MICROSTRUCTURE MANIPULATIONS TO ATTAIN DENSIFICATION WITHOUT DISTORTION DURING LIQUID PHASE SINTERING

Wuwen Yi*, Randall M. German**, Xiaoping Xu***

* Former Graduate Research Assistant  
** Brush Chair Professor in Materials  
*** Former Graduate Research Assistant

Center for Innovative Sintered Products  
P/M Lab, 147 Research Building West  
The Pennsylvania State University  
University Park, PA 16802-6809

ABSTRACT

Densification without distortion during liquid phase sintering was achieved by manipulating microstructure and its evolution during sintering. Microstructure parameters such as the solid volume fraction, dihedral angle, initial porosity, and pore size were varied to measure densification and distortion behavior during LPS using W-Ni-Cu alloys. Green compacts were formed using ethylene-bis-stearamide as a pore-forming agent with the amount of polymer controlling the initial porosity. Different initial pore sizes were generated by varying the polymer particle size. Dihedral angle was varied by changing the Ni:Cu ratio in the alloys. Finally, the solid volume fraction was adjusted via the tungsten content. Distortion was quantified using profiles determined with a coordinate measuring machine to calculate a distortion parameter. Sintering results showed that solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle, while initial porosity and pore size have no observable effect on distortion at nearly full densification. Various strategies emerge to improve distortion control in liquid phase sintering.

INTRODUCTION

Liquid phase sintering is broadly used for net-shape manufacturing [1, 2]. In many systems the liquid enhances densification, since it provides a capillary force that pulls the solid grains together and offers a fast mass transport medium [3, 4]. However, liquid phase sintering is generally limited to high solid content compositions due to shape retention difficulties. In tungsten heavy alloys, the large density difference (over 10 g/cm³) between tungsten grains and the matrix (usually Ni, Cu, or Fe) induces tungsten grain settling along the gravitational direction, especially for liquid contents over approximately 25 vol.%, resulting in significant distortion [5, 6].

5-227
Densification has long been the subject of many investigations, and distortion has also been studied in recent works [5, 6, 7], but few reports have directly addressed distortion control. A systematic investigation of distortion is lacking. Similarly, the initial pore structure effects on distortion have been neglected and are still uncertain at this time.

This work studies liquid phase sintering by investigating the microstructural effects on the combination of densification and distortion, including solid volume fraction, dihedral angle, green porosity, and green pore size. In this work, W-Ni-Cu tungsten heavy alloys with varying dihedral angles were liquid phase sintered and simultaneously monitored for densification and distortion. The sequence of densification and distortion during liquid phase sintering was investigated using quenching experiments. Processing strategies brought forth by this research aid in liquid phase sintering practice for the fabrication of high density and high precision components.

EXPERIMENTAL PROCEDURES

The W-Ni-Cu tungsten heavy alloys with varying microstructures were fabricated from mixed powders. To control the green porosity and pore size, an organic binder, EBS (ethylene-bis-stearamide) was added to the powder mixture. During heating, the binder decomposed to leave pores in proportion to added concentration. Varying binder particle sizes created different green pore sizes. Dihedral angles were varied through the Ni:Cu ratio from 8:2 to 2:8. The initial formulations were adjusted to give final solid volume fraction (poro-free) ranging from approximate 60 to 85 vol.% using initial tungsten contents and the alloy balance being Ni and Cu.

Table 1 summarizes the characteristics of the W, Ni, and Cu powders used in the study, and the particle sizes of the EBS powders are listed in Table 2. The as-received tungsten powder was first deagglomerated by rod milling for 1 h in a 2000 cm$^3$ plastic jar filled with argon. The ratio of rods to the powder was 10:1. The W, Ni, and Cu elemental powders were first mixed according to the target composition, and then mixed with the EBS binder at different particle sizes in a Turbula mixer for 20 min to achieve a homogenous distribution. The binder content in the mixture was in proportion to the desired green porosity.

The mixed powders were weighed and uniaxially die pressed at 175 MPa into cylinders 12.8 mm in diameter and 10 mm in height. The green compacts were heated to extract the binder at 550°C for 1 h in dry hydrogen with dew point of -55°C. The hydrogen flow rate was 23 turnovers/h, and the heating rate was 3°C/min. After the binder was extracted, the compacts were weighed and measured again to calculate the green porosity.

Sintering was performed at 1480°C in a CM horizontal tube furnace in dry hydrogen with dew point of -55°C. The hydrogen flow rate was 35 turnovers/h. The heating rate was 10 °C/min, and the holding time at sintering temperature was 30 min. To reduce oxidation, a 30 min hold at 1050°C was employed during heating.
Table 1. Characteristics of the Metal Powders Used in this Study.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Rod-milled W</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vendor</td>
<td>Osram</td>
<td>Novamet</td>
<td>ACuPowder</td>
</tr>
<tr>
<td>Designation</td>
<td>M-37</td>
<td>123</td>
<td>635</td>
</tr>
<tr>
<td>Particle size distribution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{10}$ ($\mu$m)</td>
<td>1.8</td>
<td>4.7</td>
<td>7.9</td>
</tr>
<tr>
<td>$D_{50}$ ($\mu$m)</td>
<td>4.8</td>
<td>10.8</td>
<td>12.1</td>
</tr>
<tr>
<td>$D_{90}$ ($\mu$m)</td>
<td>9.3</td>
<td>25.7</td>
<td>18.9</td>
</tr>
<tr>
<td>Pycnometer density (g/cm$^3$)</td>
<td>19.1</td>
<td>8.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Apparent density (g/cm$^3$) (% of pycnometer density)</td>
<td>3.7</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Tap density (g/cm$^3$) (% of pycnometer density)</td>
<td>6.1</td>
<td>3.3</td>
<td>3.9</td>
</tr>
<tr>
<td>BET surface area m$^2$/g</td>
<td>0.208</td>
<td>0.48</td>
<td>0.230</td>
</tr>
</tbody>
</table>

Table 2. Particle Sizes of the EBS Powders used in this Study (Vendor: Lonza)

<table>
<thead>
<tr>
<th>Designation</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size distribution</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{10}$ ($\mu$m)</td>
<td>1.3</td>
<td>1.9</td>
<td>3.4</td>
<td>7.7</td>
<td>29.2</td>
</tr>
<tr>
<td>$D_{50}$ ($\mu$m)</td>
<td>5.9</td>
<td>11.6</td>
<td>22.7</td>
<td>36.2</td>
<td>87.0</td>
</tr>
<tr>
<td>$D_{90}$ ($\mu$m)</td>
<td>15.3</td>
<td>25.8</td>
<td>55.4</td>
<td>83.2</td>
<td>173.8</td>
</tr>
</tbody>
</table>

5-229
Quenching experiments were employed to investigate the sequence of densification and distortion during liquid phase sintering. The 80W-16Ni-4Cu compacts with 67% green porosity were sintered at 1480°C in a CM vertical furnace in dry hydrogen atmosphere with dew point of -55°C. The hydrogen flow rate was 24 turnovers/h, heating rate was 10 ºC/min, and sintering holding times were from 0 to 30 min. After the sintering temperature and holding time were achieved, the samples were quenched into water at room temperature.

After sintering, distortion was quantified using a distortion parameter. Compact dimensions were first measured at various heights using a coordinate measuring machine (CMM). The measured sectional radii were normalized with respect to the maximum radius of the sintered compact. The distortion parameter equals the standard deviation of the normalized radii of each sample.

The densities of the sintered compacts were measured using water immersion method. Prior to measurement, the samples were infiltrated with light paraffin oil in a vacuum chamber for 15 min to fill all open pores.

Finally, the samples were sectioned along the longitudinal direction, mounted, and polished to a 0.05 µm finish for metallographic analysis. The solid volume fraction was measured manually by point-count method. Typically 3 micrographs were measured to ensure the statistical accuracy of ± 3 vol.%. Dihedral angle measurement was performed by manually measuring the angle between two connecting grains using a protractor. The median of 25 observations was reported as the true dihedral angle.

**EXPERIMENTAL RESULTS**

Figure 1 shows the photo of W-Ni-Cu (Ni : Cu 8:2) alloys with different initial tungsten contents (80, 83, 87, and 90 wt.%) after liquid phase sintering at 1480°C for 30 min. The initial porosity was 59 % and the pore size was 87 µm. The heating rate was 10°C/min. Figure 2 shows the sintered densities and corresponding distortion parameters. All samples achieved nearly full density, except the sample with 90 wt.% W content which achieved only 94% of theoretical density. Solid volume fraction increased as initial tungsten content increased. Distortion decreased as initial tungsten content and solid volume fraction increased. The 80W alloy had the lowest solid volume fraction and most distortion, while the 90W alloy had the highest solid volume fraction and only showed slight distortion.

To investigate the dihedral angle effect on distortion, the solid volume fraction was constant by decreasing the initial tungsten content with decreasing Ni : Cu ratio (As Ni : Cu ratio decreases, W solubility in Ni-Cu matrix decreases). The alloys employed were 80W-16Ni-4Cu (Ni : Cu 8:2), 78.7W-12.8Ni-8.5Cu (Ni : Cu 6:4), 78W-11Ni-11Cu (Ni : Cu 5:5), 77.3W-9.1Ni-13.6Cu (Ni : Cu 4:6), and 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8). These alloys were liquid phase sintered at 1480°C for 30 min. The heating rate was 10°C/min. The initial green porosity was 36%, and the pore size was 87 µm. Figure 3 shows the photo of the sintered samples. The measured solid volume fraction was about 0.61 for all the samples. Figure 4 shows the densities and corresponding distortion parameters of the sintered samples. All the samples achieved a sintered density of above 95% of theoretical density. The sintered density increased slightly as dihedral angle increased, except the 75.6W-4.9Ni-19.5Cu (Ni : Cu 2:8) alloy. Distortion decreased as the dihedral angle increased (Ni : Cu ratio decreased). The sample with dihedral angle of 46 degree
had the most distortion, while the sample with dihedral angle of 76 degree did not show observable distortion.

A comprehensive study of porosity effect on distortion was conducted on three different tungsten alloys, 80W-16Ni-4Cu (Ni : Cu 8:2), 83W-13.6Ni-3.4Cu (Ni : Cu 8:2), and 90W-8Ni-2Cu (Ni : Cu 8:2). Compacts with different green porosities were sintered at 1480°C for 30 min. The heating rate was 10°C/min and the pore size was 87 μm. The distortion parameters for these alloys are plotted in Figure 5, and Figure 6 shows the photo of the sintered 80W-16Ni-4Cu alloy with different green porosities. For the 80W-16Ni-4Cu alloy, all the samples with different green porosities achieved nearly full density and had similar distortion. The distortion parameter for the 80W-16Ni-4Cu alloy is about 0.38. For the 83W-13.6Ni-3.4Cu alloy, all the samples with different green porosities also achieved nearly full density and had similar distortion. The distortion parameter for the 83W-13.6Ni-3.4Cu alloy is about 0.11. The 80W-16Ni-4Cu alloy had more distortion than the 83W-13.6Ni-3.4 Cu alloy. Green porosity did not show observable effects on distortion of 80W and 83W alloys after nearly full densification. For the 90W-8Ni-2Cu alloy, samples with green porosities of 37% and 47% achieved nearly full density and showed slight distortion. Sample with green porosity of 57% achieved only 93% density, and sample with green porosity of 67% achieved only 88% density. Both samples did not show observable distortion.

Figure 7 shows the photo of the 80W-12Ni-8Cu alloys with different green pore sizes after sintering at 1480°C for 30 min. The green porosity was 51%. The distortion parameters are plotted in Figure 8. All the samples with different pore sizes achieved a sintered density of above 96% of theoretical density, and had similar distortion parameter. Green pore size did not show significant effect on distortion.

Figure 9 shows the photo of the 80W-16Ni-4Cu alloys after liquid phase sintering at 1480°C for 30 min using different heating rates. The green porosity was 68%, and pore size was 87 μm. The compacts were heated to 1300°C at 10°C/min, and then the temperature was increased to 1480°C using different heating rates. By doing this, the heating rate when the liquid formed was changed. The heating rates employed were 1, 3, 5, and 10°C/min. Figure 10 shows the sintered densities and corresponding distortion parameters with different heating rates. All the samples achieved a sintered density above 96% of theoretical density. Distortion decreased as heating rate decreased. The sample with a 10°C/min heating rate had the most distortion, while the sample with a 1°C/min heating rate only showed slight distortion.

Figure 11 shows the photo of the 80W-16Ni-4Cu (Ni : Cu 8:2) alloys with 67% green porosity after water quenching from 1480°C. The pore size was 87 μm, and the heating rate was 10°C/min. The holding times at 1480°C was 0, 2, 5, 10, 20, or 30 min. The sintered densities and distortion parameters of water-quenched samples are plotted in Figure 12. It is clearly shown that distortion increased with increasing holding time, and distortion did not occur until after nearly full density. After sintering for 0 min, the compact achieved only 94% density and did not show distortion. After sintering for 2 min, the compact achieved 98.9% density and started to distort. Distortion was significant after sintering for 5 min.
Figure 1. Photograph of W-Ni-Cu (Ni : Cu 8:2) alloys with different tungsten contents, after sintering at 1480°C for 30 min. The heating rate was 10°C/min, green porosity was 59%, and initial pore size was 87μm.

Figure 2. Distortion parameters of W-Ni-Cu (Ni : Cu 8:2) alloys with different tungsten contents, after sintering at 1480°C for 30 min. The heating rate was 10°C/min, green porosity was 59%, and initial pore size was 87μm.
Figure 3. Photo of W-Ni-Cu alloys with constant solid volume fraction but different dihedral angles, after sintering at 1480°C for 30 min. Note that dihedral angle is varied by varying the Ni : Cu ratio.

Figure 4. Sintered densities and distortion parameters of W-Ni-Cu alloys with constant solid volume fraction but different dihedral angles, after sintering at 1480°C for 30 min. The initial green porosity was 36%, and the pore size was 87 μm. Note that dihedral angle was varied by varying the Ni : Cu ratio.
Figure 5. Distortion parameters of W-Ni-Cu (Ni : Cu 8:2) alloys with different porosities, after sintering at 1480°C for 30 min. The heating rate was 10°C/min.

Figure 6. Photo of 80W-16Ni-4Cu (Ni : Cu 8:2) alloy with different porosities, after sintering at 1480°C for 30 min; (a) 37%, (b) 47%, (c) 57%, and (d) 67%. The pore size is 87 μm.
Figure 7. Photo of 80W-12Ni-8Cu (Ni : Cu 6:4) alloy with different EBS binder particle size, after sintering at 1480°C for 30 min. The heating rate was 10°C/min and initial green porosity was 51%.

Figure 8. Densities and distortion parameters of 80W-12Ni-8Cu (Ni : Cu 6:4) alloy with different EBS binder particle sizes, after sintering at 1480°C for 30 min. The heating rate was 10°C/min and the initial green porosity was 51%.
Figure 9. Photo of 80W-16Ni-4Cu (Ni : Cu 8:2) alloy after sintering at 1480°C for 30 min. The green porosity was 68%, and the pore size was 87 μm. The heating rates were: (a) 1°C/min, (b) 3°C/min, (c) 5°C/min, and (d) 10°C/min.

Figure 10. Distortion parameters of 80W-16Ni-4Cu (Ni : Cu 8:2) alloys after sintering at 1480°C for 30 min at different heating rates. The green porosity was 68% and pore size was 87 μm.
Figure 11. Photo of 80W-16Ni-4Cu (Ni : Cu 8:2) alloys after water quenching from 1480°C for different holding times. The heating rate was 10°C/min. The pore size was 87 μm, and green porosity was 67%.

Figure 12. Distortion parameters of 80W-16Ni-4Cu alloys with 67% initial porosity after sintering at 1480°C. The heating rate was 10°C/min. The initial pore size was 87 μm. The alloys were water quenched after different holding times.
DISCUSSION

In liquid phase sintering, densification and distortion are closely related to liquid content. With high liquid content full density can be achieved even at the particle rearrangement stage [1], but often is the concomitant distortion. With low liquid content the solid skeleton resists densification and also retain the compact shape. This was observed in our experiments. Low tungsten content samples achieved full density and distorted, while the 90W sample only achieved 94% density and did not distort.

Distortion in liquid phase sintering is also associated with low dihedral angles. In low dihedral angles, the reduction in solid-liquid surface energy on first melt formation leads to liquid penetration of grain boundaries [8]. Consequently, densification by rearrangement occurs rapidly and solid-solid bonds do not form before saturation of the intergrain void space [8]. Then the relatively weak capillary force is the only source of strength that disappears as the voids are filled with liquid. Distortion is the consequence of strength loss, due to loss of solid skeleton strength or capillarity induced strength. Note that full density alloys will distort on reheating to liquid phase sintering temperature, demonstrating liquid attack of grain boundary. On other hand high liquid content alloys retain shape up to point of densification or pore closure.

Liquid penetration of grain boundaries leads to compact strength loss. A high solid solubility in the liquid correlates with a low dihedral angle and easy liquid penetration of grain boundaries. The fractional atomic solid solubility in the liquid can be approximately linked to the dihedral angle by the following empirical expression [8]:

$$k_A = 0.11 - 0.14 \frac{\phi}{2} \tan \left( \frac{\phi}{2} \right)$$  \hspace{1cm} (1)

where $k_A$ is the fractional atomic solid solubility in the liquid, and $\phi$ is the dihedral angle in radians. High solid solubility in the liquid $k_A$ indicts a low dihedral angle according to Equation 1. The atomic solid solubility in liquid can also be linked to the dihedral angle by the following empirical equation [8]:

$$\phi = 75 - 638\Delta k_A$$  \hspace{1cm} (2)

where $\Delta k_A$ is the fractional atomic solid solubility change in newly formed liquid as compared with the solid solubility in the additive, and $\phi$ is the dihedral angle in radians. Equation 2 indicts that if the atomic solid solubility in liquid is much larger than the atomic solid solubility in the additive, the systems have low dihedral angles. In turn, low dihedral angles imply easier liquid penetration of the grain boundaries and often distortion.

Solid volume fraction and dihedral angle are the dominant factors controlling densification and distortion during liquid phase sintering. Table 3 summarizes the interrelation between dihedral angle and solid volume fraction with respect to distortion during liquid phase sintering [8]. As it shows, a combination of high solid volume fraction and high dihedral angle results in slow densification without distortion. On the other hand, low solid volume fraction and low dihedral angle result in rapid densification with shape distortion. A map as shown in Figure 13 [9] further illustrates these interrelations. This map consists of five zones in terms of densification and distortion. In zone I, sintering is basically via solid-state sinter due to the extremely high solid volume fraction and high dihedral angle. Thus, there is no distortion in zone I. In zone II, there is slow liquid phase sintering densification due to high solid volume fraction or high dihedral angle. No distortion is expected in zone II. In zone III, intermediate densification results in some distortion. In zone IV, low solid volume fraction and low dihedral angle result in
fast densification, compact strength loss, and consequently large distortion. In zone V, solid volume fraction is below the percolation limit (0.185 vol % solid [10]) for compact rigidity and no composition can be sintered without distortion. Our data and some previous observations [5, 6, 8] with several liquid phase sintering systems are superimposed in the sinter map, including W-Ni-Cu, W-Ni-Fe, W-Ni, W-Cu, Mo-Cu, Mo-Ni, and Fe-Cu. These experimental results agree with the sinter map. We expect this map is also representative for other liquid phase sintering systems with spherical solid grains. For systems with prismatic grains we need more experiments to confirm these.

Table 3. Interrelation between solid volume fraction and dihedral angle with respect to distortion during liquid phase sintering [8].

<table>
<thead>
<tr>
<th>Solid volume fraction</th>
<th>Dihedral angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td>rapid densification, large distortion</td>
</tr>
<tr>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td>intermediate to slow densification, little distortion</td>
</tr>
<tr>
<td></td>
<td>intermediate densification, no distortion</td>
</tr>
<tr>
<td></td>
<td>intermediate distortion</td>
</tr>
</tbody>
</table>

STRATEGIES FOR DISTORTION CONTROL IN LIQUID PHASE SINTERING

Various strategies emerge to improve distortion control in liquid phase sintering. Since the compact strength evolution determines densification and distortion onset, the design of compositions for densification without distortion requires manipulation of the microstructure and its evolution to sustain compact strength to avoid distortion. As compact strength has contributions from both sinter bonds and capillary forces, in principle, processing strategies that preserve sinter bonds and/or capillary forces will resist distortion. Liquid phase sintering systems that densify slowly resist distortion. These inherently have high solid volume fraction and high dihedral angle. So one option for distortion control is to use high solid volume fraction and high dihedral angle systems. Systems with low solid solubility in liquid inherently have a high dihedral angle and resist distortion. Compositions with presaturated liquid forming agents (for example, prealloy matrix) will inhibit dissolution of sinter bonds into liquid and resist distortion [8]. A slow heating rate at the point of liquid formation allows solid bonds to reform before capillary forces are lost with pore elimination and will resist distortion. Densification and distortion are sequential events during liquid phase sintering; the first focus is on densification. Densification occurs first. Distortion is inhibited until after nearly full densification when capillary forces are lost and a solid skeleton is not formed. So sintering without full density will also resist distortion.
Figure 13. Densification and distortion map for tungsten heavy alloys during liquid phase sintering [9].
CONCLUSIONS

Solid volume fraction and dihedral angle are the dominant factors on densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and dihedral angle. On Earth, green porosity and pore size do not have observable effects on distortion in situation of fast densification where nearly full density is achieved or pores are closed and capillary forces are lost. Quenching results show that distortion is inhibited until pores are closed and the compact is nearly fully densified. Dimensional precision can be achieved by manipulating the microstructure and its evolution to sustain compact strength to avoid distortion in liquid phase sintering. Processing strategies emerge to improve distortion control in liquid phase sintering, including use of high solid volume fraction and high dihedral angle systems, low solid solubility in liquid, compositions with presaturated liquid forming agents, slow heating rate at liquid formation. Densification before full density or pore closure can also prevent distortion.

ACKNOWLEDGEMENTS

Funding for this research was provided by NASA under grant NAG8-1452, with Mike Purvey as Project Manager.

REFERENCES