Characterization of fine-grained W–10 wt.% Cu composite fabricated by hot-shock consolidation

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A B S T R A C T
In this study the W–Cu composites have been fabricated by hot-shock consolidation and then their mechanical properties were estimated by nano-indentation experiments. The initial powders were preheated to 700–1000 °C in less than 3 min, then consolidated under shock pressure within range of 3–4 GPa instantaneously. A W–Cu composite with the highest relative density of 96.3% was obtained without any sintering activator. The grain size of consolidated sample is nearly the same as its initial size of 2 μm. The samples were characterized using light microscopy (LM) and scanning electron microscopy (SEM). It was found that the homogeneous distribution of copper is the key factor for the consolidation of W–Cu powder, which is dominated by preheating temperature. High temperature improves the distribution of copper and enhances the bonding of W–Cu, but also leads to agglomerating of Cu while exceeding a specific value. The main mechanisms of the densification of W particles are void collapse and plastic deformation, which are dominated by the shock pressure.

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1. Introduction

Tungsten–copper (W–Cu) composites combine the excellent properties of both components, such as low thermal expansion, high melting temperature, and high temperature strength of tungsten and high thermal and electrical conductivity of copper [1]. Such properties make W–Cu composites be widely used as heat-sink material, ultra-high voltage electric contact material and warhead materials [2].

The difficulties in fabricating W–Cu composites are related to the practically zero mutual solubility of tungsten and copper, the high difference between their melting points and densities [3]. In general, two common methods have been developed to fabricate W–Cu composites, which are liquid phase sintering (LPS) and the liquid infiltration (LI). It is difficult to achieve full or near density by LPS due to the poor solubility of W and Cu [4]. Therefore, activated sintering [5] and mechanical alloying [6,7] were used to enhance the sinterability of W–Cu composites. However, these methods led to unsatisfactory thermal and electrical properties due to contaminations generated during the process. In addition, high temperature (exceeding 1000 °C) and long duration (over 1 h) are necessary for both LPS and LI methods, but leading to aggregation of Cu and microstructural coarsening [8]. Novel sintering techniques have been explored to improve W–Cu composite densifications, which includes plasma spraying [9], laser sintering [10], microwave sintering [8,11,12] and powder injection molding [13]; but the deterioration due to high sintering temperature and long processing time is still not overcome. Then methods utilizing ultra-high pressure are developed to fabricate W–Cu composites, such as Hot-pressing method [14] and resistance sintering [15,16], which apparently lower sintering temperature and shorten sintering time. Resistance sintering is considered as a promising method for the fabrication of metals with a fine-grain microstructure. But the size of sample prepared by applying this method is limited due to the size of the cubic quasi-isostatic loading device, and the cost is also expensive.

Shock consolidation (SC) is a unique method that uses shock wave generated by explosion or high velocity impact to compact powders. While the shock wave propagates in powders, particles impact each other at an extremely high strain rates (107−108 s−1), generating high temperature at the particle surface and high pressure in the powder bed. Under high pressure, particles are crushed into pieces to fill the voids between them, and are bonded to each other under high temperature. Due to the rapid cooling rates of 108 K/s, the melting of particle is limited to the surface while the interior of particle remains relatively cool [17,18]. These inherent properties make the SC method suitable for consolidation of metastable powders, such as nano-sized and amorphous powders, where the consolidated bulks can retain its initial particle size with a density nearly full [19,20]. However, in the case of brittle materials, such as ceramic and refractory powders, it is difficult to achieve full density due to the cracks generated by tensile stresses and thermal residual stresses under the rapid cooling rate. Then hot shock consolidation (HSC) is explored, whereby, the powders are heated to moderate temperatures before consolidation. Heating reduces the hardness and strength and increases the ductility of powders. By preheating powders, the additional energy required to melt the powder surfaces can also be reduced. Considerable reduction in compacting pressure can be achieved by adopting preheating of powders, with which the

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cracks induced by intense reflected wave can be avoided. Successful applications of HSC have been reported; the pure tungsten \cite{21} and tungsten alloy \cite{22,23} samples are free of cracks and show good bonding. Besides preheating powders, the underwater shock wave has been considered as an effective way to eliminate the cracks \cite{24}. Utilizing preheating of powders and underwater shock wave, even the diamond powders and c-BN powders can be consolidated \cite{25–28}. For most of these researches, the powders were preheated by an external electric furnace, which was removed by a complex mechanical structure after the preheating process, then the preheating rate is less than 10°C/min, much lower than the rate of 10°C/s for chemical furnace utilized in this work.

There are a few publications on shock consolidation of W–Cu composites without preheating the powders. Wang et al. \cite{29} produced W–25 wt.% Cu nanocomposites via shock consolidation of reduced W–CuO mixture, with a final density of 97.6%T.D. and crystalline size of 27 nm. Mashimo et al. \cite{30} combined mechanical alloying and shock consolidation to fabricate W–18.7 wt.% Cu composites with a density of 88%T.D. In our previous work \cite{31}, the validity of this HSC technique in fabricating W–Cu composites has been confirmed, and preliminary study has been conducted.

In this work, the fine-grained W–Cu composites were fabricated by HSC at a preheating temperature range of 700–1100 °C. The W–Cu powders were preheated using the heat released through a SHS (Self-Propagating High-temperature Synthesis) reaction. The underwater shock wave was also applied to eliminate cracks. The effects of preheating temperature and shock pressure on consolidation were investigated; and the sintering mechanism was also discussed.

2. Experimental procedure

Fig. 1 shows the schematic illustration of the SHS assisted HSC system, which is similar to the assembly used in our previous work \cite{21} but smaller. This system consists of several parts: explosive, water column, SHS compact, W–Cu mixture and SHS reaction vessel. A liquid explosive, nitromethane with a detonation velocity of 6.3 km/s and a detonation pressure of 11.9 GPa, was used and charged in a PVC container. The water column is used to adjust the intensity of shock wave, which, when ignited, will generate a high temperature over 2000 K. As soon as the powder bed reached the designed temperature, the explosive was ignited by a detonator. After explosion, when cooling to room temperature, the powder container was extracted and the compacted sample was machined out for further testing. The preheating temperature is controlled in the range of 700–1300 °C by changing the mass of the SHS mixture. Fig. 2 shows a typical temperature history curve during preheating process. As shown in Fig. 2, the powders reach the highest temperature in less than 3 min, and then retain an isothermal state for a short time, when the explosive is ignited. The heating rate of powders is ~10 °C/s, allowing the temperature of the inner and the periphery to be identical at the peak.

The peak pressure in powder bed was estimated by numerical simulation using AUTODYN-2D, a two-dimensional finite difference program. The density of recovered sample was measured by Archimedes’ method. The microstructure was investigated using light microscopy (LM) and scanning electron microscopy (SEM). The hardness and modulus were both measured through the nano-indentation experiments.

3. Results and discussion

3.1. Hot-shock consolidation

Fig. 3 shows the W–Cu composites with the highest and lowest density, respectively. From the photograph, the samples show different colors due to different densities, but no macro-crack is observed. The experimental parameters are listed in Table 1, where the shock pressure and preheating temperature are two key parameters for hot-shock consolidation. The incident shock pressures onto the preheated powder were estimated through the AUTODYN, using the P-α model to describe the compression behavior of W–Cu powders. The E/M is the mass ratio of the explosive to W–Cu powders. The temperatures were measured using a thermocouple, which was inserted into the bottom of powders.
The relationship between the preheating temperature and final densities is shown in Fig. 4. It shows an appropriate temperature with which a high density can be achieved in hot-shock consolidation. The preheating temperature for HSC is lower than the conventional methods, in which the sintering temperature is always higher than 1100 °C. But an abnormal case (W–Cu-10) was also observed that a high temperature exceeding 1000 °C led to a decrease in density, the reason for which will be discussed in the section below.

3.2. Mechanical properties

The nano-indentation experiments were conducted at room temperature using a commercial depth-sensing instrument (MTS Nano Indenter® XP) to measure the hardness and modulus of the consolidated W–Cu composites. Experiments at constant strain rate 0.05 s⁻¹ were performed to a depth limit of 1500 nm, and the maximum load was held constant for 10 s. Five indentations were made for each sample. Fig. 5 is the relationship of load on the sample and displacement into surface, from which hardness and modulus can be calculated. Plastic and elastic deformations are distinctly presented on the curves; only a small fraction of deformation recovered after unloading. To reach an identical depth, the loading on W–Cu-8 is higher than others, indicating a stronger particle bonding. The modulus and hardness are not consistent with density, as shown in Table 1. The density of W–Cu-12 is close to W–Cu-8, but the modulus and hardness are lower than the latter. The pressures of both samples are identical, with difference in preheating temperature, 887 °C and 970 °C, respectively. This implies that high preheating temperature will improve particle bonding. Such a conclusion can also be deduced from the comparison of W–Cu-12 and W–Cu-13. However, W–Cu-13 shows a low density and poor bonding strength with the preheating temperature and pressure compared to W–Cu-8. This is due to its high E/M ratio. Increasing E/M ratio not only prolongs the duration of shock wave and increases incident shock energy, but also strengthens the tensile wave. Microcrack will occur as the intensity of tensile wave exceeds the bonding strength, leading to the decrease in hardness and modulus. Compare W–Cu-13 with W–Cu-16, the hardness of the former is higher than the latter, while the density is lower than that of the latter. Note that the temperature of W–Cu-13 is higher than W–Cu-16 while pressure is lower; it implies that the preheating temperature is responsible for bonding while the pressure for densification, which is quite different from the HSC of pure W powders [21].

Comparing with Hot-pressing method [32], the density and hardness of W–Cu composite by HSC (this work) are higher due to the high pressure and work hardening. The density and hardness achieved in this work are 95.3% and 5.94 GPa, while 93.9% and 2.09 GPa for Hot-pressing. Moreover, the preheating temperature in the HSC is lower than 1000 °C with a duration as short as 3 min, while the sintering conditions for Hot-pressing method are 1400 °C and 1 h. It demonstrates that a high sintering quality can be obtained under a relatively low temperature and a very short processing time by hot-shock consolidation.

3.3. Microstructure characteristics

Fig. 6 shows the morphology of W–Cu powders after 2 h ball-milling. The original Cu powders are fir-tree crystal with coarse grain, and the W powders are with fine grains, as shown in Fig. 6(a) and (b), respectively. The Cu powders were fractured into flake-like particles, and were partly agglomerated as large flattened particles, as shown in Fig. 6(c). The flake-like Cu particles and fine W particles were welded to the large W particle and agglomeration of W particles was also formed due to plastic deformation, as shown in Fig. 6(d).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>E/M</th>
<th>Pressure (GPa)</th>
<th>Temperature (°C)</th>
<th>Density (X.T.D.)</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W–Cu-7</td>
<td>8.65</td>
<td>4.3</td>
<td>850</td>
<td>93</td>
<td>5.94</td>
<td>306.46</td>
</tr>
<tr>
<td>W–Cu-8</td>
<td>7.78</td>
<td>3.1</td>
<td>970</td>
<td>95.3</td>
<td>5.94</td>
<td>306.46</td>
</tr>
<tr>
<td>W–Cu-9</td>
<td>7.78</td>
<td>4.3</td>
<td>770</td>
<td>90</td>
<td>3.73</td>
<td>191.72</td>
</tr>
<tr>
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<td>7.78</td>
<td>3.1</td>
<td>1028</td>
<td>92</td>
<td>5.11</td>
<td>274.57</td>
</tr>
<tr>
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<td>10.39</td>
<td>3.1</td>
<td>887</td>
<td>96.3</td>
<td>4.15</td>
<td>234.51</td>
</tr>
<tr>
<td>W–Cu-13</td>
<td>12.98</td>
<td>3.1</td>
<td>950</td>
<td>94.3</td>
<td>4.34</td>
<td>246.02</td>
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<td>W–Cu-15</td>
<td>12.98</td>
<td>4.3</td>
<td>702</td>
<td>87.3</td>
<td>3.81</td>
<td>201.32</td>
</tr>
<tr>
<td>W–Cu-16</td>
<td>12.98</td>
<td>4.3</td>
<td>890</td>
<td>95.3</td>
<td>3.46</td>
<td>254.82</td>
</tr>
</tbody>
</table>

![Fig. 3. Photograph of W–Cu composites with densities of (a) 96.3% and (b) 87.3%, respectively.](image)

![Fig. 4. The relationship between the preheating temperatures and final densities.](image)

![Fig. 5. Load on sample vs displacement into surface.](image)
Fig. 6. SEM images of (a) Cu powders, (b) W powders and (c and d) ball-milled W–Cu powders.

Fig. 7. Optical microscopy images of the W–Cu samples: a. W–Cu-15 (702 °C); b. W–Cu-9 (770 °C); c. W–Cu-7 (850 °C); d. W–Cu-8 (970 °C); and e. W–Cu-10 (1028 °C).
Fig. 7 shows the optical microscopy images of the W–Cu samples in the order of preheating temperature. As shown in Fig. 7a–d, the distribution of copper becomes more uniform as the temperature rises, with which the density also increases. At a relatively low temperature, there exist numerous aggregations of Cu, as shown in Fig. 7aa and b, which were formed during ball-milling as mentioned above. After the temperature exceeded 800 °C, the Cu matrix is quite homogeneous, especially for the W–Cu-8 with a temperature of 970 °C. It is supposed that the flowability of copper is enhanced as temperature rises. At dynamic condition, the copper flow fills most of the voids between tungsten particles, contributing to the densification process. However, due to the low shock intensity and buffering of copper, the plastic deformation and fracture of tungsten particle are not as severe as the HSC of pure tungsten [21]. Hence neither the deformation of tungsten nor the immersion of copper flow is sufficient to fill in the voids between tungsten particles, resulting in the residual pores indicated by the arrow in Fig. 7d.

As shock wave propagated through the powder bed, W particles instantaneously impact each other at a high velocity. The copper is squeezed to fill in the voids between W particles, whereas the viscosity makes copper matrix tend to stick on the surface of W particle during the collision. These effects drive copper matrix to be distributed along the boundary of W particle. It is known that high temperature can lower viscosity of material, which also means enhancement of the flowability. After the preheating temperature exceeded a value, copper begins to be extruded from the adjacent area of several tungsten particles due to the loss of viscosity, leaving plenty of W–W contacts. However, the intensity of shock pressure and temperature are insufficient to form W–W bonding, as mentioned in previous work [21]. There is no bonding between the compacted W particles, and the porosities occur while the W particles are being drawn back by the subsequently reflected tensile wave. It is presumed to be the reason for the low density of W–Cu-10, that high preheating temperature (1028 °C) doesn’t lead to high density, but pores, as shown in Fig. 7e. Nevertheless, the fact that higher temperature leads to aggregation and loss of Cu has also been reported for conventional methods [8,33].

Comparing to the morphology of W–Cu-9 shown in Fig. 8a, the distribution of copper in W–Cu-8 is quite homogeneous, as shown in Fig. 8c, which is due to the high preheating temperature. In W–Cu-9, the copper agglomerates can be clearly distinguished, as indicated by the arrow in Fig. 8b. The homogeneous distribution of the copper continuous phase modifies the mechanical property of W–Cu-8. Fig. 8d shows the ductile fracture surfaces of copper covering the surfaces of the tungsten particles, which is not observed in Fig. 8b. This indicates a strong bonding of W and Cu due to high preheating temperature. Although most W particles preserve its initial size, some of them are crushed into pieces during the shock loading and ball-milling due to its brittleness, shown as the nano-sized particles in Figs. 8d and 9.

Fig. 10 shows a tungsten particle in W–Cu-8 surrounded by fine tungsten particles and copper phase. The smooth edges on the tungsten particle surface, indicated by the dashed circle in Fig. 10, demonstrate plastic deformation of several particles, demonstrating a weak bonding between tungsten particles. Under the conditions concerning this work, the deformation is insufficient to fill the voids between tungsten...
particles. However, it is evident, from the ductile fracture in Fig. 8d and its magnified view in Fig. 9, that the copper is distributed in a connected network at the W–W boundary and a good W–Cu bonding is achieved. The distribution of copper seems to be the dominating factor for the densification of W–Cu powder, which is consistent with reports on conventional methods.

High preheating temperature improves the distribution of copper and enhances the bonding of W–Cu. In contrast, the effect of shock pressure is not as apparent as temperature, which only leads to plastic deformation of tungsten, but cannot be ignored. Under high pressure, a relative high density could be obtained within microsecond time scale due to plastic deformation and particle crush. Further densification can be obtained only by filling residual pores with Cu, which are mainly determined by temperature not pressure. A similar conclusion was also presented in resistance sintering of W–Cu composites [15], where the densification was associated with ultra-high pressure.

4. Conclusions

W–10 wt.% Cu composites were fabricated by hot-shock consolidation. High-density W–Cu composites can be obtained under a relatively low sintering temperature (less than 1000 °C) and a short sintering time (less than 3 min) without any sintering activator, which makes the hot-shock consolidation a promising method for fabricating fine-grained W–Cu alloys. The homogeneous distribution of copper is the key factor for the consolidation of W–Cu powder, which is dominated by preheating temperature. High temperature improves the distribution of copper and enhances the bonding of W–Cu, but also leads to the agglomeration of Cu while exceeding a specific value. The shock pressure is responsible for the densification of W particles, the dominating mechanisms of which are void collapse and plastic deformation.

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