Realtime Sintering Observations in W-Cu system: Accelerated Rearrangement Densification via Copper Coated Tungsten Powders Approach

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Abstract

Liquid phase sintering (LPS) is an attractive processing approach for sintering the W-Cu system. Lack of solubility between W and Cu inhibits densification via the solution-recipitation process, therefore rearrangement and solid state sintering are the only active means to densify during LPS. In this study W-50Cu compositions were prepared by two different methods. One is by use of Cu coated W powders and other is by mixing elemental powders. Compacts prepared from these powders were liquid phase sintered at 1250°C for 1h. The compact dimensional change during sintering was monitored in situ using real-time imaging. In contrast to mixed powders, the Cu coated tungsten powders undergoes more densification and at relatively faster rate. Experimental studies were also conducted with dilatometry and microstructural characterization via optical microscopy support the mechanistic interpretation.

Key Words: W-Cu system, LPS, Rearrangement, Cu coated W powders

1.INTRODUCTION

W-Cu composites are used in electrical contacts and thermal management applications owing to high thermal conductivity of copper and the low thermal expansion coefficient and arc erosion resistance of tungsten [1-3]. There are several manufacturing routes for generating the composite structure in W-Cu system including liquid phase sintering (LPS), infiltration, and combined infiltration and sintering process. Furthermore, during the past decade there have been efforts to improve the initial powder homogeneity using mechanically alloyed or coated composite particles [4-12].

Since mutual solubility in W-Cu system is almost non-existent, densification via solution-precipitation during LPS is limited. Therefore, the main driving force for densification is controlled by events associated with the rearrangement process [13-15]. Consequently, higher applied pressures during compaction may result in increased particle contacts, which limit the particle movements via rearrangement. As it is previously reported, certain amount of solid state sintering may occur between the W-W particle contacts prior to liquid formation which can lead to formation of a rigid tungsten skeleton [3-4]. This is a major barrier to reaching full densities in W-Cu system, since the rigid skeleton resists densification. Use of higher...
sintering temperature to enhance densification is also avoided as it leads to copper evaporation.

Although high densification is possible with sintering aids, most additives negatively impact conductivity, both electrical and thermal. Therefore, use of smaller W powder size as optimal solution for achieving higher density in W-Cu alloys. However, fine powders are susceptible to oxidation, which restricts densification and adversely affects both the mechanical and thermal properties.

Mechanical and physical properties of W-Cu alloys also are dependent on microstructural features as a result of the processing conditions. The level of residual porosity, contiguity of tungsten and copper phases, compositional segregations need to be minimized to sustain high properties. In certain applications (e.g. thermal management devices), use of transition metal additives, such as Ni, Fe and Co is restricted since these degrade conductivity [16-18]. One of the viable strategies therefore for densification of W-Cu compacts is through the use of Cu coated composite W powders [4-5, 7]. This study compares the densification behavior of premixed W-Cu and Cu-coated W powder compacts. The dimensional changes during sintering were monitored in situ using a dilatometer as well as through real-time imaging.

2. EXPERIMENTAL PROCEDURES

A-Preparation of W-Cu Composite Powders

In this study, W-50Cu composite powders were prepared via two methods, i.e. elemental mixing and electroless copper coating on tungsten powders. Elemental mixing operation was performed by use of turbula blender for 20 min. In the background of this study, alternative methods of coating W powders with Cu were investigated including electroless coating, electrolytic coating and physical vapor deposition (PVD). Since it is a simple process and offers exact final compositions, the electroless coating technic was selected for this study. Details of coating operation are described elsewhere [7]. Both the coated powders and spent coating solutions were subjected to chemical analysis to ensure proper control of over the coating of Cu on to the W powders.

The characteristics of the powders used in the present study are summarized in Table 1. The coarser tungsten powder was selected as substrate for preparing the copper coated composite powders whereas the finer one was only used for preparation of the elementally mixed powders.

B-Compaction of Powders and Real Time Sintering Experiment

For sintering studies, the powders having W-50Cu composition were compacted as cylindrical pellets (φ =1.27 mm) using hydraulic press. Applied compaction pressure was varied between 150 to 600 MPa. In situ monitoring of the compact dimensional change was done using a Synchrovision™ system while the compacts were sintered in a horizontal tube furnace. The compacts were heated to 1050 °C at 10 °C /min. Subsequently, in order to observe the subtle dimensional changes during sintering, the compacts were heated further to 1200 °C at 1 °C /min. Afterwards, the heating ramp was increased to 10 °C /min. The compacts were heated to 1250°C and isothermally held there for 1h. As sintering
<table>
<thead>
<tr>
<th>Powder</th>
<th>Particle Size Distribution (μm)</th>
<th>Apparent Density (g/cm³)</th>
<th>Tap Density (g/cm³)</th>
<th>Pycnometer Density (g/cm³)</th>
<th>Production Method, Particle Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>W Coarse</td>
<td>D10 2.4, D50 6.2, D90 10.8</td>
<td>4.05</td>
<td>6.06</td>
<td>19.12</td>
<td>Reduction, Polygonal</td>
</tr>
<tr>
<td>W Fine</td>
<td>D10 0.9, D50 2.9, D90 6.1</td>
<td>3.96</td>
<td>5.92</td>
<td>19.18</td>
<td>Reduction, Polygonal</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>D10 8.5, D50 13.1, D90 17.4</td>
<td>3.39</td>
<td>2.44</td>
<td>8.45</td>
<td>Atomization, Spherical</td>
</tr>
</tbody>
</table>

Atmosphere, nitrogen gas was used until 700 °C and after reaching this temperature atmosphere was changed to hydrogen. The densification responses of the compacts were also measured using a vertical dilatometer. For this purpose samples were heated up to 1250 °C with the constant heating rate of 10 °C/min.

3. RESULTS and DISCUSSION

Figure 1 shows series of pictures captured of the mixed and the coated W-50Cu at various temperatures between 1070 °C and 1200 °C. From the figure, it is interesting to note that the Cu-coated tungsten powder compact undergoes higher densification as compared to its mixed W-Cu counterpart. Initially, both compacts were pressed under same conditions. Prior to Cu-melt formation, none of the compact shows more appreciable densification. Consequently, both coated and mixed (uncoated) compacts appear similar. Once the onset of melt formation occurs, both compacts densify. However, the densification in Cu-coated W compact starts at a relatively lower temperature compared to the mixed W-50Cu. Moreover, between 1111 °C and 1120 °C, the coated W-50Cu exhibits an appreciably greater densification compared to mixed counterpart. Even at higher temperatures, the radial as well as axial shrinkage in coated compact is more than the mixed one.

Based on the real-time images (Figure 1), it is obvious that in coated W-Cu rearrangement occurs at a relatively lower temperature. This can be attributed to relatively homogenous distribution of Cu, and hence, the melt during liquid phase sintering. Moreover, Cu-coating restricts the W-W contact formation through solid-state sintering during the compact heat up. The extent of W-W bond formation and the resulting tungsten skeletal rigidity restricts capillary stress induced densification. It is obvious that the compact prepared from the elementally mixed powders has initially more W-W particle contacts in compare to sample prepared from the as-coated powders.

Figure 2 shows the variation in compact axial shrinkage with temperature of the mixed and the coated W-50Cu compacts. The powders were compacted at 150 MPa and sintering was done at 10 °C/min under H₂ gas flow. As it can also be followed from this figure, following with the liquid formation compact prepared from the coated powders (E50) shows earlier and faster rearrangement while relatively gradual shrinkage were observed in sintering of compact prepared from the elementally mixed powders (EM50). Since there is almost no densification occurs by means of the solution-recipitation contribution during LPS of W-Cu alloys, the time dependent shrinkage should be attributed to sole rearrangement supported densification. When sintering temperature exceeds copper melting point, the copper coated powders were easily make small movements and rearrange their positions whereas, most of tungsten particles in the compact prepared from the elementally mixed powders are not easily
Figure 1 Real Time Sintering Images of W-50Cu alloys between 1070°C-1200°C
(Left Sample Coated powders- Right Sample Elemental mixed)
move because of solid state bonding realized up to this temperature. Group movement of tungsten particles may probably alter this restriction however this process needs more time.

Figures 3. compares the effect of compaction pressure on the shape of the coated and the elementally mixed W-50Cu compact sintered at 1250 °C for 1h. Note W-50Cu compacts (both mixed and coated) pressed at 150 MPa exhibit structural rigidity during sintering and do not distort. The coated W-50Cu however shows greater densification as compared to the mixed compact. This is keeping with the same trend as obtained by the real time video imaging of the compacts during heating between 1070 °C and 1200 °C. Surprisingly, the dimensional behavior of compacts pressed at higher pressures was markedly different. It is interesting to note that at 400 MPa and 600 MPa, the Cu-coated W compact shows extensive compact distortion.

Typical microstructures of compacts real-time observed during sintering were given in Figure 4. Grouping and necking between tungsten particles can be seen in both micrographs. It is obvious that during powder coating or pressing, any physical effect leading tungsten-tungsten particle contact will be promote solid state bonding of tungsten particles during sintering. Since material transport rate is limited due to low sintering temperature, no abrupt grain coarsening was observed after sintering and micrograph still reflects initial tungsten particle properties.

Table 2 presents the effect of compaction pressure on the sintered density of the coated and the mixed W-50Cu compacts, liquid phase sintered at 1250 °C. Note that at 150 MPa, the coated powders have undergone higher densification (97%) as compared to mixed powder.
However, there is a marked decrease in the sintered density in the coated compacts at 400 and 600 MPa. During microstructural investigation of these samples only macro level porosity and voids were observed which are led to such a marked density decrease as mentioned in the Table 2.

Table 2: Effect of compaction pressure on the sintered density of mixed and coated W-50Cu. All compacts were sintered at 1250 °C for 1h.

<table>
<thead>
<tr>
<th>Compaction pressure, MPa</th>
<th>Sintered Density, % Theoretical</th>
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<tbody>
<tr>
<td></td>
<td>Samples prepared from Cu-coated tungsten powder</td>
</tr>
<tr>
<td>150</td>
<td>97</td>
</tr>
<tr>
<td>400</td>
<td>71</td>
</tr>
<tr>
<td>600</td>
<td>68</td>
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</table>

4. CONCLUSION

This study shows that powder processing has a significant influence on the densification response of W-Cu alloys. Early onset of rearrangement were detected via dilatometric and real-time video imaging of the copper coated W-50Cu alloys as compared to the elemental mixed counterpart. When pressed at 150 MPa, the densification in the coated compacts is significantly higher as compared to the elemental mixed counterpart. However, when pressed at higher pressure (400 and 600 MPa) the coated W-50Cu alloy shows extensively shape distortion, whereas the compact prepared by elemental mixing retains its structural rigidity. Thus, both the powder processing as well as the compaction should be optimized in conjunction to achieve the desired densification in W-Cu system.

REFERENCES