Effect of Heating Rate on Densification and Distortion in Liquid Phase Sintering of Tungsten Heavy Alloys.

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Abstract

Dimensional precision is one of the prime concerns in liquid phase sintering. The factors that lead to densification also cause distortion, leaving a narrow processing window in which to operate in, to achieve densification without distortion. Heating rate was selected as a variable parameter during liquid phase sintering of W-Ni-Fe alloys. Distortion was quantified from final profiles measured using a coordinate measuring machine. Microstructural parameters such as solid volume fraction and contiguity were measured for all heating rates. Contrary to widely held notions the distortion results indicated that there was no significant effect of heating rate nor solid state sintering on distortion behavior. Consequently, these results show the lack of structural rigidity at the point of liquid formation is the key factor leading to shape loss of the compact.

Introduction

Liquid phase sintering is a net shape fabrication technique employed to consolidate both ceramic and metal powders. The formation of a liquid during heating process enhances the diffusion and bonding process, leading to increased sintering rates [1, 2].

Heating of a powder compact from the initial green state leads to solid state sintering up to the formation of liquid phase. Concomitant with solid state sintering, the compact continuously strengthens and becomes resistant to distortion. The amount of densification achieved prior to liquid formation is as high as 90 % in W-Ni-Fe systems [3]. The solid bonds formed during heating inhibit deformation and preserve the compact shape. Upon liquid formation there is a decrease in the contiguity due to dissolution of the solid-solid bonds leading to a substantial strength loss [4, 5]. Once the contiguity falls below a critical level, the compact strength also diminishes leading to a shape distortion. Gravity plays a very important role in shape distortion of heavy alloys [6-13]. In W-Ni-Fe heavy alloys the density difference between the solid and liquid phases is as high as 10.3 g/cm³ and this leads to solid-liquid separation, bulk distortion, and microstructural gradients in the compact [14]. Factors such as solid solubility in the liquid and liquid: solid ratio affects the distortion behavior to a great extent, systems like W-Cu and Mo-Cu, which have limited intersolubility, have high dihedral angles and maintain structural rigidity for compositions in excess of 50 % liquid. But on the other hand the W-Ni system has a low dihedral angle (or high intersolubility) and distorts with only 27 % liquid [15].

Densification and distortion are sequential processes, densification occurs first as the compact softens to a point where capillary stresses exceed compact strength, resulting in self-densification. On the other hand distortion takes place if the compact does not have sufficient strength [5]. Studies have shown that microstructural parameters like solid: liquid ratio, contiguity, and connectivity affect the distortion behavior of W-Ni-Fe and W-Ni-Cu heavy alloys [16, 17]. Increasing the dihedral angle or the solid volume fraction reduce the amount of distortion. Recent studies have isolated the effects of green microstructure and initial pore size on the densification and distortion of heavy alloys. It was found that initial pore size and porosity do not significantly effect on the densification or distortion behavior of heavy alloys when sintered on Earth [18,19].
Heating rate during sintering is another important process parameter whose effect on densification and distortion is not well known. In this work, W-Ni-Fe tungsten heavy alloys were liquid phase sintered at different heating rates. Densification and distortion were quantified and related to heating rate, and microstructural changes.

**Experimental Procedures**

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. The various compositions employed were 83, 88, and 93 wt.% tungsten, with the balance being Ni: Fe in the ratio of 7:3.

**Figure 1:** Scanning electron micrographs of Fe (top left), Ni (top right) and W as-received (bottom left) and rod milled (bottom right) powders.
Table1: Powder characteristics of W, Ni, and Fe powders used in this study.

<table>
<thead>
<tr>
<th>Powder</th>
<th>Ni Vendor</th>
<th>Ni Grade</th>
<th>Ni Purity</th>
<th>Ni Fabrication Method</th>
<th>Ni Shape</th>
<th>W (as-received) Vendor</th>
<th>W (as-received) Grade</th>
<th>W (as-received) Purity</th>
<th>W (as-received) Fabrication Method</th>
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<td>Fe Purity</td>
<td>Fe Fabrication Method</td>
<td>Fe Shape</td>
<td>W (rod-milled) Vendor</td>
<td>W (rod-milled) Grade</td>
<td>W (rod-milled) Purity</td>
<td>W (rod-milled) Fabrication Method</td>
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<tr>
<td>Powder</td>
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<td>ISP</td>
<td>Osram</td>
<td>Carbonyl process</td>
<td>Spiky</td>
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<td>Grade</td>
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<td>99.2%</td>
<td>99.5%</td>
<td>Hydrogen reduction</td>
<td>Irregular faceted</td>
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<td>Fabrication Method</td>
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<td>7.9</td>
<td>19.3</td>
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<td>4.13</td>
<td>5.27</td>
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<td>6.23</td>
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<td>Pycnometer density (g/cm^3)</td>
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<td>7.89</td>
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<td>19.3</td>
<td></td>
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<tr>
<td>BET surface area (m^2/g)</td>
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<td>0.45</td>
<td>0.18</td>
<td>0.19</td>
<td></td>
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The homogenously mixed powders were compacted using a cold isostatic press at a compaction pressure of 280 ± 5 MPa. The cold isostatically pressed rods were sectioned at various heights using a band saw and green segments with height of 10 mm and diameter close to 10.6 mm were prepared for sintering. Sintering was done at 1500°C in a CM horizontal tube furnace (CM Furnaces, Bloomfield, NJ) in dry hydrogen with dew point below – 40°C. The hydrogen flow rate of 2000 cm³/min was maintained in the furnace throughout the sintering cycle. The compacts were heated at 10°C/min to 900°C and held at this temperature for 1 h to reduce oxides on the powders. Then the temperature was increased to 1400°C at 10°C/min and held for 5 min to equilibrate. The heating rate effect during liquid formation was observed by changing the heating rate from 1400°C to 1500 °C. The various heating rates are 1, 5, 10, and 15 °C/min. The samples were held at 1500°C for 30 min and cooled at 10°C/min to room temperature.

Dilatometry was used to observe the in situ shrinkage, shrinkage rate, and melt formation during sintering. Dilatometric experiments were conducted on 88W-Ni-Fe (7:3) at heating rates of 1, 5, 10, and 15 °C/min. The experiments were performed using a vertical push rod dilatometer in hydrogen atmosphere. The temperature inside the dilatometer (model: 1161V, Anter, Pittsburgh, PA, USA) was accurate to ± 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. Finally the samples were sectioned along the longitudinal direction, mounted and polished to a 0.05 μm finish for metallographic analysis. An image analysis software (PGT Imagist) was used to measure the microstructural parameters such as solid volume fraction and contiguity. Connectivity was measured manually. To ensure statistically significant results more than 500 grains per sample were measured with a coefficient of variance less than 0.05.

Results

The usual objective of net-shape liquid phase sintering is to achieve full density without distortion. Densification according to classic liquid phase sintering theory occurs through stages of rearrangement, solution-reprecipitation, and solid phase sintering. The sintered density (% of theoretical) as a function of tungsten weight percentage is shown in Figure 2. The sintered density is over 95 % for all alloys except for 83W alloy sintered at a heating rate of 1°C/min, which has a sintered density of 90 %. There is no systematic trend observed between the heating rate and densification.

Densification, shrinkage, and shrinkage rate were monitored by performing dilatometry at various heating rates for an 88W-Ni-Fe alloy. A plot of shrinkage versus temperature for four different heating rates between 1400°C and 1500°C is shown in Figure 3. A substantial amount of shrinkage occurs prior to the formation of the liquid phase for all heating rates. Sintered densities of approximately 93 % are achieved for heating rates of 5, 10, and 15°C/min, whereas for 1°C/min it is near 95 %. Note there is compact swelling before slumping in the compact sintered at 1°C/min. This could be due to the penetration of grain boundaries by the liquid and hence
pushing the grains apart before pulling them together by rearrangement process. The shrinkage prior to liquid formation increases as the heating rate decreases.

![Graph showing sinter density as function of tungsten wt.% for 83, 88, and 93W-Ni-Fe (7:3) alloys sintered at 1500°C for 30 min at heating rates of 1, 5, 10, or 15 °C/min.](image)

Figure 2: Sinter density as function of tungsten wt.% for 83, 88, and 93W-Ni-Fe (7:3) alloys sintered at 1500°C for 30 min at heating rates of 1, 5, 10, or 15 °C/min.

Since shrinkage rate plots are more sensitive to small changes in temperature than are shrinkage plots, the variation of shrinkage rate with temperature was obtained by numerical differentiation of the plots in Figure 3. These are shown in Figure 4. At any temperature the shrinkage rate is lower for a lower heating rate. The point of maximum shrinkage rate indicates the dissolution of solid-solid bonds by liquid phase and densification due to rearrangement. If the solid-state densification is suppressed, then a large burst of densification occurs at the onset of liquid formation. This can be seen in Figure 5 where the peak shrinkage rate increases with heating rate, indicating that the contribution of rearrangement to densification is higher for higher heating rates. To observe whether densification behavior was different if the period of slow heating was extended, dilatometer runs were performed by changing heating rate from 900°C. The resulting shrinkage and shrinkage rate plots are shown in Figures 6a and 6b. The shrinkage at any given temperature is higher for the slower heating rate of 1°C/min, since the slower heating rate gives more time for solid-state diffusion process. In turn, because the compact is denser on reaching the liquid formation temperature, there is a smaller shrinkage rate peak with slow heating. Figure 6b shows that shrinkage rate is constant with temperature for a heating rate of 1°C/min, but increases with temperature for heating rate of 15°C/min. The peak shrinkage is higher for the higher heating rate of 15 °C/min.
Figure 3: Shrinkage of a 88W-Ni-Fe (7:3) alloy plotted as a function of temperature at different heating rates of 1, 5, 10, and 15 °C/min.

Figure 4: Shrinkage rate of a 88W-Ni-Fe (7:3) alloy plotted as a function of temperature at different heating rates of 1, 5, 10, and 15 °C/min.
Figure 5: Peak shrinkage rate of 88W-Ni-Fe (7:3) alloy at the onset of liquid formation plotted as a function of heating rate.

Figure 6a: Shrinkage plotted as a function of temperature for a 88W-Ni-Fe (7:3) alloy sintered from 900°C to 1500°C at heating rates of 1 or 15°C/min. Note that the shrinkage at any given temperature is higher for the lower heating rate of 1°C/min.
Figure 6b: Shrinkage rate plotted as a function of temperature for 88W-Ni-Fe (7:3) alloy sintered from 900°C to 1500°C at heating rates of 1 or 15°C/min. Note that the shrinkage rate is constant for lower heating rate of 1°C/min till the point of liquid formation.

The loss of contiguity at the point of liquid formation leads to a significant reduction in structural rigidity causing distortion in sintering of heavy alloys [21]. Compacts with higher tungsten content, namely 93W-Ni-Fe(7:3), resist distortion at all heating rates; whereas, considerable distortion occurs for 83W-Ni-Fe(7:3) and 88W-Ni-Fe(7:3) alloys. The macroscopic distortion is mapped onto distortion profile maps to help calculate the distortion parameter. For this study the distortion parameter is defined as the standard deviation of the normalized radial measurements. Figure 7 shows a heavily distorted 83W-Ni-Fe, the evident shape is characteristic of alloys that undergo heavy distortion.

The effect of heating rate can be qualitatively judged by the distortion profiles of these alloys after sintering with various heating rates for a fixed tungsten content. This can be seen in Figures 8, 9, and 10. The normalized distortion profiles are of similar form for all heating rates, which indicates that the effect of heating rate on distortion is negligible. The distortion parameter plotted against the heating rate for heavy alloys containing varying amount of tungsten is shown in Figure 11. The near horizontal lines for distortion as a function of heating rate for alloys containing 83, 88, and 93 W by wt.% reiterate that distortion does not change much with heating rate. The variation of distortion parameter with tungsten content is shown in Figure 12. The fit gives a statistical correlation greater than 99 % significance. The distortion decreases linearly with increasing tungsten content in the alloy. As the tungsten content increases, solid volume fraction and contiguity also increase leading to a rigid skeletal structure, which ensures dimensional stability.
Figure 7: A representative shape of a heavily distorted 83W-Ni-Fe (7:3) heavy alloy sintered at 1500 °C for 30 min.

Figure 8: Distortion profiles of 83W-Ni-Fe (7:3) heavy alloys sintered at 1500°C for 30 min at heating rates of 1, 5, 10, or 15°C/min. The x-axis represents the normalized radius and the y-axis the normalized height.
Figure 9: Distortion profiles of 88W-Ni-Fe (7:3) heavy alloys sintered at 1500°C for 30 min at various heating rates of 1, 5, 10, or 15°C/min. The x-axis represents the normalized radius and the y-axis the normalized height.

Figure 10: Distortion profiles of 93W-Ni-Fe (7:3) heavy alloys sintered at 1500°C for 30 min at heating rates of 1, 5, 10, or 15°C/min. The x-axis represents the normalized radius and the y-axis the normalized height.
Figure 11: Distortion parameter plotted as a function of heating rate for tungsten heavy alloys containing 83, 88, or 93 W by wt.% sintered at 1500°C for 30 min.

Figure 12: Distortion parameter plotted as a function of tungsten content in wt.%. Note the linear decrease in distortion parameter with increasing tungsten content.
Discussion

The experimental results provide an insight into the densification and distortion of heavy alloys and their dependence on heating rate. The distortion behavior can be related to the microstructural parameters. The microstructural parameters from this study for different heating rates are plotted in Figures 13 and 14 and reported in Table 2. The general trend is an increase in solid volume fraction and contiguity with increasing tungsten content. This is in agreement with the studies from previous research work [6, 7,9,10,20] on W-Ni-Fe alloys. A higher solid content results in a higher contiguity, as shown in Figure 15. The present results are compared to some previous studies, which also show an increase in contiguity with increase in solid volume fraction. A higher contiguity results in a rigid skeletal structure and hence preserves the compact shape.

German [7] related the critical content required to the three-dimensional grain coordination number \( N_C \) dihedral angle \( \phi \) according to the relation:

\[
V_S = -0.83 + 0.81 N_C -0.056N^2_C + 0.0018N^3_C -0.36A +0.008A^2
\]  
(1)

where the parameter \( A=N_C\cos (\phi/2) \)

The mean connectivity \( C_g \) is related to the three dimensional grain co-ordination number and dihedral angle according to

\[
C_g = 0.68 N_C\sin (\phi/2)
\]  
(2)

For an average connectivity of 2 contacts per grain and dihedral angle of 30 degrees, the corresponding critical solid volume fraction is 0.8, as calculated from Equations 1 and 2. The observed average solid volume fraction, calculated for all heating rates, for 88W and 93W alloys are 0.78 and 0.87, respectively. The calculated critical solid volume fraction of 0.8 lies between the 88W and 93W compositions, which confirms that distortion sets in for composition lying between the 88W and 93W alloys. The 83W and 88W compacts distort at all heating rates. This indicates that the amount of solid state sintering prior to liquid formation, although creating solid-solid bonds, these bonds dissolve once the liquid forms. The dissolution of the solid-solid bonds causes a decrease in the contiguity, which will cause distortion in the compact due to lack of structural rigidity. Hence, in 83 and 88W alloys the compacts distort as the contiguity falls below the critical value.
Figure 13: Average of the top and bottom solid content plotted as a function of tungsten content for alloys sintered at 1500°C for 30 min at different heating rates.

Figure 14: Average of the top and bottom contiguity plotted as function of tungsten content for alloys sintered at 1500°C for 30 min at different heating rates.
Table 2: Microstructural data for 83, 88, and 93W alloys sintered at 1500°C for 30 min at different heating rates.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Heating rate °C/min</th>
<th>Solid Volume Fraction</th>
<th>Contiguity</th>
</tr>
</thead>
<tbody>
<tr>
<td>83W-Ni-Fe</td>
<td>1</td>
<td>0.71</td>
<td>0.095</td>
</tr>
<tr>
<td>88W-Ni-Fe</td>
<td>1</td>
<td>0.77</td>
<td>0.142</td>
</tr>
<tr>
<td>93W-Ni-Fe</td>
<td>1</td>
<td>0.86</td>
<td>0.256</td>
</tr>
<tr>
<td>83W-Ni-Fe</td>
<td>5</td>
<td>0.72</td>
<td>0.101</td>
</tr>
<tr>
<td>88W-Ni-Fe</td>
<td>5</td>
<td>0.78</td>
<td>0.166</td>
</tr>
<tr>
<td>93W-Ni-Fe</td>
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<td>0.87</td>
<td>0.300</td>
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<td>93W-Ni-Fe</td>
<td>15</td>
<td>0.87</td>
<td>0.356</td>
</tr>
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Figure 15: Contiguity plotted as a function of solid volume content for alloys sintered at 1500°C for 30 min at different heating rates.
Conclusions

Slower heating causes a higher amount of shrinkage (densification) prior to the liquid formation in W-Ni-Fe heavy alloy systems. At the point of melt formation the aggressive liquid penetrates the grain boundaries causing shape loss independent of heating rate. Hence over the range from 1 to 15°C/min solid state sintering did not have a significant effect on final distortion. The distortion profiles are self-similar for alloys sintered at different heating rates at fixed tungsten content. The distortion parameter is almost the same for a fixed tungsten content alloy sintered at different heating rates. An increase in solid content leads to an increase in contiguity leading to structural rigidity of the compacts. The distortion parameter decreases with an increasing solid content in the alloy.

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References