

Research Article

# Calcium Phosphate Formation on Titanium and Zirconium and Its Application to Medical Devices

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**Abstract** Titanium and zirconium were immersed in Hanks' solution with and without calcium and phosphate ions, and the surfaces were characterized with X-ray photoelectron spectroscopy (XPS) to determine the mechanism of calcium phosphate formation on titanium in simulated body fluids and in a living body. In addition, they were cathodically polarized in the above solutions. As a result, neither calcium nor phosphate stably exists alone on titanium, and calcium phosphate is naturally formed on it; calcium phosphate formed on titanium is stable and protective. On the other hand, calcium is never incorporated on zirconium, while zirconium phosphate, which is easily formed on zirconium, is highly stable and protective.

**Keywords** titanium; zirconium; calcium phosphate; surface analysis; cathodic polarization

## 1 Introduction

Calcium phosphates are formed on titanium and titanium alloys by being implanted in bone, by immersion in simulated body fluids and by culturing cells on it [4,6]. The ability of titanium to form calcium phosphate on itself is one of the reasons for its better hard-tissue compatibility than those of other metals. On the other hand, zirconium does not form calcium phosphate in Hanks' solution, but it forms zirconium phosphate [3].

In this study, titanium and zirconium were immersed in Hanks' solution with and without calcium and phosphate ions, and the surfaces were characterized with XPS. Titanium and zirconium were cathodically polarized in Hanks' solution with and without calcium and phosphate ions.

## 2 Materials and methods

Commercially pure titanium (Ti: 99.5%) and pure zirconium (Zr: 99.6%) disks were mechanically polished and cleaned ultrasonically in acetone and ethanol, followed by immediate storage in an auto-dried desiccator before immersion and cathodic polarization. The compositions of electrolytes and pH are summarized in Table 1. Before immersion and

polarization, the solutions were kept in a thermostatic bath to control the temperature of 310 K.

Ti and Zr disks were immersed in electrolytes in the order as follows: (1) not immersed in any electrolyte, (2) immersed in Hanks for 1 d, (3) immersed in Ca-free for 1 d, (4) first immersed in Ca-free and then immersed in P-free for 1 d, (5) immersed in P-free for 1 d, and (6) first immersed in P-free and then immersed in Ca-free for 1 d. On the other hand, they become to be thick after 1-d immersion for the detection of the whole region of them with XPS. After the above processes, the specimens were rinsed with deionized water to remove chemical species that were physically adsorbed but not chemically incorporated in the surface oxide film. After rinsing, the specimens were immediately stored in an auto-dried desiccator before XPS analysis.

XPS was performed with an electron spectrometer (SSI-SSX100). All binding energies given in this paper are relative to the Fermi level, and all spectra were excited with the monochromatized Al K $\alpha$  line (1486.61 eV). The composition and thickness of the surface oxide film were simultaneously calculated according to the method by the previous studies [1,2].

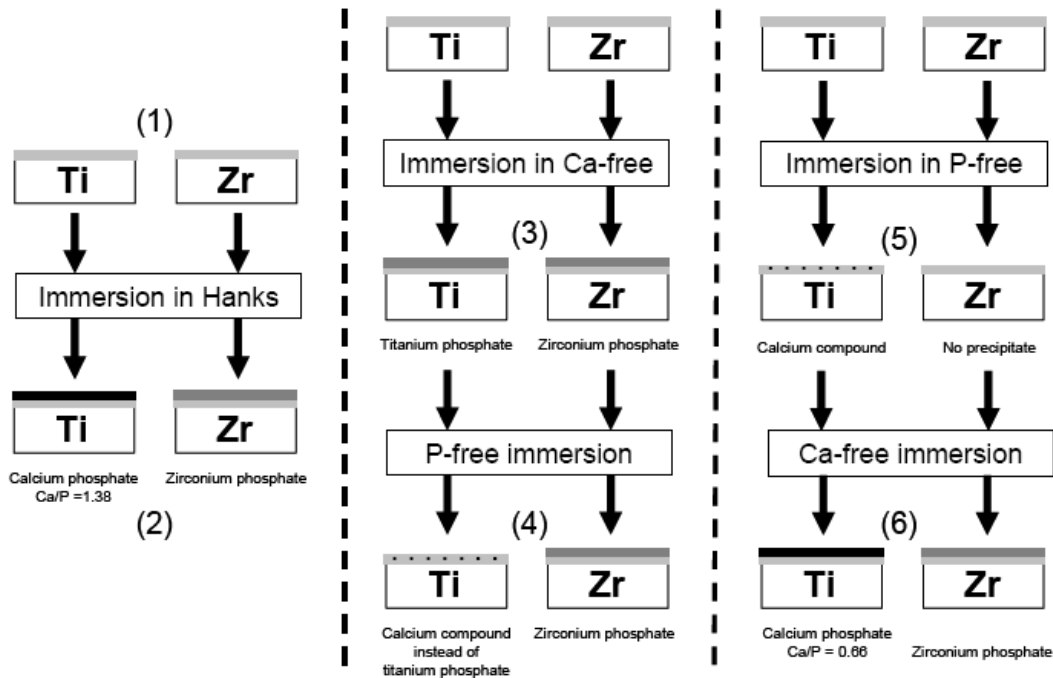
The cathodic polarization was performed with the potentiostat. After immersing the specimens into the electrolytes, the open circuit potential (OCP) was measured for 10 min. Thereafter, the cathodic potential was applied from OCP to  $-2V_{SCE}$  at a constant sweep rate of  $-20 \text{ mV min}^{-1}$ .

## 3 Results and discussion

*Composition of surface oxide film before immersion.* From XPS characterization, The surface oxide film on Zr contains only Zr<sup>4+</sup>, and that on Ti contains Ti<sup>2+</sup> and Ti<sup>3+</sup> as well as Ti<sup>4+</sup>. In other words, the surface oxide film on Zr is stoichiometrically oxidized and stable, while that on Ti is not stoichiometric and still has room for oxidation. Therefore, the surface oxide film on Zr is more stable than that on Ti. Moreover, less OH<sup>-</sup> is contained in surface oxide film on Zr than on Ti, indicating that the film on Zr is less hydrated.

Ion	Concentration (mol L <sup>-1</sup> )			
	0.9% NaCl	Hanks	Ca-free	P-free
Na <sup>+</sup>	$1.54 \times 10^{-1}$	$1.42 \times 10^{-1}$	$1.42 \times 10^{-1}$	$1.41 \times 10^{-1}$
K <sup>+</sup>	—	$5.81 \times 10^{-3}$	$5.81 \times 10^{-3}$	$5.37 \times 10^{-3}$
Mg <sup>2+</sup>	—	$8.11 \times 10^{-4}$	$8.11 \times 10^{-4}$	$8.11 \times 10^{-4}$
Ca <sup>2+</sup>	—	$1.26 \times 10^{-3}$	—	$1.26 \times 10^{-3}$
Cl <sup>-</sup>	$1.54 \times 10^{-1}$	$1.45 \times 10^{-1}$	$1.42 \times 10^{-1}$	$1.45 \times 10^{-1}$
PO <sub>4</sub> <sup>-3</sup>	—	$7.78 \times 10^{-4}$	$7.78 \times 10^{-4}$	—
SO <sub>4</sub> <sup>-2</sup>	—	$8.11 \times 10^{-4}$	$8.11 \times 10^{-4}$	$8.11 \times 10^{-4}$
CO <sub>3</sub> <sup>-2</sup>	—	$4.17 \times 10^{-3}$	$4.17 \times 10^{-3}$	$4.17 \times 10^{-3}$
pH	5.4	7.4	7.2	8.1

**Table 1:** Compositions and pH values of electrolytes used in this study.

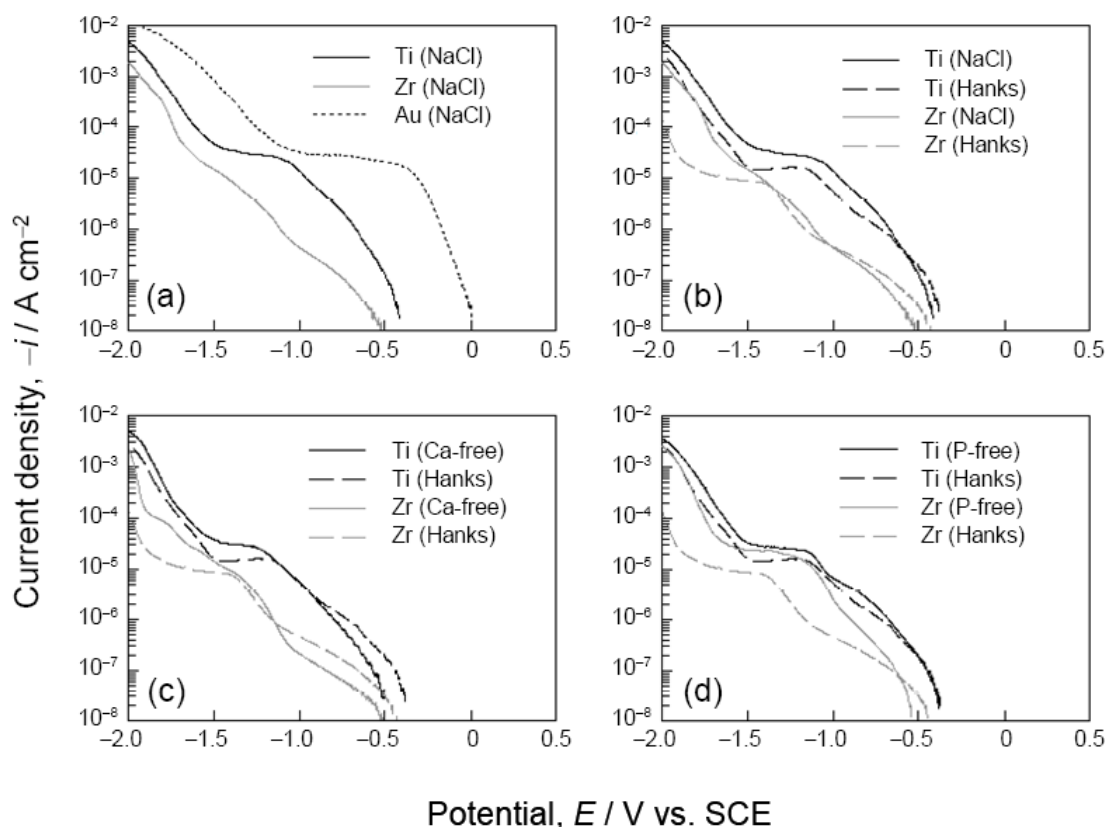


**Figure 1:** Illustrations of changes in surface layers on Ti and Zr immersed in each electrolyte determined with XPS.

The dehydration proceeds inside the surface film, while the dehydration process takes place only partly for Ti<sup>4+</sup> oxide.

*Immersion in electrolytes.* After immersion in electrolytes, calcium and/or phosphorus were detected at the binding energy region of Ca 2p and P 2p electrons with XPS. From binding energies of them, calcium and phosphorus existed as Ca<sup>2+</sup> and phosphate ions, respectively. The phenomena in the formation of the calcium and/or phosphate layer are schematically summarized in Figure 1. In the case of Ti, calcium phosphate was formed when Ti was immersed in Hanks. Calcium was incorporated on Ti by immersion in P-free; calcium did not form CaTiO<sub>3</sub>, but it formed CaO or Ca(OH)<sub>2</sub> because the binding energy of Ca 2p<sub>3/2</sub> from

this specimen was 347.6 eV, which is similar to that of CaO or Ca(OH)<sub>2</sub>, while that of CaTiO<sub>3</sub> is 346.6 eV [5]. Then, calcium phosphate was formed on it by immersion in Ca-free. On the other hand, phosphate was formed on Ti by immersion in Ca-free, but phosphate was completely substituted with calcium after immersion in P-free. This indicates that calcium or phosphate could not exist stably alone on Ti and eventually formed calcium phosphate on it in solutions containing both calcium and phosphate ions. In the case of Zr, zirconium phosphate was formed in Hanks, and calcium was not incorporated. Calcium was also never incorporated by immersion in P-free, and the original surface oxide film remained. On the other hand, phosphate was formed on Zr by immersion in Ca-free, and



**Figure 2:** (a) Cathodic polarization curves of Ti, Zr and/or Au in 0.9% NaCl; (b) those of Ti and Zr in Hanks in addition to those in 0.9% NaCl; (c) those of Ti and Zr in Ca-free with those in Hanks; (d) and those of Ti and Zr in P-free with those in Hanks.

this phosphate film maintained even after immersion in P-free. Therefore, Zr does not react with calcium because phosphate is more stable with Zr and zirconium phosphate is formed. Therefore, Zr does not form calcium phosphate on it in the human body.

**Cathodic polarization.** Figure 2(a) shows the cathodic polarization curves of Ti, Zr, and Au in 0.9% NaCl; Figure 2(b) shows those of Ti and Zr in Hanks in addition to those in 0.9% NaCl; Figure 2(c) shows those of Ti and Zr in Ca-free with those in Hanks; and Figure 2(d) shows those of Ti and Zr in P-free with those in Hanks. In Figure 2(a), from the result of Au, there was no barrier layer on Au obstructing the diffusion of oxygen because Au had no oxide or hydroxide layer on it. The polarization curve of Ti showed a similar tendency to that of Au: the curve had flat region. On the other hand, the cathodic current density of Zr was much smaller than that of Ti. In other words, the density (or compactness) of the passive film of Zr was much higher than that of Ti. That is, the surface oxide film on Zr is electrochemically stronger and more protective than that on Ti against the metal dissolution. This difference between the surface oxide films on Ti and Zr might be

caused by their compositions, as determined with XPS. Figure 2(b), (c) and (d) show polarization curves of Ti and Zr in NaCl, Hanks, Ca-free, and P-free. The cathodic reaction on the Ti surface was totally suppressed in Hanks but not in 0.9% NaCl. In this study, it is obvious that Ti formed the calcium phosphate layer on itself and acted as a barrier against mass transfer because the calcium phosphate layer was dense and insulated. On the other hand, the cathodic reaction on Zr is still more significantly prevented than that on Ti. In Figure 2(c), the cathodic reaction in Ti was accelerated in Ca-free than in Hanks, indicating that protective calcium phosphate formed on Ti in Hanks. Titanium phosphate formed in Ca-free is not protective. On the other hand, the cathodic current in Zr is almost the same in Hanks and Ca-free. In Figure 2(d), the cathodic reactions in Ti and Zr were more accelerated in P-free than in Hanks. Therefore, a calcium compound formed on Ti and Zr by itself was unstable in P-free. This indicated that the presence of phosphate ion was important in protectiveness and reactivity for both metals. In fact, calcium phosphate on Ti and zirconium phosphate on Zr were formed after immersion in Ca-free to be stabilized with the reactions from (5) to (6).

## 4 Conclusions

The surface oxide film on Ti is not completely oxidized and is relatively reactive, while that on Zr is stably oxidized; that on Zr is more passive and protective than that on Ti. Neither calcium nor phosphate stably exists alone on Ti, and calcium phosphate is formed in biological environments; calcium phosphate formed on Ti is stable and protective. On the other hand, calcium is never incorporated on Zr, while phosphate zirconium formed on Zr is highly stable and forms a protective layer; therefore, no calcium reacts with the layer. Finally, we demonstrate that surface oxide films as passive films on Ti and Zr are almost amorphous and different from crystallized titanium oxide and zirconium oxide bulk ceramics with regard to those chemical properties [7]. This property of zirconium could be applied to internal fixators used in bone marrow, such as bone screws and bone nails, to avoid assimilation with bone because bone sometimes refractures when devices consisting of titanium alloy are retrieved.

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