Original Article

Fabrication of ultrafine W-Cu composite powders and its sintering behavior

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ABSTRACT

Ultrafine W-Cu composite powders with various copper (Cu) contents (5%, 20% and 40 wt.%) have been fabricated by a method consisting of a carbothermic pre-reduction step and a subsequent hydrogen reduction step. After roasting the mixture of ammonium tungstate \((\text{NH}_4)_2\text{WO}_4\) and copper nitrate trihydrate \((\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O})\), the mixture of CuWO₄ and CuO (or WO₃) was obtained. Subsequently, this mixture was pre-reduced by insufficient carbon black to generate the products containing W, Cu and a small amount of WO₃ which was further reduced to W in the following hydrogen reduction process. Thus, the ultrafine W-Cu composite powders were successfully produced. After sintering the green compacts made of these powders at 1100 °C, 1150 °C, 1200 °C and 1250 °C, respectively, the microstructure, relative densities, electric conductivity and thermal conductivity of the sintered alloys were measured. The experimental results indicated that the higher the sintering temperature is, the better the performance of alloys will be.

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1. Introduction

Tungsten (W) possesses a low thermal expansion coefficient, high temperature behavior and excellent mechanical properties, while copper (Cu) has a high thermal conductivity and electrical conductivity. Therefore, tungsten-copper (W-Cu) composites have the advantages of both of them. W-Cu composites are widely used as resistance welding electrodes, electrode materials for electro discharge machining, heat sink materials, heavy-duty electrical contacts, welding electrodes and thermal management devices for microelectronics packaging [1–6]. Properties of the composites determine the application fields and the performances of the composite are largely affected by the relative density. Conventionally, the most widely used method to prepare W-Cu alloy is to prepare a sintered W skeleton with a desired density and then Cu is infiltrated in the W skeleton pore. However, the relative density of alloy obtained by this method is poor, especially for the composition with a low Cu content. Because W-Cu system exhibits mutual insolubility or negligible solubility [7,8], when the Cu content was low, the porosity in the W skeletons will be relatively small, and there may be some isolated pores. Therefore, the homogeneous microstructure cannot be obtained by the infiltration process. An approach can improve the relative density of W-Cu composites by adding a small amount of Fe, Co, or Ni in the W powder as sintering activators. However, the
thermal and electrical conductivity of W-Cu alloys would be deteriorated by these additives \[9,10\].

However, if using the ultrafine W-Cu composite powders as the raw materials, W-Cu alloys could be prepared by the traditional sintering. It is well known that the sintering activity of W-Cu composite powders depends on the particle size and uniformity. The smaller the particle size of powders is, the better the sintering activity of powders will be. Therefore, in the recent years, many methods like mecanochemo synthesis \[11–14\], mechanical alloying \[15–18\], injection molding \[19,20\] and mecano-thermochemical method \[21–24\] were used to fabricate ultrafine W-Cu composite powders. Kim et al. prepared W-20 wt.% Cu composite powder by mecanochemochemical process, and then obtained the alloy with a relative density of 95% by sintering at 1200 °C \[11\]. Hong et al. produced W-20 wt.% Cu composite powder through ball milling, and after sintering at 1250 °C for 1 h, the relative density of the alloys was 98.5% \[15\]. Yoon et al. synthesized W-20 wt.% Cu powder by hydrogen reducing the precursor from the spray drying, obtained the W-Cu alloy with a relative density of 95% after sintering at 1200 °C for 2 h \[25\]. Although lots of investigations have been carried out, lots of efforts are still needed before the above processes could be used in the industrial production, due to the contamination during ball milling process, as well the cost, etc.

In our previous investigation \[26\], ultrafine W-10 wt.% Cu composite powder have been fabricated via carbothermic pre-reduction followed by hydrogen reduction process, and the sintered compact by this powder has excellent performances. Herein, the method was extended to prepare W-Cu composite powders with a Cu content of 5, 20, 40 wt.% respectively. Meanwhile, the relative density, thermal conductivity, and electrical conductivity of the sintered compacts were also investigated in detail.

1.1. Experimental procedures

The raw materials used to fabricate the ultrafine W-(5, 20, 40 wt.% Cu composite powders were \((\text{NH}_4)_2\text{[H}_2\text{W}_{12}\text{O}_{42}]\)\(\times\)\(\text{H}_2\text{O}\) (>99%, Aladdin Holdings Group Co., Ltd.); carbon black (98.5%, MA100, Mitsubishi Chemical Corporation) and \(\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}\) (99%–100%, Sinopharm Chemical Reagent Co., Ltd.). Fig. 1(a) and (b) are the scanning electron micrographs (SEM) of \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\) and carbon black, respectively. From which it can be seen that the particle sizes of \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\) and carbon black were about 37 \(\mu\text{m}\) and 24 nm (The value was obtained from the Mitsubishi Chemical Corporation), respectively.

Stoichiometric ratios of \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\) and \(\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}\) were weighted and mixed in the agate mortar for 30 min. The mixtures were calcined at 500 °C for 4 h under an air atmosphere in the horizontal-chamber furnace, to produce the mixture of CuWO\(_4\) and WO\(_3\) (or CuO). In the current study, the molar ratio of carbon to CuO used for reducing CuO was kept at 0.5, while the molar ratio of carbon to WO\(_3\) used for reducing WO\(_3\) was in the range of 2–2.75 (2, 2.25, 2.5, 2.75). After evenly mixing of calcined products in an agate mortar, the powders were reduced by insufficient carbon black in high-purity argon (Ar, >99.999%) atmosphere. The carbothermic pre-reduction process was carried out first at 600 °C for 2 h and then at 1050 °C for 2 h, respectively, with Ar flow rate of 400 mL/min. After the carbothermic pre-reduction, the further deep hydrogen reduction of the as-prepared pre-reduced W-Cu powders was done at 800 °C in a constant flowing hydrogen atmosphere of 200 mL/min. The ultrafine W-Cu composite powders prepared at a C/WO\(_3\) molar ratio of 2 (for 5% Cu) and 2.25 (for 20%, 40% Cu) was used for the following sintering processes. The powders were compacted into a disc with a diameter of 20 mm and a height of 4 mm at a pressure of 300 MPa. The relative density of the green compact was about 50% (The relative of green compact was derived from the Eq. \(10\)). Then, the green compacts were heated at a ramping rate of 5 °C/min under a stable hydrogen flow rate of 20 mL/min, to the desired sintering temperature of 1100 °C, 1150 °C, 1200 °C and 1250 °C, and maintained for 3 h. Finally, the furnace was cooled down to room temperature before taking out and collecting for characterization.

The microstructures of sample were analyzed by scanning electron microscopy (SEM, ZEISS SUPRA 55, Germany). The crystal structure was established by X-ray diffraction (XRD; TTR III, Rigaku Corporation, Japan) using Cu Ka radiation in the range of 2θ = 10–90 degree with a scanning rate of 10 deg./min. In the experiment, the average particle sizes were measured rigorously by the statistics of >300 particles from five different fields in the FE-SEM micrographs. Residual carbon content of composite powders was examined by using an infrared carbon-sulfur analyzer (EMIA-920V2, HORIBA, Japan). The thermal conductivity of the sintered compacts was measured by Laser Flash thermal constant analyzer (LFA 467; Naichi Corporation, Germany) at different temperatures (100 °C, 200 °C, 300 °C, 400 °C). The electrical conductivity was measured by the Four-Point Probe method on Hall effect measurement system (HL5500PC; DNIV Electronics Trading Co. Ltd., Germany, United Kingdom), with the sample size of 8 × 8 × 1 mm\(^3\). Vickers hardness of the sample was measured using automatic turret digital micro hardness tester (THV-1MDX; Elite precision instrument Corporation, China) under a maximum load of 3 kg and a dwell time of 10 s at room temperature.

2. Results and discussion

2.1. Preparation of ultrafine W-Cu composite powders

2.1.1. XRD analysis

According to our previous research \[26,27\], the appropriate reaction factors could be determined. The calcination temperature of the mixture of \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\) and \(\text{Cu(NO}_3)_2\cdot3\text{H}_2\text{O}\) was 500 °C; the temperature for the carbothermic pre-reduction was 600 °C and 1050 °C, and the temperature for hydrogen reduction is 800 °C.

When the mixture of \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\) and \(\text{Cu(NO}_3)_2\) \(\times\)\(\text{H}_2\text{O}\) was used as raw materials, CuWO\(_4\) can be directly formed after calcination treatment, which contributed to the uniform distribution of W and Cu after the reduction. Meanwhile, in the industrial production, WO\(_3\) is also prepared by roasting \((\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\) \(\times\)\(\text{H}_2\text{O}\). Thus, the addition of \((\text{Cu(NO}_3)_2\) \(\times\)\(\text{H}_2\text{O}\) to this process is a very simple operation to get the composite powders of WO\(_3\) and CuO. Therefore, this preparation method is relatively economical.
Fig. 1 – SEM of: a: (NH₄)₁₀[H₂W₁₂O₄₂]·xH₂O; b: carbon black.

Fig. 2 – XRD patterns of the calcination products mixture of (NH₄)₁₀[H₂W₁₂O₄₂]·xH₂O and Cu(NO₃)₃·3H₂O at 500 °C for 4 h.

Fig. 2 shows the XRD pattern of the calcined products of mixture of (NH₄)₁₀[H₂W₁₂O₄₂]·xH₂O and Cu(NO₃)₃·3H₂O at 500 °C for 4 h, which is composed of CuWO₄ and WO₃ (or CuO), dependent on the Cu content.

The C/WO₃ molar ratio is derived from the Eqs. (1)–(4). If the gaseous product of carbothermal pre-reduction is only CO, as shown in Eqs. (1) and (2), the theoretical C/WO₃ ratio will be 3; while if the gaseous product is only CO₂, as shown Eqs. (3) and (4), the ratio will be 1.5. Therefore, the theoretical ratio should be between 1.5 and 3 in the experiment.

\[ \text{WO}_3 + \text{C} = \text{WO}_2 + \text{CO} \]  
(1)

\[ \text{WO}_2 + 2\text{C} = \text{W} + 2\text{CO} \]  
(2)

\[ 2\text{WO}_3 + \text{C} = 2\text{WO}_2 + \text{CO}_2 \]  
(3)

\[ \text{WO}_2 + \text{C} = \text{W} + \text{CO}_2 \]  
(4)

Fig. 3 shows the XRD patterns of the products in different reaction stages (a: d: W-5 wt% Cu; b: e: W-20 wt% Cu; c: f: W-40 wt% Cu) with different carbon additions (2–2.75). Fig. 3(a), (b) and (c) show that the products generated by the carbothermic pre-reduction are mainly composed of W, Cu and a small amount of WO₂, while W-Cu composite powders were obtained after hydrogen reduction as shown in Fig. 3(d), (e) and (f). As the Cu content increases, the diffraction peaks of Cu gradually become stronger; the main peak of W gradually becomes weaker; the diffraction peaks of WO₂ gradually become weaker and finally disappear as shown in the Fig. 3(a), (b) and (c). When the molar ratio of C/WO₂ is 2.75, WO₂ disappears and W₂C appears in the products of carbothermal pre-reduction from Fig. 3(a), (b) and (c). The formation of W₂C means that the carbon addition is excessive [28]. Since W₂C is difficult to be removed in the process of hydrogen reduction, the molar ratio of C/WO₂ should be lower than 2.75. When the carbon ratio was 2, the product of carbothermal pre-reduction contains a certain amount of WO₂. If continue to reduce the carbon ratio, the WO₂ content in carbothermal pre-reduction product will be increased, and more WO₂ will need to be reduced by hydrogen in the second stage. However, during the hydrogen reduction process, the existence of CVT mechanism will cause the growth of W particles. Therefore, the C/WO₃ molar ratio in this study is in the range of 2–2.75.

Because carbon black is amorphous and could not be detected by XRD analysis, the residual carbon content of reduction product is detected by a high-frequency combustion infrared absorption method. Table 1 shows residual carbon contents in different reaction stages for samples with different Cu contents. As shown in Table 1, with the increase in the C/WO₃ molar ratio, there is an increase in residual carbon content. Meanwhile, by comparing the carbon contents of samples before and after the hydrogen reduction, it can be concluded that residual carbon content could be decreased in hydrogen reduction process, probably owing to the reaction between C and H₂O produced by hydrogen reduction.

The chemical reactions (5–9) will occur during the carbothermal pre-reduction of WO₃. According to the thermodynamic software FactSage 7.0, the changes of the standard Gibbs free energy of these reactions are calculated and shown in Fig. 4, from which the initial reaction temperature of Eqs. (5–9) are 570 °C, 749 °C, 720 °C, 898 °C and 950 °C under the standard condition, respectively. Therefore, the generation of W is thermodynamically feasible by Eqs. (6) and (8), and the formation of WC is more difficult than W. Consequently, W will be formed firstly, and then react with C to generate WC.

\[ \text{WO}_4 + \text{C} = \text{WO}_2 + \text{CO} \]  
(5)

\[ \text{WO}_2 + 2\text{C} = \text{W} + 2\text{CO} \]  
(6)
Table 1 – Residual carbon content of products with different Cu contents at different reaction stages.

<table>
<thead>
<tr>
<th>C/WO$_3$</th>
<th>2</th>
<th>2.25</th>
<th>2.5</th>
<th>2.75</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-5 wt% Cu Carbothermic pre-reduction</td>
<td>0.053 %</td>
<td>0.063 %</td>
<td>0.063 %</td>
<td>0.077 %</td>
</tr>
<tr>
<td>Hydrogen reduction</td>
<td>0.030 %</td>
<td>0.033 %</td>
<td>0.034 %</td>
<td>0.067 %</td>
</tr>
<tr>
<td>W-20 wt% Cu Carbothermic pre-reduction</td>
<td>0.049 %</td>
<td>0.057 %</td>
<td>0.090 %</td>
<td>0.929 %</td>
</tr>
<tr>
<td>Hydrogen reduction</td>
<td>0.041 %</td>
<td>0.046 %</td>
<td>0.087 %</td>
<td>0.739 %</td>
</tr>
<tr>
<td>W-40 wt% Cu Carbothermic pre-reduction</td>
<td>0.043 %</td>
<td>0.048 %</td>
<td>0.057 %</td>
<td>0.200 %</td>
</tr>
<tr>
<td>Hydrogen reduction</td>
<td>0.033 %</td>
<td>0.034 %</td>
<td>0.055 %</td>
<td>0.199 %</td>
</tr>
</tbody>
</table>

2WO$_2$ + 5C = W$_3$C + 4CO  
WO$_2$ + 2W$_2$C = 5W + 2CO  
WO$_2$ + 2C = WC + 2CO

2.1.2. Microstructure

Fig. 5 shows the morphologies of the powders with various Cu contents prepared after the carbothermic pre-reduction and hydrogen reduction (The reaction temperature is 800 °C) at different C/WO$_3$ molar ratios. It can be seen that many small spherical particles and dendritic particles are formed. Fig. 5(A) shows that the large particles and nano-sized spherical particles are Cu and W, respectively.

From Fig. 5, it can be concluded that the products of carbothermic pre-reduction is a mixture of W, Cu and WO$_2$ (Fig. 3(a, b, c)), while it is reduced to W-Cu composite powder by hydrogen (Fig. 3(e, d, f)). As the C/WO$_3$ molar ratio increases, large sized WO$_2$ gradually decrease, and the particle size of the products of carbothermic pre-reduction gradually becomes smaller as shown in Fig. 5 (A: a, b, c; B: a, b, c; C: a, b, c, d), which is in accordance with the results of the XRD described above.

This is because the number of nano nuclei of W increases as the amount of carbon black addition increases, meanwhile,
no gaseous intermediate phase like WO$_2$(OH)$_2$ (which could result in the growth of W grain during the hydrogen reduction process [29]) is formed in the carbothermic pre-reduction stage [30]. In addition, the particle size of W almost unchanged before and after the deep reduced by hydrogen, as shown in Fig. 5 (A: e, f; B: e, f; C: e, f, g, h), due to the small content of WO$_2$. Large Cu particles don’t have much negative effect on the sintering process of the sample, since when the sintering temperature exceeds the melting point of Cu, Cu will be melted and infiltrated into the surrounding gap of W particles [10].

2.2. Sintering of compact

2.2.1. Morphology features of compact after sintering

Fig. 6 shows the fracture micrograph of samples sintered at different temperatures. In the temperature range of 1100 °C to 1250 °C (1100 °C, 1150 °C, 1200 °C, 1250 °C), with the increase of sintering temperature, the particle size of compact is gradually increased from the cross-section.

Generally speaking, densification during liquid phase sintering occurs through the particle rearrangement due to capillary forces, but additional W particle contacts are made and form W–W bonds as rearrangement densification occurs [31]. In the case of W-Cu composites, the low solubility of W and Cu makes the contribution of solution re-precipitation negligible. Similar conclusion has been reported by some researchers [29,31]. The main restriction of rearrangement is the bonds between W and W particles which generate during the sintering process of the samples. The rearrangement of W particles appears when the W skeleton was weaker than the capillary forces according to conclusions of Johnson et al. [32]. Because the particle size of W is small in the experiment, and with the decrease of the particle size of W, capillary forces gradually increase, enabling more rearrangement shrinkage. When the Cu was melted, W-Cu alloys with higher Cu mass fractions give rapid shrinkage, since weak bonds exist between the W particles, so the W particles were sufficient rearranged.

From Fig. 6(a, e, i) (Fig. 6(b, f, j)), it can be seen that as the Cu content increases, the porosity of sample become smaller. Thereby, a high Cu content is beneficial to increase the relative density of the sample. However, the further increase in the Cu content will isolate the W particles. These particles are completely separated by thin liquid layers, and the influence of temperature on the growth of W particles becomes smaller as shown in Fig. 6(i, j, k, l). Because the possibility of particle contact is lowered, the growths of particles produced by coalescence are greatly suppressed.

Fig. 7 show that the microstructures of W-5 wt.% Cu, W-20 wt.% Cu and W-40 wt.% Cu alloys sintered at various sintering temperatures (1100 °C, 1150 °C, 1200 °C, 1250 °C). It can be seen that during the liquid-phase sintering, an obvious growth of W particles appear and the particles become spherical (Fig. 6) [33]. As the Cu content increases, the distribution of W and Cu becomes more uniform. Furthermore, the higher the Cu content is, the less the porosity will be. When the sintering temperature was gradually increased, Cu is fully melted, and the viscosity of liquid Cu is decreased, which further promotes the sufficient rearrangement of W particles. This means that a high Cu content and high temperature contributes remarkably to improve the densification degree. Because the mutual solution is poor between W and Cu, the densification and accompanying particle growth during liquid-phase sintering are dependent strongly on particle rearrangement and particle coalescence, respectively. As the increase of Cu content, the effect of capillary forces becomes more obvious, that causes the rearrangement of W particles and leads to the elimination of pores. Whereas, a further increase of Cu content would isolate the W particles. Hence, the grain growth induced by coalescence is greatly inhibited, because the possibility of particle contact is limited.

2.2.2. Relative density and shrinking percentage

The W-5 wt.% Cu, W-20 wt.% Cu and W-40 wt.% Cu composite powders prepared at a Cu/WO$_3$ molar ratio of 2, 2.25 and 2.25 are sintered at different temperatures (1100 °C, 1250 °C). Ardestani et al. found that W-Cu composite powders cannot achieve a high densification by solid phase sintering [34]. Therefore, the sintering temperature in the current experiment is higher than the melting point of Cu. Fig. 8 shows the relative density of the sintered compacts at 1100–1250 °C for 3 h by ultrasonic W-Cu composite powders with different Cu contents. The relative density of compact is calculated by the ratio of the mass of compact to its volume; and the relative density of compact is the ratio of actual density to the theoretical density, as shown by Eq. (10).

$$\rho_{W-Cu} = \frac{(X_W \cdot \rho_{Cu} + X_{Cu} \cdot \rho_W) \cdot m}{(\pi h^2) \cdot \rho_W \cdot \rho_{Cu}} \cdot 100\%$$  \hspace{1cm} (10)

where $\rho_{W-Cu}$ is the relative density of compact; $\rho_W$ is theoretical density of tungsten; $\rho_{Cu}$ is theoretical density of copper; $m$ is quality of compact; $h$ is height of sample; $r$ is radius of sample; $X_{Cu}$ and $X_W$ are the mass fractions of Cu and W in the sintered alloys, respectively.

At a sintering temperature of 1100 °C, alloys of W-5 wt.% Cu, W-20 wt.% Cu, W-40 wt.% Cu had relative densities of 90.97...
Fig. 5 – SEM and Energy Dispersive Spectrum (EDS) images of W-Cu composite powders with various Cu contents and C/WO₃ molar ratios after hydrogen reduction and carbothermic pre-reduction (A: W-5 wt% Cu, B: W-20 wt% Cu, C: W-40 wt% Cu; a, e: C/WO₃ = 2; b, f: C/WO₃ = 2.25; c, g: C/WO₃ = 2.5; d, h: C/WO₃ = 2.75; a, b, c, d: obtained after carbothermic pre-reduction at 600 °C and 1050 °C; e, f, g, h: obtained after hydrogen reduction at 800 °C).

%, 91.30 %, and 92.47 %, respectively. It is obvious that the relative densities of the samples are increased by raising the sintering temperature (Fig. 8). At 1100 °C, the viscosity of liquid phase Cu is relatively large due to the low temperature, which limits the movement of the W particles. Therefore, the W particles are not sufficiently rearranged, leading to a low relative density of the sample. As increasing the sintering temperatures to 1200 °C and 1250 °C, the fluidity of Cu phase is greatly improved, and the rearrangement of the W particles are enhanced [30]. Under the effect of capillary force, the W
particles are fully rearranged. Therefore, the relative density of the sample is further increases. When the sintering temperature was 1250 °C, the relative density of the compact of W-5 wt% Cu, W-20 wt% Cu and W-40 wt% Cu reached 96.76 %, 98.1 % and 98.80 %, respectively. The relative density of W-5 wt% Cu alloy was obviously lower than W-20 wt.% Cu and W-40 wt.% Cu alloys obtained at the same sintering temperature. When the Cu was melted, W-Cu alloys with higher Cu mass fractions give rapid shrinkage, since weak bonds exist between the W particles, so the W particles were sufficient rearranged. Table 2 shows the shrinkage of W-Cu alloys with different Cu contents at different sintering temperatures (1100 °C-1250 °C). As the sintering temperature increases, the shrinkage rate of the sample increases. The higher the Cu content in the sample is, the higher the shrinkage will be, as shown in Table 2. Meanwhile, from Table 2, it can be found that the radial shrinkage of the compacts is always larger than the axial shrinkage, owing to that the radial pressure is smaller than the axial pressure in a uniaxial press. Therefore, the density of the green body after pressing is different in the radial direction and the axial direction.
Table 2 – Radial and axial shrinkage rates of W-Cu specimens prepared at different sintering temperatures.

<table>
<thead>
<tr>
<th>Sintering temperature(°C)</th>
<th>1100</th>
<th>1150</th>
<th>1200</th>
<th>1250</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-5 wt% Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radial shrinkage rate(%)</td>
<td>10</td>
<td>12.5</td>
<td>14.1</td>
<td>15.5</td>
</tr>
<tr>
<td>Axial shrinkage rate(%)</td>
<td>7.8</td>
<td>9.3</td>
<td>10.1</td>
<td>10.3</td>
</tr>
<tr>
<td>W-20 wt% Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radial shrinkage rate(%)</td>
<td>12.1</td>
<td>13.4</td>
<td>16.3</td>
<td>16.5</td>
</tr>
<tr>
<td>Axial shrinkage rate(%)</td>
<td>9.5</td>
<td>9.8</td>
<td>10.5</td>
<td>11.1</td>
</tr>
<tr>
<td>W-40 wt% Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radial shrinkage rate(%)</td>
<td>12.4</td>
<td>13.6</td>
<td>16.5</td>
<td>16.7</td>
</tr>
<tr>
<td>Axial shrinkage rate(%)</td>
<td>9.55</td>
<td>9.9</td>
<td>10.7</td>
<td>11.25</td>
</tr>
</tbody>
</table>

Fig. 8 – The relative density of samples with various Cu contents obtained at different sintering temperatures (1100~1250 °C).

![Relative Density Graph](image)

Fig. 9 – Vickers hardness versus sintering temperature of W-Cu alloys with various Cu contents.

![Hardness vs Temperature Graph](image)

2.2.3. Properties

The effect of sintering temperature on hardness of the sintered specimens is shown in Fig. 9. The hardness of compacts increases with the increase of W content. In addition, for the same composition, there is a higher hardness at a higher sintering temperature. When the sintering temperature was 1250 °C, the Vickers hardness of W-wt.%5 Cu, W-wt.%20 Cu and W-wt.%40 Cu composites reached 395 HV, 299 HV and 244 HV, respectively. These results can be attributed to the effect of Cu content and porosity. With the decreases of Cu content and porosity, the hardness of compact increases [36], since W has a higher hardness value than Cu.

Fig. 10 shows the effects of temperature and Cu content on the thermal conductivity of W-Cu composites. At the same detection temperature, as the Cu content increases, the thermal conductivity of sample gradually increases, since the thermal conductivity of Cu is much larger than W [35–37]. Moreover, for alloys with the same composition, the higher the sintering temperature is, the better the thermal conductivity of sample will be. The reason should be that as the sintering temperature increases, the relative density of sample increases, which leads to an increase in the thermal conductivity of alloy [38]. When the sintering temperature reached 1250 °C, the thermal conductivity of W-5 wt.% Cu, W-20 wt.% Cu and W-40 wt.% Cu samples are 87 W/(m·K), 176 W/(m·K) and 235 W/(m·K), respectively. The theoretical thermal conductivity of W-Cu alloy is calculated by Eq. (11) [32], which are 172 W/(m·K), 208 W/(m·K) and 256 W/(m·K) for W-5 wt.% Cu, W-20 wt.% Cu and W-40 wt.% Cu alloys, respectively. The measured values of thermal conductivity are less than the theoretical values, which may be due to the presence of some micropores in the sample. The measurement value of thermal conductivity for W-5 wt.% Cu alloy is much smaller than the theoretical value, since its relative density is lower, and there are a larger number of pores in the compact, which makes the heat diffusion in sample difficult. In addition, the thermal conductivity of sample decreases as the detection temperature increases, since the thermal conduction of the W-Cu composite is impeded by
the phonon at a higher temperature. The higher the temperature, the more intense the thermal motion of the atom, and the more obvious the effect of the phonon on the thermal conductivity [10].

\[
\lambda = \lambda_{Cu}X_{Cu} + \lambda_{W}X_{W}
\]

where \(\lambda\) is thermal conductivity of W-Cu alloy; \(X_{Cu}\) and \(X_{W}\) are the mass fractions of Cu and W in the sintered alloys; \(\lambda_{Cu}\) and \(\lambda_{W}\) are the theoretical thermal conductivities of Cu and W, respectively.

Meanwhile, as the sintering temperature increases, the electric conductivity of sample continuously increases as shown in Fig. 11, since the relative density of sample increases and the Cu mesh distribution of sample becomes more uniform. As shown in Table 3, the electric conductivity of W-20 wt.% Cu and W-40 wt.% Cu alloys are 33.52 % IACS and 49.53 % IACS at the sintering temperature of 1250 °C, respectively. In the relevant literature [41], electric conductivity of W-25 wt. % Cu and W-40 wt. % Cu alloys were 34 % IACS and 41.5 % IACS at the sintering temperature of 1400 °C, respectively. Therefore, the prepared W-Cu alloy in this study has excellent performance (Fig. 11).

<table>
<thead>
<tr>
<th>Sintering temperature/°C</th>
<th>Electric conductivity/% IACS</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-5 wt.% Cu</td>
<td>1250</td>
</tr>
<tr>
<td>W-20 wt.% Cu</td>
<td>1250</td>
</tr>
<tr>
<td>W-40 wt.% Cu</td>
<td>1250</td>
</tr>
<tr>
<td>W-25 wt.% Cu [41]</td>
<td>1400</td>
</tr>
<tr>
<td>W-30 wt.% Cu [39]</td>
<td>1350</td>
</tr>
<tr>
<td>W-40 wt.% Cu [40]</td>
<td>1100</td>
</tr>
<tr>
<td>W-18 wt.% Cu [39]</td>
<td>1350</td>
</tr>
<tr>
<td>W-40 wt.% Cu [41]</td>
<td>1400</td>
</tr>
</tbody>
</table>

Fig. 11 – Relationship between electric conductivity of sample and sintering temperature.

3. Conclusions

A new process was proposed to fabricate ultrafine W-Cu composite powder by combining the carbothermic pre-reduction and hydrogen reduction processes. The mixture of CuWO₄ and CuO (or WO₃) was obtained by roasting the mixture of ammonium tungstate and copper nitrate trihydrate. After that, the composite oxides are reacted with insufficient carbon black to produce the pre-reduced W-Cu composite powder containing a few amount of WO₂. Then, the pre-reduced powder was further reduced by hydrogen at 800 °C to remove the residual oxygen. Finally, the ultrafine high purity W-Cu composite powder was obtained. The prepared composite powder has a high sintering activity. As increasing the sintering temperature or Cu content, the relative density of the sintered compact increases. At a sintering temperature was 1250 °C, the relative densities of W-5 wt.% Cu, W-20 wt.% Cu, and W-40 wt.% Cu compacts are 96.76 %, 98.1 % and 98.80 %, the hardness of samples is 395 HV, 299 HV and 244 HV, the thermal conductivity of compact is 87 W/(m·K), 176 W/(m·K) and 235 W/(m·K); and the electrical conductivity of alloy are 8.72 % IACS, 33.52 % IACS and 49.53 % IACS, respectively.

Conflicts of interest

The authors declare no conflicts of interest.

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