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


INTRODUCTION

The military employs long-rod kinetic energy (KE) penetrators to defeat armor.1 This armor-piercing ammunition is essentially a rod with a high aspect ratio (length (L) to diameter (D) ≥10) that is launched at velocities in excess of 1,500 m/s at an armored target.1 For a given L/D ratio, the denser the penetrator material, the higher the energy delivered to the impacted area. To date, depleted uranium (DU) alloys have been found to be the best performing long-rod KE penetrators. There is no replacement presently available for U-0.75 w/o Ti and there exists a need for an alternative material that performs at least as well as, and preferably better than, DU should it become necessary to replace DU. Tungsten-base materials have been extensively studied as a potential replacement for DU because of their high strength and density; however, when used in a high L/D configuration, tungsten fails marginally short in penetration capability, the most important performance criterion in comparison to DU.

The deformation of penetrators and armor occurs at extremely high strain rates, which leads to adiabatic heating with attendant extensive plastic deformation at the penetrator head. Thermal softening, due to an increase in temperature and strain, and strain-rate hardening due to deformation, compete with each other during this process. In the case of DU alloys, adiabatic shear failure is observed as softening develops rapidly at low strain values and shear bands form during deformation. This results in a chiseled-head formation which improves penetration performance due to a self-sharpening effect.2 However, conventionally fabricated tungsten and tungsten heavy alloys (WHAs) show a mushrooming effect, causing the diameter of the penetration head to increase, thereby degrading performance in penetrator applications.

Ramesh et al.3 have observed that the deformation mechanism and failure modes for fine-grain materials can be very different from those in coarse-grain materials. In the case of nanophase iron they observed the formation of shear bands under dynamic loading at high strain

Recently, there has been a renewed interest in fine-grain dense objects of refractory metals containing no liquid-phase sintering aids. This has been the motivation for exploring new sintering techniques, and using ultrfine powders as the starting material. In the work reported here, two different types of commercially available and two experimental grades of tungsten powders were microwave sintered in the absence of additives. The effects of primary particle size, phase purity, aggregate size, and morphology on densification behavior have been studied. There was no direct correlation between the characteristics of the as-received powders and the sintered density; for example, a smaller initial particle size did not lead to higher sintered densities, even with higher green densities. The densification behavior was governed by a combination of particle characteristics. In contrast to conventional sintering, it was found that in microwave sintering, the degree of densification increased with increasing aspect ratio. Densities ≥98.5% of the pore-free level were achieved with a grain size in the range of 2–4 μm by microwave sintering followed by hot isostatic pressing (HIPing) at temperatures as low as 1,500°C. In the absence of HIPing, the density of microwave sintered tungsten was 12%–18% higher than the density of conventionally sintered tungsten.

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rates. However, this behavior was not observed in coarse-grain iron. It is expected that tungsten will show similar behavior if the grain size is sufficiently fine. It is therefore necessary to develop a processing technique to fabricate fine-grain tungsten in order to at least match the performance of DU.

In this paper, we describe a method to consolidate tungsten using microwave radiation. In microwave sintering, the material is heated volumetrically at significantly higher rates compared with conventional heating. These high rates of volumetric heating are not limited by thermal diffusion, hence they prevent recrystallization and grain growth, and result in a finer and more-uniform microstructure, which is a prerequisite for improving the performance of tungsten-base materials in penetrator applications. Permittivity and permeability are the two most important properties that control the interaction of a material with microwave radiation. The relative permittivity $\varepsilon_r'$ of a material is described by the relation:

$$\varepsilon_r' = \varepsilon_r - j\varepsilon_r''$$

where $\varepsilon_r'$ and $\varepsilon_r''$ are real and imaginary parts of the relative permittivity respectively, and $j = \sqrt{-1}$.

When microwaves penetrate the material, the electric field induces motion in charged particles (e.g., electrons and ions). The resistance to this motion causes a departure from equilibrium, and leads to the dissipation of energy. This loss due to attenuation of the electric field from the microwave radiation results in the generation of heat in the material. The loss tangent, $\tan \delta$, defines the losses and is described by the relation:

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'}$$

The average power dissipated per unit volume of the material is given by:

$$W = \frac{1}{2} \varepsilon_0 \omega E_0^2 \varepsilon_r' \tan \delta$$

where $E_0$ is the amplitude of the electric field, $\omega$ is the angular frequency of the microwave radiation, and $\varepsilon_r'$ is the permittivity in vacuum. Similar equations can be derived for the interaction of the magnetic field with a material due to microwave radiation.

The rapid and volumetric heating capability of microwave radiation makes it particularly appealing to employ this sintering technique for refractory metals, which are generally difficult to sinter. In the absence of sintering aids due to high melting temperatures. For porous materials, microwave heating is volumetric, whereas in a fully dense material there is a skin-depth effect. Thus, microwave radiation was employed to study the effect of the initial particle characteristics on densification behavior and the resulting microstructure of tungsten.

**EXPERIMENTAL PROCEDURE**

Four types of tungsten powders, all with different particle characteristics, were used in this study. The powders were coded: commercial powder-1 (CP-1), commercial powder-2 (CP-2), experimental powder-1 (EP-1), and experimental powder-2 (EP-2). The powders were mixed with a 1 w/o binder of poly (vinyl butyral).

Compaction of the powder was performed uniaxially at 70 MPa into discs, 16 mm dia. x ~2 mm in thickness. The disks were then cold isostatically pressed (CIPed) at 255 MPa. In addition, rods 38 mm long x 15 mm dia. were fabricated by CIPing powders in a polymer die at 255 MPa. The CIPed disks and rods were heated at 600°C for 4 h in hydrogen to remove the binder.

The green disks and rods were subsequently microwave sintered in a pure-hydrogen atmosphere and in a hydrogen/nitrogen mixture. A 6 kW microwave generator operating at 2.45 GHz frequency was used for the microwave sintering experiments. The disks and rods were sintered for 20 min at temperatures of 1,400°C, 1,450°C, and 1,500°C.

The microwave sintered disks and rods were then hot isostatically pressed (HIPed) by placing the samples in a graphite die, and applying temperature and pressure simultaneously. Argon was used as the pressure-transmitting medium. Microwave-sintered samples were HIPed for 1 h at 1,500°C and 100 MPa pressure. A plate of Al₂O₃ was used to prevent contact of the tungsten with the graphite die, as a precaution against possible embrittlement of the tungsten by carbon.

The mean aggregate size of the as-received powders was measured by laser light scattering (HORIBA LB-500 particle size analyzer). The powders were suspended in a mixture of ethylene glycol and isopropanol prior to particle-size measurement.

The densities of the green samples were calculated from their weight and geometry. In the sintered condition, densities were determined using
Archimedes’ principle.

The morphology of the tungsten powders and the microstructure of the sintered samples were characterized using a field emission scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Powder Characterization

Table I lists the average aggregate particle sizes of as-received tungsten powders. CP-1 exhibited the largest aggregate size, while EP-1 was essentially not aggregated. The aggregate size was in the order: CP-1 > EP-2 > CP-2 > EP-1.

Figures 1 (a) through (d) show the shape and size of the as-received tungsten powders. The particles of the EP-1 powder are spherical in shape, whereas the other three powders are irregular in shape. Additionally, the primary particle-size distribution is much wider in the case of the EP-1 powder, compared with the other powders. Some aggregates of the EP-2 powder are needle-shaped, whereas the aggregates of CP-1 and CP-2 are irregular. EP-1, the non-aggregated powder, is composed of α tungsten and β tungsten, while CP-1, CP-2, and EP-2 powders consist of α tungsten.

<table>
<thead>
<tr>
<th>Powder Code</th>
<th>Mean Aggregate Size (μm)</th>
</tr>
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<tbody>
<tr>
<td>CP-1</td>
<td>0.70</td>
</tr>
<tr>
<td>CP-2</td>
<td>0.41</td>
</tr>
<tr>
<td>EP-1</td>
<td>0.16</td>
</tr>
<tr>
<td>EP-2</td>
<td>0.50</td>
</tr>
</tbody>
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Figure 1(a). Representative morphology of CP-1 tungsten powder. SEM

Figure 1(b). Representative morphology of CP-2 tungsten powder. SEM

Figure 1(c). Representative morphology of EP-1 tungsten powder. SEM

Figure 1(d). Representative morphology of EP-2 tungsten powder. SEM
Green Compact Characterization

Relative green densities of the compacts after binder burnout are given in Table II. The EP-1 powder achieved the highest relative green density. This is attributed to the absence of any significant aggregation of the spherical particles, in combination with a wide particle-size distribution. In contrast, the relative green density of the EP-2 powder was only ~35% of the pore-free density, due in part to the non-uniform aggregates, and the small size of the primary particles. The CP-1 and CP-2 powders exhibited faceting, which generally inhibits flow and results in a lower green density.

<table>
<thead>
<tr>
<th>Powder Code</th>
<th>Relative Green Density (%)*</th>
</tr>
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<tbody>
<tr>
<td>CP-1</td>
<td>45</td>
</tr>
<tr>
<td>CP-2</td>
<td>48</td>
</tr>
<tr>
<td>EP-1</td>
<td>63</td>
</tr>
<tr>
<td>EP-2</td>
<td>35</td>
</tr>
</tbody>
</table>

*Based on a pore-free density of 19.3 g/cm³ for tungsten

MICROWAVE SINTERING

The time-temperature history of a typical tungsten sample during microwave sintering is illustrated in Figure 2. The temperature was monitored using a C-type thermocouple and/or a pyrometer. Microwave power was controlled manually to achieve the desired temperature. Initially, the temperature of the sample was increased slowly at a heating rate of 10°C-20°C/min. Above 300°C, the sample heats up at a much faster rate (100°C-125°C/min.). The change in heating rate with increasing temperature is due to the change in the absorbance mechanism of microwave radiation. With an increase in temperature, the loss tangent becomes larger, leading to a significantly higher heating rate. Notwithstanding the high heating rates, neither microcracking nor macrocracking was observed in any of the samples. This is testimony to the efficacy of volumetric heating intrinsic to microwave furnaces.

Disks and rods fabricated from the CP-1 and CP-2 powders exhibited the highest level of densification. In contrast, EP-1 disks and rods did not show any significant densification during microwave sintering. Figure 3 shows the relative densities of the disk compacts microwave sintered at 1,400°C, 1,450°C, and 1,500°C for 20 min in pure hydrogen.

The CP-1, CP-2, and EP-2 disks had relative densities in the range of 85%-90% of the pore-free level after microwave sintering. In contrast, the relative density of EP-1 was ~75% of the pore-free level. The poor densification behavior of the EP-1 powder is tentatively attributed to a wide particle-size distribution, and the presence of α and β tungsten.
Figure 4 shows the relative densities of disk compacts that were HIPed, following microwave sintering. The sintered CP-1, CP-2, and EP-2 powder compacts achieved higher densities than EP-1 after HIPing, as the initial microwave-sintered densities were high. The microwave-sintered and HIPed CP-2 powder attained densities ~98% of the pore-free density of tungsten. The density of the EP-2 and CP-1 powders after microwave sintering and HIPing was ~93% of the pore-free level. The relatively low green density of EP-2 and CP-1, and the relatively low final density, are attributed to the poor packing efficiency of the powder aggregates.

A study is underway to alter the characteristics of the EP-2 powder, thereby modifying its sintering characteristics. For example, a reduction in the aggregate size by a factor of three has resulted in an increase in green density to ~45% of the pore-free level. It is anticipated that this will enhance the final sintered density and grain size.

The atmosphere present in the microwave cavity during sintering also had an effect on the sintered densities. Reducing the proportion of hydrogen in the atmosphere decreased the final density of the compacts. Figure 5 shows the effect of hydrogen concentration on the densification behavior of the CP-1, CP-2 and EP-1 disks. The compacts were microwave sintered in 30 v/o H₂-70 v/o N₂ for 20 min at 1,400°C, 1,450°C, and 1,500°C. The samples showed 15%-20% lower relative densities compared with disks sintered in pure hydrogen. The reason for the reduced densification was the residual amount of oxide present on the surface of the particles which was not reduced at the lower hydrogen concentration.

The effect of aspect ratio on densification during microwave sintering was studied by sintering a rod and a disk under identical conditions of time, temperature, and sintering atmosphere. It was observed that the sintered density of the rod was consistently higher than that of the disk, irrespective of the type of powder used. Figure 6. The rods show ~11% higher density, compared with the disks, for the three powders. Similar behavior was observed in case of the EP-2 powder, when disks and rod were sintered simultaneously at 1,500°C for 20 min in pure hydrogen. The rod was 96% dense, compared with a relative density of 93% for the disk. It appears that as L/D increases, microwave sintering is enhanced. The reason(s) for this effect of aspect ratio are not clear at the present time, but could be related to the larger surface-to-volume ratio of the disks compared with that of the rods. In conventional sintering, and in some advanced consolidation techniques, it is easier to sinter smaller parts than large parts. This is attributed to the large thermal gradients that exist from the surface to the interior of a large compact, which leads to thermal stresses and cracking.

Figure 7 shows representative micrographs of disks compacted from CP-2 powder and microwave sintered at 1,450°C for 20 min in pure hydrogen,
followed by HIPing at 1,500°C for 1 h in nitrogen. The compact, which was 98.5% dense after HIPing, shows uniform densification with a grain size in the range of 2–4 μm. In the absence of a sintering aid, conventionally processed tungsten typically exhibits average grain sizes >>20 μm.

The advantage of microwave sintering over conventional sintering was confirmed by comparing the density of compacts prepared from CP-1 and CP-2 powders conventionally sintered at 1,450°C for 20 min in pure hydrogen in a tube furnace. The compacts were fabricated under conditions identical to those used for fabricating the compacts for microwave sintering. Table III shows the relative densities achieved via the two sintering modes. The densities were 12%–18% higher for microwave sintered samples compared with conventionally sintered samples, confirming the advantage of microwave sintering.

CONCLUSIONS

1. Microwave sintering, coupled with HIPing, resulted in near pore-free density for tungsten powder, with an attendant fine grain size.
2. A small primary particle size, and the absence of aggregation in the starting tungsten powder, do not necessarily lead to high sintered densities. Single-phase powders with a narrow particle-size distribution and a larger particle size exhibited the best sinterability.
3. In the absence of HIPing, the density of microwave-sintered tungsten was 12%–18% higher than the density of conventionally sintered tungsten.
4. The decrease in density in some of the samples with increasing temperature is attributed to variations in porosity.
5. An increase in aspect ratio enhances the response of tungsten to microwave sintering.

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REFERENCES