Effect of tungsten dissolution on the mechanical properties of Ti–W composites

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Abstract

Blends of 90 wt.% Ti and 10 wt.% W powders were consolidated by powder metallurgy, using an initial W powder size that was very fine (0.7 and 2 $\mu$m) or very coarse (<250 $\mu$m). Dissolution of W powders in the Ti matrix during consolidation was almost complete for the former blends (thus forming Ti–10W "alloys") but very limited for the latter blend (thus forming a Ti–10W "composite"). The Ti–10W alloys exhibit much higher yield and tensile strengths than the Ti–10W composite, indicating that tungsten strengthens titanium more efficiently as a solute atom (solid-solution strengthening) than as a second phase (composite strengthening by load transfer). The Ti–10W alloys also exhibit much higher ductility than the Ti–10W composite, whose brittle W particles exhibit fracture or pull-out from the matrix.

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1. Introduction

Titanium and its alloys, originally developed as aeronautical materials, are used as bone-replacement implants due to their bio-compatibility, low density, static and fatigue strength, corrosion resistance, and lack of magnetism (important for magnetic resonance imaging after implantation)\cite{1,2}. Another critical requirement for implants is wear resistance, as wear debris can cause severe inflammatory responses in surrounding tissue\cite{1,2}. However, the wear resistance and strength of commercially pure titanium (CP-Ti) is relatively poor, which makes it insufficient for highly stressed bone implants or wear-prone prostheses\cite{3}. A solution to both strength and wear-resistance limitations is to add a hard ceramic reinforcement that is thermodynamically stable with the matrix, e.g. titanium carbide or boride. The resulting metal matrix composites however exhibit low ductility and toughness\cite{4}. Recently, it has been shown that tungsten particles can be added to a titanium matrix, resulting in a Ti–W composites with outstanding strength and hardness (which generally scales with wear-resistance), and only a minor ductility penalty\cite{5}. Moreover, tungsten is non-magnetic and, in solid solution, is known to decrease the elastic modulus of titanium\cite{5}, which helps alleviate stress-shielding arising from differences in compliance between the implant and the host tissue\cite{1}. Unlike ceramic reinforcement, tungsten has unlimited solubility in titanium at the composite densification temperature. For short processing times when partial dissolution of the W particles occurs, the composite then consists of a Ti–W matrix containing partially dissolved W particles, as shown in a previous study\cite{5}. In that study, however, the relative importance of solid-solution strengthening and composite strengthening was not investigated.

Here, we present a study of the microstructure and mechanical properties for a series of Ti–10 wt.% W alloys produced by powder metallurgy using W powders with size varying over a wide range. This allows to vary the degree of W dissolution from small to nearly complete, and to probe the relative importance of solid-solution strengthening and composite strengthening for tungsten in titanium.
2. Materials and methods

Three Ti–10 wt.% W blends were mixed using different W powder sizes. The W powder sizes spanned two orders of magnitude: 0.72 μm (for Alloy 1), 2 μm (for Alloy 2), and <250 μm (for Alloy 3), as summarized in Table 1.

Processing was by the combined cold and hot isostatic pressing (CHIP) technology [6] as follows. A blend of Ti powders (<150 μm) and W powders were compacted into green billets by cold-isostatic pressing at a pressure of 379 MPa. The billets were then vacuum-sintered at 1230 °C for 4 h and densified by hot-isostatic pressing (HIP) at 900 °C for 2 h at 100 MPa [5], followed by slow cooling within the press. Billet density was, within experimental error, equal to the theoretical value of 4.9 g/cm³, indicating that complete densification had been achieved.

3. Results

The microstructure of the Ti–W alloys was evaluated by optical microscopy on cross-sections produced by grinding on SiC paper, polishing with diamond and alumina slurries, and etching with a modified Kroll’s reagent (5% nitric acid, 10% HF, and 85% water). Chemical composition profiles were achieved by energy-dispersive spectroscopy (EDS, Hitachi S-3500) with a spot size of 15 nm. Matrix micro-hardness was measured with a Vickers indenter using a 100–200 g load and an indent time of 10 s on epoxy-mounted cross-sections in matrix regions far from W particles.

Tensile tests were preformed at ambient temperature on one specimen of each alloy, machined to ASTM E-8 proportional standards with 36 mm gauge length and 6.4 mm gauge diameter. The cross-head speed was 12.7 mm/min, corresponding to an initial strain rate of 6.2 × 10⁻³ s⁻¹. The strain was measured with an extensometer with 25.4 mm gauge length. Fracture surfaces were examined in a scanning electron microscope (SEM).

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>W powder type</th>
<th>Average size of initial W powders (μm)</th>
<th>Size of W particles (μm) in compositea</th>
<th>Volume fraction of W particles in composite (%)</th>
<th>Extent of W powder dissolution in composite (%)</th>
<th>Matrix average W concentration in compositeb (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>FSSS 0.72</td>
<td>0.3</td>
<td>11 ± 8</td>
<td>0.006</td>
<td>99.8</td>
<td>9.98</td>
</tr>
<tr>
<td>2</td>
<td>FSSS 2.02</td>
<td>2</td>
<td>20 ± 8</td>
<td>0.07</td>
<td>97</td>
<td>9.74</td>
</tr>
<tr>
<td>3</td>
<td>40 mesh</td>
<td>&lt;250</td>
<td>119 ± 54</td>
<td>2.25</td>
<td>10</td>
<td>1.23</td>
</tr>
</tbody>
</table>

a Apparent size in metallographic sections with error given as standard deviation.

b Calculated from measured W particle volume fraction assuming an overall W content of 10 wt.%.

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Tensile tests were preformed at ambient temperature on one specimen of each alloy, machined to ASTM E-8 proportional standards with 36 mm gauge length and 6.4 mm gauge diameter. The cross-head speed was 12.7 mm/min, corresponding to an initial strain rate of 6.2 × 10⁻³ s⁻¹. The strain was measured with an extensometer with 25.4 mm gauge length. Fracture surfaces were examined in a scanning electron microscope (SEM).
3, but the matrix composition is \( \sim 0 \) wt.\% W at a distance of \( \sim 170 \) \( \mu \)m from the particle edge (Fig. 2). The hardness profile measured for the same Alloys 1 and 3 (Fig. 3) shows that particles are much harder than the matrix, whose hardness reaches a minimum in the diffusion zone adjacent to the particles, before achieving values of ca. 400 and 300 HV for Alloys 1 and 3, respectively, in good agreement with average matrix values listed in Table 2.

Fig. 4 shows the tensile stress–strain curves for the three Ti–10W alloys together with that of pure CP-Ti fabricated by the same powder route [5]. The corresponding mechanical properties are listed in Table 2, and also included for comparison is a Ti–10W alloy produced from 3 \( \mu \)m W powders [5]. Alloys 1 and 2, with almost all the W in solid solution, have nearly overlapping stress–strain curves which show very high yield and ultimate strengths as compared to CP-Ti. On the other hand, Alloy 3, with large W particles, fractured shortly after reaching its ultimate tensile strength (UTS) which, together with its yield strength, is closer to that of CP-Ti than those of Alloys 1–2. Table 2 also shows that good agreement exist between the mechanical properties of Alloy 2 (made with 2 \( \mu \)m W powders) and those of a previously studied Ti–10W alloy produced from 3 \( \mu \)m W powders [5].

SEM pictures of fracture surfaces for Alloys 1 and 3 are shown in Fig. 5. The stronger and more ductile Alloy 1 is characterized by pockets of spherical dimples in the matrix (Fig. 5a). For Alloy 3, matrix dimples are larger than for Alloy 1 (Fig. 5c), and fractured W particles are observed (Fig. 5d), together with particle pull-out (Fig. 5b).

4. Discussion

4.1. Microstructure

The equilibrium Ti–W phase diagram is characterized by a eutectoid reaction at 740°C where a Ti–W solid solution decomposes into Ti-rich and W-rich phases, without any intermediate intermetallic phases [7]. Above 882°C, there is complete solubility between Ti and W, so that the sintering and HIP steps at 1230 and 900°C are expected to promote complete dissolution of the W powders. The W particle vol-
due to hardening by Ti in solid solution following diffusion reaching a steady state value of 10 wt.% at a distance of 175 μm from the W particles (Fig. 2). This unexpected result is probably due to the formation of complex metastable phases whose structure (and thus probably hardness) change with W content. In binary Ti–W alloys, hexagonal martensite (α′′) is formed below ~8 wt.% W, orthorhombic martensite (α″) exists between ~8 and ~24 wt.% W, beyond which orthohombic α precipitates can form. Additionally, the formation of the metastable phases is further complicated by their quenching and aging history [7,10,11].

4.2. Strength and hardness

Two mechanisms may contribute to the increase in yield strength of the Ti–10W alloys as compared to CP-Ti: (i) solid solution strengthening of Ti by W, which is influenced by the W content of the matrix (both average and local); (ii) composite strengthening by the W particles, which is affected by their volume fraction, size and shape. Direct composite strengthening by load transfer is expected to be negligible, given the low volume fraction and equiaxed shape of the particles. Eshelby calculations based on elastic load transfer to spherical particles [12] predict an increase in yield stress with respect to CP-Ti by 6 MPa for Alloy 3 with the highest un-dissolved W volume fraction. Indirect composite strengthening by thermal-mismatch dislocations and grain size refinement is similarly negligible given the low volume fraction and relatively large size of the W particles. Finally, W particles are much too large for any significant dispersion strengthening. We thus conclude that the large differences in yield strength between Alloys 1–2 and Alloy 3 is due to differing extent in solid-solution strengthening. For Alloys 1 and 2 with the smallest initial W powders, the matrix composition is uniform, except in the immediate vicinity of the very few remaining W particles (Fig. 2). By contrast, for Alloy 3 with only one-tenth of its W content in solid solution, the matrix W composition drops to near zero at a distance of 175 μm from the particle edge (Fig. 2). Yielding is then controlled by the W-poor matrix regions between the W particles and their associated W-rich matrix regions. The volume fraction of W-poor region is estimated as 30 vol.%, calculated by con-
sidering a W content of 5 wt.% at a distance of 190 μm from the particle center (Fig. 2) and an average particle radius of 60 μm (Table 1).

The average matrix hardness of Alloys 1 and 2 (ca. 430 HV) is exceptionally high: it exceeds the hardness of pure annealed W (350 HV) [9] and is close to that of work-hardened W (445 HV) [9], thus indicating that Ti–10W alloys are very wear-resistant. The hardness of Alloys 1 and 2 is higher than that reported previously for a Ti–10W alloy (300 HV) [5] which however used different W powder size (3 μm) and cooling rate after HIP, the latter being known to affect the non-equilibrium phases in the Ti-W system. Depending on composition and cooling process, it is possible to obtain a martensitic structure leading to a range of non-equilibrium phases, namely, α′, α″, and γ with a coexistent change in mechanical properties [5,7,11]. By contrast, Alloy 3 is expected to be less wear-resistant due to its lower matrix average hardness and strength: in particular, W particle pull-out may become an issue for biomedical implant applications.

4.3. Ductility

The three Ti–10W alloys have very different ductilities: Alloys 1 and 2 exhibit large strain to failure (ca. 18%) and extensive necking, while Alloy 3 fractured shortly after reaching its UTS. This difference can be explained by the different volume fractions of hard and brittle W particles which can trigger early fracture. For the highly ductile Alloy 1, it is apparent that the inherent ductility of the Ti–10W matrix (as illustrated by the fine dimples typical of ductile tensile fracture, Fig. 5a) controls the fracture behavior, despite the occasional presence of W particles (Table 1). The low ductility of Alloy 3 is then not due to the limited ductility of its matrix but to the presence of the large, brittle W particles. Indeed, Alloy 3 shows evidence of both particle fracture and pull-out (Fig. 5d and b), indicative of particle cracking and reinforcement/matrix debonding, respectively, which are known in metal matrix composites to lead to a relatively brittle fracture behavior [13]. The clustering and relatively large size of W particles in Alloy 3 (Fig. 1c) are further reasons for its low ductility, as observed in other metal matrix composites [14–16]. In particular, the simulation work by Segurado et al. [17] shows that a small degree of particle clustering causes the fraction of broken particles to increase dramatically, leading to a large decrease in the overall composite flow stress and ductility.

5. Conclusions

• Blends of Ti–10 wt.% W powders were densified by powder metallurgy using W powders from very small (0.7–2 μm) to very large (>250 μm) sizes. After processing, almost all the W is dissolved within the Ti matrix for the former materials, which are thus solid-solution “alloys” with a transformed α/β microstructure at ambient temperature. By contrast, for the latter materials, most of the W remains un-dissolved in the form of large metallic particles, resulting in a particulate-reinforced “composite”.

• The strength of the Ti–10W alloys is much higher than that of the Ti–10W composite, indicating that W is more efficient as a solid-solution strengthener than as a particle strengthener.

• The hardness of the Ti–10W alloys is higher and more uniform than that of the Ti–10W composite, and achieves values of ~400 HV, indicative of excellent wear resistance.

• The Ti–10W alloys are also much more ductile than the Ti–10W composite, which suffers from particle pull-out and fracture.

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References