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Corrosion behavior of Ti–5Ag alloy with and without thermal oxidation in artificial saliva solution

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1. Introduction

Ti and Ti-based alloys have been widely used in dental devices, such as CP Ti dental implants and TiMo alloy arc wires [1]. Their wide applications are mainly due to their good mechanical properties, outstanding corrosion resistance and excellent biocompatibility. Ti–Ag binary alloys are recently developed as dental materials with several advantages: (1) The yield strength of as-cast Ti–5Ag alloy is about 280 MPa [2], which is higher than that of CP Ti. (2) It was reported that Ti–Ag alloys possess better grindability [3] than that of CP Ti. (3) Ti–5Ag alloy fabricated by three-dimensional printing (3DPTM) and sintering at 1300 °C shows good passivation behavior in a simulated body fluid [4]. Additionally, the corrosion studies carried out by Shim et al. [5] revealed that, among Ti–Ag alloys, Ti3.0Ag (at.%) alloy had a higher resistance against the attack of fluoride ions in fluoride-containing solution.

The human mouth presents a very aggressive environment for metals used for therapy. For dental alloys, systemic and local toxicity allergy, and carcinogenicity all result from elements in the alloys being released into the mouth [6]. Although titanium alloys exhibit superior corrosion resistance due to the presence of stable and dense titanium oxide film, released alloying element ions into the surrounding tissues and into the serum had been reported [7]. To minimize biologic risks, dental titanium alloys should have the best corrosion resistance and the lowest release of elements. Therefore, it is necessary to improve the corrosion resistance of titanium alloys for dental usage.
The corrosion resistance of Ti and Ti-based alloys in biological environments are ascribed to the rapid formation of passive titanium-dioxide film at the surface. The thicknesses of the passive film formed on titanium alloys in aqueous solutions are usually about several tens of nanometers [8]. Since the corrosion resistance is known to increase with the thickness of the oxide layer [8], several attempts have been made to form thicker TiO2 layer on the Ti alloy substrate by different methods, such as anodization [9], thermal oxidation [9–12], and the sol–gel process [13]. Among these methods, the simple and effective method is developing oxide films by thermal oxidation. Velten et al. [9] found that thermally oxidized Ti and Ti–6Al–4 V alloys exhibited much lower passive current density compared with non-treated Ti alloys. López et al. [10] reported that thermally oxidized Ti–6Al–7Nb alloy exhibited excellent corrosion behavior in Hank’s solution. Moreover, it has been reported that the TiO2 layer formed by thermal oxidation provided good wear resistance and excellent osseointegration [11].

The purpose of this study was to further investigate the effect of thermal oxidation on the corrosion behavior of Ti–5Ag alloy. Scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) tests were carried out to analyze the surface characteristics of Ti–5Ag alloy without and with thermal oxidation, with CP Ti as control. Electrochemical measurements were used to evaluate their corrosion resistance.

2. Materials and methods

2.1. Sample preparation

CP Ti and Ti–5Ag (wt.%) alloy was prepared by arc-melting method with titanium wire (99.9%) and silver wire (99.9%) as raw materials. They were melted four times to ensure the homogeneity. The plate samples with the size of 10 mm × 10 mm × 1 mm were cut from the buttons by wire-cut electric discharge machine, mechanically polished step by step, with 400#, 1000# and 2000# silicon carbide papers, and then ultrasonically cleaned in acetone and alcohol for about 10 min. For thermal oxidation, samples were heat treated at 700 °C in air for 10 min. For thermal oxidation, samples were heat treated at 700 °C in air for 2 h, and then quenched into water. Fifteen specimens for each group were prepared for the following tests.

2.2. Surface analyses

Table identification was carried out by XRD using X’plo from Philips Panalytical. The surface morphology and the chemical composition were analyzed using SEM (Phillips, Quenta 200) and energy dispersive spectroscopy (EDS), respectively. The XPS data were taken on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at 284.80 eV.

2.3. Electrochemical behavior tests

For electrochemical impedance spectrum (EIS) measurements, a potentiostat (Solartron 1287A) combined with a frequency response analyzer (Solartron 1260) was used. The potentiostat (Solartron 1287A) was used alone in open circuit potential tests, cyclic voltammetric tests and potentiostatic tests. The cell used was conventional three-electrode configuration with a Pt electrode and a saturated calomel electrode (SCE) as the counter electrode and reference electrode, respectively. The test solution was Fuayama Mayer artificial saliva (NaCl 0.4 g/L; KCl 0.4 g/L; CaCl2 0.6004 g/L; NaH2PO4 · 2H2O 0.78 g/L; KSCN 0.300 g/L; Na2S · 9H2O 0.05% g/L; urea 1.000 g/L). The pH value of the test solutions was adjusted to 4.0 by adding lactic acid, the concentration of lactic acid used was no more than 0.02 wt. %.

In the corrosion potential tests, the specimens were submerged into the electrolyte without any imposed potential for 3 h. Cyclic voltammetric tests were started at a potential in the hydrogen evolution region (~1.0 V vs. SCE) by scanning at 50 mV/s towards more positive potentials up to 8.0 V (vs. SCE), then the scanning was reversed towards the initial potential. Different potentials (0 V and 2 V) were added on CP Ti and Ti–5Ag alloy with and without thermal oxidation treatment in the potentiostatic tests, the samples were aged for 15 min in the test.

Before the electrochemical impedance spectrum measurements (EIS), the specimens were immersed in artificial saliva solution for 3 h. Electrochemical impedance spectrum (EIS) measurements were performed by applying a sinusoidal potential perturbation of 10 mV at the open circuit potentials. The impedance spectra were measured with frequency sweep from 10 kHz to 10 mHz in logarithmic increment.

3. Results

3.1. Surface analyses

Table The X-ray diffraction patterns of CP Ti, Ti–5Ag alloy with and without thermal oxidation were shown in Fig. 1(a). Only α-Ti phase can be identified in CP Ti and Ti–5Ag alloy without thermal oxidation. Corresponding EDS results revealed that the concentration of Ag was about 4.67% in the α-Ti matrix, and the amount of Ag was not enough to form intermetallic compound, according to the Ti–Ag phase diagram. For Ti–5Ag alloy with thermal oxidation, two phases, α-Ti and TiO2 with rutile structure, were identified from the XRD pattern.

The XPS survey spectrum for Ti–5Ag alloy with thermal oxidation was shown in Fig. 1(b), with the inset showing enlarged view at about 460 eV. Apart from carbon, elements titanium and oxygen were detected and no peak from element silver was found. It was evident that the surface of thermal oxidized Ti–5Ag alloy mainly consisted of TiO2.

The surface and the cross-sectional morphologies of Ti–5Ag alloy with thermal oxidation were further observed using SEM, as shown in Fig. 2, with the surface morphology of Ti–5Ag alloy without thermal oxidation also be shown as reference. The surface morphology of CP Ti was similar to that of Ti–5Ag alloy so the picture was not shown here. Fig. 2(a) shows the typical...
mechanically polished surface morphology with tiny grooves of Ti–5Ag alloy without thermal oxidation. After thermal oxidation, the surface became flat, as shown in Fig. 2(b). The thickness of the thermal oxidation layer was evaluated to be about 5 μm, as indicated by Fig. 2(c). EDS results revealed that the Ag concentration of the Ti–5Ag alloy substrate beneath the oxide layer was 5.02 wt.%.

3.2. Electrochemical behavior

In corrosion potential tests, all experimental samples exhibited stable corrosion potentials after short time immersion. After 3h immersion, stable potential values, −203 mV, −186 mV and −157 mV, were reached for CP Ti, Ti–5Ag alloy without and with thermal oxidation, respectively. Both Ti–5Ag alloy without and with thermal oxidation exhibited nobler potential than that of CP Ti, suggesting their less corrosion susceptibility.

Fig. 3 compares the cyclic voltammetric curves of CP Ti, Ti–5Ag alloys without and with thermal oxidation treatment

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**Fig. 1** – XRD patterns of different alloys (a) and XPS survey spectrum obtained from Ti–5Ag alloy with thermal oxidation (b).

**Fig. 2** – SEM micrographs showing the surface morphologies of Ti–5Ag alloy without thermal oxidation (a), Ti–5Ag alloy with thermal oxidation (b) and the cross-sectional morphology of Ti–5Ag alloy with thermal oxidation (c).
in artificial saliva solution. For CP Ti and Ti-5Ag alloy without thermal oxidation, the cyclic voltammetric curves were characteristic of the formation and growth of the passive film on the sample’s surface. The shape of the voltammetric charging curves strongly revealed valve–metal behavior of all experimental samples, with anodic formation of barrier-type oxide films. The current densities firstly increased sharply at about 500 mV, indicating the thickening of oxide film. In the inverse scan, the current density rapidly decreased, suggesting that stable passive films had been formed at the surface of CP Ti and the Ti–5Ag alloy without thermal oxidation. For Ti–5Ag alloy with thermal oxidation, the cyclic voltammetric curve exhibited low current densities in the positive scan. In the reversed scan, the curve reversed with almost the same path.

Fig. 4 illustrates the potentiostatic curves of CP Ti, Ti–5Ag alloy without thermal oxidation and Ti–5Ag alloy with thermal oxidation at different potentials: (a) 0 V and (b) 2 V.

The EIS profiles obtained from CP Ti and Ti–5Ag alloy without thermal oxidation possessed much lower current densities after 15 min immersion, compared to CP Ti. The current density could be further depressed by thermal oxidation.

After potentiostatic tests, the surface of experimental alloys were observed by SEM. Compared with the samples before tests, the samples after tests exhibited no visible difference, so the results were not given here.

The impedance spectra for CP Ti, Ti–5Ag alloy without and with thermal oxidation treatment at E_{corr} in artificial saliva solution were represented as Bode plots, as shown in Fig. 5. The EIS profiles obtained from CP Ti and Ti–5Ag alloy without thermal oxidation were quite similar. Their Bode-magnitude plots could be characterized by two distinct regions. In the high frequency range (100–10,000 Hz), straight horizontal line was shown. In the broad low and middle frequency range (0.01–100 Hz), the spectrum displayed a linear slope of about −1. For the Bode-phase angle plots of CP Ti and Ti–5Ag alloy without thermal oxidation, the phase angle observed at high frequency for was nearly −10°. However, at intermediate frequency, the phase angle decrease to −75° and remained constant over a wide range of frequency.

For Ti–5Ag alloy with thermal oxidation, the impedance spectra exhibited two distinct capacitive behaviors, indicating the presence of two time constants. High impedance values can be observed in the low frequency (near 0.01 Hz), suggesting the superior corrosion resistance. In coincidence, a two distinct capacitive behavior could be observed in the Bode-phase angle plot.

4. Discussion

4.1. Effect of Ag addition

It was evident in this study that addition of Ag was effective in increasing the corrosion resistance of Ti, as reflected by the increase in corrosion potential and impedance values, and the decrease in current densities (at potentials below 5 V vs. SCE). The increased corrosion resistance was expected for the addition of Ag, which is a nobler element than the element Ti. The presence of 5 wt.% Ag (standard
reduction potential, $E_{\text{Ag}}^{0} = 0.799 \text{ V vs. SCE}$) was proved to be enough to raise the corrosion potential of the Ti–Ag system. On the other hand, because of the high corrosion resistance of Ag, in the process of corrosion, Ag atoms may accumulate on the surface of the Ti–Ag alloy because of the loss of Ti. A higher Ag content further increased the electrode potential of the Ti–Ag alloy. Moreover, it was consumed that [4] silver enhances the oxygen anion uptake in the oxide layer, thus consuming oxygen anion vacancies. This vacancy deficit may result in a reduced current density.

The rutile type TiO$_2$ formed on the surface of CP Ti during thermal oxidation at 700 °C [12]. The surface film formed on Ti–5Ag alloy with thermal oxidation exhibited similar structure, with no Ag or Ag compounds being found on the surface as identified by the present XPS and XRD results, indicating that the 5 wt.% Ag addition does not change the structure of surface film formed on Ti–5Ag alloy.

To verify the feasibility of new titanium alloys to be applied as dental materials, it is usual to analyze their corrosion resistance in hard and general conditions, usually up to very high potentials. In the cyclic voltammetric tests, typical valve–metal behavior was shown in Fig. 4 for CP Ti and Ti–5Ag alloy without thermal oxidation. The increase of current densities at about 1000 mV might be due to the evolution reactions, such as oxygen (O$_2$) evolution which was thermodynamically possible at potentials >580 mV (vs. SCE) [14]. Similar valve–metal behavior had been obtained from pure Ti, Ti–Mo...
and Ti–13Nb–13Zr alloys in different biological solutions, and no pitting corrosion was observed [14].

4.2. Effect of thermal oxidation

It was obvious that the thickness of the surface film formed on Ti–5Ag alloy could be greatly improved by thermal oxidation. The present XRD and XPS results indicated that the surface film of Ti–5Ag alloy with thermal oxidation was mainly composed by TiO2. However, The EIS behavior of the Ti–5Ag alloy with thermal oxidation was different in nature compared to CP Ti and Ti–5Ag alloy without thermal oxidation, and it exhibited a two time constant system suggesting the formation of two layers.

In this study, the EIS profiles strongly indicated a near capacitive response for CP Ti and Ti–5Ag alloy without thermal oxidation. The model $R_0(R_1;Q_1)$ was used to fit the EIS data of CP Ti and Ti–5Ag alloy without thermal oxidation and the model $R_0(Q_1(R_1;R_2;Q_2))$ was used to fit the EIS data of Ti–5Ag alloy with thermal oxidation. $R_0$ corresponded to the resistance of the solution. $R_1$ or $R_2$ was the resistance of the layer, and $Q_1$ or $Q_2$ represented the capacitance or Warburg impedance of the layer. The model $R_0(Q_1;R_1)$ was used to fit the EIS data in the case of single passive film presented on the metal surface, as shown in Fig. 5(c). The model $R_0(Q_1(R_1;R_2;Q_2))$, as shown in Fig. 5(d), assuming that the oxide film formed on the surface of the alloy consisted of two layers. The fitted results of the analysis were presented in Table 1. The good agreement between the experimental data and fitted data could be obtained with the $x^2$ of about $10^{-4}$. High impedance values ($>3 \times 10^5 \Omega \text{cm}^2$) were obtained for all alloys, suggesting the high corrosion resistance.

Comparing with Ti–5Ag alloy without thermal oxidation, Ti–5Ag alloy with thermal oxidation exhibited better electrochemical parameters, such as higher corrosion potentials, lower current densities and larger impedance values. Obviously, the presence of thick oxide layer protected the alloy against the attack of the electrolyte. Of the same effect, Ti–5Ag alloy with thermal oxidation may not be easily affected by other factors such as applying potentials which were often achieved in biomaterials practical applications.

5. Conclusions

1. Adding 5 wt.% Ag did not change the phase constitution of titanium. A dense surface film can be obtained by aging at 700 °C for 2 h. The film was mainly composed of TiO2 with rutile structure.
2. Compared to CP Ti, Ti–5Ag alloy without thermal oxidation exhibited higher open circuit potential and larger impedance value. Moreover, the current densities were smaller at potentials below 5 V (vs. SCE). These suggested a nobler electrochemical corrosion behavior for Ti–5Ag alloy.
3. All experimental samples exhibit high impedance values in artificial saliva solution. The EIS results indicated the presence of a single passive layer for CP Ti and Ti–5Ag alloy without thermal oxidation. Ti–5Ag alloy with thermal oxidation in artificial saliva solution exhibited the presence of two time constants.
4. Compared to Ti–5Ag alloy without thermal oxidation, Ti–5Ag alloy with thermal oxidation exhibited thicker surface film, lower current densities and larger impedance values. Thermal oxidation was an effective way to improve the corrosion resistance of the surface film formed on Ti–5Ag alloy.

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References


Table 1 – Impedance parameters for CP Ti, Ti–5Ag alloy without and with thermal oxidation treatment.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$R_0$ (Ω cm$^2$)</th>
<th>$Q_1$ (Ω$^{-1}$ s$^{0.5}$ cm$^{-2}$)</th>
<th>$R_1$ (Ω cm$^2$)</th>
<th>$Q_2$ (Ω$^{-1}$ s$^{0.5}$ cm$^{-2}$)</th>
<th>$R_2$ (Ω cm$^2$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Ti</td>
<td>290</td>
<td>4.02E–6</td>
<td>0.83</td>
<td>3.11E5</td>
<td></td>
<td>1.7E–4</td>
</tr>
<tr>
<td>Ti–5Ag alloy without</td>
<td>281</td>
<td>3.85E–6</td>
<td>0.83</td>
<td>3.20E5</td>
<td></td>
<td>1.1E–4</td>
</tr>
<tr>
<td>thermal oxidation</td>
<td></td>
<td></td>
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<tr>
<td>Ti–5Ag alloy with</td>
<td>394</td>
<td>1.70E–6</td>
<td>0.81</td>
<td>3.70E4</td>
<td>2.30E–5</td>
<td>6.4E–4</td>
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<tr>
<td>thermal oxidation</td>
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