Influence of sulfide concentration on the corrosion behavior of titanium in a simulated oral environment

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ABSTRACT

This study assessed the corrosion behavior of titanium in response to sulfide by determining the effects of sulfide concentration and pH over immersion period. Corrosion was evaluated through changes in color, glossiness, surface characterization, and titanium release. Sulfide solutions were prepared in 3 different concentrations with Na_2S, each in pH unadjusted (sulfide-alkaline) and pH adjusted to 7.5 (sulfide-neutral). Titanium discoloration increased and glossiness decreased as sulfide concentration and immersion period increased in sulfide-alkaline solutions. Coral-like complexes were observed on the surface of these specimens, which became more pronounced as concentration increased. Small amounts of titanium release were detected in sulfide-alkaline solutions; however, this was not affected by immersion periods. Corrosion was indicated through considerable surface oxidation suggesting the formation of a thick oxide layer. No significant changes in color and glossiness, or titanium release were indicated for titanium specimens immersed in sulfide-neutral solutions indicating that pH had a significant effect on corrosion. Our findings suggest that a thick oxide layer on the titanium surface was formed in sulfide-alkaline solutions due to excessive oxidation.

1. Introduction

The use of a titanium dental implant system is common to restore the function of lost teeth. The clinical success of dental implants is dependent on biomechanical factors that determine the integrity of the implant [1–3]. The physical properties of pure titanium or titanium alloys, such as high strength to weight ratio, superior fatigue strength, tensile strength, modulus of elasticity, and cytotoxicity make them very attractive and suitable for the fabrication of any dental prosthesis [4–7]. Titanium is also known for its corrosion resistance, which is a result of the materials' ability to form passive oxide films (TiO_2) in normal physiological conditions. However, the nature, composition, and thickness of this protective film depend on environmental conditions [8–10].

Electrochemical corrosion in fluid electrolytes such as saliva can possibly trigger allergic reactions by releasing elements from the alloy [11]. This can also be an issue since titanium ions have a biological effect on the viabilities of osteoblast and osteoclast and on their differentiation which may influence prognosis after implant placement [12]. The dynamicity of the oral cavity makes it essential to determine the causes of material corrosion and subsequent wear. These aspects serve as the foundations to develop materials resistant to corrosion or methods to treat unfavorable conditions.

Literatures have reported that fluoride, peroxide, organic acids, and released-cell products induce titanium corrosion [13–22]. Fluorides found in prophylactic agents, affect the titanium surface by dissolving the passive oxide layer leading to ion dissolution and surface discoloration [19,20]. Peroxides found in denture cleanser affect titanium through surface oxidation in acidic conditions or by inducing dissolution in alkaline solutions [20]. Released-cell products such as lactic acid and formic acid which can be produced by oral bacteria have also shown to affect the corrosion behavior of titanium [14,21]. The biomedical application of titanium is common due to its exceptional properties discussed earlier as well as corrosion resistance, however these papers suggest that titanium may be susceptible to corrosion in the oral environment.

Sulfur products are of particular concern in regards to titanium dental implants because periodontopathic bacteria secretes considerable amounts of sulfide byproducts, such as hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and dimethyl sulfide (($CH_3)_2S$), as a result of their metabolism [23]. Sulfide has been reported to have the potential to cause discoloration in dental alloys. Silver based alloys have shown to tarnish at various degrees in 0.1% sulfide solutions based on chemical composition and microstructure [24]. When silver palladium alloys were placed in cultures containing *Fusobacterium nucleatum*, discoloration occurred and sulfur was identified on the metal surface [25]. Titanium is known for its corrosion resistance however, Rodrigues et al. retrieved failed implants due to peri-implantitis and reported that titanium dental implants were highly susceptible to pitting attack

in the oral environment [26]. Yoshida et al. reported discoloration of titanium and titanium alloys in sulfide solutions [27]. These suggest the possibility of sulfides in the oral cavity affecting the corrosion behavior of titanium, however factors which affect the corrosion behavior of titanium in sulfide environments have not yet been studied in detail.

The objective of this study is to assess the corrosion behavior of titanium in response to sulfide by determining the effects of sulfide concentration and pH over immersion period. The null hypothesis is that sulfide concentration, pH, and immersion period have no effect on the corrosion behavior of titanium.

2. Materials and methods

2.1. Specimen and solution preparation

Commercially available pure titanium disks 1.3 mm thick and 13 mm in diameter were prepared from wrought titanium rods (Grade 2, Tokyo Titanium, Tokyo, Japan). The disks were mirror polished with a polishing machine (Automet 250 and Ecomet, 250 Buehler, Tokyo, Japan) using silicon carbide paper from 320 to 1200 grit, diamond suspension, and colloidal silica suspension according to metallographic procedure. These were ultrasonically washed with acetone and distilled water for 5 min and dried.

Ultrapure water (Milli-Q®; Merck Millipore Corporation, Tokyo, Japan: MQ) was used as a representative immersion medium. Sulfide solutions were prepared by adding to 500 mL of 3.12 g, 12.12 g, and 24.00 g of $Na_2S \cdot 9H_2O$ (Wako Pure Chemical Industries, Ltd., Osaka, Japan) to MQ abbreviated as MQS-L, MQS-M, and MQS-H respectively. The pH of sulfide solutions with pH unadjusted (sulfide-alkaline solutions) ranged from 11.6–12.1. Sulfide solutions with pH adjusted to 7.5 using hydrochloric acid (Wako Pure Chemical Industries, Ltd., Osaka, Japan), denoted as -AD (sulfide-neutral solutions), were also prepared.

Titanium disks were immersed in 20 mL of solution in a polypropylene bottle and sealed to prevent evaporation and stored at 37 °C for 1, 3, and 7 days. All assays were performed using triplicate samples of each solution in at least 2 different experiments.

2.2. Color and glossiness measurements

Initial color and glossiness of the titanium specimens were measured using a colorimeter (MCR-A Luck Office, Tokyo, Japan) and glossmeter (GM-26D, Murakami Color Research Laboratory, Tokyo, Japan). Color difference ($\Delta E * ab$) of titanium specimens were calculated for each condition at 1, 3, and 7 days by measuring CIE L*a*b* color coordinates against reflected light. The colorimeter was calibrated with a white calibration tile before being used. The $\Delta E * ab$ was determined using the following equation:

$$\Delta E^* ab = \left[(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2 \right]^{1/2}$$

where L_0^*, a_0^*, b_0^* were values before immersion, while L^*, a^*, b^* were values after immersion.

For glossiness, incidence light angle of 20° from the surface normal was selected and reflected light was measured using a detector. The glossmeter was calibrated with a black tile with a standard reference value of 86.7% for Gs(20°).

2.3. Surface characterization

Surface texture of specimens was observed under a field emission scanning electron microscope (FE-SEM SU6600; Hitachi, Tokyo, Japan) operating at a voltage of 15 kV. The specimens were subsequently coated with carbon using a carbon coater (VC-100S, Vacuum Device, Ibaraki, Japan) before observation.

Crystal structure on titanium specimens were investigated by X-ray diffraction (XRD) using CuKα radiation operating at a voltage of 40 kV and current of 30 mA. Two theta diffraction angle were set between 20–70° with an incremental angle of 5° per minute using a diffractometer (Ultima IV, Rigaku, Tokyo, Japan) with a semiconductor detector. Thin film XRD (TF-XRD) pattern was also analyzed to determine surface at an incident angle of 1° at a 2θ diffraction angle of 10–50° and incremental angle of 0.5° per minute (Smartlab®, Rigaku, Tokyo, Japan).

The chemical composition and binding state of the titanium specimens were analyzed by X-ray photoelectron spectroscopy (XPS); (AxisUltra, Kratos-Shimadzu, Kyoto, Japan). The X-ray resource was monochronized AlKα electrode at 15 kV, 10 mA emission current. The area of measurement was 200×600 μm, and take-off angle of photoelectrons was 45°. All XPS spectra were calibrated to the standard carbon C1s hydrocarbon peak at around 285.0 eV. The quantitative analysis and the curve fitting were conducted by the CasaXPS software (Casa Software Ltd., Teignmouth, UK).

2.4. Released element analysis in solution

Titanium release into the test solutions was determined using an inductively coupled plasma optical emission spectroscopy (ICP-OES, Vista-MPX, SII, Japan). Release values were calculated by using the concentration (ppm or mg/L) to derive the total amount released titanium in the bottle then dividing the amount by the exposed area (μg/cm²). The detection limit of titanium release from the specimens used in this study was above 0.01 μg/cm².

2.5. Statistical analysis

Data analysis was performed using one-way analysis of variance (ANOVA) and Tukey's HSD multiple comparison tests using software (Excel Tokei, 2010, SSRI, Tokyo, Japan) to compare $\Delta E * ab$, glossiness, and titanium ion release with immersion period. Color difference with respect to immersion period, sulfide concentration, pH, and titanium ion release were statistically analyzed with two-way ANOVA. The influence of pH was compared for each sulfide concentration at constant immersion periods. Statistical significance was set at $\alpha = 0.05$. Triplicate samples were used in the experiments to ensure the reproducibility of the results.

3. Results

3.1. Color and glossiness change

Fig. 1 displays the $\Delta E * ab$ of titanium specimens immersed in various sulfide solutions over immersion period. For sulfide-alkaline solutions, $\Delta E * ab$ value was significantly higher in order of MQ, MQS-L, MQS-M, and MQS-H at each immersion period. For each sulfide-alkaline solution, $\Delta E * ab$ value demonstrated significant increase on day 1 and 3, however no further changes were indicated after day 3. In contrast, no significant differences in $\Delta E * ab$ were found between titanium specimens immersed in MQ and all sulfide-neutral solutions (−AD), and no significant changes in $\Delta E * ab$ were indicated with increasing immersion period.

Fig. 2 shows the change in glossiness of titanium specimens immersed in various sulfide solutions over immersion period. Glossiness decrease was greater in order of MQ, MQS-L, MQS-M, and MQS-H at all immersion periods, however no significant differences were found between MQ and MQS-L at all immersion periods. Glossiness decreased with time by day 1 and 3, however no significant changes were indicated after day 3 for all sulfide-alkaline solutions. No significant changes in glossiness were found among MQ and all sulfide-neutral solutions with increasing immersion periods.