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

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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.

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

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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 successively finer SiC papers up to #2000 and were then ultrasonically cleansed in distilled water. Subsequently, the polished samples were etched with Keller's solution (distilled water: 65% HNO_3:32% HCl:40% HF$=$95:2.5:1.5:0.5).

2.2. Material characterization

Phase analysis and structural characterization were performed using X-ray diffractometer. The XRD diffraction patterns were collected on the bulk sample using an X'Pert PRO Multi Purpose X-ray Diffractometer (40 kV and 40 mA) with Cu K_α (λ=1.54056 Å). The scanning speed was 2°/min and the scanning angle ranged from 20° to 80° 2θ. 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 microscopy (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–*x*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 $4.5 \times 4.2 \times 14.0\ \text{mm}^3$ 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 (Postfach4350, 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 cm^2. 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–*x*Zr/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 cm^2, 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–*x*Zr alloys has been prepared by arc melting. The X-ray diffraction patterns as a function of *x* for the Ti–*x*Zr (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–*x*Zr alloys can be indexed in the hexagonal α-Ti type structure, the space group of $P6_3/mmc$, 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–*x*Zr 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–*x*Zr 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

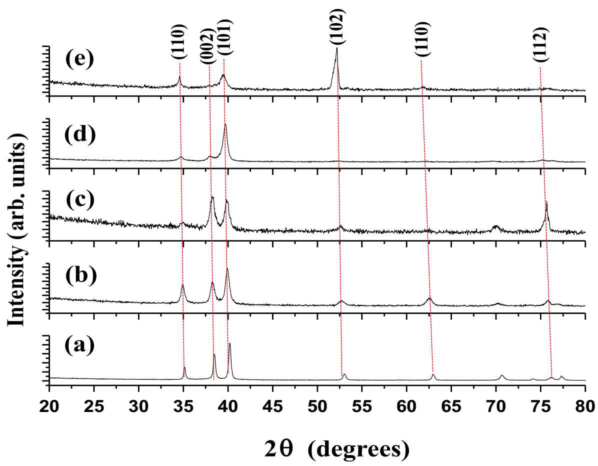

Fig. 1. XRD patterns of cast cp-Ti and the series of binary Ti–*x*Zr alloys: (a) cp-Ti, (b) Ti–5Zr, (c) Ti–10Zr, (d) Ti–15Zr, and (e) Ti–20Zr.