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Corrosion behavior and surface characterization of titanium in solution containing fluoride and albumin

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Abstract

The objective of this study was to demonstrate the role of albumin on the corrosion behavior of titanium in a solution containing 2.0 g/l fluoride and either 0.1 or 1.0 g/l albumin. The corrosion behavior and surface characterization of passive films on titanium immersed in such a solution were examined. In addition, the change in pH and the concentration of dissolved titanium in the solution were examined. The results showed that the corrosion of titanium in a solution containing fluoride was distinct, and that adding albumin to the solution containing fluoride suppressed corrosion. Fluorine was detected on the titanium surface immersed in the solution containing fluoride, and dissolution of the titanium was confirmed. The titanium immersed in a solution containing both fluoride and albumin had an albumin film regardless of the albumin concentration. In addition, the amount of dissolved titanium from the titanium immersed in the solution was less than when the solution contained no albumin. It was suggested that the formation of adsorbed albumin films on or in the passive film acted to not only protect the titanium from attack by the fluoride but also suppressed dissolution of the titanium-fluoride compounds.

Keywords: Titanium; Albumin; Fluoride; Corrosion; X-ray photoelectron spectroscopy

1. Introduction

Titanium and its alloys are widely used in dentistry as prosthetic appliances because of a high corrosion resistance and good biocompatibility. These valuable properties are caused by passive films that are rapidly formed in the body fluid environment [1–3]. Recently, mouth-rinses, toothpastes, and prophylactic agents containing fluoride are utilizing to prevent the dental caries. However, decreasing the corrosion resistance of titanium in solutions containing fluoride has been reported [4–12]. The corrosion behaviors are related to the concentration of fluoride and the surrounding environment (e.g., pH, concentration of dissolved oxygen, and temperature). Therefore, the surface reaction on titanium under the existence of fluoride is important to understand the corrosion and tarnish of titanium in oral environment.

The influence of protein on the corrosion resistance of the implant materials is important because saliva contains 200–500 mg/dl of salivary protein. Williams et al. [13] reported that the corrosion of titanium in serum was enhanced. Khan et al. [14] suggested that the corrosion behavior of titanium alloys in protein solutions was dependent on the kind of alloy. In addition, they indicated that the alloys immersed in the protein solutions reduced the hardness of the surface oxides. However, how proteins are related to surface oxides has not been examined.

Recently, Ide et al. [15,16] reported that the corrosion of titanium was suppressed in solutions containing fluoride and albumin. They suggested a possible mechanism for suppression of the corrosion of the titanium. The albumin adsorption on the titanium prevented fluoride attack, or the buffering effect of the albumin increased the pH. Furthermore, Huang [17] also indicated that Ti-6Al-4 V alloys in artificial saliva containing fluoride and albumin had higher corrosion resistance than they did in saliva without albumin. He suggested that albumin adsorption could prevent

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destruction of the passive films by the fluoride ion. However, the mechanism of suppressing corrosion of titanium and its alloys in the presence of albumin is not clear, that is, the corrosion products and the composition of the surface oxide caused by albumin adsorption have not been examined in detail.

The present study was to examine the surface characterization of titanium and the dissolved titanium concentration after the titanium was immersed in solution containing fluoride and albumin, and to determine the effects of the addition of albumin on the corrosion behavior of the titanium. These results will enhance the understanding of the surface reaction of titanium prosthetic appliance in oral environment.

2. Experimental procedure

2.1. Materials

Titanium specimens 14 × 14 × 1 mm in size or 4 mm in diameter and 1 mm in thickness were cut from a sheet of commercially available pure titanium (Ti grade 2, Kobe Steel, Japan). The former were prepared as specimens for the corrosion tests and surface characterization; the latter were prepared for X-ray photoelectron spectroscopy (XPS) measurement. The specimens were polished with silicon carbide papers No. 120, 240, 400, and 600 grits in series. They were ultrasonically washed in acetone and ethanol for 10 min.

2.2. Test solution

The solution was composed of sodium chloride (NaCl, Wako Chem., Osaka, Japan), sodium fluoride (NaF, Wako Chem., Osaka, Japan), bovine serum albumin (BSA, Wako Chem., Osaka, Japan), and distilled water. The starting composition in 1000 ml of each solution and the specimen codes are listed in Table 1. All solutions containing fluoride (NAF, BSA.01, and BSA.1) were adjusted to pH 5.0 using lactic acid (Wako Chem., Osaka, Japan) at 37°C, while SAL solution was not adjusted.

Table 1
Code, composition and pH of 1000 ml preparation solutions at 37°C

Code	NaCl/g	NaF/g	BSA/g	pH
SAL	9.00	None	None	5.5
NAF	9.00	2.00	None	5.0
BSA.01	9.00	2.00	0.10	5.0
BSA.1	9.00	2.00	1.00	5.0

2.3. Electrochemical measurement

The apparatus for electrochemical measurement consisted of a potentiostat/galvanostat (Model 273A, EG&G, USA) controlled by a computer using research corrosion software M352C (EG&G, USA), a saturated calomel electrode (SCE) as reference electrode, a platinum plate as counter electrode, and a sample holder (the exposed area of the specimen was 1.0 cm^2) as working electrode. A volume of 500 ml of test solution was deaerated with pure nitrogen gas for 30 min before measurement. The open circuit potential (E_{open}) was measured after the specimen was immersed in the solution for 30 min. The polarization resistance (R_{p}) of the specimen in the test solution was measured in a scanning range of −20 to 20 mV from the open circuit potential at a scanning rate of 0.1 mV/s. The potentiodynamic polarization behavior of the specimens was recorded in a scanning range of −1.2 to +2.5 V (vs. SCE) at a scanning rate of 0.33 mV/s. The passive current density at 0.5 V ($I_{0.5}$) was obtained from the potentiodynamic polarization curve. Each measurement was maintained at 37°C. Five specimens were tested for each condition.

2.4. Surface characterization and analysis of dissolved titanium

Some of the specimens were immersed in 10 ml per unit area (cm^2) of the test solutions at 37°C. The specimens were picked up from the solutions after immersion for 3 days and gently washed with distilled water. Their surface structure was examined by a thin-film X-ray diffractometer (TF-XRD), an electron probe microanalyzer (EPMA), and XPS. The TF-XRD profiles were taken with a Rint 2000 (Rigaku, Japan) equipped with a Cu K_α radiation (40 kV and 200 mA) source and with a thin film attachment; the incidence angle was 1°. EPMA measurements were performed with an X-3010 (Hitachi, Japan). The profiles of each element were obtained with voltage 15 kV and current 100 nA. All XPS spectra were measured with an ESCA 750 (Shimadzu, Japan) and obtained with a Mg K_α: energy 1253.6 eV, voltage 8 kV, and current 30 mA. The reflectance angle for photoelectron detection was 0°. The binding energy was normalized to the C 1s peak (285.0 eV) of hydrocarbon on the titanium specimen. The surface texture of the specimens was observed under a scanning electron microscope (SEM; JSM-6340F, JEOL, Japan). The titanium ion concentration and pH in the test solution after immersion of specimen were monitored with an inductively coupled plasma emission spectrometer (ICP; Vista-MPX, SII, Japan) and pH meter (BASIC, Denver Instrument, USA), respectively. Three specimens were prepared for each condition to examine the analysis of dissolved titanium.