MICROWAVE SINTERING: A NEW APPROACH TO FINE-GRAIN TUNGSTEN—II


INTRODUCTION

In Part I of this study the benefits of using microwave radiation as a volumetric heating source for sintering tungsten were delineated. Grain growth was curtailed when submicron size particles were used as the starting material followed by sintering in a microwave furnace. Prior research has shown that grain growth in refractory metals and ceramics can also be reduced by the addition of suitable secondary phases. Examples of this effect are the addition of $\text{Al}_2\text{O}_3$ to $\text{ZrO}_2$, $\text{ZrO}_2$ (tetragonal or cubic) to $\beta'$-$\text{Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3$ to cubic $\text{ZrO}_2$, and $\text{Al}_2\text{O}_3$ and molybdenum alloys utilizing TiC as a secondary phase. By means of hot isostatic pressing (HIPing), followed by forging, they were able to develop grain sizes in the range 50 nm to 1.6 μm. However, the addition of the secondary phase to tungsten or molybdenum involved ball milling, and this resulted in a non-uniform dispersion of the inclusions, with an attendant wide distribution in grain size.

In this paper, we describe a method to synthesize ultrafine tungsten powders doped with small amounts of HfO$_2$ and Y$_2$O$_3$. The oxide phases were formed in situ during formation of the tungsten phase, which insured a uniform dispersion. The doped powders were subsequently sintered in a microwave furnace. At the outset, the premise was that the combined effects of oxide doping and microwave radiation should lead to an ultrafine grain size in the sintered tungsten.

EXPERIMENTAL PROCEDURE

Tungsten powders were synthesized by the thermal decomposition of ammonium metatungstate (AMT) of composition $[\text{NH}_4\text{H}_2\text{W}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ to WO$_3$, followed by reduction to the metal in a hydrogen atmosphere. In the AMT, $x > 2$. An aqueous solution of AMT was spray dried and doping of the tungsten powder, with either HfO$_2$ or Y$_2$O$_3$, was achieved by dissolving hafnium oxychloride (HfOCl$_2$) or yttrium nitrate (Y(NO$_3$)$_3$) in the aqueous AMT solution prior to spray drying. This resulted in the...
introduction of the dopant/second phase at the molecular level. The spray-dried AMT powder was then heated at 500°C in oxygen to convert it to WO3. Subsequently, the WO3 was reduced to tungsten by heating at 700°C in hydrogen. The amount of Y2O3 was varied from 0.06 w/o to 2.48 w/o, and the amount of HfO2 was varied from 0.14 w/o to 2.28 w/o. These weight percentages correspond to volume percentages of 0.23 to 8.92 for Y2O3, and 0.23 to 4.45 for HfO2.

The as-synthesized tungsten-base powders were compacted into disks 12 mm dia. x ~2 mm thick. Prior to compaction, the powders were mixed with a binder (3 w/o polyethylene glycol). Subsequently, the disks were cold isostatically pressed (CIPed) at 255 MPa (37,000 psi). The CIPed disks were then heated at 600°C for 4 h in hydrogen to remove the binder, and microwave sintered in a hydrogen atmosphere. The microwave generator was operated at 2.45 GHz frequency. The disks were microwave sintered for 20 min at 1,400°C, 1,600°C, and 1,800°C.

The specific surface areas of the as-synthesized powers were determined using a BET Micromeritics FlowSorb II 2300 single-point instrument. The as-synthesized powders were characterized by means of x-ray diffraction (Siemens diffractometer). The microstructures of the as-synthesized powders and the microwave-sintered compacts were monitored utilizing a Leo-Gemini field emission scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Synthesis of Doped Tungsten Powder

The variation in specific surface area as a function of composition is shown in Figure 1. The specific surface area increases with the addition of both HfO2 and Y2O3 dopants, compared with the non-doped tungsten powder. The increase in specific surface area with Y2O3 as the dopant saturates above 0.3 w/o. In the case of HfO2, the specific surface area increases with an increase in the level of HfO2, up to 2.28 w/o. The reason for this difference in the dependence of specific surface area with dopant level could be due to a difference in the interaction of these oxides with WO3 during the formation of tungsten. It is likely that the level of HfO2 needed to saturate the specific surface area is much higher compared with that of Y2O3, and that this level was not reached in the present study.

Figure 2 shows the change in primary particle size with the level of dopant. The increase in specific surface area is the result of a reduction in particle size, not from any contribution to specific surface area by the ultrafine oxides.

X-ray diffraction patterns of the as-synthesized tungsten powder doped with Y2O3 and HfO2 are shown in Figures 3 and 4 respectively. WO2 and/or WO3 impurity phases were not observed in any of the powders. Table I shows the effect of the dopants on the crystallite size of the as-synthesized tungsten powder, as measured from the x-ray diffraction peak broadening. The crystallite size was 25 nm in the tungsten powder doped with Y2O3, compared with 48 nm for the undoped tungsten powder. The corresponding reduction in crystallite size due to HfO2 as the dopant was from 48
Representative morphologies of the as-synthesized tungsten powders, with and without the two dopants, are illustrated in Figure 5. The particle size decreased from ~350 nm in the pure tungsten to ~80-100 nm in the tungsten doped with 1.14 w/o HfO$_2$. The particle morphology also

<p>| TABLE 1. Effect of Dopants on Crystallite Size of Tungsten Powder |
|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>$Y_2O_3$ (w/o)</th>
<th>Crystallite Size (nm)</th>
<th>HfO$_2$ (w/o)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>48</td>
<td>0</td>
<td>48</td>
</tr>
<tr>
<td>1.24</td>
<td>25</td>
<td>1.14</td>
<td>32</td>
</tr>
</tbody>
</table>

nm to 32 nm. This confirms that both the crystallite size and the primary particle size (calculated from surface area) are reduced by the dopants. The as-synthesized tungsten powders contained 1–1.5 w/o oxygen, and 0.001–0.01 w/o aluminum.
changed with the level of HfO$_2$: the surfaces of the particles in the doped powder were rougher than those of the pure tungsten. With 1.24 w/o Y$_2$O$_3$ dopant in the tungsten, the particle size was 50-100 nm.

**MICROWAVE SINTERING**

Representative micrographs of the pure tungsten and tungsten doped with HfO$_2$ and Y$_2$O$_3$ after microwave sintering at 1,400°C for 20 min are shown in Figure 6. The grain size was reduced significantly when 1.14 w/o HfO$_2$ or 0.61 w/o Y$_2$O$_3$ were introduced as dopants, namely, from 2 μm to 0.5 μm. The reduction in grain size for both the HfO$_2$-doped and Y$_2$O$_3$-doped tungsten was comparable for similar volume levels of the second phase: 0.61 w/o Y$_2$O$_3$ corresponds to 2.30 v/o Y$_2$O$_3$, and 1.14 w/o HfO$_2$ corresponds to 2.25 v/o HfO$_2$.

Figure 7 shows a representative fractograph of tungsten doped with 1.14 w/o HfO$_2$, microwave sintered at 1,400°C for 20 min. The grains are

![Figure 6. Representative micrographs of tungsten powder microwave sintered at 1,400°C for 20 min in pure hydrogen, (a) no dopant, (b) doped with 1.14 w/o HfO$_2$, (c) doped with 0.61 w/o Y$_2$O$_3$, SEM.](image)

![Figure 7. Representative fractograph of tungsten doped with 1.14 w/o HfO$_2$ and microwave sintered at 1,400°C for 20 min, showing HfO$_2$ particles dispersed in the tungsten, SEM.](image)

![Figure 8. Representative micrograph of tungsten doped with 2.48 w/o Y$_2$O$_3$ and microwave sintered at 1,400°C for 20 min. SEM.](image)
faceted, with an average grain size ~0.5 μm. Some residual porosity can be observed on the fracture surface. The fractograph also shows particles (~<50 nm) on the surface of the tungsten grains. These particles are brighter than the tungsten grains in the secondary electron image mode which cannot be explained by topological contrast alone. A possible reason for the contrast could be the higher amount of charging due to the lower electrical conductivity of the particles, coupled with the fact that hafnium has a lower work function than pure tungsten (3.9 Φ/eV for hafnium compared to 4.55 Φ/eV for tungsten), hence more efficient electron emission, and evidence that the particles are HfO₂.

A representative micrograph of tungsten containing 2.48 w/o Y₂O₃, microwave sintered at 1,400°C for 20 min is shown in Figure 8. A significant reduction in sinterability was observed compared to the tungsten doped with HfO₂. The same effect was observed in the tungsten powder doped with 2.28 w/o HfO₂. A possible explanation for this reduction in microwave sinterability is that there exists an optimal concentration of HfO₂ or Y₂O₃, above which the dopant hinders sintering.

An additional study is underway to examine the effect of processing parameters, such as milling conditions, compaction pressure, and amount of binder, on the compaction behavior of fine-grain tungsten powder.

CONCLUSIONS
1. The present study has demonstrated that high-purity oxide-doped tungsten-base powders with an ultrafine particle size can be synthesized.
2. The introduction of a secondary oxide (HfO₂ and/or Y₂O₃) had a significant effect on the powder morphology, and in reducing the primary particle size of the as-synthesized tungsten powders. The particle size was reduced from 350 nm to 80-100 nm, and the crystallite size was reduced from 48 nm to 25 nm with the addition of the dopants.
3. The grain size in microwave-sintered tungsten can be controlled via the composition of the secondary phase, and an average grain size ≤0.5 μm can be achieved in the microwave-sintered tungsten.
4. It appears that there is an optimum level of the dopant that exerts the maximum effect in reducing the grain size.

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REFERENCES