Effect of zirconium content on the microstructure, physical properties and corrosion behavior of Ti alloys

Mi-Kyung Han a, Moon-Jin Hwang a, Min-Soo Yang b, Hong-So Yang b, Ho-Jun Song a, Yeong-Joon Park a, b

a Department of Dental Materials and MRC for Biomineralization Disorders, School of Dentistry, Chonnam National University, Gwangju 500-757, Republic of Korea
b Department of Prosthodontics, School of Dentistry, Chonnam National University, Gwangju 500-757, Republic of Korea

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ABSTRACT

A series of Ti–xZr alloys with Zr contents ranging from 5 to 20 wt% was prepared and the effects of Zr addition on the microstructure, physical properties, and corrosion behavior of Ti alloys were investigated. The phase and microstructures were characterized using X-ray diffractometry (XRD), optical microscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The Ti–xZr alloys exhibited α-Ti structure at Zr content of 20 wt% or below. Commercially pure titanium (cp-Ti) was used as a control. We also investigated the effects of alloying element Zr on the mechanical property, oxidation protection ability, and corrosion behavior of Ti–xZr binary alloys. The physical properties and corrosion behavior of Ti–xZr alloys were sensitive to the Zr content. The addition of Zr did contribute to the hardening of cp-Ti due to solid-solution strengthening of α-Ti. Ti–xZr alloys containing up to 10 wt% Zr resulted in good oxidation resistance, while Ti–xZr alloys with above 10 wt% Zr demonstrated higher oxidation weight gain than cp-Ti. Electrochemical experiments showed that the Ti–xZr alloys exhibited better corrosion resistance compared to that of cp-Ti.

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1. Introduction

The favorable mechanical properties including high specific strength, excellent corrosion resistance both in air and in biological fluids, and high biocompatibility have made titanium (Ti) and titanium alloys suitable for applications in dental and medical fields [1,2]. New titanium alloys with improved mechanical properties have been developed by alloying Ti with a variety of elements such as Al, V, Cu, Zn, Cr, Mo, Nb, Ge, Ag, Au, Zr, and Sn [3–11]. The Ti–6Al–4V alloy and TiNi (Nitinol) are the most widely used Ti alloys [12,13]. However, the release of metal ions, such as Ni, Al, and V from the alloy sometimes causes allergic, cytotoxic effect and neurological disorders [14]. Therefore, the search continues for developing new Ti-based alloys with desired properties, while lacking any toxic effects, to be used successfully in dentistry.

Zirconium has been recognized as a nontoxic and nonallergic element and belongs to the IVB group in the periodic table. This is the same as titanium and is known to have chemical structure and properties like titanium. The binary phase diagram presents a continuous solid solution between titanium and zirconium [15]. The fusion temperature becomes lowered by alloying Ti with Zr, thus facilitating the casting process [16]. Recently, binary Ti–Zr alloys have been developed for dental applications due to their good corrosion resistance and biocompatibility [16–22]. It was reported that alloying Ti with Zr significantly improved osteoblast adhesion [23–25]. Therefore, it was reasonable to employ zirconium as a strengthening alloying element to improve the clinical performance of cp-Ti.

In the present study, with the goal of developing a dental titanium alloy with better corrosion resistance and physical properties compared to those of cp-Ti, the effect of alloying element Zr were investigated on the microstructure, physical properties and corrosion behavior of Ti–Zr binary alloys, with the addition of 5, 10, 15 and 20 wt% Zr. Therefore, ‘Ti–xZr’ will be replaced for ‘Ti–xwt% Zr’ in this work.

2. Experimental procedures

2.1. Material preparation

A commercially available cp-Ti (ASTM grade 2, Daito Steel Co. Ltd., Japan) was used as a control titanium material. Experimental
Ti–Zr alloys (5, 10, 15, and 20 wt% Zr) were prepared by arc-melting the stoichiometric quantities of the elements on a water-cooled copper hearth using a tungsten electrode under a high-purity argon atmosphere. The starting materials (Ti sponge, Alfa Aesar, USA, 99.9%; Zr ingot, LS-Nikko, Korea, 99.95%) were used without purification. During the arc-melting procedure, a titanium getter was heated prior to melting the reactant mixture to further purify the argon atmosphere. The samples were remelted seven times to promote sample homogeneity. At each step, the arc melting time was approximately 30 s. The average weight, diameter, and height of ingots were 10.5 g, 20 mm, and 9.5 mm, respectively. Subsequently, the samples were heat treated using a tube furnace under argon atmosphere (99.9999%) for 4 h at 150 °C below the respective solidus temperatures. This was followed by cooling inside the furnace to 600 °C with a cooling rate of 10 °C/min, and then air-cooling to room temperature. These heat treatment conditions were chosen in accordance with the binary Ti–Zr phase diagrams [15]. Samples embedded in epoxy resin were cut and polished into disks of about 1.2 mm thickness with an angle ranged from 20 ° to 80 °. The lattice parameters were obtained by least squares refinement of data in the 2θ range of 20–80 ° with the aid of a Rietveld refinement program. The microstructure of the samples was examined using a metallurgical microscope (Epiphot FX-35WA, Nikon, Japan), scanning electron microscope (SEM; S-3000N, Hitachi, Japan), high-resolution transmission electron microscope (HRTEM; Technai-F20, Philips, Netherlands), selected area energy diffraction (SAED), and energy dispersive X-ray analysis (EDX; EMAX, Horiba, Japan). The phase transformation of Ti–Zr alloys was investigated by heating approximately 200 mg of the sample to 1000 °C at a heating rate of 20 °C/min using differential scanning calorimeter (DSC; DSC 404C, Netzsch, Germany). The oxidation behaviors of Ti alloys with different Zr content were tested with Thermogravimetric Analysis (TGA; SDTA 851e, Mettler-Toledo, USA), which measured the change in mass due to the oxidation. The samples 4.5 × 4.2 × 14.0 mm³ in size were heated to 795 °C or 1000 °C at a heating rate of 10 °C/min with air flowing rate of 50 mL/min.

The microhardness of the polished alloys was measured using a Vicker’s microhardness tester (Postfach 4350, Zwick, Germany) with a load of 500 g for 30 s. To observe the corrosion behaviors of the materials, potentiodynamic anodic polarization tests were conducted with a scan rate of 0.005 V/s from −1.5 V to +1.5 V (vs. SCE) using a potentiostat (WAT100, WonA Tech Co., Korea) in a 0.9% NaCl solution at 37 ± 1 °C. The surface of the sample with 10 mm diameter was mechanically polished with up to 2000 grit SiC paper. At least three samples were tested to ensure the repetition of the experimental results. A three-electrode cell was used. The counter electrode was a high-density graphite electrode, and the reference electrode was a saturated calomel electrode (SCE) [26]. The electrolyte was bubbled with Ar gas at 150 mL/min for over 20 min to eliminate the residual oxygen. The used electrolyte was replaced with fresh electrolyte before each measurement. The exposed surface area in the electrolyte was about 0.283 cm². The potentiodynamic polarization curves were plotted using an automatic data acquisition system. Both corrosion current density and potential were estimated with Tafel plots by using both anodic and cathodic branches.

The galvanic voltage and the galvanic current density of the various Ti–xZr/cp-Ti galvanic pairs were measured over a 20 min period by using Potentiostat/Galvanostat (ZIVE SP2, WonA Tech Co., Korea) at ambient conditions. The experimental setup for the electrochemical measurements consisted of a three-electrode cell with the sample as a working electrode with exposed area of 0.785 cm², a saturated calomel electrode (SCE) as a reference electrode, and a cp-Ti as the counter electrode.

3. Results and discussion

3.1. Phase and microstructure

A series of binary Ti–xZr alloys has been prepared by arc melting. The X-ray diffraction patterns as a function of x for the Ti–xZr (x=5, 10, 15 and 20 wt%) samples are shown in Fig. 1, which were compared with that of cp-Ti. The vertical dotted lines in the figure are guides to the eye, connecting the peak positions. The patterns of Ti–xZr alloys can be indexed in the hexagonal α-Ti type structure, the space group of P63/mmc, with no indication for the existence of a secondary phase. This result was consistent with the previous analysis of phases in the Ti–Zr system [16].

Rietveld refinements were done in this work to investigate the effect of Zr on the lattice parameters. The lattice parameter variations of Ti–xZr alloys as a function of Zr content are presented in Fig. 2. Due to the bigger atomic radius of Zr (≈1.62 Å) compared to Ti (≈1.47 Å), the addition of Zr atoms caused the lattice parameters to increase, which in turn caused the XRD peaks to shift toward low angle side. The lattice parameters a and c increased linearly with increasing Zr content in Ti–xZr alloys, whereas c/a ratios remained nearly constant as the content of Zr was increased. This indicated that alloying between Ti and Zr has occurred as a complete solid solution. Unit cell constants of cp-Ti were a=2.95(1) Å and c=4.68(1) Å (c/a ratio=1.587), which corresponded well with those in the literature (JCPDS card no. 44-1294), whereas the unit cell parameters of Ti–20Zr were a=3.02(1) Å and c=4.79(1) Å (c/a ratio=1.587).

It is widely known that the mechanical properties of Ti alloys depend essentially on the microstructure. A good understanding of the microstructure is therefore a prerequisite for controlling the properties. To investigate the influence of the addition of Zr on the microstructures of Ti, the samples were investigated using a
metallurgical microscope and a scanning electron microscope (SEM). Fig. 3 shows the microstructures of Ti–xZr alloys with different Zr contents (5, 10, 15, and 20 wt%). All the microstructures belonged to Widmanstätten lamella structures, which were related to the inherent anisotropy of the hexagonal crystal structure of α phase. With the increase of Zr content in Ti–xZr alloy, Widmanstätten lamella structures became coarser. Pits or holes were observed at the grain boundaries of Ti–15Zr and Ti–20Zr alloys (Fig. 3c and d, right). A large number of holes were observed especially at the Ti–20Zr alloy sample. Those defects were inferred to be formed during the etching process with Keller’s reagent for metallurgical structure observation, and would reduce the corrosion resistance of Ti–xZr alloys. A detailed analysis of the phases was conducted using TEM. Typical representative TEM images and SAED patterns of Ti–10Zr and Ti–20Zr alloys are shown in Figs. 4 and 5. Very fine and irregularly shaped grains were observed in TEM microstructures of Ti–10Zr and Ti–20Zr alloys (Figs. 4a and 5a). HR-TEM showed imperfect atomic arrays at the interface between the primary phase and the bar-shaped phase (Figs. 4b and 5b). Compared to Ti–10Zr, the increase of imperfect atomic arrays was observed at Ti–20Zr as shown in Figs. 4b and 5b. The SAED patterns from the region marked with an ‘A’ in the TEM image consisted of characteristic single crystalline α-Ti phase (Fig. 4c), showing a perfect atomic arrangement, while the SAED pattern acquired from the ‘B’ region consisted of main peaks of α-Ti phase with satellite peaks indicated by the arrow (Fig. 4d). The SAED patterns of Ti–20Zr obtained at ‘A’, ‘B’, and ‘C’ regions showed characteristic single crystalline α-Ti phase (Fig. 5c–e), which were similar to those of Ti–10Zr (Fig. 4c and d). Weaker satellite peaks indicated the formation of stacking fault in the α-Ti phases of Ti–10Zr and Ti–20Zr alloys (Figs. 4d and 5e). This sub-microstructure was due to the formation of a solid solution between Zr and Ti, which was most likely related to the dominancy of hardening effect of Ti–xZr alloys.

Differential scanning calorimetry (DSC) analysis was performed to detect any abnormal thermal effects from room temperature to 1000 °C. As shown in Fig. 6, very smooth temperature-dependent traces were found at about 150 °C for all Ti–xZr alloys with the content up to 20 wt%. This peak resulted from the stabilization of thermally unstable structure such as grain boundary relaxation or grain boundary reordering. The second exothermic peak at around 900 °C resulted from the martensitic transformation of β-Ti to α-Ti. Other than those two peaks, no extraneous exothermic or endothermic peaks were detected. The martensitic transformation temperature decreased with increasing Zr content as shown in Fig. 6.

The oxidation behaviors of Ti–xZr alloys were conducted using thermogravimetric analysis (TGA). Fig. 7 shows the result of the TGA experiment when the cp-Ti and Ti–xZr alloys were heated up to 795 °C and 1000 °C with a heating rate of 10 °C/min in air. Each of the samples was oxidized and the weight gain was compared with that of non-oxidized samples. All the samples showed a single parabolic increment of mass during the oxidation. The change in mass did not appear between room temperature to 500 °C in all Ti–xZr alloys, which was indicative of oxidation resistance. At temperature higher than 500 °C, Ti–xZr alloys were exponentially increased in mass as shown in Fig. 7(a). At temperatures below 500 °C, the oxidation was relatively slow; beyond 500 °C, the weight was changed by an exponential function thus suggesting that the oxidation mechanism is different above and below 500 °C. The final mass change of Ti–5Zr (0.666%) was significantly lower than that (0.991%) for the oxidation of cp-Ti (p < 0.05), indicating that Ti–5Zr could restrain the oxidizing of the alloy and had higher oxidation protection ability. Ti–10Zr had slightly lower final mass change (+0.889%) compared to cp-Ti, but there was no statistically significant difference. The weight change in Ti–xZr alloys was increased with increasing Zr contents.

### 3.2. Mechanical property

The Vicker’s hardness values of Ti–xZr alloys are shown in Table 1. All the Ti–Zr alloys had significantly higher (p < 0.05) hardness than the cp-Ti tested. The hardness value tended to rise with increasing Zr content up to 15 wt%, and then slightly decreased with further increase of the Zr content. As for the Ti–15Zr alloy, the microhardness was about 412 VHN. This result indicated that the Zr element could effectively increase the microhardness values of the cp-Ti, which was mainly caused by the solid-solution strengthening of the α-phase.

### 3.3. Corrosion behavior

The purpose of this study was to evaluate the corrosion resistance of experimental Ti–Zr alloys. Potentiodynamic polarization and galvanic couple technique were used in order to investigate the effect of Zr content on corrosion resistance. The potentiodynamic polarization curves of cp-Ti and Ti–xZr alloys were recorded at a sweep rate of 0.005 V/s, between −1.5 and 1.5 V of potential range in 0.9% NaCl solution, and the results are shown in Fig. 8. Except for the Ti–5Zr alloy, the corrosion potential of Ti–xZr alloys showed a shifting to positive direction as compared to that of cp-Ti. This shift suggested the positive influence of Zr on the corrosion resistance of cp-Ti.

Using the Tafel extrapolation method, we calculated corrosion potential (E\text{corr}) and corrosion current density (i\text{corr}) of cp-Ti and Ti–xZr alloys from both of the anodic and cathodic branches of the potentiodynamic polarization curves; and these are listed in Table 2. There was a cathodic shift of E\text{corr} in Ti–xZr alloys (x = 10, 15, and 20 wt%). In comparison with cp-Ti, Ti–xZr alloys (x = 5, 15, and 20 wt%) exhibited much reduced i\text{corr} values. The decrease in i\text{corr} and increase in E\text{corr} indicate the increased corrosion resistance of Ti–xZr alloys compared to cp-Ti.
Fig. 3. Typical micrographs of (a) Ti–5Zr, (b) Ti–10Zr, (c) Ti–15Zr, and (d) Ti–20Zr. In each micrograph, the left side images are metallurgical micrographs (400x; scale bar, 10 μm) and the right side images are SEM micrographs (scale bar, 1 μm).
Fig. 4. (a) TEM micrographs of Ti–10Zr alloy, (b) HR-TEM image, (c) and (d) SAED patterns of matrix (region A) and grain boundary (region B), respectively.

Fig. 5. (a) TEM micrographs of Ti–20Zr alloy, (b) HR-TEM image, (c), (d), and (e) SAED patterns of A, B, and C regions, respectively.
The passivation phenomenon may be better studied by the galvanic couple technique. Mean values of galvanic current versus time of the couplings of cp-Ti/Ti–xZr alloys are shown in Fig. 9. Ti–xZr alloys (x=5, 10, and 15 wt%) except Ti–20Zr alloy exhibited negative current values indicating the electron flows from cp-Ti to Ti–xZr alloys, which implies that cp-Ti is prone to corrode because it loses electrons when coupled with Ti–xZr alloys. On the other hand, a positive current was measured for Ti–20Zr alloy, which indicates that the Ti–20Zr alloy is more prone to corrode, while cp-Ti remains protected. The galvanic current of all Ti–xZr alloys reached a stable value, indicating the formation of TiO₂ film on the metal surface which grew with time and partially protected the material. A steady state current value was more rapidly attained when Zr content increased, indicating a passive film grew more rapidly on Ti–xZr alloys. The Ti–15Zr alloy showed the fastest passivation tendency among the Ti–xZr alloys, since the time taken by the Ti–15Zr alloys to attain the stable rest potential was less as compared to that taken by other Ti–xZr alloys.

### 4. Conclusions

This study investigated the influences of Zr on the microstructure, physical properties, and corrosion behavior of commercially pure titanium (cp-Ti). Based on the results of XRD and optical microscopy, all the Ti–xZr alloys showed hcp α structures up to 20 wt% Zr content in Ti alloy. As a result of solid-solution strengthening of α-Ti, the Ti–xZr showed better hardness than...
that of the cp-Ti. Ti–5Zr and Ti–10Zr alloys exhibited higher oxidation protection ability, while Ti–15Zr and Ti–20Zr had higher weight gain compared to cp-Ti. The corrosion experiments data revealed that the Ti–15Zr had the best corrosion resistance among all the samples.

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References


Fig. 9. Mean values of galvanic currents versus time of the couplings cp-Ti/Ti–xZr alloys.