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Corrosion and hydrogen absorption of commercially pure zirconium in acid fluoride solutions

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ABSTRACT

The corrosion and hydrogen absorption of commercially pure zirconium have been investigated in acidulated phosphate fluoride (APF) solutions. Upon immersion in 2.0% APF solution of pH 5.0 at 25 °C, a granular corrosion product (Na_3ZrF_7) deposits over the entire side surface of the specimen, thereby inhibiting further corrosion. In 0.2% APF solution, marked corrosion is observed from the early stage of immersion; no deposition of the corrosion product is observed by scanning electron microscopy. A substantial amount of hydrogen absorption is confirmed in both APF solutions by hydrogen thermal desorption analysis. The amount of absorbed hydrogen of the specimen immersed in the 2.0% APF solution is smaller than that in the 0.2% APF solution in the early stage of immersion. The hydrogen absorption behavior is not always consistent with the corrosion behavior. Hydrogen thermal desorption occurs in the temperature range of 300–700 °C for the specimen without the corrosion product. Under the same immersion conditions, the amount of absorbed hydrogen in commercially pure zirconium is smaller than that in commercially pure titanium as reported previously. The present results suggest that commercially pure zirconium, compared with commercially pure titanium, is highly resistant to hydrogen absorption, although corrosion occurs in fluoride solutions.

1. Introduction

The group IV elements in the periodic table, such as titanium and zirconium, are considered to be highly corrosion-resistant. In biological environments, titanium exhibits high corrosion resistance. In addition, titanium exhibits osseointegration and superior biocompatibility. Hence, titanium and its alloys are extensively used and are essential biomedical materials. However, to use them as materials of dental devices in the oral cavity, high corrosion resistance against fluoride is required. Fluoride, such as NaF, is added in toothpastes, prophylactic agents and dental rinses, because of its cariostatic effect. For titanium and its alloys, marked corrosion occurs in the presence of fluoride [1–6]. The corrosion often leads to a substantial amount of hydrogen absorption, thereby causing hydrogen embrittlement [7–10].

On the other hand, zirconium exhibits lower cell cytotoxicity than titanium [11] and good biocompatibility. Moreover, because zirconium does not form calcium phosphate in Hanks' solution [12,13], it is a candidate material for a removable bone fixator. Zirconium is now being used and is anticipated as an alloying element for biomedical titanium alloys [14–18]. Zirconium and its alloys have potential applications as materials of dental devices. Dental implants made of titanium–zirconium alloys have attracted interest [19–24]. Zirconium is resistant to corrosion in many environments, such as those containing most mineral acids, organic acids and salt solutions [25,26]. However, there are no data on the corrosion and hydrogen absorption of zirconium in oral environments containing fluoride, although, in the field of nuclear materials, they have been investigated in severe environments [27–38]. Therefore, if the hydrogen absorption of zirconium is confirmed in a mild environment, such as an oral environment containing fluoride at nearly room temperature, it will be the first observation of this phenomenon. In addition, to our knowledge, there are no data on the hydrogen thermal desorption behavior of zirconium. The desorption behavior is a useful key to understanding the mechanism of hydrogen embrittlement. Fundamental data must be accumulated for the future application of zirconium.

The present study is conducted to investigate the corrosion and hydrogen absorption of commercially pure zirconium in acid fluoride solutions at room temperature. This article focuses on comparing the corrosion and hydrogen absorption behavior of commercially pure zirconium with those of commercially pure titanium reported previously [8].

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2. Experimental procedures

A commercially pure zirconium (nominal 99.5 mass%, Nilaco Corp.) wire of 0.50 mm diameter was cut into specimens of 50 mm length. The impurities of combined iron and chromium levels were 0.1 mass%. Percentages in this paper refer to mass percent, unless otherwise stated. The specimens were carefully finished with 600-grit SiC paper and ultrasonically washed in acetone for 5 min.

For comparison with the results of commercially pure titanium, the present study was performed under the same experimental conditions as those reported previously [8]. The immersion test solutions used were 2.0% acidulated phosphate fluoride (APF; 0.48 M NaF + 0.15 M H_3PO_4) and 0.2% APF aqueous solutions with pH 5.0 at room temperature (25 ± 2 °C). The fluoride concentrations were 9000 and 900 mass ppm, corresponding to those in prophylactic agents and toothpastes, respectively.

The potentiodynamic polarization curves of each specimen were measured at least three times from the corrosion potential towards the anodic and cathodic directions with a scan rate of 20 mV/min at room temperature in the test solutions under aerated conditions. The counter and reference electrodes used were a platinum electrode and a saturated calomel electrode (SCE), respectively. The measurement was started 10 min after immersion in the solution. The changes in the corrosion potentials of the specimens in the test solutions were measured at room temperature under aerated conditions.

The specimens were immersed separately in 50 ml of the test solutions. The mass and diameter changes of the immersed specimens were measured using a microbalance and a micrometer caliper, respectively. Standard deviations were calculated from the results obtained for five specimens. The side surface of the immersed specimens was observed by scanning electron microscopy (SEM). The corrosion product on the surface of the immersed specimens was examined using an X-ray diffractometer with Cu Kα radiation of wavelength $\lambda = 0.154056$ nm in the 2θ angle range from 20° to 90° operated at 40 kV and 20 mA. A surface chemical analysis of the immersed specimens was performed by X-ray photoelectron spectroscopy (XPS) with Al Kα radiation at 12 kV.

The amount of desorbed hydrogen was measured by the hydrogen thermal desorption analysis of the immersed specimens. The immersed specimens were cut at both ends and subjected to ultrasonic cleaning with acetone for 2 min. Subsequently, the specimens were dried in ambient air and then subjected to measurement. A quadrupole mass spectrometer (ULVAC, Kanagawa, Japan) was used for hydrogen detection. Sampling was conducted at 30 s intervals at a heating rate of 100 °C/h.

3. Results and discussion

3.1. Corrosion

The representative polarization behavior observed in the 2.0% and 0.2% APF solutions are shown in Fig. 1. At a noble potential, the anodic current density of commercially pure zirconium immersed in the 2.0% APF solution is one order of magnitude smaller than that in the 0.2% APF solution. For commercially pure titanium, the anodic current density increases with fluoride concentration in solutions [3–6]. In 2.0% APF solution, the anodic current density of commercially pure zirconium is smaller than that of commercially pure titanium as reported previously [3–6]. In contrast, in 0.2% APF solution, the anodic current density of commercially pure zirconium is larger than that of commercially pure titanium.

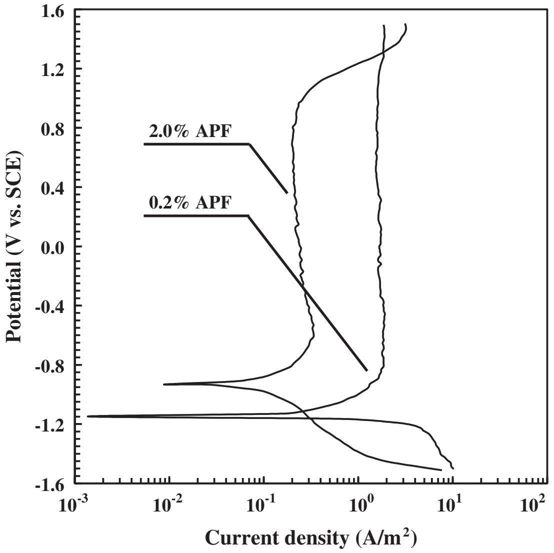

Fig. 1. Polarization curves for specimens immersed in 2.0% and 0.2% APF solutions.

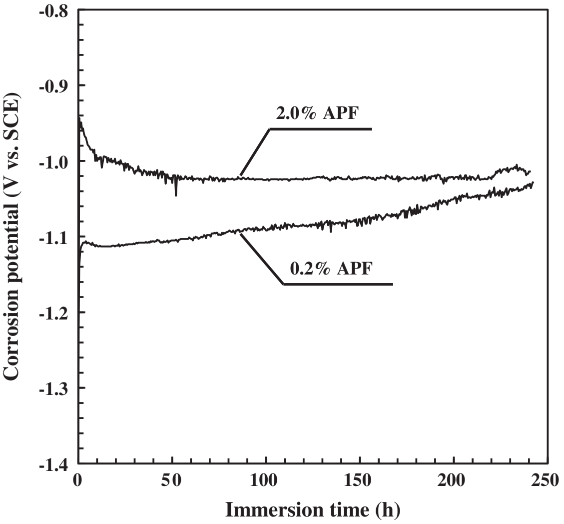

Fig. 2. Changes in corrosion potentials of specimens immersed in 2.0% and 0.2% APF solutions.

Changes in the corrosion potentials of commercially pure zirconium in the 2.0% and 0.2% APF solutions are shown in Fig. 2. The corrosion potentials in both solutions were stable at approximately −1.0 to −1.1 V (vs. SCE) for a long immersion time. For commercially pure titanium and titanium alloys, similar results have been reported by several workers [3–6]. These electrochemical results suggest the hydrogen evolution on the surface of the specimen upon immersion in APF solutions.

Mass and diameter changes of commercially pure zirconium immersed in the 2.0% and 0.2% APF solutions are shown in Figs. 3 and 4, respectively. The amounts of scatter of the mass and diameter changes were very small. In the 2.0% APF solution, the mass and diameter of the specimen were increased by the deposition of the corrosion product. The deposition of a corrosion product has also been observed for commercially pure titanium or titanium alloys, as reported previously [8]; however, the corrosion product (Na_3TiF_6) readily peels off the surface of the specimen [39,40]. In the present study, the corrosion product hardly peeled off the surface of the specimen. In the 0.2% APF solution, the mass and diameter of the specimen were gradually decreased by dissolution. The mass and diameter losses of commercially pure zirconium are