

**ADVANCED COPPER-TUNGSTEN COMPOSITE
MATERIALS FOR THERMAL AND ELECTRICAL
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Abstract. *The contacts and fingers in the traditional high-voltage circuit breakers are all made of copper-tungsten alloy materials by powder metallurgy process at present. The conductivity and hardness of existing materials have reached the bottleneck, which can't meet the requirements of working conditions. Graphene has good electrical conductivity, mechanical properties and high specific surface area. Doped into the traditional copper-tungsten alloy, graphene is expected to greatly improve the electrical conductivity and hardness of copper-tungsten electric contacts, which could make the alloy have excellent mechanical and electrical properties at the same time. It has become the main development direction of current electrical contact materials research. In this paper, the research progress of strengthening methods of traditional copper-tungsten electric contact materials by graphene and other reinforcing agents is systematically reviewed, and the strengthening mechanism of graphene on copper-tungsten electric contact materials is explored, which can provide technical guidance for the development and application of new high strength and high conductivity graphene-reinforced copper-tungsten electric contact materials with new performance and long electrical life.*

Keywords: *powder metallurgy, tungsten (W), tungsten–cobalt (WCo) alloys, tungsten–titanium (WTi) alloys, metal powders, mechanical properties, sintering, hard materials, composite materials, cutting tools.*

1. Introduction

Metal matrix composites (MMC) consists of continuous metal matrix and a certain content of reinforcing material. Unlike conventional alloys, no new phase is formed in metal-based composites, only components uniformly mixed [1]. Metal matrix composites have been widely used in industries like aerospace, military and electrical applications due to their outstanding electrical, thermal and mechanical properties. Copper tungsten (Cu-W) alloy is a metal matrix composite consisting of tungsten (W) matrix and copper (Cu) dispersed therein, and both tungsten and copper maintain their original physical and mechanical properties. Therefore, copper tungsten composite can have excellent conductivity and thermal conductivity of copper as well as excellent mechanical properties, extremely low thermal expansion coefficient and excellent arc resistance of tungsten [2,3]. In the power industry, copper-tungsten composites are the most commonly used material for high-voltage circuit breaker electrical contacts. Arcs arise when arc contacts in the circuit break separate, accompanied by high temperature and arc erosion. For the high-voltage circuit breaker prepared by copper tungsten contacts during separation, a lot of heat can be consumed by the evaporation of copper phase, which can reduce the damage of arc to the contact [4, 5].

According to the copper tungsten equilibrium phase diagram [6], there is no solid soluble region in the phase diagram when temperatures are below 1084 °C. Under this condition, both copper and tungsten exist in solid state. Meanwhile, due to the large difference in melting boiling point of copper and tungsten, there is no coexistence region of liquid copper and liquid tungsten in the phase diagram. This means that both tungsten and copper are completely insoluble not only in solid phase, but also in liquid phase. Therefore, the so-called copper-tungsten alloy is a fake alloy. The Hume-Rother rule is often used to predict whether metal combinations will form replacement solid solvents (a solid solvent where solute atoms randomly replace solvent atoms), which can also support the phenomenon

that copper-tungsten alloys are false alloys. First, the Hume-Rothery rule suggests that the difference in ionic radius of the two atoms forming displaced solid solvents should be within 15%. But for copper and tungsten atoms, the difference of their ionic radius is greater than 20% (atomic radius of tungsten is 1.93 Å and copper is 1.45 Å). Second, to make sure both elements have the proper solubility, the crystal structure must be same. However, the crystal structure of copper is the face-centered cubic (FCC), while tungsten is the body-centered cubic (BCC) structure. Finally, the atoms forming solid solvents should have similar electronegativity that is used to characterize the power of atom to attract electrons. Atoms with high electronegativity can absorb electrons from neighboring atoms with low electronegativity. For two atoms with great different electronegativity, they will attract to each other, which will form a chemically bonded compound rather than a metal-bonded solid solvent. According to the Hume-Rothery rule, the negativity difference between the two atoms should be less than 0.3, which is much bigger for copper tungsten alloy (1.9 for copper and 2.36 for tungsten) [7]. Therefore, it is difficult to form solids between copper and tungsten.

Due to the incompatibility between copper and tungsten, a high-density copper-tungsten composite [8] cannot be prepared using conventional alloy techniques (e. g. copper casting process). Melting fusion has commonly used to prepare copper tungsten composites. The melting technique may be performed under conditions of high pressure or no pressure. The latter case is generally known as no pressure melt, where the metal/ alloy ingot is placed and melted on a lower density raw billet, then the molten metal flows under gravity into the preformed billet. That's why the melting method belongs to the liquid metallurgical process [9]. Tejado et al. [10] prepared copper tungsten composites with high compaction and excellent mechanical properties by liquid copper melting porous tungsten rods. As the requirements for the stability of power system and reliability of power supply become higher, the working conditions of contact materials are increasingly severe.

During successive opening cycles, copper on the contact surface is lost through the splashing of liquid droplets, which would cause damage to the contact structure [3]. Moreover, due to the low solubility and wetting properties between copper and tungsten, it is getting difficult to prepare more compact and evenly microstructured copper and tungsten composites. Therefore, traditional copper-tungsten composites are unable to meet the needs of electrical contacts, and strengthening the performance of copper-tungsten composites is imminent.

2. Strengthening method of copper and tungsten composites

Usually, adding the reinforcing phase and optimizing the preparation process are the main methods to enhance the properties of copper-tungsten composites. Since the great properties of the tungsten and copper phases, it is relatively difficult to develop new manufacturing techniques to prepare the fully dense copper tungsten composites [11]. Therefore, adding reinforced phase to copper-tungsten composites is more promising. By hindering the crystal boundary and dislocation motion, the reinforced phase particles scattered in the substrate can effectively inhibit the growth of copper grain. Thereby refining the microstructure of the copper tungsten composite and improving its mechanical properties, such as the tensile strength [3]. Furthermore, the intrinsic properties of the reinforcing phase can also affect the properties of composite material. In recent years, multiple reinforcing materials have been added in copper-tungsten composites. Common reinforcing materials can be divided into the following four types. Alloy elements are reinforced with copper-tungsten composites According to the effect of alloy elements on the copper tungsten matrix, the alloy elements used for reinforcement can be divided into three categories: action with copper, tungsten and interface [3]. The first category of elements such as zinc (Zn) and silver (Ag) can form solid solvents or compounds with copper but are insoluble in tungsten. The effects of zinc content on the performance of copper-tungsten composites was investigated. Experimental results show that the maximum bending strength of copper tungsten composite reached 960

MPa after added 14 wt.% Zn, which increased more than twice that of copper tungsten composite without zinc. At the same time, because the zinc fixation temperature of copper is lower than pure copper, the sintering temperature of zinc is also much lower. The second category of alloy elements such as cobalt (Co) and iron (Fe) can form intermetallic compounds with tungsten to enhance the diffusivity of tungsten, thus improving the sintering density, hardness and strength of the composites. Finally, the elemental zirconium (Zr) has some solubility in both tungsten and copper and can also spread into the copper tungsten interface [1] prepared a copper zirconium tungsten (Cu-Zr-W) composite by using the infiltration of the copper zirconium (Cu-Zr) alloy into the tungsten skeleton. The results show that zirconium particles can enhance the copper tungsten interface and copper rich region, and maintain the high conductivity of copper as well. The vacuum arc can be effectively scattered on the surface of copper zirconium tungsten composite to reduce molten copper splash. Compound particles reinforced copper-tungsten composites. Compound particles (ex. oxides, carbide, nitride, and boride) are also used to reinforce copper-tungsten composites. Li et al [14] prepared W-25 wt.% Cu nanopowder doped with lanthanide oxide (La_2O_3) by hydrothermal-coreduction method. The fine-grain and high-density W-25 Cu- La_2O_3 composite powders were fabricated by hot extrusion technology. The results indicate that the composite shows the best comprehensive performance when the content of La_2O_3 is 2.0 wt.%. The value of conductivity, hardness and tensile strength is 52.5% IACS, 288 HB and 375.9 MPa. Zhang et al [11] reported that the tungsten carbide (WC) doped W-Cu composites prepared by vacuum hot-press sintering had excellent thermal conductivity ($287.5 \text{ W/m}\cdot\text{K}$) compared with previous research. Compared to oxides, carbide can also remove free oxygen, eliminate oxide impurities, improve the density of the composite and reduce the brittle of the material [7].

Carbon nanotubes (CNT) reinforced copper-tungsten composites

Although alloy elements such as iron, cobalt and nickel as well as hard materials like oxide or carbide particles can greatly improve the mechanical properties of copper tungsten composites, these additives also cause damage to their electrical and thermal properties. Therefore, it is necessary to find more effective reinforcing materials that can improve the mechanical properties of copper-tungsten materials while maintaining good thermal and electrical properties. In recent years, due to their excellent electrical, mechanical and thermal properties, carbon nanotubes (CNT) and graphene have been considered as highly attractive nanofillers in metal-based composites [9, 17-19]. Structurally, CNT is a piece of graphene rolled into a tube, as shown in figure 1a. CNT can be divided into different types depending on the direction of the tube shaft relative to the carbon network, including an armchair type CNT exhibiting metal conductivity ($n=m$), a serrated CNT with semiconductor properties ($m=0$) and a helical type CNT ($n \neq m$) [20]. In addition, CNT can be classified by the number of carbon layers on their tube wall as shown in figure 1b, including single wall carbon nanotubes (SWCNT), double wall carbon nanotubes (DWCNT) and multi wall carbon nanotubes (MWCNT) [8].

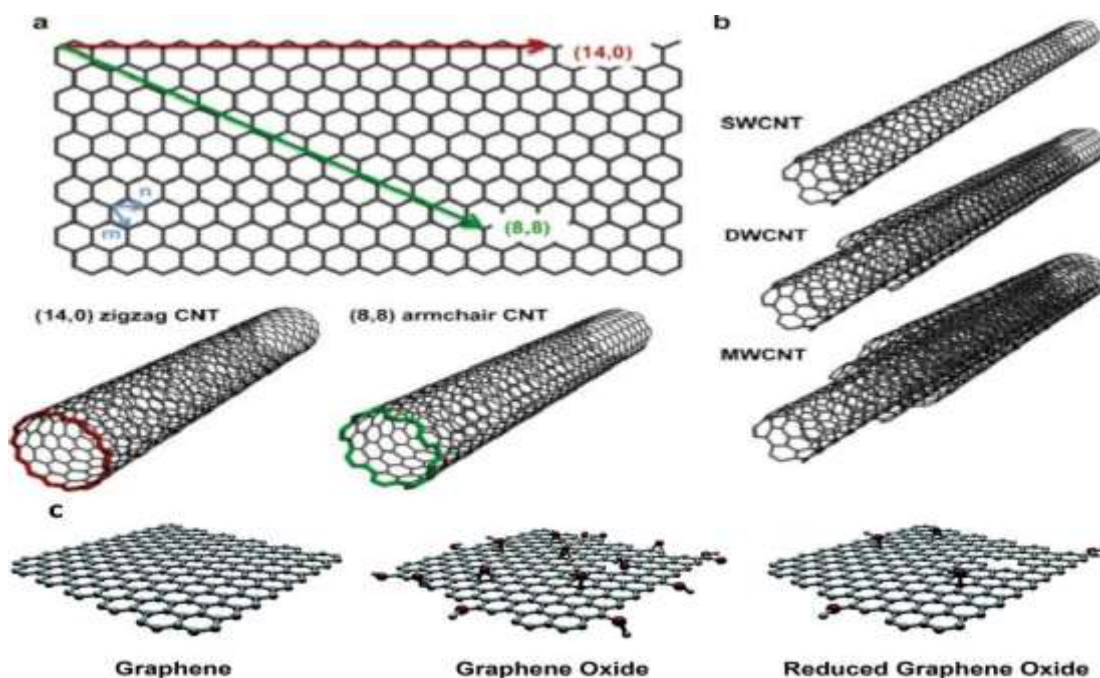


Figure 1. Structure of carbon nanotubes and graphene a) armchair CNT (n, n) and zigzag CNT ($n, 0$).

Over the past two decades, CNT has been widely used as a reinforcing phase in various metal-based composites. Most of these studies have focused on aluminum-carbon nanotubes (Al-CNTs) and copper-carbon nanotubes (Cu-CNTs). For example, He et al. [9] prepared a 96% relative density of Al-5wt.%CNT composite material combined with chemical vapor deposition (CVD), compaction and sintering techniques. The hardness and tensile strength of the composite are 4.3 and 2.8 times that of pure Al, respectively.

Carbon nanotube-reinforced copper-tungsten composites are relatively poorly studied. MWCNTs-copper tungsten composite was prepared by thermal pressure sintering process by Shi et al [10]. The results showed that the addition of 0.4 wt.% MWCNTs increased the bending strength and thermal conductivity of the copper-tungsten composites by 8.8% and 27.8%, respectively. However, due to high cost and the complexity of carbon nanotube distribution in the metal matrix, further development of the carbon nanotube reinforced metal-based composites becomes a difficult task [11].

Graphene-reinforced copper-tungsten composites

Graphene is a two-dimensional (2D) sheet-like structure, covalently bonded to the sp^2 hybridized carbon atomic composition with excellent electrical conductivity (carrier mobility of $1.5 \times 10^4 \text{ cm}^2/\text{V}\cdot\text{s}$ [25]), thermal conductivity ($5 \times 10^3 \text{ W}/\text{m}\cdot\text{K}$ [5]) and mechanical properties (Young's modulus reaches 1 TPa, tensile strength of 130 GPa [8]). The structures of graphene and its two derivatives: GO (GO) and reduced GO (rGO) are shown in figure 1(c). GO is a monolayer of graphene sheet, where the number of carbon atoms has been reduced to 40- 60% to support more oxygen atoms. As a "hydrophilic derivative" of graphene, GO has higher surface activity due to the presence of the oxide group. rGO is a monolayer graphene sheet where GO still retains some functional groups after reduction. rGO can be seen as an intermediate structure between ideal graphene sheets and highly oxidized GO [6].

Compared to carbon nanotubes, graphene can be manufactured by relatively inexpensive chemical and electrochemical peeling of graphite [4]. Alternatively, graphene has a larger surface area than CNT, whose properties can better reflect in composites [10]. Therefore, graphene may be more suitable for a reinforcing material than carbon nanotubes. Nowadays, graphene-reinforced metal matrix composites have attracted increasing attention from researchers. For example, copper-graphene composites with 8 vol. % graphene has great mechanical properties that the yield strength and Young's modulus increased by 114% and 37% [3], respectively; the hardness and strength of aluminum-graphene composites is 2-3 times higher than pure aluminum [2]; moreover, the addition of graphene to the magnesium-titanium (Mg-10 wt.% Ti) composite can also improve its yield strength and malleability [7].

So far, few studies have been conducted on the preparation and performance of graphene-reinforced copper-tungsten composites. Xi'an University of Technology has done relatively more research in this field. Graphene/ W70Cu30 composites were prepared by mechanical alloying and pressure-free melting techniques, and the mechanical hardness and electrical conductivity of copper-tungsten-doped graphene composites were investigated. In addition, materials which were [2] prepared a copper-coated graphene-reinforced W80Cu20 composite using fusion technology and spark plasma sintering (SPS).

Since the van der Waals force between graphene layers is stronger than the mechanical adhesion force of graphene to copper, graphene tends to form aggregates to reduce its surface energy rather than being evenly dispersed into the metal substrate [9]. Similarly, because copper neither moistens nor reacts with graphene, the interface bond between graphene and copper is very weak. Only the weak mechanical adhesion and van der Waals force interaction are leaving at the interface [6]. Therefore, the key to develop graphene-metal composites is keeping the uniform dispersion and complete structure of graphene in the matrix during the preparation.

3. Preparation method of graphene reinforced metal-based composites

With the development of graphene-reinforced metal-based composites, its manufacturing technology is also constantly improving. To date, multiple processing techniques have been used to optimize the structure and properties of graphene reinforced metal-based composites.

The melting technique is mainly used for composites like copper-tungsten composites, which cannot be prepared by conventional metallurgical methods due to its insolubility. In addition, melting method can be used to prepare graphene reinforced copper tungsten composites. Graphene / W70Cu30 complexes were prepared in a manner of combining mechanical alloy with the melting method [5]. The process is shown in figure 2, where the synthesized graphene is firstly dispersed in the C₂H₅OH solution. Then, the copper and tungsten powder were mixed by mechanical agitator in the C₂H₅OH solvent. Graphene dispersion was slowly added to the copper-tungsten mixed solution and stirred for several minutes. Afterwards, the graphene mixture with copper-tungsten powder was ball ground in protective atmosphere and the ball ground mixture was dried in the vacuum oven. After pressing the complex powder into a cylindrical bar, a copper block was placed at its top to form a raw blank. The raw blank was sintered at 1350°C under H₂ protective atmosphere. During sintering, the tungsten solid grains coexisted with the copper liquid and the grains were rearranged. The subsequent composite compaction process, accompanied by grain coarsening, the removal of voids in composite were effectively facilitated. [2]

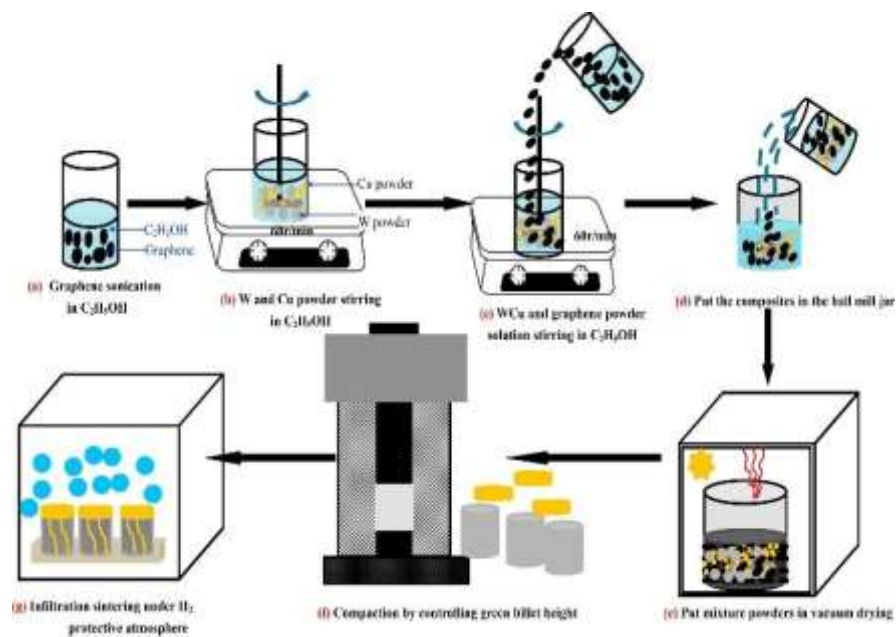


Figure 2. Preparation Process of Graphene / W70Cu30 Composite [32].

It is shown that graphene can strengthen the mechanical properties and conductivity of copper-tungsten composites [11, 8]. It is important to understand the principle that graphene additives affect the arc breakdown properties of copper tungsten contacts. Dong et al [8] estimated the arc resistance using contact mass loss and dielectric strength. It was shown that when graphene was added to 0.5 wt.%, the weight loss of W70Cu30 composites decreased by 45.5% compared to graphene-free contacts. Furthermore, the breakdown intensity values showed a trend of linear increase. When the arc breakdown times reach more than 20 times, the maximum breakdown intensity value is 54.5% greater than that without added graphene.

Figures 3(a), (b) show the morphology of CuW alloy with and without adding 0.5 wt.% graphene, respectively. The surface SEM images of the W70Cu30 materials of graphene after the first electro breakdown show that the size of the erosion region is reduced by about 25%: the length of the W70Cu30 complex without graphene is about 240 mm, and the addition of graphene is 180 mm. Meanwhile, from the amplified image figure.3(a1) and (b1), with 0.5wt.% The W70Cu30 complex of graphene has a small number of smaller pits. figures 3(c) and

3(d) are SEM images of the sample surface after electro breakdown 100 times, and c1 and d1 are local amplification plots, containing 0.5wt.% The W70Cu30 composite of graphene has a flat surface and a smaller corrosion area. Therefore, the addition of graphene effectively reduces the splash of liquid copper and slows down arc corrosion.

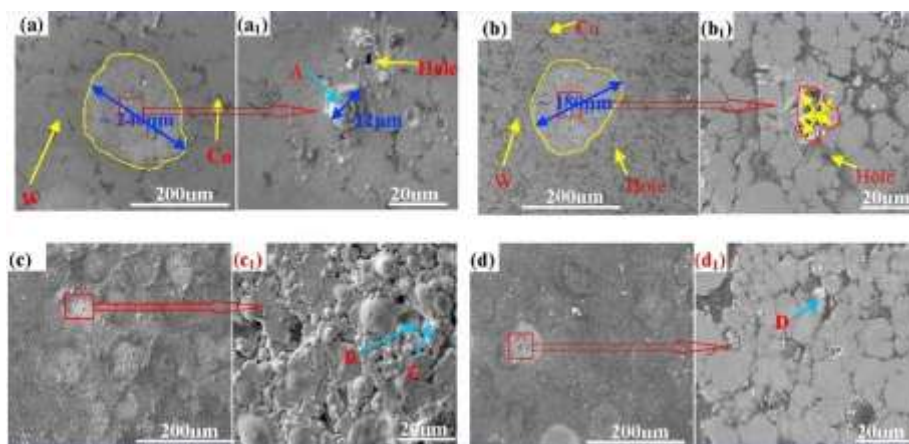


Figure 3. The surface SEM micrographs after first electro breakdown of the W70Cu30 alloy a) without b) with 0.5 wt.% graphene.

The surface SEM micrographs after 100 times electro breakdown of W70Cu30 alloy c) without d) with 0.5 wt.% graphene. (The figure marked below 1 is the enlarged image) [9].

This phenomenon can be explained by work function that defined as the minimum energy required for electrons to escape out of the material surface. Arc breakdown usually preferentially focus on the phases with low work function. Thus, for graphene-W70Cu30 complexes, due to the low work function of graphene (ϕ_{rphn} (4.2 eV) $<$ ϕ_u (4.36 eV) $<$ ϕ (4.55 eV)), arc breakdown occurs first in the graphene phase and subsequently moves towards the copper and tungsten phases. Moreover, graphene has no reaction with other alloy elements because of its high melting points and chemical stability. When the arc breakdown occurs through graphene, graphene can consume much of the arc energy, reduce the arc action on the copper phase and ultimately reduce copper sputtering. Second, graphene can

effectively refine tungsten particles, improve the wettability of tungsten and copper, make the copper phase more homogeneous in the tungsten skeleton and generate more crystal boundaries. Furthermore, due to the different work functions of graphene, copper and tungsten, there is electron migration and charge redistribution at the three-phase interface. The internal electric field is formed at the interface. Arc breakdown preferentially forms at these interfaces rather than concentrating in local regions. Therefore, the presence of graphene effectively improves the viscosity of copper liquid under the arc, effectively reduces the splash of copper liquid, improves the arc stability and extends the service life of the copper tungsten contact.

Conclusion

In short, the electrical conductivity and hardness of traditional copper and tungsten alloy materials can be double improved through graphene doping modification, which provides new ideas for the component design and preparation of new high-voltage electric contacts. Due to the addition of graphene realizing the high force electric performance and corrosion resistance of copper tungsten electric contact, it can provide theoretical basis and technical guidance for the material selection and development of high voltage high current circuit breaker, and has an important role in promoting the development of graphene technology and high voltage electric contact technology.

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