Effect of Sn addition on the corrosion behavior of Ti-Ta alloy

B. Guo, Y. X. Tong, F. Chen, Y. F. Zheng*, L. Li and C. Y. Chung

In the present paper, the effect of Sn addition on phase constitution and corrosion behavior of Ti$_{65}$Ta$_{35-	ext{x}}$Sn$_x$ ($x = 0, 1, 3, 5$ at%) alloys has been investigated using X-ray diffraction and electrochemical measurements. The results show that the β phase is stabilized when quenching after the addition of Sn into Ti$_{65}$Ta$_{35}$ alloy, with Ti$_{65}$Ta$_{30}$Sn$_5$ alloy consisting of single β phase at room temperature. The corrosion resistance is enhanced with increase in the Sn content. When the Sn content increases up to 5%, the addition of Sn results in a decrease of corrosion current density from 0.690 μA/cm$^2$ of the Ti$_{65}$Ta$_{35}$ alloy to 0.098 μA/cm$^2$, and corresponding passive current density decreased from 37.7 μA/cm$^2$ of the Ti$_{65}$Ta$_{35}$ alloy to 9.30 μA/cm$^2$.

1 Introduction

Recently, Ti-Ta binary alloys have attracted great interest due to a good combination of high strength and low modulus, as well as its potential as shape memory alloys, indicating potential application for implant materials [1, 2]. It was shown that Ti-70Ta (mass%) alloy with metastable β phase had a good combination of high strength (600 MPa) and low modulus (67 GPa), which is beneficial for avoiding “stress shielding” problem [1, 3]. The martensitic transformation start temperature ($M_s$) decreased by 30 K per 1 at% Ta in Ti-Ta alloys with a Ta content ranging from 30 to 40 in at%, while the shape memory effect was confirmed in these Ti-Ta alloys by using thermal cycling test under a constant stress [2].

The addition of alloying elements has been proved to be an effective method to adjust the properties of Ti-Ta binary alloy. Phase constitution, aging behavior, and shape memory behavior of Ti-Ta-$X$($X$= Zr, Hf, Mo, Sn) ternary alloys have been systematically investigated [4–6]. The additions of Zr, Hf, Mo, and Sn elements decreased the martensitic transformation temperature of Ti$_{70}$Ta$_{30}$ (at%) alloy. Among the elements, the Sn element seems to be more attractive, since the addition of Sn suppressed the effect of aging on shape memory behavior due to its strongly suppressing effect in α' phase formation [4].

Besides being the alloying element to adjust the transformation temperature and shape memory behavior, the Sn element also plays an important role in changing the corrosion behavior of biomedical alloys due to its biocompatibility. From a biomedical application point of view, the excellent corrosion resistance of metallic biomaterials in the body fluids is a crucial prerequisite [7]. However, up to now, the effect of Sn element on corrosion properties of binary Ti-Ta alloys has not been systematically investigated. The aim of the present study is to investigate the effect of Sn addition on phase constitution and electrochemical corrosion behavior of Ti-Ta-based alloy in 0.9% NaCl solution.

2 Materials and methods

Ti$_{65}$Ta$_{35-	ext{x}}$Sn$_x$ ($x = 0, 1, 3, 5$ at%) samples were prepared using an arc melting furnace with water-cooled copper crucible under a high purity argon atmosphere from Ti wire (99.8%), Ta wire (99.9%), and Sn sheet (99.9%) as raw materials. The ingots were melted for 10 times, and flipped over after each melting to achieve chemical homogeneity. The button shaped ingots were hot rolled into around 1 mm thick plate at 900 °C by a thickness reduction of 90%, then solution-treated at 900 °C for 3.6 ks and quenched in water.

Phase constitution at room temperature was determined by X-ray diffraction (XRD) analysis using Cu Kα radiation in the typical range of 2θ = 10° to 100° at an accelerating voltage of 40 kV and a current of 40 mA.

The samples prepared for electrochemical measurements were cut from the solution treated samples with an area of 1 cm$^2$. After mechanically polishing with water-proof silicon carbide paper up to 2000# grid, all the samples were cleaned with acetone, ethanol, and de-ionized water in turn in an ultrasonic bath and then dried in heat flow air. The electrochemical measurements were performed using an electrochemical analyzer CHI 660C. The sample, a platinum electrode, and a saturated calomel electrode (SCE) were used as working electrode, counter
electrode, and reference electrode, respectively. The simulated physiological electrolyte was 0.9% NaCl solution prepared from the analytical reagent and de-ionized water. The experiments in 0.9% NaCl solution were carried out at 25 °C and neutral pH range (of about 6.8).

The open circuit potential (OCP) measurements were maintained up to 3.6 ks in 0.9% NaCl solution. The dynamic polarization curves were conducted from −0.5 V (vs. SCE) to 1.5 V (vs. SCE) with a scan rate of 1 mV/s after 3.6 ks immersion. The corrosion behavior for the passive film formed on the surface of the alloys after 3.6 ks immersion was studied by using electrochemical impedance spectroscopy (EIS) technique. The impedance spectrum was acquired in the frequency range of 10⁴ to 10⁻² Hz with a 10 mV amplitude sine wave. To obtain quantitative information, appropriate model (Zview version) for equivalent circuit quantification was used.

3 Results and discussion

The XRD patterns of Ti₆₅Ta₃₅−ₓSnₓ (x = 0, 1, 3, 5 at%) samples are shown in Fig. 1(a). It can be seen that Ti₆₅Ta₃₅ binary alloy exhibits a mixture of β phase with a body-centered cubic (b.c.c) structure and α’’ martensite phase with an orthorhombic structure. It is noticed that the diffraction peak corresponding to α’’ martensite gradually becomes weak and finally disappears with the Sn content increasing from 1 to 5%. When Sn content reaches up to 5%, Ti₆₅Ta₃₀Sn₅ consists of only β phase at room temperature. This indicates that the β phase is stabilized when quenching by the addition of Sn in Ti₆₅Ta₃₅ alloy. In another word, the addition of Sn may decrease the transformation temperature of β phase to α’’ martensite, which is consistent with the report for the effect of ternary alloying elements on Ti₇₀Ta₃₀ (at%) alloy [4]. Figure 1(b) shows the dependence of lattice parameter of β phase on the Sn content. The lattice parameter increases obviously with increase in Sn content up to 3%, and remains almost constant with further increase up to 5%.

OCP values as a function of immersion time of the samples in 0.9% NaCl solution are shown in Fig. 2. It can be seen that in the initial immersion period, there are obvious fluctuation for the curves; after 3.6 ks immersion, the OCP values become stable for all the curves, indicating that protective passive oxide films have been formed on the surface of the samples.

The potential dynamic polarization measurements of the samples were carried out after immersion for 3.6 ks in 0.9% NaCl solution. The electrochemical parameters, such as corrosion potential (Ecorr) and corrosion current density (Icorr), can be estimated from the polarization curves by Tafel analysis using both cathodic and anodic branches of the polarization curves, as shown in Table 1. It is noted that in 0.9% NaCl solution, the Ecorr values of Ti₆₅Ta₃₅−ₓSnₓ (x = 0, 1, 3, 5 at%) are close to the OCP curves analyzing. The Icorr for Ti₆₅Ta₃₅ sample is 0.690 μA/cm², and it decreases with increase in the Sn content, reaching to 0.098 μA/cm² at the Sn content of 5%, demonstrating an increased corrosion resistance.

Figure 3 shows that in 0.9% NaCl solution, all the samples exhibit self-passivated characteristic, translating directly into the passive region from the Tafel region. The oxide films become stable at about 0.2 and 0.1 V for the Ti₆₅Ta₃₅ and Ti₆₅Ta₃₅−ₓSnₓ alloys.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Ecorr (V)</th>
<th>Icorr (μA/cm²)</th>
<th>Ipass (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₆₅Ta₃₅</td>
<td>-0.302</td>
<td>0.690</td>
<td>37.7</td>
</tr>
<tr>
<td>Ti₆₅Ta₃₅Sn₁</td>
<td>-0.303</td>
<td>0.138</td>
<td>10.6</td>
</tr>
<tr>
<td>Ti₆₅Ta₃₅Sn₃</td>
<td>-0.401</td>
<td>0.098</td>
<td>9.76</td>
</tr>
<tr>
<td>Ti₆₅Ta₃₀Sn₅</td>
<td>-0.375</td>
<td>0.098</td>
<td>9.30</td>
</tr>
</tbody>
</table>
(x = 1, 3, 5 at%), respectively. It is worth noting that there are broad and distinctive passivation regions for all these samples (up to 1.5 V), which means the passive films forming on the surface of samples are stable and protective, thus preventing corrosion. As shown in Fig. 3, the curves shift to left side with Sn content increasing in passivation regions, meaning decrease in passive current density. Passive current density ($I_{pass}$) as determined at initial passivated potential (as indicated by the arrows in Fig. 3) is about 36.4 μA/cm² for Ti65Ta35 binary alloy, and the alloying element additions of 1, 3, and 5% Sn into Ti65Ta35 alloy result in the lower $I_{pass}$ of 10.6, 9.76, and 9.30 μA/cm², respectively, which indicates the formation of more protective passive films with Sn addition. It has been reported that when an active–passive metal was exposed to a corrosive medium and the current density of the metal was lower than about 100 μA/cm², the metal would spontaneously passivate [8]. Therefore, the Ti-Ta-Sn alloys in the present study should easily be passivated in human body environment, as evidenced by the low corrosion current density and low passive current density, showing the promising potential for biomedical application.

To make clear the effect of Sn addition on the electrochemical behavior, EIS tests were performed. Figures 4(a) and (b) shows the experimental and the simulated EIS results for all the Ti65Ta35$_{1-x}$Sn$_x$ (x = 0, 1, 3, 5 at%) samples after 3.6 ks immersion in 0.9% NaCl solution, respectively. The Nyquist plots and Bode plots are characterized by similar behavior for all the samples. From Fig. 4(a), it is obvious that all the Nyquist plots in the impedance spectrum are characterized by two semicircles showing two relaxation time constants and the diameter of the semicircles become larger with the increase in Sn content, which indicates the electrochemical behavior become nobler [9, 10]. From the Bode-magnitude plots shown in Fig. 4(b), it can be seen that there are two distinct regions for the samples immersed 3.6 ks in 0.9% NaCl solution. In the high frequency range (100–10 kHz), a flat portion of curves (slope $\approx$ 0) is observed due to the response of electrolyte. In the low- and middle-frequency ranges, the impedance spectrum displays a linear slope of about $-1$, which is the characteristic response of a capacitive behavior of passive film [10, 11]. There are three characteristic regions for all the alloys in the Bode-phase plots in Fig. 4(b). In the high-frequency range, the phase angle drops to 0° with the response of electrolyte resistance; in the middle frequency, the phase angle is found to lie in the range of approximately $-65^\circ$ to $-75^\circ$ indicating a typical passive film presented on the surface and a near capacitive response for passive film; and in the low frequency range, the impedance spectrum displays a linear slope of about $-1$, which is the characteristic response of a capacitive behavior of passive film comparing with Ti65Ta35 binary alloy. Higher impedance and phase angle lead to a nobler electrochemical behavior. The evidence presented in Fig. 4 confirms that the addition of Sn is helpful to increase the resistance of the passive film of Ti65Ta35 binary alloy in 0.9% NaCl solution. There are two peaks in each of the Bode-phase plots, demonstrating the formation of bi-layered oxide film for each of these alloys in 0.9% NaCl solution.
Table 2. Values of fitting parameters obtained using the $R_s(Q_0(R_0Q_b))$ model to fit the experimental electrochemical impedance spectra (EIS) data for the Ti-Ta-based alloys after immersion for 3.6 ks in 0.9% NaCl solution

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ti65Ta35</th>
<th>Ti65Ta34Sn1</th>
<th>Ti65Ta32Sn3</th>
<th>Ti65Ta30Sn5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$ (Ω/cm$^2$)</td>
<td>24.2</td>
<td>24.5</td>
<td>24.1</td>
<td>24.9</td>
</tr>
<tr>
<td>$Q_0$ ($µF/cm^2$)</td>
<td>88.9</td>
<td>83.3</td>
<td>68.2</td>
<td>74.5</td>
</tr>
<tr>
<td>$n_0$</td>
<td>0.88</td>
<td>0.80</td>
<td>0.86</td>
<td>0.90</td>
</tr>
<tr>
<td>$R_0$ ($10^5$ Ω cm$^2$)</td>
<td>0.067</td>
<td>0.208</td>
<td>0.348</td>
<td>0.352</td>
</tr>
<tr>
<td>$Q_b$ ($µF/cm^2$)</td>
<td>450</td>
<td>58.8</td>
<td>56.4</td>
<td>54.0</td>
</tr>
<tr>
<td>$n_b$</td>
<td>0.62</td>
<td>0.80</td>
<td>0.80</td>
<td>0.68</td>
</tr>
<tr>
<td>$R_b$ ($10^5$ Ω cm$^2$)</td>
<td>0.046</td>
<td>1.98</td>
<td>2.07</td>
<td>6.09</td>
</tr>
<tr>
<td>$\chi^2$ ($10^{-4}$)</td>
<td>2.98</td>
<td>7.25</td>
<td>5.06</td>
<td>3.03</td>
</tr>
</tbody>
</table>

In order to quantify the experimental EIS results, equivalent circuit analysis has been carried out. The impedance parameters supply quantitative support for the discussion of EIS results and were obtained by Zview software by adopting a well known equivalent circuit $R_s(Q_0(R_0Q_b))$ as shown in Fig. 4(c). The fitting quality was evaluated by chi-squared ($\chi^2$) values of about $10^{-4}$, which were interpreted by ZView software and are shown in Table 2. The agreement between experimental and simulated results indicates that the experimental results are well fitted to the proposed equivalent circuit.

The physical significance of the elements in $R_s(Q_0(R_0Q_b))$ model with two time constants has been intensively reported in the literature [10, 12–13]. The proposed model assumes that a bi-layered oxide consisting of a porous outer layer and a barrier inner layer formed on the surface of these four kinds of experimental Ti-Ta-based alloys. In this model, $R_s$ corresponds to the resistance of the electrolyte (0.9% NaCl solution). $R_0$ and $R_b$ are the resistances of the porous and barrier layer. $Q_0$ and $Q_b$ are defined as capacitances of the porous and barrier layer, respectively.

All impedance parameter values are shown in Table 2. It can be seen that the values of $R_s$ do not change notably for all the experimental. The inner layer exhibits much higher resistance ($R_b$) compared to the outer layer ($R_0$) for Ti65Ta35Sn$_x$ ($x = 1, 3, 5$ at%) alloys. This result suggests that the corrosion protection is dominated by the inner layer. With the addition of Sn, the inner barrier layer capacitance $Q_b$ has significantly decreased (of about 7 to 8 times) and its resistance $R_b$ has increased significantly (of about 40 to 130 times) compared to Ti65Ta35 binary alloy. This indicates that the thickness and the oxide density of the inner barrier layers have increased with Sn content increasing, resulting in corrosion resistance improvement. It is reported that the porous outer layer may be responsible for the osseointegration between implant and human bone [12].

Zhou’s investigation confirmed the corrosion resistance of Ti60Ta70 (mass%) alloy with $\beta$ phase and unrecrystallized structure in 5% HCl solution was better than that of pure Ti and Ti-6Al-4V alloy used as standard biomaterials [14]. Marecz’s results further confirmed that the corrosion resistance of Ti60Ta40 (mass%) alloy with $\beta$ phase and small fraction of $\alpha$ phase was better than that of Ti-6Al-7Nb alloy in artificial saliva, showing the promising potentials for dental applications [15]. In the present study, the association of values of $I_{corr}$, $I_{pass}$, and the impedance parameters permit us to conclude that the substitution of Sn for Ta improves the corrosion resistance of Ti65Ta35 alloy in 0.9% NaCl solution. Several factors can be related to the corrosion performance of the Ti-Ta-based alloys, including composition, environment, and microstructure. The single $\beta$ titanium alloys generally exhibit superior corrosion resistance in comparison to $\alpha^\prime$ + $\beta$ alloys, attributed to the even distribution of the alloying elements in the phase of $\beta$ titanium alloys [16]. In the present work, the substitution of Sn for Ta suppresses the formation of $\alpha''$ martensite when quenching, as shown in Fig. 1(a), leads to the improvement of corrosive resistance. Ti65Ta30Sn$_5$ alloy consisting of single $\beta$ phase without $\alpha''$ martensite exhibits the noblest corrosion resistance among all the samples. Whilst, the results in Table 2 and Fig. 3 show that $I_{corr}$ and $I_{pass}$ can be greatly reduced even for the samples containing little Sn element and consisting of a mixture of $\alpha''$ and $\beta$ phases.

4 Conclusions

(i) The substitution of Sn for Ta causes the stabilization of $\beta$ phase in Ti65Ta35 alloy. When the Sn content is 5%, Ti65Ta30Sn$_5$ alloy consists of only $\beta$ phase at room temperature. With the increase of Sn up to 5%, the lattice parameter of $\beta$ phase increases.

(ii) All the experimental alloys passivated spontaneously when immersed in 0.9% NaCl solution. The substitution of Sn for Ta improves the electrochemical corrosion resistance of Ti65Ta35 alloy in 0.9% NaCl solution. The $I_{corr}$ decreases from 0.690 to 0.098 $mA/cm^2$ with Sn content increasing up to 5%, reaching for Ti65Ta30Sn$_5$ alloy. The $I_{pass}$ decreases from 37.7 to 9.30 $mA/cm^2$ with Sn content increasing up to 5%.

(iii) The EIS results demonstrate that the resistance of the passive film increases with the addition of Sn content, and a bi-layered oxide formed on the surface of the samples. The corrosion resistance improvement might result from the effect of the $\beta$ phase stability increase with Sn addition.

Acknowledgements: This work was supported by the Outstanding Youth Funding of Heilongjiang Province (JC200608) and the fundamental Research Funds for the Central Universities (HEUCFZ 1017).

5 References


(Received: June 11, 2010) W5824
(Accepted: July 6, 2010)