Microstructures and mechanical properties of tungsten-tantalum alloys consolidated by electron beam melting, hot pressing and spark plasma sintering

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Abstract. The effect of consolidation process conditions and the tungsten concentration on the microstructures and mechanical properties of tantalum–tungsten alloys has been investigated. Ta–10W (in weight percent) and Ta–20W (in weight percent) alloys have been consolidated by electron beam melting (EBM), hot pressing (HP) and spark plasma sintering (SPS) techniques. The results show that the tantalum–tungsten alloys consolidated by EBM exhibit the highest relative density while by HP or SPS exhibit smaller grain-size compared to that by EBM, which may be attributed from the lower process temperature and the existence of oxide on the grain boundary hindering the growth of grain. The alloys with fine grain size (HP or SPS) have a higher microhardness and compression strength than that with coarse grain size (SPS) under the same tungsten concentration. It has been shown that these two alloy systems exhibit a similar general trend of strength increasing and the ductility decreasing when applying different consolidation process, while an enhanced strength-ductility synergy can be achieved for the Ta–10W alloy.

1. Introduction

Tantalum (Ta) and tantalum alloys are widely used in electronics, chemical industries, industrial furnace, aerospace, atomic energy due to their unique properties such as high density, high melting point, low ductile-to-brittle transition temperature and moderately high elastic modulus [1–6]. Ta–W alloy is a kind of Ta-based solid-solution strengthened refractory alloy with body-centered cubic crystal structure, which is widely used in high-tech applications, such as power, aerospace and nuclear engineering [1, 2].

Ta–W alloys are usually prepared by electron beam melting (EBM) method or powder metallurgy method [7, 8]. The alloys prepared by EBM method have coarse grains and lower content of impurities, compared with those prepared by powder metallurgy method. However, there was very little work reported in the literatures to compare the mechanical properties of Ta–W alloys fabricated by these two methods. Therefore, this study mainly focused on this issue. Ta–10W and Ta–20W alloys have been consolidated by EBM, hot pressing (HP) and spark plasma sintering (SPS) techniques separately. Subsequently, the effect of consolidation process conditions and the tungsten concentration on the microstructures and mechanical properties of tantalum-tungsten alloys were investigated.
2. Experimental
The Ta and W powder had 99.9% nominal purity and an average particle size \(D\) of 15 \(\mu\)m and 10 \(\mu\)m, respectively. Ta–W composites with 10 and 20 wt % of W were consolidated by EBM, HP and SPS.

- **EBM**: The powder mix was cold isostatically pressed at 100 MPa in order to obtain cylindrical rods, and then the formed billet was sintered in vacuum furnace under 1900°C. The ingot was obtained by melting the sintered billet in the vacuum electron beam melting furnace.

- **HP**: Powders were mixed in a conventional ball mill for 12 h using ZrO balls with ball to powder ratio (BPR) of 1:1. Then the powders were transferred from mill pots to a graphite die in a glove box which was filled with pure argon gas. HP was performed for 1 h at 2000°C with high purity Ar under 30 MPa. The heating rate was maintained 20°C/min.

- **SPS**: The samples were sintered by spark plasma sintering (SPS) in vacuum under a pressure of 30 MPa, and the maximum temperature was 1800°C with heating rate of 100°C/min. The holding time was chosen to be 10 min in order to limit grain growth. Afterwards, the surface of all samples was mechanically polished to mirror-like finish. The processing parameters are summarized in table 1.

| Table 1. Chemical composition of the Ta–10W and Ta–20W plates (% mass fraction). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Material        | W               | Nb              | Ti              | Mo              | Si              | C               | N               | Ta              |
| Ta–10W          | 10.24           | 0.003           | 0.001           | 0.001           | 0.001           | 0.0008          | 0.0015          | Bal             |
| Ta–20W          | 20.4            | 0.004           | 0.002           | 0.008           | 0.001           | 0.0012          | 0.002           | Bal             |

The consolidation cycles are presented in figure 1.

![Figure 1. HP and SPS consolidation cycles.](image)

The densification achieved was measured using the Archimedes method. Microstructure observation was carried out by scanning electron microscope (SEM). The samples for the examination were metallographically polished and etched using hydrofluoric acid solution for 5 s before the microstructural investigation was carried out. Phase compositions were investigated by a X-ray diffractometer (XRD-6000, Shimadzu, Japan) with Cu \(K_a\) radiation in a scanning range of 10°–80°. A scanning electron microscope (Sigma 500, Zeiss Gemini, Germany) fixed with energy-dispersive spectroscopy (EDS) was used to investigate the chemistry of the interested phases.

The hardness and compressive properties of the Ta–W alloys were evaluated using Brinell hardness testing, tensile testing, respectively. The specimens for hardness test were ground and polished before carrying out multiple hardness indentations. The hardness values within the range of ±2% were
averaged to obtain the hardness value.

A universal compressive testing machine operated at a strain rate of 0.5 mm/min was used for the compressive testing of the composite samples which were machined as a rectangular solid with a dimension of $3 \times 3 \times 6$ mm. The compressive properties evaluated from the engineering stress–strain curves are yield strength, compressive strength and percent elongation. Multiple compressive tests were performed for each test composition in order to guarantee the reliability and reproducibility of the results.

3. Results and discussions

Engineering compressive stress-strain curves are shown in figure 2a. The distinctive behavior of displacement controlled compression was observed in these curves.

![Figure 2](image)

**Figure 2.** (a) Compressive engineering stress–strain curves of Ta–W alloys obtained by different preparing method; (b) relationship between compression strength and uniform elongation of Ta–W alloys; (c) corresponding true stress-strain curves and (d) work hardening rate ($d\sigma/d\varepsilon$)-true strain curves.

Corresponding compressive properties are listed in table 2. The results show that the range of yield strength (YS) values is from 585 to 1502 MPa, the range of compression strength (CS) is from 1204 to 2785 MPa and the range of elongation varies is from 24.9 to 40.5%.

The Ta–10W and Ta–20W alloys consolidated by HP and SPS exhibited a better strength-ductility combination than consolidated by EBM. More crucially, compared with the Ta–20W, the Ta–10W with lower solution of atoms exhibits simultaneously high strength and ductility consolidated by different method, as illustrated in figure 2b.
Table 2. Mechanical properties of Ta–W alloy samples.

| Material     | YS, MPa | CS, MPa | UEL  | TEL  | HV, GPa |
|--------------|---------|---------|------|------|---------|
| Ta–10W-EBM   | 585     | 1619    | 0.405| 0.405| 2.74    |
| Ta–20W-EBM   | 669     | 1204    | 0.262| 0.262| 3.41    |
| Ta–10W-HP    | 1502    | 2785    | 0.344| 0.318| 4.53    |
| Ta–20W-HP    | 1432    | 2300    | 0.278| 0.249| 4.17    |
| Ta–10W-SPS   | 1389    | 2523    | 0.358| 0.379| 3.98    |
| Ta–20W-SPS   | 1198    | 2115    | 0.268| 0.296| 3.68    |

In order to reveal the work hardening behavior of the present samples, the engineering stress–strain curves in figure 2a were converted into the true stress–strain curves in figure 2c. Work-hardening rate \( \Theta \) vs. true strain (\( \varepsilon \)) are shown in figure 2d. It has been widely acknowledged that the ductility of metallic materials is controlled by strain hardening [9]. In macroscale, the Consideré criterion governs the onset of localized deformation [10].

\[ \Theta = d\sigma/d\varepsilon \leq \sigma \]

Where \( \sigma \) is true stress and \( \varepsilon \) is the true strain, it is noted that the mechanical properties of the two Ta–W alloys exhibit a similar trend.

The high strength of the Ta–W alloys consolidated by HP is attributed to the grain size effect in terms of Hall–Petch relation [11]. Figure 3 shows a Hall–Petch plot using measured \( \sigma_{ys} \) of Ta–W alloys consolidated by different methods (as listed in table 2). According to the Hall-Petch relationship, the YS of an alloy can be approximated as

\[ \sigma_{ys} = \sigma_0 + kd^{-1/2} \]

Where \( \sigma_{ys} \) is the yield strength, where \( \sigma_0 \) is the friction stress, \( k \) is the Hall–Petch parameter, and \( d \) is the mean grain size. As for Ta–10W and Ta–20W alloys, the \( k \) value was 5.45 MPa · m\(^{1/2}\) and 4.24 MPa · m\(^{1/2}\); the \( \sigma_0 \) value was 336 MPa and 458 MPa.

Figure 3. Plots of grain size and yield strength of Ta–W alloys showing the Hall-Petch relation.

Figure 4a shows the X-ray diffraction patterns for the Ta–20W alloy consolidated by EBM, HP and SPS. No peaks of W can be detectable in all of the Ta–20W alloys. The lattice size of the Ta–20W becomes smaller after solid solution W atoms. There are axial offset to high angle for the diffraction peaks, take (200) as an example. And the width of diffraction peaks of alloy after EBM is wider than...
that after HP and SPS sintering, which can be explained by larger grain size of the Ta–20W after the EBM.

The average grain size, Vickers hardness and density of Ta–W alloy samples obtained by different preparing method are recorded in table 3. The alloys with fine grain size (HP or SPS) have a higher micro-hardness than that with coarse grain size (SPS) under the same tungsten concentration.

Table 3. Characteristics of Ta–W alloy samples.

| Material     | Average grain size, μm | Density, g cm⁻³ | Theoretical density, g cm⁻³ | Relative density, % |
|--------------|------------------------|-----------------|-----------------------------|---------------------|
| Ta–10W-EBM   | 455                    | 16.91           | 16.92                       | 99.94               |
| Ta–20W-EBM   | 487                    | 17.21           | 17.25                       | 98.23               |
| Ta–10W-HP    | 23                     | 16.69           | 16.92                       | 98.64               |
| Ta–20W-HP    | 21                     | 16.75           | 17.25                       | 97.1                |
| Ta–10W-SPS   | 32                     | 16.35           | 16.92                       | 96.63               |
| Ta–20W-SPS   | 29                     | 16.52           | 17.25                       | 95.78               |

Figure 4. (a) XRD patterns of Ta–20W alloys obtained by different preparing method; (b) SEM and EDS of Ta–20W alloy obtained by EBM; (c) SEM and EDS of Ta–10W alloy obtained by HP; (d) SEM and EDS of Ta–20W alloy obtained by SPS.

Figure 4b showed the SEM images of Ta–20W alloy after EBM. It can be seen that the grain size is about 400–500 μm. The high temperature in the melting process of EBM was the cause of these large particles. The content of W of the alloy under the light color contrast and the dark color contrast was 22.1%, indicating that the chemical homogeneity of the alloy was high. Figures 4c and 4d are SEM images of Ta–10W alloy manufactured by HP or SPS, respectively. The grain size after HP was around 20 μm, the grain size after SPS is about 30μm. The porosity could both be observed after preparation process of HP or SPS, which was mainly formed during the process of solidification. The brittleness of alloy increased due to the existence of these porosities [12]. The surface of the alloy at grain boundary and the porosity is mainly composed of Ta and O two elements, mass ratio was 82.3% and 17.7% respectively. The crystal grain size of the alloy by HP or SPS is small compared to that by EBM. The powder metallurgy method (HP or SPS) of the alloy will form tantalum oxide at the grain boundary. The formation of oxide plays a role of pinning grain boundary, thus inhibiting the grain
growth [13].

4. Conclusions
The Ta–W alloys consolidated by SPS exhibits the smallest grain-size and relative density, which may be attributed from the existence of oxide in the grain boundary hindering the growth of grain and the lower process temperature. The alloy with fine grains has a higher micro-hardness and compression strength than that with coarse grains under the same tungsten concentration. It is shown that these two alloy systems exhibit a similar general trend of the strength increasing and the ductility decreasing when applying different consolidation process, while an enhanced strength-ductility synergy can be achieved for the Ta–10W alloy.

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