Effect of Inhomogeneity on Dimensional Precision in Liquid Phase Sintering

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Abstract

A rigid skeleton during liquid phase sintering is the key to achieving high tolerances in liquid phase sintered compacts. The initial errors (due to inhomogeneities) induced during powder processing, powder mixing, powder compaction add up and this effects the sintering behavior of the material. This is usually observed as warpage, cracking or even compact shape distortion after sintering. Inhomogeneities were deliberately induced in a non-distorting 93W-Ni-Fe (7:3) alloy. Green compacts were formed using ethylene-bis-stearamide as a pore-forming agent with the amount of polymer controlling the local porosity. Layers with varying amount of porosities were generated by using different amount of wax in each layer. The distortion profiles of the sintered samples were measured using a co-ordinate measuring machine. A green density inhomogeneity parameter was defined and the measured distortion parameter was correlated to the inhomogeneity parameter.

Introduction

Liquid phase sintering (LPS) is used for net shape manufacturing of high performance materials for a wide range of applications [1]. LPS is limited to systems with high solid content due to distortion associated with slumping in unit gravity conditions. Tungsten heavy alloys based on W-Ni-Fe/Cu systems are the classic liquid phase sintering system. During LPS the solid phase consists essentially of pure tungsten (density 19.3 g/cm³) in a liquid approximately 53 % Ni- 23% Fe-24% W (density 10.3 g/cm³) [2]. This large difference in densities between the solid and liquid phases causes segregation, hence leading to slumping and microstructural gradients [3, 4]. Upadhyaya and German [5,6] have shown that the microstructural parameters such as solid content, contiguity, connectivity and dihedral angle influence the distortion behavior of liquid phase sintered alloys. An increase in the solid content and the dihedral angle will result in an increased contiguity of the compact. As long as the contiguity is above the critical value the compact has sufficient strength to retain its shape [7].

Recent studies have looked into the effect of porosity and pore size on densification and distortion in liquid phase sintering [8-12]. Yi et al. [10,11] have done experiments on W-Ni –Cu system with varying amounts of porosity and pore sizes. They have found that porosity and pore size do not have observable effects on distortion in situations where full density is achieved. Xu et al. [8] have done similar experiments with W-Ni-Fe heavy
alloys with porosities ranging from 37.5% to 70% and varying tungsten content from 78 to 93-wt% W. The 78W-Ni-Fe compacts distorted and had same amount of distortion for different porosities. 93W-Ni-Fe compacts did not distort for different amount of green porosities. Greater the amount of porosity of the green compact higher the shrinkage of the sintered compact. Experiments on W-Cu system also did not show any effect of porosity on distortion. No apparent effect of porosity on microstructural evolution was found. Lu et.al[12] have done experiments on the W-Ni-Cu system with varying porosity from 34% to 71% and the pore size from 6 to 87 μm. They have shown that higher the amount of porosity and pore size, smaller the distortion. The distortion was not significantly different for different porosity and pore sizes.

Although these studies looked at effect of porosity and pore size on densification and distortion, the porosity introduced was homogenous. This study aims at looking at the effect of inhomogeneous porosity in the green compacts and its effect on densification and distortion.

**Experiments**

W-Ni-Fe tungsten heavy alloys were fabricated from elemental W, Ni, and Fe powders. Table 1 summarizes the characteristics of the powders used in this study. The as-received tungsten powder was deagglomerated by rod milling with pure tungsten rods for 1 h in a 2000 cm³ plastic jar filled with argon. The weight ratio of the rods to the powder was 10:1. Figure 1 shows the powders employed in this study. The W, Ni, and Fe powders were then weighed to the target composition and mixed in a Turbula for 30 min to achieve homogenous distribution. A non-distorting alloy with composition of 93W-Ni-Fe was used for studying the effect of inhomogeneity. The 93W-Ni-Fe alloy was then mixed with different amounts of Acrawax varying from 0.5% to 6% (weight %) and homogenized in the turbula for 30 min. Acrawax is a clean burning polymer leaving behind porosity equivalent to the amount of wax added. The different layers were compacted in a carver hand press with a load of approximately 550 MPa. The green parts were then debound in an inconel retort furnace (Supplier: Lindberg/Blue, Asheville, NC). The samples were placed on a ceramic plate and put into the retort under a flowing atmosphere of H₂, the samples were heated at a rate of 5°C/min to 300°C, then at 2°C/min to 600°C and held at 600°C for 1 h. The temperature was then increased to 1000°C at a rate of 5°C/min and held there for 1 h. Finally, the samples were cooled at 5°C/min to room temperature. The retort was calibrated using a standard temperature cycle measured by a thermocouple inserted into the furnace. At 1000°C, the temperature offset was 20°C with an accuracy of 2°C. After debinding the compact dimensions were measured.
Figure 1: Scanning electron micrographs of Fe (top left), Ni (top right) and W as received (bottom left) and rod milled (bottom right) powders.

A horizontal alumina tube batch type furnace (Supplier: CM, Bloomfield, NJ) was used to sinter the samples. The samples were placed in a ceramic dish and inserted into the hot zone of the furnace. Sintering was performed in a dry H₂ atmosphere with a constant gas flow rate of 2000 cm³/min.

The samples were initially heated at a rate of 10°C/min to a temperature of 900°C and held there for 1h. The temperature was then increased at 10°C/min to 1500°C and held for 30 min. The samples were then cooled at 3°C/min to 1400°C followed by cooling at a rate of 10°C/min to room temperature. The CM horizontal furnace was calibrated using a standard temperature cycle measured by a thermocouple inserted into the furnace. The accuracy of the furnace was ± 2°C. After sintering, the compact dimensions were measured at various heights using a coordinate measuring machine (CMM). The measured sectional radii and heights were normalized with respect to the maximum
radius and height of the sintered compact. The normalized radii were plotted against the normalized height to give the profile of the compact shape. These profiles provide a framework for comparing the relative degree of distortion. The amount of distortion was quantified using a distortion parameter, which is measured as the standard deviation of the radius measurements. The densities of the sintered samples were measured using the Archimedes method.

Table 1: Powder characteristics of W, Ni and Fe

<table>
<thead>
<tr>
<th>Powder</th>
<th>Ni</th>
<th>Fe</th>
<th>W (as-received)</th>
<th>W (rod-milled)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vendor</td>
<td>Novamet</td>
<td>ISP</td>
<td>Osram</td>
<td>Osram</td>
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<tr>
<td>Grade</td>
<td>123</td>
<td>CIP-R1470</td>
<td>M-37</td>
<td>M-37</td>
</tr>
<tr>
<td>Purity</td>
<td>99.8%</td>
<td>99.2%</td>
<td>99.5%</td>
<td>99.5%</td>
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<td>Fabrication Method</td>
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<td>carbonyl process</td>
<td>hydrogen reduction</td>
<td>hydrogen reduction</td>
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<tr>
<td>Particle Size, μm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{10}$</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$D_{50}$</td>
<td>10</td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>$D_{90}$</td>
<td>24</td>
<td>10</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>Shape</td>
<td>Spiky</td>
<td>Spherical</td>
<td>Irregular faceted</td>
<td>Irregular faceted</td>
</tr>
<tr>
<td>Theoretical density (g/cm$^3$)</td>
<td>8.9</td>
<td>7.9</td>
<td>19.3</td>
<td>19.3</td>
</tr>
<tr>
<td>Apparent density (g/cm$^3$)</td>
<td>2.30</td>
<td>2.43</td>
<td>4.13</td>
<td>5.27</td>
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<tr>
<td>Tap density (g/cm$^3$)</td>
<td>3.26</td>
<td>4.63</td>
<td>6.23</td>
<td>7.66</td>
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</tbody>
</table>
Results and Discussion

To quantify the heterogeneous porosity of these samples, an inhomogeneity parameter was devised that is calculated using the following equation:

\[
IP = \left( \frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N} \right) \left( \sum_{i=1}^{N} X_i \right)
\]

(1)

Where \(X_i\) is the weight percent polymer added to the \(i^{th}\) layer of a sample, \(\bar{X}\) is the mean of the weight percent polymer in the sample, and \(N\) is the number of layers in the sample. This specific inhomogeneity parameter was chosen because it integrates several aspects of the heterogeneous porous structure that contribute to distortion. These aspects are the number of layers in the sample, the variation in polymer added to the different layers, and the total polymer present in the structure.
Figure 3 shows a plot of the inhomogeneity parameter versus the average sintered density of each layer configuration. The graph shows that all but one of the samples had an average density of 98% or higher, with the standard deviation for the averages above 98% being less than 0.6. The configuration that fell below the 98% level was sample 1, which had no porosity added. The low average value (97.31%) was due to one of the three samples having an exceptionally low density of only 92%. The other two samples of that configuration had densities above 99%, and therefore the low value is attributed to experimental error. Prior experiments [8,9,10,12] have found that final density varies with a change in the initial porosity. Figure 4 shows the plot between the sinter density and the initial green porosity. The plot indicates that no trend could be established between the initial porosity and the final sintered density.

Figure 3: Sintered density variation with inhomogeneity parameter showing that most compacts achieved near full density.
Figure 4: Scatter plot showing the sintered density of different W heavy alloys with different starting porosity.

Distortion was quantified using a distortion parameter calculated by taking the standard deviation of the normalized radius measurements according to the following equation:

$$
\Delta = \sqrt{\frac{\sum_{i=1}^{N} (X_i - \bar{X})^2}{N}}
$$

(2)

Where $X_i$ is the normalized radius of the $i^{th}$ observation, $\bar{X}$ is the mean of the normalized radii, and $N$ is the number of observations. Figures 5 through 9 show the distortion profiles of all the sintered compacts.
Figure 5: Distortion profiles of samples 2 and 4.

Figure 6: Distortion Profiles of sample 3 and 5
Figure 7: Distortion Profiles of samples 1 and 9.

Figure 8: Distortion profiles of samples 8 and 10.
As can be seen from the distortion profiles, introducing an inhomogeneous porosity in the green compact of a nondistorting 93W-Ni-Fe alloy distorts it. This distortion is attributed to the different amount of shrinkage associated with different layers of the compact. This can be clearly seen in Figure 9 where samples 6 has a higher porosity at the top than bottom corresponding to a higher shrinkage at the top. Sample 7 on the other hand has a higher porosity at the bottom corresponding to a higher shrinkage.

Figure 10 further illustrates this differential shrinkage of different layers. Porosity gradients or density gradients translate into poor dimensional control during the sintering process. Both the layers with low and high porosity undergo different amounts of shrinkage to achieve near full density. This effect has been observed in die compaction of powders. The average distortion parameter was plotted against the inhomogeneity parameter for each layer configuration to see the effect of heterogeneous green porosity on distortion. The standard deviation of the distortion parameters was less than 0.002 for all configurations. The inhomogeneity versus distortion plot is shown in Figure 11. TableCurve statistical software was used to fit a sigmoid curve to the data, which yielded the following empirical equation:

\[
y = \frac{a + b}{1 + \exp(-(x - c)/d)}
\]  

(3)
where \( a = 3.4e-4, \ b = 2.2e-2, \ c = 9.0, \) and \( d = 3.1. \) The curve and actual data show good correlation, as the correlation coefficient is 0.989 and all of the data lie within two standard deviations of the curve, indicating a statistical significance of greater than 99%. The plot shows that as inhomogeneity increases, distortion generally increases. Initially,
Figure 11. Plot of inhomogeneity parameter vs. distortion parameter indicating a sigmoid relationship between the inhomogeneity and distortion. The critical value for inhomogeneity is around 15 above which any change in inhomogeneity does not have a significant effect on distortion.

Conclusions

Introducing heterogeneous porosity in a non-distorting 93W-Ni-Fe alloy causes distortion. Heterogeneity was quantified using an inhomogeneity parameter. The inhomogeneity parameter did not have a significant effect on densification i.e., regardless of the inhomogeneity parameter all the compacts sintered to near full density. Heterogeneity has a significant effect on the distortion behavior during liquid phase sintering. Inhomogeneity parameter and distortion parameter were related by a sigmoid relationship. Increasing the inhomogeneity parameter causes an increase in the distortion. There exists a critical inhomogeneity value beyond which distortion doesn’t change much with inhomogeneity. This critical value for the 93W-Ni-Fe alloy was shown to be around 15. Further experiments need to be done on different systems with different inhomogeneities to conclusively validate the model.
Acknowledgements

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References