Original Article

Microstructure and properties of ultrafine-grained W-25 wt.%Cu composites doped with CNTs

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**A B S T R A C T**

In the present work, the ultrafine-grained W-25 wt.%Cu composites doped with multi-walled carbon nanotubes (CNTs) have been prepared through combined processes of high-energy ball-milling, liquid-phase sintering and infiltration. Furthermore, the microstructure, hardness and electrical conductivity of the ultrafine-grained W-Cu composites doped with different contents of CNTs were investigated. Meanwhile, the wear resistance, compressive performance at different temperatures and arc erosion resistance were evaluated in comparison with the W-Cu composite without CNTs. The results revealed that the hardness, wear resistance, compressive performance and arc erosion resistance of the W-Cu composites doped with CNTs were enhanced dramatically due to the introduction of tungsten carbide phases after sintering and infiltration.

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1. **Introduction**

As a typical pseudo alloy due to the mutual insolubility between tungsten and copper, the W-Cu (tungsten-copper) composite successfully combines high melting point, high hardness as well as low thermal expansion coefficient of tungsten, with good electrical and thermal conductivity of copper. It has been widely used in various industrial fields, such as ultrahigh-voltage electrical contacts, heat sink materials, welding electrodes and other high temperature components [1–8]. With the need for constantly increasing service lifetime, more stringent requirements are put forward for W-Cu composites. Extensive efforts have been reported to show that the introduction of rare earth oxides, WC particles and other metal elements into W-Cu composites can effectively improve the hardness and arc erosion resistance of materials [9–12].

On the other hand, with doughnut shaped structure and large length to diameter ratio, carbon nanotubes (CNTs) are considered to be the ideal reinforcements in various materials such as polymers, metals, ceramics and so on [13–20], as they exhibit outstanding mechanical properties and excellent electrical properties [21–24]. Recently, Dong et al. [25,26] have utilized graphene to reinforce the W-Cu composites, which...
Fig. 1 – XRD phase analysis results of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs.

Fig. 2 – Secondary electron SEM images of the ultrafine-grained W-25 wt.%Cu composites doped with CNTs of 0 wt.% (a), 1 wt.% (b) and 3 wt.% (c).
indicated that the carbon source with special structure significantly improved the density, microstructure, thermal and electrical conductivity, as well as some mechanical properties. Also, they agreed that the formation of tungsten carbide (WC or W$_2$C) would deteriorate or could not enhance the mechanical properties of W-Cu composites (especially high temperature performances). In contrast, our recent work [7,12] has shown that the introduction of in situ or extraneous tungsten carbide particles would remarkably improve the arc erosion resistance, wear resistance and high temperature compressive performance of W-Cu composites. Therefore, it could be anticipated to prolong the service lifetime of W-Cu composites as ultra-high voltage capacitor group switch and other high temperature components.

Accordingly, in this work, the multi-walled carbon nanotubes (CNTs) were attempted to be introduced to improve the comprehensive performance of the W-Cu composite. On the hand, tungsten powders would be partially carbonized by CNTs to produce tungsten carbide phases during the sintering and infiltration processes. The generated tungsten carbide ceramics with good hardness, strength and stability [27,28] are expected to improve the hardness, wear resistance, compressive performance and arc erosion resistance of the W-Cu composite. On the other hand, the residual carbon source would provide self-lubricating effect during the friction and wearing processes [29,30]. The influence of the content of doped CNTs on microstructure, hardness, wear resistance, high temperature compressive strength and arc erosion resistance of the W-Cu composite has been systematically investigated and discussed.

Fig. 3 – TEM bright field image of the ultrafine-grained W-25 wt.%Cu composite doped with 3 wt.% CNTs (a) and SAED patterns taken from region I (b), region II (c), region III (d), region IV (e) and region V (f).

Fig. 4 – Raman spectra of raw CNTs, mixed W-Cu powders and resultant W-Cu composites doped with different contents of CNTs.

2. Experimental materials and methods

Tungsten powders (purity ≥ 99.9%) with an average particle size of 400 nm and copper powders (purity ≥ 99.9%) of 50 μm were used as raw materials. Multi-walled carbon nanotubes (purity ≥ 95.0%) (purchased from Nanjing XFNANO Materials Tech Co., Ltd.) were used as the potential reinforcement
Table 1 – Hardness and electrical conductivity of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs.

<table>
<thead>
<tr>
<th>CNTs content</th>
<th>0 wt.%</th>
<th>1 wt.%</th>
<th>3 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HB)</td>
<td>229</td>
<td>244</td>
<td>275</td>
</tr>
<tr>
<td>Electrical conductivity (%IACS)</td>
<td>51.7</td>
<td>37.9</td>
<td>29.3</td>
</tr>
</tbody>
</table>

materials. The ultrafine-grained W-25 wt.%Cu composites doped with CNTs were fabricated through the following processing techniques: first, mechanical mixing of mixed powders with 25 wt.% copper powders and different contents of CNTs (0 wt.%, 1 wt.% and 3 wt.%) was performed in a planetary ball mill using a stainless steel container and balls at 400 r/min for 8 h, and the ball to powder weight ratio was 5:1. Subsequently, the mixed powders were pressed into green compacts with the dimensions of $\psi$ 21 mm $\times$ 15 mm and $\psi$ 48 mm $\times$ 10 mm under the pressure of 340 MPa in a XTM-108-200T Hydraulic Press. Finally, the green compacts were sintered and infiltrated at 1350 °C for 40 min under H$_2$ atmosphere followed by furnace cooling.

The hardness was measured on the polished surface of the W-Cu composites by Brinell Hardness Tester with a load of $7.5 \times 10^5$ g and dwell time of 30 s, and the average of 5 indents was used to ensure the acquisition of a reasonable value. Also, the electrical conductivity of polished composites was measured by an Eddy Current Conductivity Meter and 5 times measurements were conducted for each sample. The microstructure of the W-Cu composites was observed materials.
by JEOL-6700F Field Emission Scanning Electron Microscope (SEM). The phase composition was investigated using 7000S X-ray diffraction instrument (XRD) with Cu-Kα radiation at a scan speed of 8° min⁻¹ from 10° to 90°. Bright field images and selected area electron diffraction (SAED) patterns were obtained on a JEM-3010 Transmission Electron Microscopy (TEM). The carbon-related phase composition in mixed powders and composites was verified at room temperature using HR800 Laser Raman Spectrometer. Raman spectra was excited with an output powder of 17 mW at the laser wavelength of 633 nm and collected in the spectral range from 1000 cm⁻¹ to 2000 cm⁻¹. The friction and wear experiments (wear time of 180 min, wear radius of 8 mm, rotating speed of 80 r/min and loading of 500 g) were carried out on a HT-1000 Pin-on-Disk Tester with the wear pin made of GCr15 stainless steel ball and wear disk made of investigated W-Cu composites at room temperature. The compressive stress–strain curves at different temperatures (room temperature, 300 °C, 500 °C, 700 °C and 900 °C) were obtained by a Gleeble 3500 Thermal Cycle Simulation Testing Machine. For compression tests, the W-Cu composites were firstly machined into cylindrical samples with the dimension of φ 6 mm × 9 mm and then welded to a thermo-couple to measure the real-time temperature. The samples were heated to the target temperature at a heating rate of 10 °C s⁻¹, and then compressed with a strain rate of 0.02 mm s⁻¹ at the target temperature. The vacuum electrical breakdown tests were conducted in a vacuum arcing indoor chamber modified by a TDR-40A Single-crystal Furnace under the voltage of 8 kV, to evaluate the arc erosion resistance of the W-Cu composites doped with different contents of CNTs.

### 3. Results and discussions

#### 3.1. Phase constituents and microstructure

Phase analysis for the resultant W-25 wt.%Cu composites doped with different contents of CNTs by XRD experiments as shown in Fig. 1 reveals that, in addition to W and Cu phases, tungsten carbides of WC and W₂C were introduced into the W-Cu composites doped with CNTs. With the increase of CNTs content, the relative intensity of the peaks for tungsten carbides increased significantly. In order to verify the morphology and distribution of introduced tungsten carbides, detailed SEM and TEM observations were carried out as follows.

![Fig. 7](image)

**Fig. 7** – The surface worn micrographs and average line roughness of the ultrafine-grained W-25 wt.%Cu composites doped with CNTs of 0 wt.% (a), 1 wt.% (b) and 3 wt.% (c).
**Fig. 2** displays the microstructure of the resultant W-25 wt.%Cu composites doped with different contents of CNTs. As shown in **Fig. 2(a)** for the W-Cu composite without CNTs, the gray phase corresponds to spherical tungsten particles with the average size of ~1 μm, and the phase with black contrast is copper. In **Fig. 2(b)** for the W-Cu composite doped with CNTs of 1 wt.%, a few angular particles (triangle, rectangle or polygon) with slightly different contrast in comparison with W or Cu can be detected. With the increase of CNTs content, both the number and size of the angular particles increased as shown in **Fig. 2(c)**. Considering the above XRD results and the fact that tungsten carbide particles generally present regular shapes (such as triangular or rectangular) [31,32], it can be concluded that the angular particles are tungsten carbide phases generated during sintering and infiltration. The quantities of the angular particles as shown in **Fig. 2(b) and (c)** exhibit well accordance with the intensity change of the peaks for tungsten carbides as presented in Fig. 1.

Furthermore, TEM analysis was performed to characterize the angular particles in the W-Cu composite doped with 3 wt.% CNTs, as shown in **Fig. 3**. The SAED patterns (**Fig. 3(b)–(f)**) collected from regions I, II, III, IV and V of **Fig. 3(a)** indicated that the angular particles of region I and region V were WC and the region II was W$_2$C. The WC phase has an hexagonal structure with lattice parameters of $a = 2.907$ nm, $b = 2.907$ nm, $c = 2.837$ nm, and the W$_2$C phase has an hexagonal structure with lattice parameters of $a = 2.997$ nm, $b = 2.997$ nm, $c = 4.728$ nm. Also, region III was identified to be Cu and region IV was W. This further confirms that the angular particles in W-Cu composites doped with CNTs are tungsten carbide phases (WC or W$_2$C), which are considered to improve their hardness, wear resistance, compressive performance and arc erosion resistance [7,12].

**3.2. CNTs characteristics**

The purpose of doping CNTs into the W-Cu composites is that, the tungsten carbide ceramics generated from CNTs and tungsten could improve the properties such as hardness, wear resistance, high temperature strength and arc erosion resistance of the W-Cu composites. Besides, due to the excellent mechanical and electrical properties of CNTs, the comprehensive performances of the W-Cu composites could be further improved; however, the residual carbon resource has not been found in the W-Cu composites doped with CNTs according to the results of XRD, SEM and TEM analysis.

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**Fig. 8** - The value of compressive strength at different temperatures (a) and stress–strain curves of the ultrafine-grained W-25 wt.%Cu composites doped with CNTs of 0 wt.% (b), 1 wt.% (c) and 3 wt.% (d).
It is generally accepted that Raman spectra is an effective method to reveal the information of internal CNTs in various materials [33,34]. Therefore, the Raman spectra for raw CNTs, mixed W-Cu powders and the resultant W-Cu composites with different contents of CNTs (1 wt.% and 3 wt.%) was tested as shown in Fig. 4. It can be observed that the spectra of raw CNTs shows two characteristic peaks of disordered-band (D-band) at 1318 cm$^{-1}$ and graphite-band (G-band) at 1580 cm$^{-1}$. It should also be pointed out that the intensity of D-band and G-band decreased with the decrease of CNTs content in mixed powders. Comparatively, characteristic peaks of CNTs could not be revealed in the W-Cu composites doped with 1 wt.% or 3 wt.% CNTs. As the intensity of D-band and G-band qualitatively reflects the content of CNTs in tested materials [35], it can be concluded that the CNTs may be completely consumed to form tungsten carbides during the sintering and infiltrating processes. On the other hand, the intensity ratio of the D-band and G-band peaks ($I_D/I_G$) can semi-quantitatively reveal the structural integrity of CNTs in materials [21,36]. The greater the value, the higher the defect density of the CNTs in materials. In this study, the measured $I_D/I_G$ values of raw CNTs, as well as mixed W-Cu powders doped with 1 wt.% and 3 wt.% CNTs are 1.06, 1.10 and 1.10, respectively. The increased $I_D/I_G$ value of mixed powders after ball-milling indicates the damaged structure of CNTs after milling.

In order to further understand the damage degree of CNTs, the TEM morphologies and HRTEM images of the raw CNTs and mixed W-Cu powders doped with 3 wt.% CNTs were observed as shown in Fig. 5. Fig. 5(a) displays the TEM morphology of the tangled raw CNTs used in this experiment, with slender shapes and obvious bending. The multi-walled CNTs, formed by the tangled raw CNTs, are usually found to be several layers to 10 layers. From the HRTEM image as presented in Fig. 5(b), the carbon nanotube with a hollow channel has 6–7 layers, and the layer spacing is less than 0.5 nm. Fig. 5(c) shows the TEM morphology of mixed W-Cu powders with 3 wt.% CNTs after ball-milling. It can be seen that the fragmented CNTs are mixed with W-Cu powders, and a few small particles are embedded in the tangled CNTs. Fig. 5(d) displays the high magnification view and characteristic selected area electron diffraction (SAED) pattern of CNTs taken from the red region in Fig. 5(c). It should be noticed that, the CNTs are intricately intertwined, and the hollow channel does not exist anymore, which could be attributed to the mechanical impact of milling balls on CNTs and mixed powders during high-energy ball-milling process. This accords well with the results obtained from the above Raman spectra of the mixed W-Cu powders doped with 3 wt.% CNTs as shown in Fig. 4. So the result of CNT addition is to provide carbon source but not CNT reinforcement, and the tungsten carbide phases present different properties with CNTs.

![Figure 9](image.png)

**Fig. 9** – Breakdown strength of the ultrafine-grained W-25 wt.%Cu composites doped with CNTs of 0 wt.% (a), 1 wt.% (b) and 3 wt.% (c).
3.3. Hardness and electrical conductivity

The hardness and electrical conductivity of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs are listed in Table 1. It is obvious that the hardness of the W-Cu composites increased with the increase of CNTs content, but with certain sacrifice of electrical conductivity. The increase of hardness and decrease of electrical conductivity probably arose from the formation of tungsten carbides [7,31,37] through the reaction of W and CNTs during sintering and infiltration processes. Besides, with the increase of CNTs content, the contact probability among CNTs would increase, leading more agglomeration due to Van der Waals force. The agglomeration would facilitate the formation of blind holes after copper infiltration [38], contributing to the further decrease of electrical conductivity. Therefore, the electrical conductivity of the W-Cu composites decreased with the increase of CNTs content.

3.4. Wear resistance

The friction coefficient changing curves of the ultrafine-grained W-25 wt.%Cu composites with different contents of CNTs are shown in Fig. 6. It can be clearly seen that, the average friction coefficients of W-Cu composites reduced obviously with the increase of doped CNTs content. Table 2 summarizes the mass loss rate of the ultrafine-grained W-25 wt.%Cu composites with different contents of CNTs. It can be concluded that, for each composite, the dominant mass loss originated from the grinding ball which endured continuous wear during the whole process. Moreover, with the increase of CNTs content, the mass loss rate for either grinding disk, or grinding ball, or even overall system, presented a gradually reducing trend. The surface worn micrographs and average line roughness of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs in Fig. 7. It can be seen that the worn surface maintain relatively dense microstructure, but several scratches can be observed on the worn surface. For the ultrafine-grained W-25 wt.%Cu composites without doped CNTs, as shown in Fig. 7(a), the severely worn surface and copper-rich area were observed. With the increase of the content of doped CNTs, the worn extent and copper-rich area decreased. Namely, these behaviors are consistent with the surface roughness changes.

The improvement of wear resistance is considered to be attributed to the generated tungsten carbides after sintering and infiltration. The generated tungsten carbide ceramic particles can be used as effective carrier in the wear and friction process, and the higher hardness was accompanied with higher surface smoothness due to the reduced plastic
deformation of the surface during wearing. Thus, the generated tungsten carbides reduced the adhesive wear degree of the W-Cu composites, and further avoided the falling out of tungsten particles, leading to the reduction of the abrasive wear and the friction coefficient as well as the mass loss rate. Therefore, with the increase of doped CNTs content, the wear resistance of W-Cu composites has been improved significantly.

3.5. Compressive performance

To further validate the superiority of mechanical properties for the W-Cu composites doped with CNTs, we also investigated the compressive behaviors at 300 °C, 500 °C, 700 °C and 900 °C, as well as room temperature for comparison. The compressive strength at different temperatures and the stress–strain curves of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs are presented in Fig. 8. It can be observed that, with the increase of doped CNTs content, the compressive strength increased with certain sacrifice of plasticity at any definite temperature. At room temperature, especially, the compressive strength of the W-Cu composite doped with 3 wt.% CNTs increased by 55.7% compared with the composite without CNTs, which demonstrated the significant strengthening effect of the tungsten carbide particles at room temperature. In addition, it should be mentioned from Fig. 7(b)–(d) that, all samples showed obvious strain hardening at deformation temperatures below 500 °C; while at the temperatures of 700 °C and 900 °C, the stress–strain curves presented a typical rheological steady state, indicating that the high-temperature induced dynamic softening exceeded the strain hardening [39].

3.6. Arc erosion resistance

Arc erosion resistance ability is a crucial indicator for the W-Cu composites used as arc contacts. The breakdown strength of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs are presented in Fig. 9. The average breakdown strength of the W-Cu composites doped with 0 wt.% , 1 wt.% and 3 wt.% CNTs are calculated to be $5.56 \times 10^4$ V/m, $7.91 \times 10^4$ V/m and $9.36 \times 10^4$ V/m, respectively. With the increase of doped CNTs content, the breakdown strength of W-Cu composites gradually increased, which could be attributed to the tungsten carbide ceramic phases generated in the W-Cu composites after doped CNTs. Under the heat effect of arc, the tungsten carbide phases with good stability at high temperature distributed in the W-Cu composites could prevent the flow or the accumulation of molten copper, and also avoid the large area splash of copper liquid. On the other hand, the tungsten carbide ceramic particles with high melting point can be used as the core of heterogeneous nucleation, which shortened the solidification time of molten copper liquid and reduced the size of particles formed on the composite surface. Both the above two factors would contribute to an improved smoothness of the surface morphology. The surface morphologies after breakdown for 50 times of the ultrafine-grained W-25 wt.%Cu composites doped with different contents of CNTs are presented in Fig. 10. It can be seen that, the W-Cu composites doped with different contents of CNTs suffered serious arc erosion right underneath the tungsten anode. With the increase of doped CNTs content, the breakdown pit of W-Cu composites became gradually shallower and more diffuse. The resulted surface with lower roughness would reduce the local electric field and thereby reduce the field emitter of electric breakdown. Therefore, the arc erosion resistance of W-Cu composites could be enhanced significantly by adding CNTs into the W-Cu composites [40,41].

4. Conclusions

(1) Tungsten carbide phases of WC and W2C formed through the reaction of CNTs and tungsten during sintering and infiltration. With the increase of the content of doped CNTs, the quantities of generated tungsten carbide phases increased.

(2) The generated tungsten carbide phases improved the hardness of W-Cu composites, with certain sacrifice of electrical conductivity. The W-Cu composites doped with 1 wt.% and 3 wt.% CNTs exhibited improved hardness of 244 HB and 275 HB, respectively.

(3) With the increase of the content of doped CNTs, the friction coefficient and the mass loss rate of the W-Cu composites decreased. When the content of doped CNTs reached 3 wt.%, the average friction coefficient and mass loss rate decreased by 66.2% and 65.2% compared to the W-Cu composite without CNTs.

(4) The W-Cu composites doped with CNTs showed highly improved high temperature compressive performances. The compressive strength of the W-Cu composite doped with 3 wt.% CNTs increased by 55.7% at room temperature and 18.4% at 900 °C, respectively in comparison with the W-Cu composite without CNTs.

(5) The W-Cu composites doped with CNTs showed highly improved arc erosion resistance. The average breakdown strength of the W-Cu composite doped with 3 wt.% CNTs increased by 68.3% in comparison with the W-Cu composite without CNTs.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

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