

Surface characteristics of HA coated Ti-Hf binary alloys after nanotube formation

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Abstract: Ti-Hf binary alloys contained 10%, 20%, 30% and 40% (mass fraction) Hf were manufactured in the vacuum furnace system. And then, specimens were homogenized for 24 h at 1 000 °C in argon atmosphere. The formation of oxide nanotubes was conducted by anodic oxidation on the Ti-Hf alloy in 1 mol/L H₃PO₄ electrolytes containing small amounts of NaF at room temperature. The hydroxyapatite (HA) coating made of tooth ash prepared by electron-beam physical vapor deposition (EB-PVD) method. The corrosion behaviors of the specimens were examined through potentiodynamic test in 0.9% NaCl solution by potentiostat. The microstructures of the alloys were examined by field emission scanning electron microscopy (FE-SEM) and x-ray diffractometer (XRD). It was observed that the lamellar structure translated to needle-like structure with Hf contents. Nanotube formed and HA coated Ti-xHf alloys had a good corrosion resistance.

Key words: Ti-Hf alloy; nanotube; hydroxyapatite; EB-PVD; corrosion resistance

1 Introduction

Titanium and its alloys are widely used as implants in orthopedics, dentistry and cardiology due to their outstanding properties, such as high strength, high level of enhanced biocompatibility.

For dental applications, elements alloying with titanium should not adversely affect the corrosion behavior of titanium in the oral environment[1–2]. Hafnium element belongs to the same group as titanium in the periodic table of elements[3]. And the Ti-Hf alloy system does not form any intermetallic compounds, which is also beneficial for good corrosion resistance[4]. As an effective surface coating technology, the electrochemical anodization process is useful because of large area coating, good mechanical adhesion, and electrical conductivity due to the nanotube being directly connected to the substrate, while limited thickness of these anodic TiO₂ nanotubes must be adjusted by controlling the anodic conditions[5].

Hydroxyapatite (HA) is a bioactive material with a calcium to phosphorous ratio that is similar to that of

mineral bone. It has been used as a bone replacement material in restorative dental implant[6]. Electron-beam physical vapor deposition (EB-PVD) method has very high deposition rate and offers good structural and morphological control of films. This process has wide application for wear and corrosion resistance[7–8]. In this work, Ti-xHf binary alloys were manufactured in the vacuum furnace system. And then, specimen was homogenized for 24 h at 1 000 °C. The formation of oxide nanotubes were conducted by anodic oxidation. The HA coatings were prepared by EB-PVD method. The corrosion behavior was examined by potentiodynamic test. Microstructure was examined by SEM and XRD.

2 Experimental

2.1 Alloy preparation

Ti-xHf binary alloys with Hf contents ranging from 10% to 40% (mass fraction) by 10% increment were prepared using Cp-Ti (G&S TITANIUM, Grade 4, USA) and hafnium (Kurt J. Lesker Company, 99.95% in purity).

Ti-xHf alloys were prepared by using the vacuum arc melting furnace. The weighed charge materials were prepared in the vacuum arc furnace (vacuum arc melting system, SVT, KOREA), the refined Ar gas was filled up to water cooling copper hearth chamber in vacuum atmosphere of 0.133 Pa, and atmosphere in chamber was controlled by method to keep vacuum by fine gage. After that, the samples were re-melted at least six times by reversing the alloy sponges in order to avoid the chemical gradient of samples, and then homogenized for 24 h at 1 000 °C in Ar atmosphere followed by furnace cooling and quenching into 0 °C water.

2.2 Nanotube formation of Ti-xHf alloy

Specimens were cut from Ti-xHf alloys, and then mechanically polished using 1 μm Al_2O_3 paste, degreased by ultrasonic cleaning in acetone, and dried in air. The counter electrode was prepared for platinum and all experiments were carried out at room temperature in glass cell, at constant applied voltage (20 V) for 2 h. Electrolyte was stirred during anodization in 1 mol/L H_3PO_4 and 0.5% (mass fraction) HF solution. After the anodization, the samples were rinsed in distilled water and subsequently in acetone, and dried in air. Crystallization treatment was performed in Ar atmosphere at 550 °C for 1 h.

2.3 Hydroxyapatite coating

The hydroxyapatite (HA) coating made of tooth ash was prepared by electron-beam physical vapor deposition (EB-PVD) method. For the electron-beam deposition, an electron-beam evaporator (Telemark, Co., USA) was employed. After the chamber was evacuated to 6.65 Pa by a mechanical rotary pump, a high vacuum of 1.33×10^{-5} Pa was attained using a cryopump. After the substrate was cleaned in situ by means of an Ar ion beam for 15 min, an electron-beam was generated at a voltage of 7 kV to heat the evaporant. At the early stage of heating, the electron-beam current was fixed to within 40 mA, in order to degas the evaporant and heat it evenly. Once stabilized, the current was increased to 150 mA and the vapor flux generated was deposited on the rotating substrate at a rate of 1.5 $\text{\AA}/\text{s}$. Since the as-deposited coatings were amorphous, a heat treatment was conducted subsequently to crystallize them. The as-deposited coatings were heat treated in Ar atmosphere 550 °C for 1 h.

2.4 Characterization of surface treatment

The phase and composition of the coatings were analyzed by means of X-ray diffraction (XRD, Philips, X'pert PRO) with a Cu K_α radiation. The surface and cross-sectional morphology were observed by field-emission scanning electron microscopy (FE-SEM,

HITACHI 4800, Japan).

2.5 Electrochemical test

Electrochemical characteristics were tested in a standard three-electrode cell with specimen as a working electrode and a high carbon as counter electrode. The potential of working electrode was measured against 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 $-1\,500$ – $2\,000$ mV) at scan rate of 1.67 mV/s in 0.9% NaCl solution at (36.5 ± 1) °C (Model PARSTAT 2273, EG&G Co., USA). After electrochemical corrosion tests, the surfaces of each specimen were investigated by using FE-SEM.

3 Results and discussion

Fig.1 shows the XRD result of Ti-xHf alloys by heat treatment in Ar atmosphere for 24 h at 1 000 °C. The peaks were identified using the JCPDS diffraction data of Ti-xHf alloys. It can be seen that reflections from α' -phase (101) was identified at $2\theta \approx 40.17^\circ$. The α' -phase reaction in Ti-xHf alloys proceeds, leading to the formation of hcp phase[3].

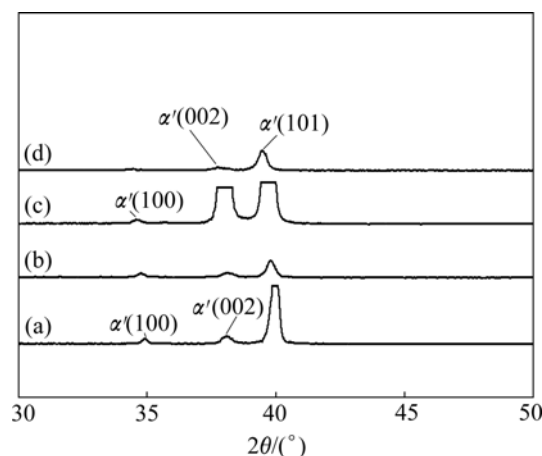


Fig.1 XRD patterns of Ti-xHf alloys after heat treatment in Ar atmosphere for 24 h at 1 000 °C: (a) Ti-10Hf; (b) Ti-20Hf; (c) Ti-30Hf; (d) Ti-40Hf

Fig.2 shows the XRD result of nanotube formed Ti-xHf alloys after crystallization treatment in Ar atmosphere for 1 h at 550 °C. There are anatase phase and α' -phase in Ti-xHf alloys. These peaks can be assigned to crystal phase of TiO_2 (JCPDS File No. 21-1272). Anatase (101) was detected from reflection peaks of crystallized Ti-xHf alloy at 25.03° . Anatase peaks were observed with higher intensity as Hf contents increased. It is suggested that Hf plays role in the formation of anatase on the nanostructure surface[6].

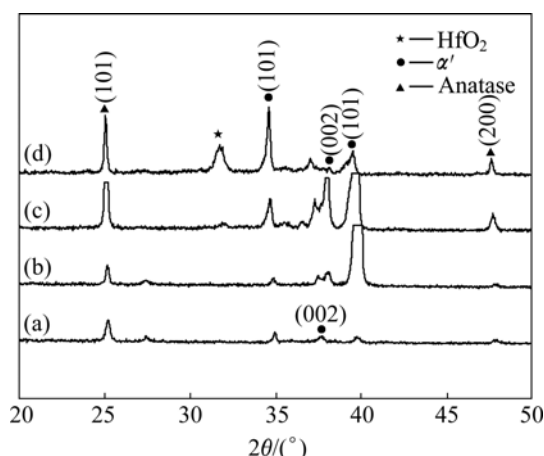


Fig.2 XRD patterns of nanotube formed Ti-xHf alloys after crystallization treatment in Ar atmosphere for 1 h at 550 °C: (a) Nanotube formed Ti-10Hf; (b) Nanotube formed Ti-20Hf; (c) Nanotube formed Ti-30Hf; (d) Nanotube formed Ti-40Hf

Fig.3 shows the microstructures of the Ti-xHf alloys after heat treatment at 1 000 °C for 24 h in Ar atmosphere followed by 0 °C water cooling. All specimens showed martensitic structure. Ti-10Hf alloy had lamellar structure, and Ti-30Hf had complex structure that consists of lamellar and needle-like structure. The Ti-40Hf had fine needle-like structure.

Fig.4 shows the microstructure of nanotube formed Ti-xHf alloys in 1.0 mol/L H_3PO_4 +0.5% NaF solution at constant applied voltage 10 V for 2 h. It was apparent that tube-like porous structures were formed with various diameter as a function of Hf content. In Fig.4(a), surface

was covered by the nanopowder. In Figs.4(b) and (c), nanotube structures were formed with a diameter of around 150 nm and 100 nm, respectively. In Fig.4(d), the surface shows mixed morphology of nanopowder and nano porous structure. It had a porous diameter of around 70 nm. Consequently, the high Hf contents led to more narrow size distribution of porous nanotube. The self-organized structure of Hf oxide layer was in the same range as that of porous Zr oxide layer[6].

Fig.5 shows the microstructure of nanotube formed and HA coated Ti-xHf alloys. HA particles were slightly covered on the top of the nanotube structures and these were well spread on the surface of nanotube formed alloys. The size of nanotube decreased with increasing the Hf contents. In the case of Ti-40Hf alloy, HA film was not coated on the tip of nanotube. But in the case of Ti-20Hf alloy, HA film was coated well on the tip of nanotube due to the formation of the nanotube on the surface.

Fig.6 shows the polarization curves of HA coated and nanotube formed Ti-xHf alloys as tested in 0.9% NaCl solution at (36.5 ± 1) °C. The corrosion potential (ϕ_{corr}) ranged from -690 mV to -770 mV for all samples. HA coated and nanotube formed Ti-40Hf alloy had the highest corrosion potential and the lowest current density that may be presented good corrosion resistance for dental application. The results of ϕ_{corr} (corrosion potential) and J_{corr} (corrosion current density) from the polarization curves were given in Table 1. From Table 1, high value of ϕ_{corr} and low value of J_{corr} show at Ti-40Hf alloy. The passive current density of Ti-40Hf alloy was

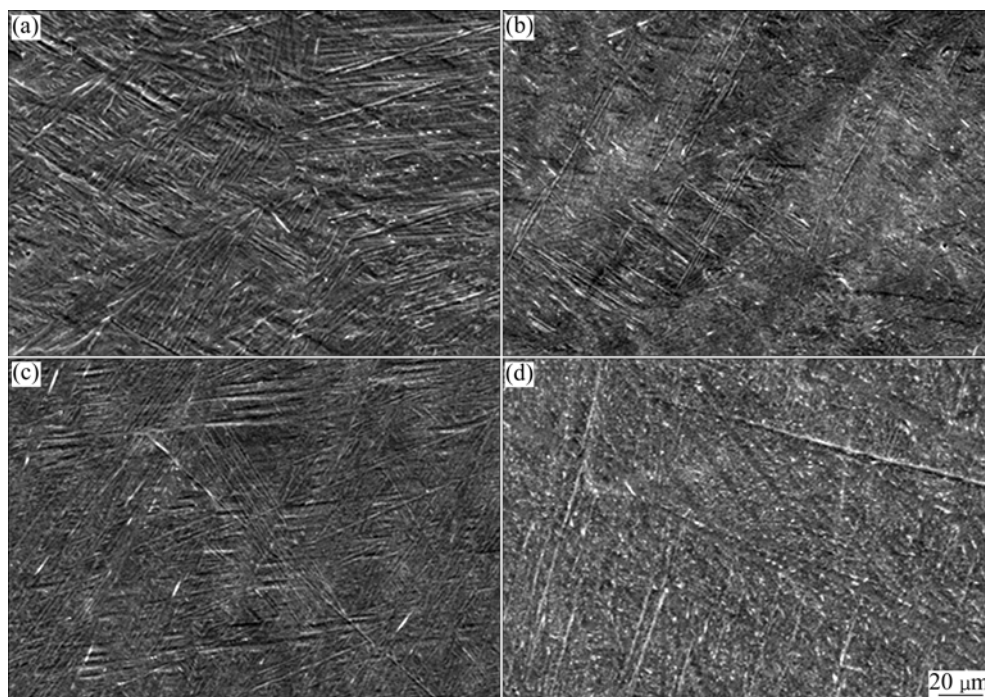


Fig.3 Microstructures of Ti-xHf alloys after heat treatment at 1 000 °C for 24 h in Ar atmosphere followed by 0 °C water cooling: (a) Ti-10Hf; (b) Ti-20Hf; (c) Ti-30Hf; (d) Ti-40Hf

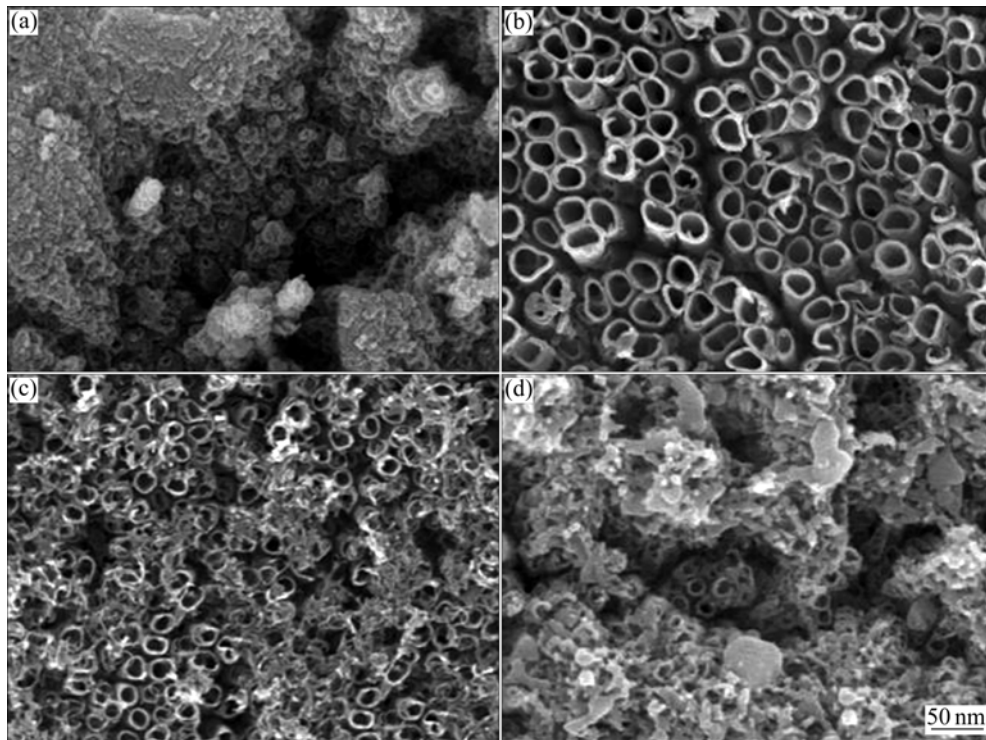


Fig.4 Microstructures of nanotube formed Ti-xHf alloys in 1.0 mol/L H_3PO_4 +0.5% NaF solution at constant applied voltage 10 V for 2 h: (a) Ti-10Hf; (b) Ti-20Hf; (c) Ti-30Hf; (d) Ti-40Hf

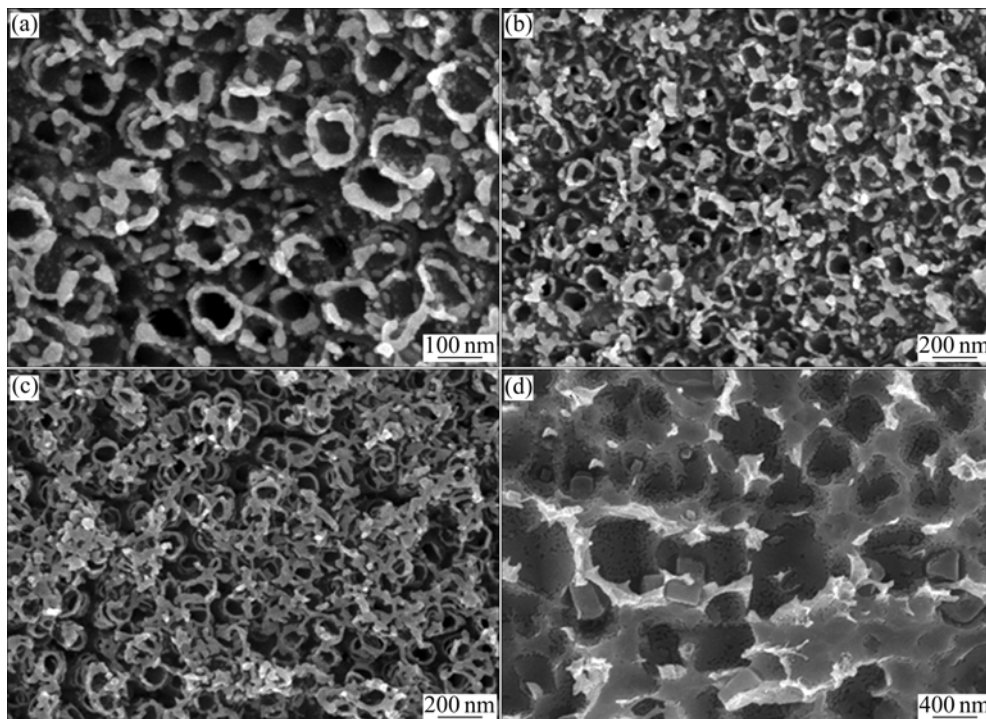


Fig.5 Microstructures of HA coated Ti-xHf alloys after nanotube formation in 1.0 mol/L H_3PO_4 +0.5% NaF solution at constant applied voltage 10 V for 2 h: (a) Ti-10Hf; (b) Ti-20Hf; (c) Ti-30Hf; (d) Ti-40Hf

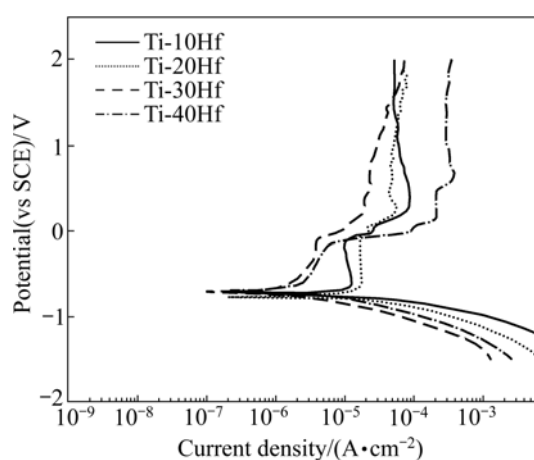
lower than that of Ti-10Hf in 0.9% NaCl solution.

And the corrosion potential of Ti-40Hf alloy showed the highest value because Hf has excellent corrosion resistance[4]. From Table 1, the nanotube

formed Ti-40Hf alloy had the highest resistance to corrosion. It was thought that the increase of corrosion resistance with Hf content was attributed to the passive film, such as TiO_2 and HfO_2 formed rapidly on the

Table 1 Corrosion potential (ϕ_{corr}), corrosion current density (J_{corr}) and current density at constant 300mV (J_{300}) of Ti-xHf with various surface modification after electrochemical test in 0.9% NaCl solution at $(36.5 \pm 1)^\circ\text{C}$

State of alloy	Item	Ti-10Hf	Ti-20Hf	Ti-30Hf	Ti-40Hf
As-prepared	$J_{\text{corr}}/(\text{A}\cdot\text{cm}^{-2})$	5.378×10^{-7}	2.062×10^{-7}	1.487×10^{-7}	3.540×10^{-7}
	$\phi_{\text{corr}}/\text{mV}$	-570	-550	-500	-550
	$J_{300}/(\text{A}\cdot\text{cm}^{-2})$	2.7×10^{-6}	3.41×10^{-6}	2.7×10^{-6}	3.26×10^{-6}
Nanotube formed	$J_{\text{corr}}/(\text{A}\cdot\text{cm}^{-2})$	4.136×10^{-6}	9.469×10^{-6}	1.321×10^{-6}	4.649×10^{-7}
	$\phi_{\text{corr}}/\text{mV}$	-1 270	-1 320	-1 000	-580
	$J_{300}/(\text{A}\cdot\text{cm}^{-2})$	2.0×10^{-5}	2.73×10^{-5}	2.02×10^{-5}	1.06×10^{-5}
Nanotube formed and HA coated	$J_{\text{corr}}/(\text{A}\cdot\text{cm}^{-2})$	1.233×10^{-5}	2.039×10^{-5}	1.901×10^{-6}	2.731×10^{-6}
	$\phi_{\text{corr}}/\text{mV}$	-740	-770	-710	-690
	$J_{300}/(\text{A}\cdot\text{cm}^{-2})$	8.88×10^{-5}	5.58×10^{-5}	2.02×10^{-5}	2.29×10^{-4}

**Fig.6** Anodic polarization curves of HA coated and nanotube formed Ti-xHf alloys after potentiodynamic test in 0.9% NaCl solution at $(36 \pm 1)^\circ\text{C}$

surface. A few nanometer thick passive films could restrict the movement of metal ions from the metal surface to the solution[9–10].

4 Conclusions

1) Microstructure of Ti-xHf alloy showed that lamellar structure translated to needle-like structure with increased Hf contents.

2) The XRD result of Ti-xHf alloys showed α' -phase and that of nanotube formed Ti-xHf alloys showed mainly anatase-phase on the surface.

3) The nanotube structure with narrow diameter was obtained in the Ti-xHf alloys as Hf content increased.

4) HA film coated Ti-xHf alloys after nanotube formation showed a good corrosion resistance in the 0.9% NaCl solution compared to nanotube formed Ti-xHf alloys.

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