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Electrochemical behavior of Ti–Cr alloys in artificial saliva

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ABSTRACT

In this study, the corrosion behavior of commercially pure titanium (c.p. Ti), Ti–6Al–4V and five new experimental Ti–Cr alloys was evaluated through open-circuit potential (OCP) and potentiodynamic polarization measurement in an artificial saliva containing fluoride. Electron spectroscopy for chemical analysis (ESCA) was used to characterize the composition of the passive films on the alloy after potentiodynamic polarization measurement. It was found that in standard artificial saliva the OCP increases with higher Cr content in Ti–Cr alloys. In 0.5% NaF artificial saliva, the OCP decreases with decreasing Cr in Ti–Cr alloys, and all but Ti–5Cr remain consistently higher than those of c.p Ti and Ti–6Al–4V. Linear polarization results show that artificial saliva and artificial saliva containing 0.5% NaF result in different corrosion behavior in Ti–Cr alloys, c.p.Ti and Ti–6Al–4V. The Ti–Cr alloys had greater resistance to corrosion in the fluoride-containing artificial saliva than c.p. Ti and Ti–6Al–4V, respectively. ESCA results verify that after potentiodynamic polarization a passive film consisting of TiO_2 and Cr_2O_3 forms on the surface of Ti–Cr alloys. These experimental results show that the electrochemical corrosion behavior of Ti–Cr alloys in artificial saliva containing 0.5% NaF can be improved by increasing Cr content. This further indicates that Ti–Cr alloys could successfully be used for crown, bridge, and metal-ceramic restorations.

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1. Introduction

Commercially pure titanium (c.p. Ti) and its alloys have been widely used for dental restorative applications such as crown/bridge, framework and dentures [1]. The advantages of titanium alloys in these applications are due to their excellent mechanical properties, good corrosion resistance in biological fluids, and biocompatibility [2]. For a metal to be used in an oral environment, it should be biocompatible and have high corrosion resistance. Among the various titanium alloys, the Ti–6Al–4V alloy is the most frequently used in medical implants. It also shows better physical and mechanical properties in comparison to c.p. Ti. However, this alloy might cause some long-term health problems because of the release of Al and V ions [3,4]. Previous studies also showed that the surface of the Ti–6Al–4V alloy was roughened by corrosion in the acidic fluoride-containing saliva [5]. In the present study the corrosion resistance of Ti–6Al–4V alloy will be further investigated.

Cr is suitable for alloying with titanium (Ti) for several reasons. For example, Cr is known to control the anodic activity of the alloy and increase the tendency of Ti to passivate [6]. In fact, it has already been used for many years as a major constituent in dental casting alloys [7]. An additional advantage of alloying Cr to Ti is that the liquidus temperature is gradually reduced from the high melting point of pure Ti (1670 °C) until reaching a minimum of 1410 °C at Cr content of 46% [8]. Thus, a number of Ti–Cr alloys have previously been developed for dental applications [9,10]. Among these, β-titanium alloys are the most versatile, and a large number of studies have been performed on them [11]. Ho et al. [9] have studied the structure and properties of a series of binary Ti–Cr alloys with Cr content up to 30 wt%. While the Ti–Cr alloys have been shown to have better mechanical properties than c.p. Ti [9], their corrosion resistance behavior remains unknown. Therefore, in this study the electrochemical behavior of these alloys was specifically investigated.

Since Ti alloys are used in the dental field, and the oral environment is exposed to fluoride, the degree of corrosion resistance offered by the Ti alloys in a fluoride-containing medium becomes an important property for their use in dentistry. In addition, some reports have shown the negative influence of fluoride on the corrosion resistance of titanium [5,12]. Therefore, in this research, corrosion behavior of all alloys was studied in simulated oral environments with and without fluoride.

2. Experimental method

2.1. Specimen preparation

Commercially pure titanium (Kobe Steel Co. Ltd., Kobe, Japan), the Ti–6Al–4V (Daido Steel Co. Ltd., Nagoya, Japan) alloy, and the experimental Ti–(5–30) wt% Cr

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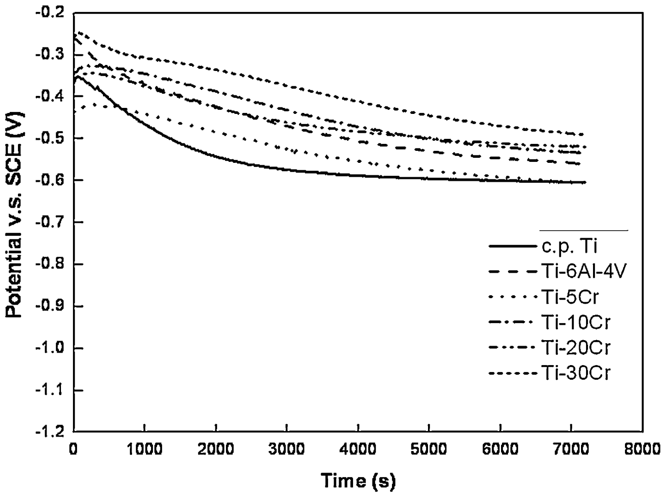

Fig. 1. OCP of c.p. Ti, Ti–6Al–4V and Ti–Cr alloys over a period of 2 h in standard artificial saliva.

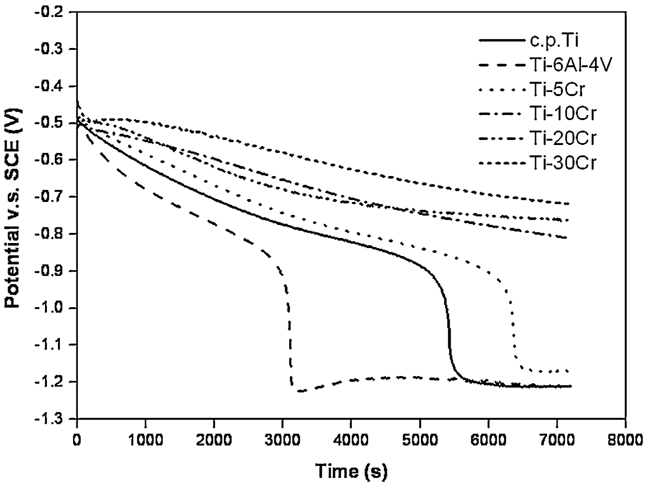

Fig. 2. OCP of c.p. Ti, Ti–6Al–4V and Ti–Cr alloys over a period of 2 h in saliva solution with 0.5 wt% NaF.

alloys were examined in this study. The Ti–Cr alloys were made from c.p. Ti and Cr (99.95%) using an argon-arc melting furnace (1000 Miller Dimension, USA). For the electrochemical measurement, specimens were cut into 1.0 mm in thickness from a rod. The specimens were grinded with silicon carbide paper until #1500 and then polished with 0.3 μm Al_2O_3 suspension. After polishing, the samples were cleaned by means of ultrasonic sound in ethanol.

2.2. Electrochemical tests

In this study, two artificial saliva solutions were used. The first was a standard artificial saliva (NaCl 400 mg/l, KCl 400 mg/l, $CaCl_2{\cdot}2H_2O$ 795 mg/l, $NaHPO_4{\cdot}H_2O$ 690 mg/l, KSCN 300 mg/l, $Na_2S{\cdot}9H_2O$ 5 mg/l, urea 1000 mg/l). The second also contained 0.5 wt% NaF (corresponding to 2500 ppm F). The pH level of both test solutions was adjusted to 4.0 by adding lactic acid in a simulated oral environment [12]. A three-electrode system was used for all the electrochemical measurements. The apparatus for electrochemical measurement consisted of a potentiostat (Versa Stat TM $^{\text{II}}$ Potentiostat/Golvanostat Model 263A; Princeton Applied Research, NJ, USA), controlled by a personal computer with dedicated software (PowerSuit-2.56, Princeton Applied Research), a saturated calomel electrode (SCE) as reference electrode, a platinum plate as counter electrode, and the specimen as working electrode. For each test, the open-circuit potential was measured for 2 h. The potentiodynamic polarization of the specimens was recorded in a scanning range from −1.2 to +2.5 V (v.s. SCE) at a scanning rate of 0.1 mV/s. In every test, the medium was maintained at 37 °C. Five specimens were tested for each condition.

2.3. Surface characterization

After electrochemical measurement, surface morphology of specimens was examined using by a scanning electron microscope (S-3000N, HITACHI, Japan) and the surface composition was examined with ESCA 750 (Shimadzu, Japan).

3. Results and discussion

3.1. Electrochemical measurement

Fig. 1 shows the change in OCP of c.p. Ti, Ti–6Al–4V and Ti–Cr alloys over a period of 2 h in standard artificial saliva. For all specimens, the potential changed in the negative direction over time until a steady-state potential was reached, and gradually decreased. For c.p. Ti, the initial potential was around −256 mV (SCE), but it gradually decreased after 3500 s, and a value of −586 mV (SCE) was reached. The potential then remained almost constant and after 7200 s its value was −580 mV (SCE). The initial potential for Ti–6Al–4V was approximately −265 mV (SCE), which decreased gradually and after 5000 s remained stable at approximately −496 mV (SCE). After 7200 s the potential for this alloy was −506 mV (SCE). The variation of potential over time for the other four Ti–Cr alloys was similar to those of c.p. Ti and Ti–6Al–4V. The steady potentials of Ti–Cr alloys ranged from −418 to −580 mV (SCE). The corrosion potential of the Ti–Cr alloys increased with

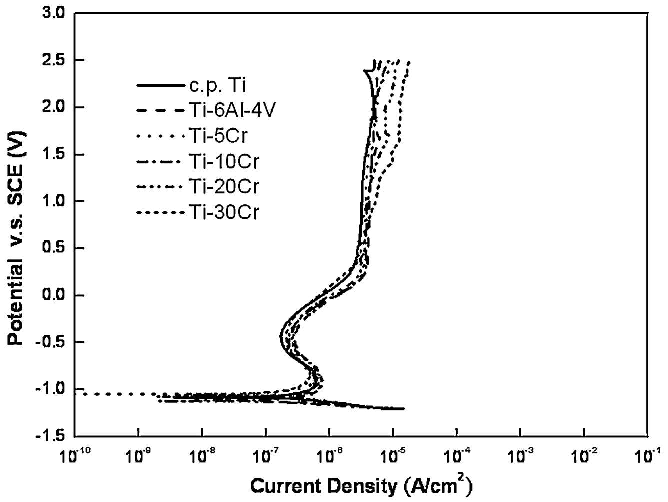

Fig. 3. Linear polarization diagrams of c.p. Ti, Ti–6Al–4V and Ti–Cr alloys in the standard artificial saliva.

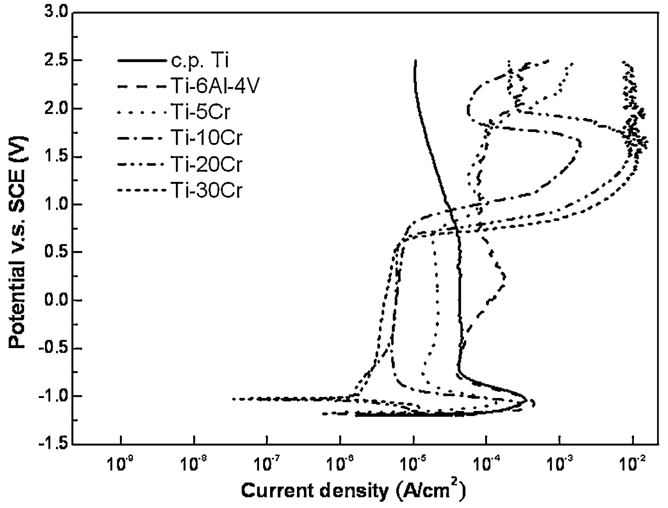

Fig. 4. Linear polarization diagrams for c.p. Ti, Ti–6Al–4V and Ti–Cr alloys in the artificial saliva containing 0.5 wt% NaF.

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