope and SEM observations. Prior to observation, the samples were prepared through a grinding process with a fineness of 80-2000 grade sandpaper. Afterwards, the process continued with polishing. ZrO_2 powder was used as the abrasive particles. As for the etching process, a solution of 5% H_2SO_4, 10% HF, 30% HNO_3, and 55% H_2O was prepared. For tensile testing, all test samples used micro-sized samples which were cut using wire cutting and followed the standards of ASTM E8-04 and DIN EN 2002-001:2006-11. The test was performed using a SHIMADZU AGS-X axial servo hydraulic testing machine with a capacity of 10 kN and an average compression speed of 1 mm/min.

RESULT AND DISCUSSION

The result of observing the microstructure of the alloy Zr–6Mo–4Ti–xY, with x = 0, 1, and 3 %wt of melting before annealing using an optical microscope are demonstrated in Figure 1. There is a significant effect on the alloy grains caused by the addition of the element yttrium. Figure 1a-1c shows that the grain size of the alloy is getting smaller from 30-40 µm to 1-10 µm (3 %wt). Grain boundaries are also seen more clearly with the addition of the element yttrium. From the observation of the microstructure, it can also be explained that the alloy phase is seen in the form of phase α and β.

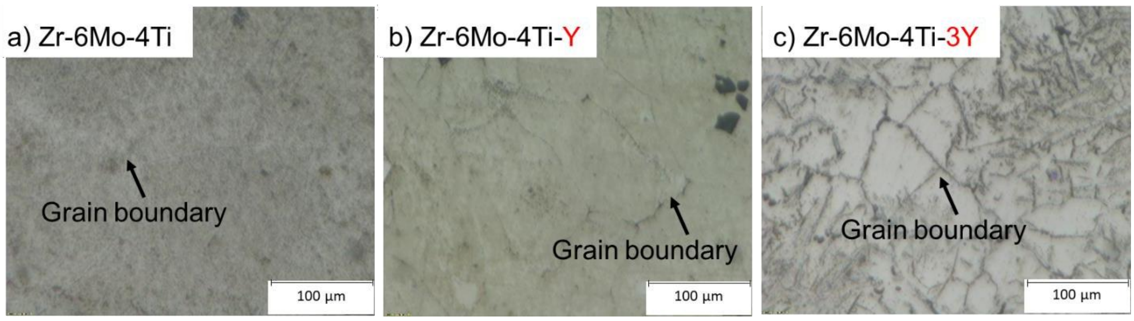

Figure 1. Microstructure of Zr-6Mo-4Ti-xY alloy with x = 0, 1, and 3 %wt before annealing process

Figure 2 projects the result of observing the microstructure of the alloy Zr–6Mo–4Ti–xY, with x=0, 1, and 3 %wt after the annealing process was carried out using an optical microscope. Based on Figure 2a-2c, the grain size of the alloy is between 10-32 µm. The annealing process emphasizes the grain boundaries of the alloy and reduces the grain size. From the observation of the microstructure, the alloy phase is seen in the form of a single phase of β.

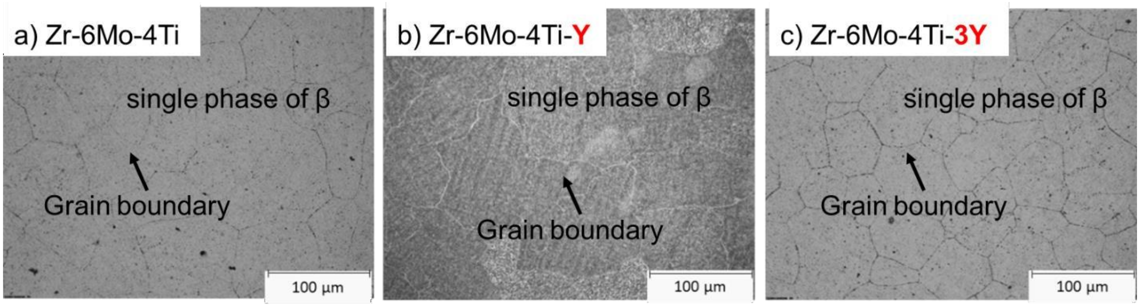

Figure 2. Microstructure of Zr-6Mo-4Ti-Xy alloy with x = 0, 1, and 3 %wt after annealing process

The morphological and topographical observations in detail were made using the JEOL JSM-6510LA Scanning Electron Microscope (SEM) as shown in Figure 3. Observations were conducted on the Zr-6Mo- 4Ti-xY alloy with x = 0, 1, and 3 %wt. after the annealing process to observe the matrix and grain boundaries of the alloy and to confirm the results of the optical microscope that has been carried out. The result proofs that there is an effect of adding element Y to the visibility of the grain boundaries and alloy matrix.

Figure 3a is the SEM result of the Zr-6Mo-4Ti alloy, that looks clean, and the grain boundaries are not clearly visible, this is different from the alloy with the addition of Y. Figures 3b and 3c shows the alloys of Zr-6Mo-4Ti-Y and Zr -6Mo-4Ti-3Y, in which the grain boundaries started to be clear and there are dendritics in the alloy. Grain and dendritic boundaries are clearly visible in the Zr-6Mo-4Ti-3Y alloy, which indicates a significant effect of adding element Y and the annealing process is able to stabilize the phase in the alloy.

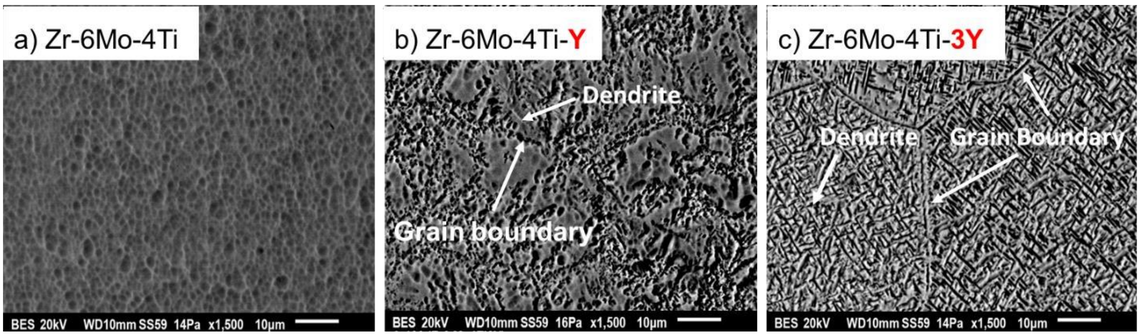

Figure 3. Scanning Electron Microscope (SEM) observations of Zr-6Mo-4Ti-xY alloy with x = 0, 1, and 3 %wt after the annealing process

In the tensile test, the test sample used is as shown in Figure 4. The length of the test sample is 27 mm with a width of 5 mm. The length of the gauge is 10 mm with the radius of 1.5 mm, and the width of the tension area is 2 mm (Figure 4.a). Cutting was performed using wire cutting in a water bath (in a cold state), which is intended to reduce deformation or changes in the structure of the alloy. The actual sample can be seen in Figure 4.b, where the length dimension for gripping follows the size of the ingot. Tensile testing was carried out 5 times for each alloy, with a pulling speed of 0.01 mm/min.

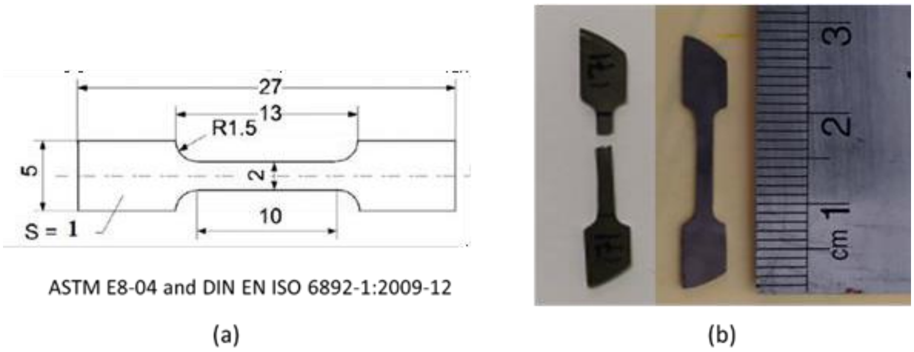

Figure 4. Specimen Size for Tensile Test; a) Standard; b) *Actual Sample*

Figure 5 is the stress-displacement curve of the tensile test results for the Zr–6Mo–4Ti-xY alloy (x = 0, 1, 2 and 3 wt%) before the annealing process. The Zr-6Mo-4Ti alloy has an ultimate strength of 647.77 N/mm^2 and a modulus elasticity of 199.67 GPa, while the Zr-6Mo-4Ti-Y alloy has an ultimate strength of 411.84 N/mm^2, and a modulus elasticity of 40.29 GPa. Meanwhile, the Zr-6Mo-4Ti-3Y alloy has an ultimate strength of 360.00 N/mm^2, and a modulus elasticity of 24.72 GPa. This means that the addition of the element yttrium results in a decrease in the tensile strength and modulus of elasticity in the Zr-Mo-Ti alloy. This is in line with the analysis of the microstructure of the alloys where the grain boundaries also decreased due to the addition of the element yttrium. The strain value increased with the addition of yttrium from 3.24% to 10.22%. This means that the addition of yttrium causes the material to have better elasticity.

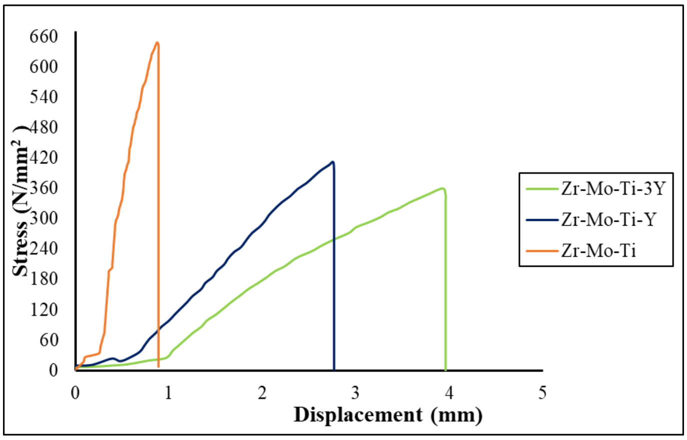

Figure 5. Stress-displacement curve of tensile test results of Zr–6Mo–4Ti-Xy alloy (x = 0, 1, 2 and 3 wt%) before annealing process

Figure 6 demonstrates the correlation between the stress and the displacement curves of the tensile test results of biomaterials Zr–6Mo–4Ti-xY (x = 0, 1, and 3 wt%) alloy after annealing. From the results, it can be inferred that there was an effect of adding yttrium to the decrease in yield and ultimate stress in the alloy. The resulting curve becomes stable after the annealing process was carried out.

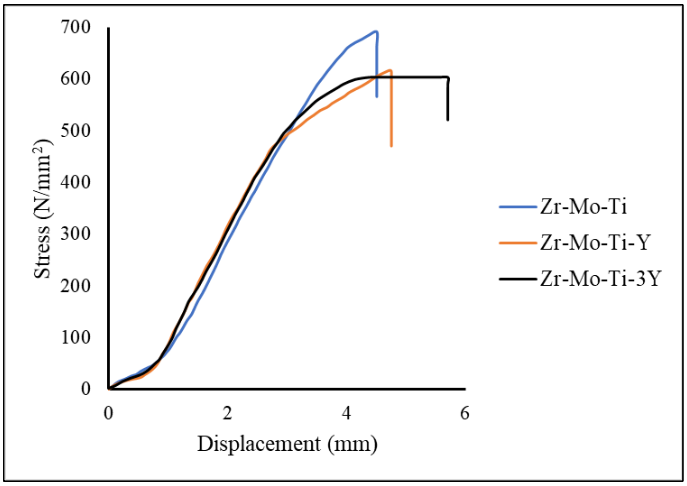

Figure 6. The stress-displacement curve of the tensile test results for the Zr–6Mo–4Ti-Xy alloy (x = 0, 1, 2 and 3 wt%) after the annealing process

The results of this study can also be analyzed based on the grain size of the fracture test sample (see Figure 7), in which the grain size affects the yield stress of the alloys. In this study, based on Figure 6, the yield strength of the tensile test using micro specimens after annealing for 3 hours was in the range of 603.23 – 690.51 MPa close to cortical bone 78-151 Mpa (tested in the longitudinal axis) and 51-66 Mpa (tested in the transverse axis) [20] and lower than the alloy of Ti-6Al-4V (720-950 Mpa) [21].

Based on Table 1, the modulus of elasticity of the tensile test results after being annealed is 40.93-44.3 GPa which indicates that this alloy has a modulus of elasticity close to human bone, which is 15-30 Gpa [12]. By producing a low modulus of elasticity, it is expected to prevent decay resulted by the incongruity of mechanical substances between the implant material and human bone especially bone plate.

Table 1. Tensile test results before and after annealing for Zr–6Mo–4Ti-xY alloy (x = 0, 1, 2 and 3 wt%)

	Annealing							
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Alloy	σ_y (Mpa)	σ_y (Mpa)	σ_u (Mpa)	σ_u (Mpa)	E (Gpa)	E (Gpa)	Ultimate Strain (%)	Ultimate Strain (%)
Zr-6Mo-4Ti	647.77	660.16	647.77	690.51	199.7	44.3	3.24	16.71
Zr-6Mo-4Ti-Y	411.84	502.24	411.84	617.48	40.29	43.52	10.22	17.55
r-6Mo-4Ti-3Y	360	583.33	360	603.23	24.72	40.93	14.56	21.11

The results of the observations on the fractures of the surface of biomaterial alloys before and after annealing in the tensile test results using scanning electron micrographs (SEM) can be seen in Figure 7. In the alloy before annealing the fracture is clearly hilly with wide grain boundaries. In the alloy after annealing the fracture also looks hilly but lower than the alloy before annealing with smoother fracture and smaller grain boundaries. It means that it is in line with the results of the yield strength and ultimate strength testing of the alloy, so it can be concluded that annealing and the addition of yttrium can increase the grain boundaries and affect the mechanical properties of the alloy.

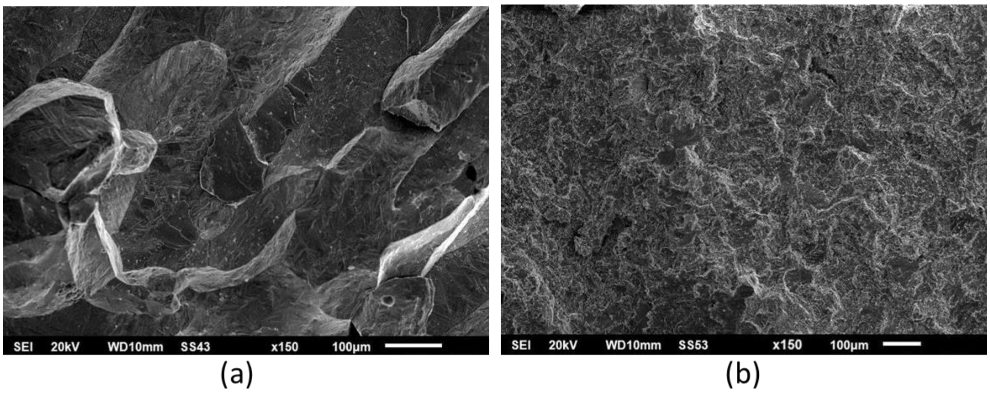

Figure 7. Cross section of tensile test results; a) before annealing; b) after annealing

CONCLUSIONS

These works investigated the effect of the annealing on the improvement of the mechanical properties of Zr-Mo-Ti-xY alloy (x = 0, 1, 2 and 3 wt%). Based on the results, the annealing process causes the grain size of the alloy to be smaller and clearly. The annealing process also improve the mechanical properties of the alloys i.e., strain, modulus elastic, and ultimate strength. Furthermore, annealing increases the strength and strain by forming more grain boundaries and dendrities.

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