Microstructures and Electrochemical Behavior of Ti-Mo Alloys for Biomaterials

Back-Sub Sung, Tae-Eon Park, and Young-Hoon Yun

1Department of Mechanical Engineering, Chosun University, Gwangju 501-759, Republic of Korea
2Ecotech Korea Co. Ltd., Jeonnam Advanced Ceramics Center, Jeonnam 530-370, Republic of Korea
3Department of Hydrogen & Fuel Cell Technology, Dongshin University, Jeonnam 520-714, Republic of Korea

Correspondence should be addressed to Young-Hoon Yun; yunemail@naver.com

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1. Introduction

Both commercial-grade pure titanium (CP Ti) and the Ti-6Al-4V alloy have been widely used for orthopedic and dental implant materials because of their excellent combination of biocompatibility, corrosion resistance, and beneficial mechanical properties [1, 2]. However, an alternative to the Ti-6Al-4V alloy that is currently being utilized should be developed because the release of Al and V ions into the human body causes long-term health problems [3–5]. Another disadvantage of this material is the mismatch of Young’s modulus between the Ti implant (100–120 GPa) and bone (10–30 GPa), which is unfavorable for bone healing and remodeling [6, 7]. To address these problems and further improve the biological and mechanical properties of Ti alloys, many Ti alloys have been developed for biomedical applications [6–8]. These efforts have focused on the development of novel titanium alloys using nontoxic elements. For this purpose, β-type titanium alloys composed of nontoxic elements, such as niobium (Nb), tantalum (Ta), zirconium (Zr), molybdenum (Mo), and tin (Sn), with lower moduli of elasticity and greater strengths should be developed [7–10]. In recent studies, binary Ti alloys employed as biomaterials have been investigated, with emphasis on their microstructure and mechanical properties [10–13].

In the present study, the elastic modulus, corrosion behavior, electrochemical properties, and microstructures of homogenization-treated binary Ti-Mo alloys with Mo contents ranging from 3 to 15 wt% were investigated.

2. Experimental

The elastic modulus, corrosion resistance, and biocompatibility of binary Ti-Mo alloy specimens with Mo contents of 3, 7, 10, and 15 wt% were investigated. Ingots of the studied alloys, consisting of commercially pure sponge titanium (99.5%, grade 4) and pellet Mo (99.95%), were melted under an argon atmosphere using a nonconsumable tungsten electrode. These alloys were melted 10 times with inversion of the liquid metal to obtain homogeneous structures. This process was followed by homogenization treatments that were performed at 1000°C under an Ar atmosphere for 24 hrs and then quenched in water. The chemical compositions of the studied Ti-Mo alloys, as determined through wet chemical and gas analysis, are summarized in Table I; this
Figure 1: SEM micrographs showing the microstructures of the Ti-xMo alloys: (a) Ti-3Mo, (b) Ti-7Mo, (c) Ti-10Mo, and (d) Ti-15Mo.

Table 1: Chemical compositions of the studied Ti-Mo alloys.

<table>
<thead>
<tr>
<th>Alloy code</th>
<th>Mo (wt%)</th>
<th>O (wt%)</th>
<th>Ti (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-3Mo</td>
<td>2.9</td>
<td>0.064</td>
<td>Balance</td>
</tr>
<tr>
<td>Ti-7Mo</td>
<td>6.8</td>
<td>0.035</td>
<td>Balance</td>
</tr>
<tr>
<td>Ti-10Mo</td>
<td>9.9</td>
<td>0.048</td>
<td>Balance</td>
</tr>
<tr>
<td>Ti-15Mo</td>
<td>14.6</td>
<td>0.088</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table shows that the actual chemical composition of each designed alloy was similar to its nominal composition.

Young’s modulus were measured using a dynamic ultra-microhardness tester (DUHW 201S, Shimadzu Co., Japan). The apparent elastic modulus of each sample, $E^*$, was calculated using the load-displacement curve and the standard Hertzian contact theory [14]:

$$E^* = \left( \frac{9}{16} \right)^{1/2} Ph^{-3/2} R^{-1/2},$$  \hspace{1cm} (1)

where $h$ is the depth of elastic penetration of the indenter, $P$ is the load, and $R$ is the indenter radius. The true modulus of the sample, $E_s$, can be calculated from the apparent modulus by accounting for the elastic properties of the indenter.

The microstructural morphologies of the homogenization-treated Ti-Mo alloys were observed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). Crystal phases were identified using an X-ray diffractometer (X’Pert MPD PW3040, Philips, Netherlands).

Anodic polarization tests and an ion-release test in a simulated body fluid (SBF) were conducted. The electrodes for the anodic polarization tests were prepared via cold mounting with epoxy resin followed by mechanical polishing with emery paper of up to 2000 grit. The SBF solution, which was composed of NaCl (8 g), KCl (0.22 g), K$_2$HPO$_4$·12H$_2$O (0.15 g), NaSO$_4$ (0.08 g), NaHCO$_3$ (0.35 g), and CaCl$_2$ (0.27 g), was used as an electrolyte solution at a pH of 7.4 and a temperature of 37$^\circ$C. Potentiodynamic polarization scans were performed at a scan rate of 1 mV/s in the range from $-1500$ to $1500$ mV/SCE. Immersion tests to assess the metal-ion release were conducted in the SBF solution (pH 7.4) and in 0.1% lactic acid (pH 3.4) at 37$^\circ$C. Each solution was collected every 5 days for 30 days. The concentrations (average values of three times) of metal ions that were released into the solutions were analyzed up to 10 ppb (0.01 $\mu$g/mL) via inductively coupled plasma-mass spectrometry (ICP-MS, JY 70Plus, Longjumeau, France).

In order to evaluate cytocompatibility of the alloys, MC3T3-E1 cells (RCB 1126, an osteoblast-like cell line from C57BL/6 mouse calvaria) were cultured on Ti-Mo alloy plates in DMEM-HG and in 5% CO$_2$ at 37$^\circ$C with a cell seeding density $1.5 \times 10^4$ cells/well. The cell viability was measured with a 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide (MTT) assay and was carried out after 1 and 3 days of culturing using an ELISA plate reader (precision microplate reader, Molecular Devices, Sunnyvale, CA, USA).

3. Results and Discussion

3.1. Microstructures and Elastic Modulus of Ti-Mo Alloys

Figure 1 shows the microstructures of the Ti alloys with 3, 7, 10, and 15 wt% Mo after heat treatment for homogenization. The specimens of the Ti-Mo alloys with 3 and 7 wt% Mo exhibited a fine acicular, martensitic structure of the $\alpha''$
phase in their surface microstructures [11]. When the Mo content increased, the fine acicular patterns in the Ti-Mo alloys disappeared. These results confirmed that the Mo content influences the formation of the martensitic phase and effectively suppresses grain-growth behavior [13, 14].

Figure 2 presents the elastic modulus of the homogenization-treated Ti-Mo alloys with respect to the varying Mo contents. The elastic modulus of the Ti-Mo alloys decreased with the addition of Mo, although the actual value of the modulus fluctuated with different Mo contents. The elastic modulus decreased as the Mo content increased up to 7 wt% but then increased as the Mo content was further increased to 15 wt%. It is interesting to note that the elastic modulus of Ti-7Mo was very low (i.e., approximately 55 GPa); this result is in good agreement with that of Ho et al. [15].

Figure 3 shows the X-ray diffraction patterns of the Ti-Mo alloys. When a Mo content of 3 wt% was added, the homogenized alloy exhibited peaks corresponding to the hexagonal α' and orthorhombic α'' phases. It was found that, in certain alloys (i.e., Ti-Mo, Ti-Nb, Ti-Ta, etc.), the hexagonal α' phase distorts and transforms into an orthorhombic α'' phase [16]. The Ti-7 wt% Mo showed just the martensitic α'' phase. When the Mo content increased to 10 wt% or higher, only the β phase was observed in the XRD patterns. The retention of the β phase at higher Mo contents is consistent with the results of Ho et al. [15].

3.2. Corrosion Resistance of Ti-Mo Alloys. Figure 4 presents the potentiodynamic polarization curves for the Ti-Mo alloys compared with CP Ti as tested in the SBF solution at 37°C. Some shift in the corrosion potential (Ecorr) and a remarkable reduction in the corrosion current densities (Icorr) are evident, which indicate enhanced corrosion resistance. The differences in corrosion potential among the alloys may be attributable to tiny differences in surface conditions [17], despite the fact that the specimens were prepared using the same procedure. The corrosion potentials (Ecorr), corrosion current densities (Icorr), and passive current densities (Ipass) for the alloys, as obtained from their polarization curves, are summarized in Table 2. The corrosion densities (Icorr) were obtained from the polarization curves using the Tafel extrapolation method and ranged from 0.358 to 0.524 μA/cm² for the Ti-Mo alloys. The passive current densities (Ipass) were in the range of 1.78–2.22 μA/cm² for the Ti-Mo alloys, compared with a value of 3.77 μA/cm² for the CP Ti. These results suggest that a protective passive film was formed for the Ti-Mo alloys. The potentiodynamic polarization curve of the Ti-7 wt% Mo exhibited stable passivation behavior throughout the entire range of potentials. These results indicate that the addition of Mo to pure Ti does not appear to modify the protection characteristics of its spontaneous oxides [18].

3.3. Electrochemical Impedance Spectroscopy (EIS) of Ti-Mo Alloys. Electrochemical impedance analysis between 10 mHz and 10⁵ Hz with an amplitude of 10 mV at an applied potential was performed for the surfaces of the Ti-Mo alloy during immersion to investigate the electrode/electrolyte interfaces and the processes that occur on these surfaces.

![Figure 2: Elastic moduli of the Ti-xMo alloys.](image)

![Figure 3: XRD patterns of the Ti-xMo alloys.](image)

**Table 2**: Corrosion potentials (Ecorr), corrosion current densities (Icorr), and passivation current densities (Ipass) determined from the polarization curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ecorr (mV/SCE)</th>
<th>Icorr (μA/cm²)</th>
<th>Ipass (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Ti</td>
<td>−320</td>
<td>1.775</td>
<td>3.77</td>
</tr>
<tr>
<td>Ti-3Mo</td>
<td>−460</td>
<td>0.524</td>
<td>1.78</td>
</tr>
<tr>
<td>Ti-7Mo</td>
<td>−400</td>
<td>0.503</td>
<td>1.88</td>
</tr>
<tr>
<td>Ti-10Mo</td>
<td>−380</td>
<td>0.385</td>
<td>2.18</td>
</tr>
<tr>
<td>Ti-15Mo</td>
<td>−390</td>
<td>0.358</td>
<td>2.22</td>
</tr>
</tbody>
</table>
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4.3. Metal-Ion Release of Ti-Mo Alloys. Table 4 presents the concentrations of metal ions released into the SBF solution and the 0.1% lactic acid over a period of 30 days. In the SBF solution, the elution of Ti and Mo ions was below the detection limit of 0.01 μg/mL, regardless of the alloy composition. By contrast, in the 0.1% lactic acid, Ti-ion release was detected in the range from 0.04 to 0.11 μg/mL, depending on the Mo content of the alloy. Moreover, the Ti-ion release from the Ti-7 wt% Mo alloy was slightly lower than that of conventional Ti-Mo alloys. This result indicates that the corrosion resistance of the Ti alloy with 7 wt% Mo was slightly better than the corrosion resistance of conventional Ti-Mo alloys, consistent with the results of the electrochemical tests.

3.5. Biocompatibility of Ti-Mo Alloys. The MTT assay was used to determine mitochondrial activity of the cultured osteoblasts on the surface of CP Ti and Ti-Mo alloys. Figure 7(a) shows the proliferation behavior in MC3T3-E1 cell adhesion after 1 day and 3 days during cell culturing. A sharp difference in the viability of MC3T3-E1 cells was scarcely found in all samples. It seems that the initial cell attachment was not affected by the alloy chemistry. After 3 days, proliferation in cell adhesion slightly increased compared to that of 1 day. Figure 7(b) shows the absorbance obtained from cells adhered to the surface at 3 days. The proliferation and absorbance of the cell showed rather high values for Ti-7 wt% Mo alloy.

4. Conclusion

The elastic modulus, electrochemical properties, and microstructures of homogenization-treated binary Ti-Mo alloys with Mo contents ranging from 3 to 15 wt% were investigated. The elastic modulus decreased when the Mo content increased up to 7% and then increased as the...
Table 4: Concentrations of metal ions released into two different solutions after various durations at 37°C.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Days</th>
<th>Ti-3Mo</th>
<th>Ti-7Mo</th>
<th>Ti-10Mo</th>
<th>Ti-15Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBF solution</td>
<td>10–30</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.11</td>
<td>0.01</td>
<td>0.08</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>0.07</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>0.1% lactic acid</td>
<td>20</td>
<td>0.05</td>
<td>&lt;0.01</td>
<td>0.06</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>0.04</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>

Mo content was further increased to 15%. Microstructure morphology of the Ti-7 wt% Mo alloy showed only a fine acicular martensitic structure of the orthorhombic ($\alpha''$) phase. An EIS data analysis confirmed that the polarization resistance of the Ti-Mo alloys increased as the Mo content was increased. The corrosion resistance of the Ti-Mo alloys increased with increasing Mo content. The Ti-7Mo alloy exhibited a relatively low elastic modulus and low metal-ion release. Near-capacitive behavior of the passive films was observed in the electrochemical impedance analysis, which reflected the corrosion resistance of the Ti-Mo alloys. MC3T3-E1 cell proliferation on Ti-7 wt% Mo was rather
active than other Ti-Mo alloys and CP Ti. The low elastic modulus and good biocompatibility suggest that Ti-7Mo alloy is promising metallic biomaterials.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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**References**


