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Electrochemical Behaviors of Binary Ti-Zr Alloys

M. Y. Oh†, W. G. Kim, H. C. Choe†, and Y. M. Ko

Dept. of Dental Materials & Research Center of Nano-Interface Activation for Biomaterials, College of Dentistry, Chosun University, Gwangju, 501-759 Korea

Pure Ti as well as Ti-6Al-4V alloy exhibit excellent properties for dental implant applications. However, for a better biocompatibility it seems important to avoid in the composition the presence of V due to the toxic effects of V ion release. Thus Al and V free and composed of non-toxic element such as Nb, Zr alloys as biomaterials have been developed. Especially, Zr contains to same family in periodic table as Ti. The addition of Zr to Ti alloy has an excellent mechanical properties, good corrosion resistance, and biocompatibility. In this study, the electrochemical characteristics of Ti-Zr alloys for biomaterials have been investigated using by electrochemical methods. Methods: Ti-Zr(10, 20, 30 and 40 wt%) alloys were prepared by arc melting and homogenized for 24 hr at 1000 °C in argon atmosphere. Phase constitutions and microstructure of the specimens were characterized by XRD, OM and SEM. The corrosion properties of the specimens were examined through potentiodynamic test (potential range of -1500 ~ 2000 mV), potentiostatic test (const. potential of 300 mV) in artificial saliva solution by potentiostat (EG&G Co, PARSTAT 2273. USA).

***Keywords** : zirconium, titanium, electrochemical characteristic, corrosion*

1. Introduction

Titanium alloys are expected to be much more widely used for implant materials in the medical and dental fields because of their superior biocompatibility, corrosion resistance and specific strength compared with other metallic implant materials. The use of titanium and its alloys implant applications has mainly been limited to the alloy Ti-6Al-4V and to cp-titanium.[1),2)] For medical application titanium and Ti-6Al-4V have been used since 1960s, with Ti-6Al-4V gradually replacing cp-titanium due to the increased mechanical strength of plates, nails, screws and endoprostheses.[3)]

Recently, however, much concern has developed over the issue of biocompatibility with respect to the dissolution of aluminum and vanadium ions and the possibility of any toxic effects.[4)-6)] Consequently, other titanium alloys are currently being considered as alternatives to the Ti-6Al-4V alloy. Therefore, Ti-alloy, Al and V free and composed of non-toxic element such as Nb and Zr as biomaterials has been developed. Especially, Zr element belongs to same family in periodic table as Ti element. Addition of Zr to Ti alloy has an excellent mechanical properties, good corrosion resistance, and biocompatibility.[7)]

In this study, the electrochemical characteristics of Ti-Zr alloys for biomaterials have been researched using by electrochemical methods.

2. Experimental

Ti (G&S TITANIUM, Grade. 4, USA)alloys containing Zr (Kurt J. Lesker Company, 99.95 % wt% in purity) up to 10, 20, 30 and 40 wt% were melted six times to improve chemical homogeneity using the vacuum arc melting furnace. And heat treatment was carried out at 1000 ℃ for 24h in order to homogenization in argon atmosphere. The specimens for electrochemical test were prepared by using various grit emery papers and then finally, polished with 0.3 ㎛ Al_2O_3 powder. All of polished specimen was ultrasonically cleaned and degreased in acetone.

Microstructures of the alloys were examined by optical microscopy (OM, OLYMPUS BM60M) and scanning electron microscopy (SEM, HITACHIS-3000). The specimens for the OM and SEM analysis were etched in Keller's solution consisting of 2 ㎖ HF, 3 ㎖ HCl, 5 ㎖ HNO_3 and 190 ㎖ H_2O. In order to identify the phase constitutions of the Ti-xZr alloys, X-ray diffraction (XRD) analysis with a Cu-K α radiation were performed.

Electrochemical characteristics were performed in a standard three-electrode cell having specimen as a working electrode and a high dense carbon as counter electrode. The potential of working electrode was measured against

† Corresponding author: hcchoe@chosun.ac.kr

a saturated calomel electrode (SCE) and all given potentials were referred to this electrode.

The corrosion properties of the specimens were examined through potentiodynamic test (potential range of -1500 ~ 2000 ㎷), potentiostatic test (const. potential of 300 ㎷) at scan rate of 1.67 ㎷/sec in artificial saliva solution at 36.5±1 ℃by potentiostat (EG&G Co, PARSTAT 2273. USA).

3. Results and discussion

From the results of X-ray diffraction patterns, the α-phase peak was observed only in as-cast and heat treated Ti-xZr alloy. It suggested that $\beta \rightarrow \alpha$ transformation progressed gradually with increasing Zr content due to Zr displacement.[8)] Each diffraction peak shifted to a lower angle with increasing Zr content. The absence of additional peaks is consistent with single-phase. Fig. 1 and 2 show microstructures of Ti-xZr alloys with different Zr contents. In the Fig. 1 and 2, β- phase appeared dark part and α -phase was bright part.[9)] The microstructures of Ti-10Zr and Ti-20Zr alloy showed lamellar structure and needle-like structure, these phase changed gradually to almost needle-like structure in Ti-40Zr alloy. Consequently, microstructures of Ti-xZr alloys were changed from lamellar structure to needle-like structure as Zr content increased.

Fig. 3 shows the results of potentiodynamic test (potential range of -1500 ~ 2000 ㎷) in artificial saliva, which was conducted in order to investigate the effect of Zr content on the polarization curve. From the results of polarization behavior, Zr addition effect on polarization behavior did not show in the as-cast Ti-xZr alloys due to heterogeneous of cast structure, but it found that the corrosion resistance was increased with increasing Zr content, in the homogenized Ti-xZr alloys. It is thought that increase of corrosion resistance with Zr content is attributed to the a few nm thick passive film such as TiO_2 and ZrO_2 formed[10),11)] rapidly on the specimen surface. A few nm thick passive films could restrict the movement of metal ions from the metal surface to the solution, thus minimiz-

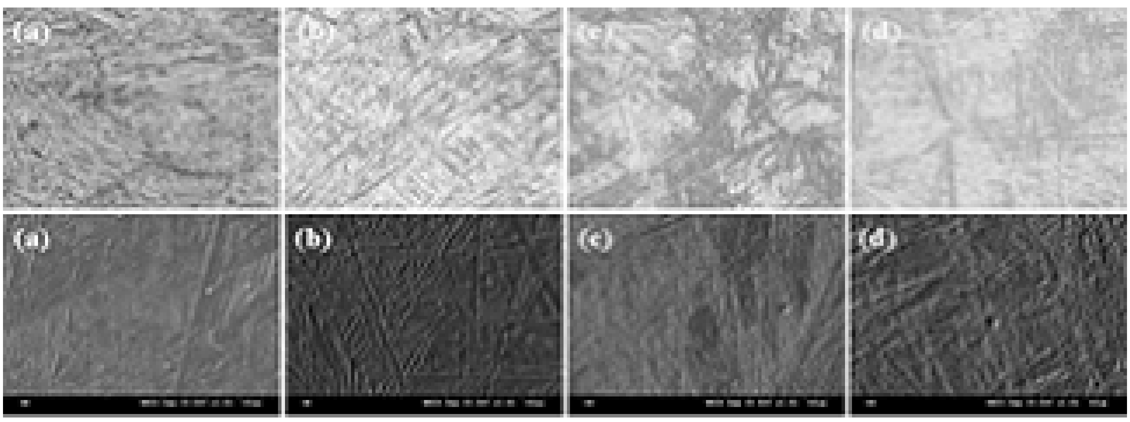

Fig. 1. OM, SEM micrographs of as-cast Ti- xZr alloys. (a) Ti-10Zr (b) Ti-20Zr (c) Ti-30Zr (d) Ti-40Zr

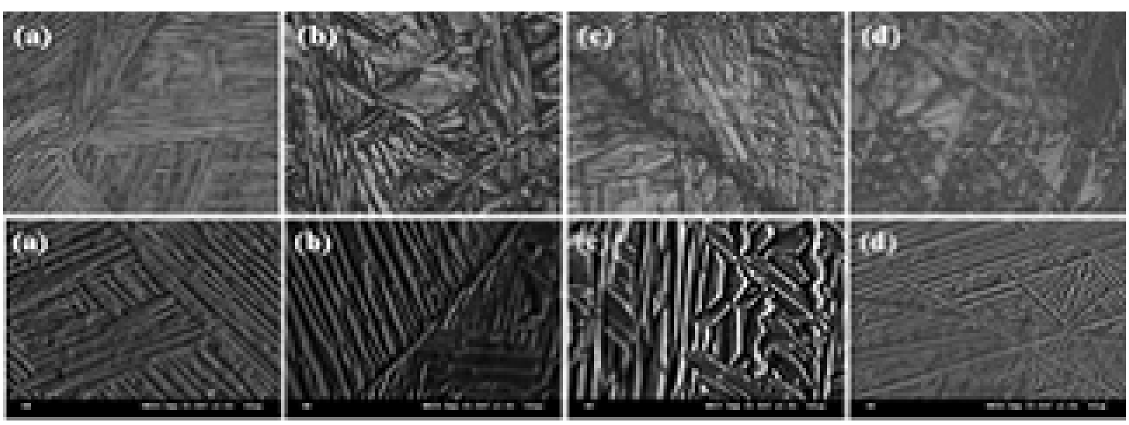

Fig. 2. OM, SEM micrographs of homogenized Ti-xZr alloys. (a) Ti-10Zr (b) Ti-20Zr (c) Ti-30Zr (d) Ti-40Zr

Table 1. Corrosion current density (I_{corr}) and corrosion potential (E_{corr}) of Ti-xZr alloys after electrochemical test in artificial saliva solution at 36.5±1 ℃

As·cast	Ti·10Zr	Ti·20Zr	Ti·30Zr	Ti·40Zr
E_{corr}(mV)	-770	-690	-970	-400
I_{corr}(A/cm^2)	3.648×10^{-7}	2,681×10^{-7}	8,436×10^{-7}	4,734×10^{-7}
Homogenized	Ti·10Zr	Ti·20Zr	Ti·30Zr	Ti·40Zr
E_{corr}(mV)	-810	-850	-860	-760
I_{corr}(A/cm^2)	2,518×10^{-7}	1,508×10^{-7}	1,507×10^{-7}	5,436×10^{-6}

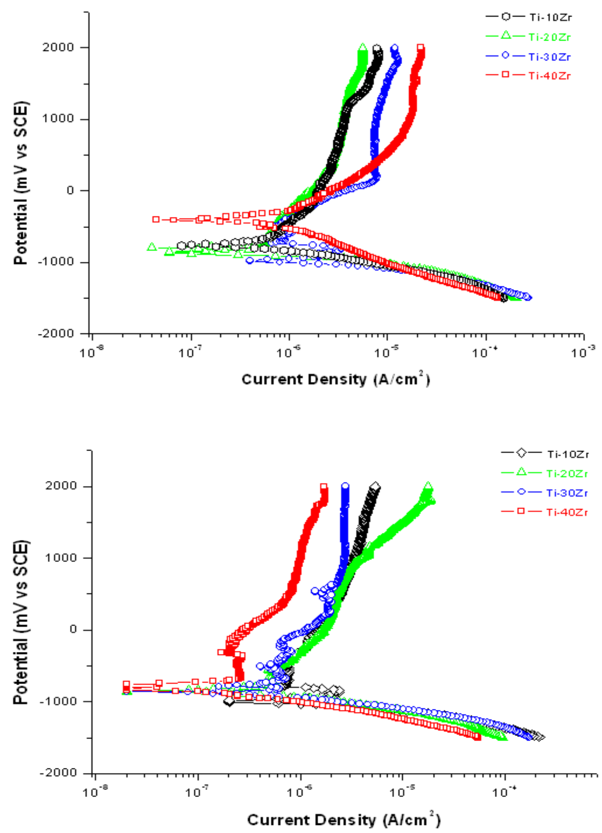

Fig. 3. The polarization curves of Ti-xZr alloys after potentiodynamic test in artificial saliva solution at 36.5±1 ℃. (a) as-cast (b) homogenized

ing corrosion. Corrosion current density (I_{corr}) and corrosion potential (E_{corr}) of Ti-xZr alloys after electrochemical test in artificial saliva solution at 36.5±1 ℃, was given in Table 2. It was confirmed that I_{corr} decreased and E_{corr} increased as Zr content increased in Ti-xZr alloys from Table 1.

Fig. 4 shows the results of potentiostatic test (const. potential of 300 ㎷) in artificial saliva solution at 36.5±1 ℃by potentiostat (EG&G Co, PARSTAT 2273. USA). From results of passivation stability test, current density

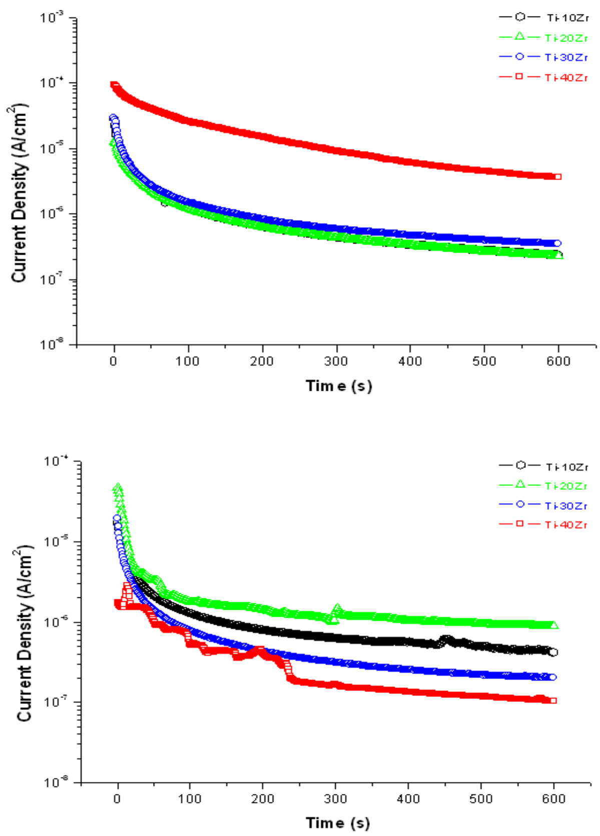

Fig. 4. Current density-time curves (const. 300 ㎷) of Ti-xZr alloys after potentiostatic test in artificial saliva solution at 36.5±1 ℃. (a) as-cast (b) homogenized

of homogenized specimen (5.436×10^{-8} A/cm^2) showed lower than that of as-cast specimen (4.734×10^{-7} A/cm^2) with 1-order difference. Current density of Ti-40Zr decreased with increasing corrosion time. Generally, when current density (I_{corr}) in passive region get lower, amount of ion release through the passive film is small due to formation of thick passive film such as TiO_2 and ZrO_2.[10] Therefore, pitting corrosion resistance is better.

4. Conclusions

In as-casted and homogenized Ti-xZr alloys, α-phase was identified by XRD. Microstructures were changed from lamellar structure to needle-like structure as Zr content increased. From the results of anodic polarization behavior in the Ti-xZr alloys, it was found that the corrosion resistance was increased with increasing Zr content. From results of passivation stability test, current density of homogenized specimen showed lower than that of as-casted specimen with 1-order difference. Current density of Ti-40Zr decreased with increasing corrosion time. Consequently, in the Ti-xZr alloys, surface stability for biomaterials increased as Zr content increased.

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