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Research on the Properties of Graphene/ Copper Composites

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Abstract:

In response to the trends of electrical products, graphene/copper composites have emerged as a highly promising material choice due to their unique advantages. But these materials still face some problems such as performance antagonism in the process of service. So in response to such phenomena, this paper starts from the preparation process of graphene/copper composites and enhances the mechanical properties of the material by exploring the strengthening mechanisms. In addition, interface regulation is also introduced to improve its strength, toughness, electrical conductivity, and thermal conductivity. Moreover, the paper lists the current technical challenges faced by this material and proposes relatively feasible solutions accordingly. Through this research, graphene/copper composites can, to a certain extent, overcome the issue of performance antagonism, achieving a balance between high strength and toughness while maintaining good electrical conductivity and thermal conductivity, thereby having stronger application potential, and better serving the field of electrical manufacturing.

Keywords: Graphene; copper; strength; toughness; electrical and thermal conductivity.

1. Introduction

Since the beginning of the 21st century, the development of electronic and electrical products has been trending towards portability, lightweight, and integration, thus placing higher demands on the performance of the materials that we use. Copper-based materials, known for their excellent thermal, electrical, and mechanical properties, have been widely applied in fundamental manufacturing fields. However, for most copper-based materials, there is often an antagonism between electrical conductivity and strength. So, to simultaneously enhance multiple properties, incorporating other materials into copper to form composites is a viable solution. From the perspectives of structure and performance, adding graphene as a secondary phase to copper-based materials can be an effective method for reinforcement. This approach not only avoids the orientation limitations posed by carbon nanofibers (CNF) as a reinforcing phase but also mitigates the potential agglomeration issues associated with carbon nanotubes (CNT). Nevertheless, graphene as a secondary phase still faces challenges, such as difficulties in achieving uniform dispersion, which can lead to formation of defect, and the tendency for its structure to be damaged, causing the material to lose its original functionality.This paper aims to improve the physical and mechanical properties of graphene/copper composites by delving into the reinforcement mechanisms and the methods of interface regulation. These improvements are intended to make the material better suited to the demands of the electrical manufacturing industry.

2. Organization of the Text Preparation Processes

2.1 Section Headings Powder Metallurgy

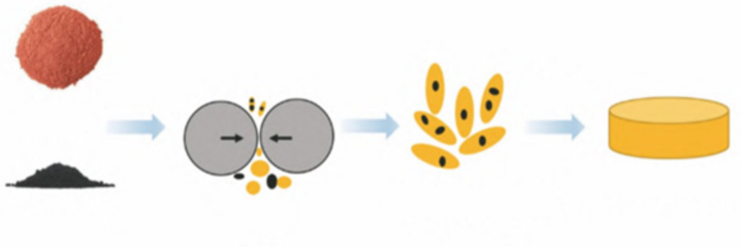

Fig. 1 Schematic of powder metallurgy process principle [1]

Powder metallurgy is a commonly used preparation method, and its process principle is shown in Fig.1. The method mainly involves mixing graphene powder with copper powder through ball milling, followed by compaction and sintering densification to obtain the graphene/copper composite [1]. As the most mature preparation process for the material, this method imposes almost no restrictions on the matrix and reinforcement, thus offering it high design flexibility. However, during the mixing process, the structural integrity of graphene is prone to be damaged, which lead to the final reinforcement effect reduce [2].

2.2 Molecular-Level Mixing

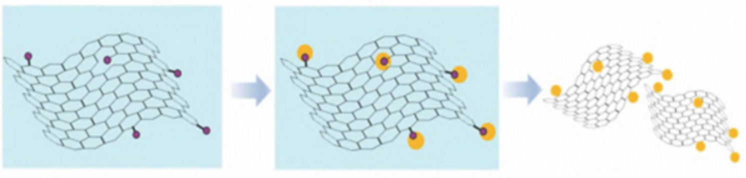

Fig.2 Principle schematic of molecular-level mixing prepared rGO/Cu composite powder [1]

Molecular-level mixing involves mixing graphene oxide with a solution containing Cu^{2+} ions, allowing them to adsorb onto the surface of graphene oxide, as shown in Fig.2. This is followed by high-temperature treatment or the use of a strong reducing agent to reduce the graphene oxide to reduced graphene oxide (rGO), forming a composite powder of rGO and copper. The final graphene/copper composite is then obtained through sintering [1]. This method ensures good dispersion of graphene in the solution, and as a result, the composite material prepared by this method typically exhibits high interfacial bonding strength, leading to a significant improvement in mechanical properties.

2.3 Chemical Vapor Deposition

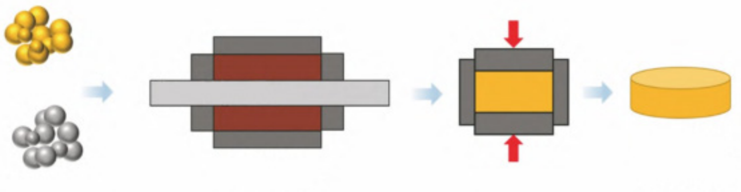

Fig.3 Schematic of chemical vapor deposition process principle [1]

Chemical vapor deposition uses carbon-containing organic compounds as a carbon source, directly generating graphene on the surface of the matrix under certain conditions, resulting in composite powder or a graphene film. The composite material is then prepared through sintering, as it shown in Fig.3 [1]. This method can produce high-quality graphene reinforcements with a controllable number of layers. Moreover, due to the large two-dimensional planar size of graphene, it can form a strong bond with the matrix metal. This method is also conducive to achieving high electrical and thermal conductivity in the composite material. However, the overall process is complex, and the equipment required is relatively expensive, making it more suitable for small-scale material preparation.

3. Properties Reinforcement and Interface Regulation

3.1 Mechanical Properties Reinforcement

The mechanisms of mechanical property reinforcement of graphene in copper matrix primarily include load transfer strengthening, grain refinement strengthening, thermal mismatch strengthening, and dispersion strengthening. Load transfer strengthening occurs when the composite material is subjected to stress, and the load is directly transferred to the graphene reinforcement through the interface, enhancing the overall strength of the composite. This is the primary strengthening mechanism in the composites, contributing to more than 30% of the overall strength improvement [1].Grain refinement strengthening involves the introduction of graphene into the metal matrix, where it can pin grain boundaries as seen in powder metallurgy, preventing grain growth. This results in grain refinement, which eventually increases the strength of the composite [3].Thermal mismatch strengthening happens during the thermal processing of the composite, where the difference in thermal expansion coefficients between the matrix and the graphene leads to localized plastic deformation. This creates regions with high dislocation density, hindering dislocation motion and, ultimately, enhancing the material's strength [4].Dispersion strengthening refers to the physical barrier that graphene creates in the copper matrix impeding dislocation motion. Then dislocations tend to accumulate near the graphene, thereby increasing the material's strength [1]. However, it is important to note that this mechanism requires the reinforcement to be at the nanoscale and dispersed within the grains to restrict the movement of intragranular dislocation. Since graphene is predominantly located at the grain boundaries, the contribution of dispersion strengthening to the overall strength of this type of composite is relatively minor [5].

In addition to enhancing strength, improving the structure of the reinforcement and designing the configuration of the composite can further compensate for the toughness of the material. In aspect of structural improvement, experimental results indicate that preparing graphene nanoribbons by shearing and unrolling carbon nanotubes, followed by sintering through spark plasma sintering, leads to the composites with higher strain hardening and uniform elongation rates [6]. Additionally, biomimetic blade-like composite reinforcements formed by partially unrolling the outer walls of carbon nanotubes help improve the efficiency of load transfer while increasing the energy dissipation during deformation. Simulation results show that the load borne by the nanoribbon sections is approximately 10% higher than that of the matrix regions, which significantly enhances the toughness of the material [1].

In aspect of configuration design, the pull-out mechanism of graphene, along with the "brick-and-mortar" structure inspired by nacre, allows cracks to deflect between the layers, increasing the energy dissipation during material failure. This design results in the composite material requiring 1.8 times more energy to fracture compared to pure copper produced using the same process, indicating significantly higher toughness [1]. Additionally, in-situ synthesis methods can be used to produce composites with a discontinuous network structure. Compared to continuous network structures, these composites exhibit more pronounced grain refinement effects and greater strength improvements. Experimental data shows that the fracture elongation rates of the materials are nearly 40% higher than the pure copper [1], significantly improving the material's toughness.

3.2 Physical Properties Enhancement

The interface between graphene and copper is crucial in determining the electrical and thermal conductivity of the composite. Due to graphene's tendency to agglomerate and its poor wettability with the matrix, nano-voids can form easily at the composite interface. They will significantly affect the conduction of electrons and phonons [7], which in turn reduces the electrical and thermal conductivity of the composite eventually.

In term of electrical conductivity, rare earth elements can be inserted to imporve it at the graphene nanosheet/copper interface using impregnation reduction or in-situ growth methods. The oxides formed during this process embed into the graphene nanosheets, enhancing the interfacial bonding and increasing the electrical conductivity of the composite from 84.5% of pure copper to 90%. In term of thermal conductivity, for improving it, graphene can be treated with 4-ethynylaniline to establish delocalized conjugated π-bonds at the graphene/copper interface, forming new electron pathways to transfer heat. At 100 °C, the thermal conductivity of this composite can reach 497 $W \cdot m^{-1} \cdot K^{-1}$, which is 1.61 times that of pure copper.

Additionally, adjusting the number of graphene layers can also control the anisotropy of the material. For example, when the number of graphene layers is between 5 and 6, the thermal conductivity can reach 394 W·m⁻¹·K⁻¹, 1.28 times that of pure copper [1].

Besides, the orientation of the matrix also significantly affects the composite's electrical and thermal properties. A composite with a nanolamellar structure can improve the orientation of graphene within the matrix. given the two-dimensional nature of graphene, the composite will have higher electrical conductivity along the graphene/copper interface. Therefore, using single-crystal copper foil as the matrix, compared to polycrystalline copper foil, enhances the electron transport capacity of the composite [8].

3.3 Interface Regulation Strategies

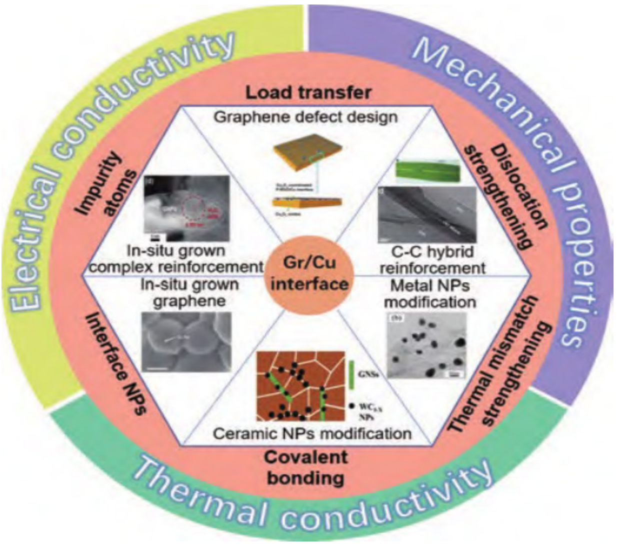

Fig. 4 Schematic diagram of the main strategies for graphene/ copper interface regulation [9]

Fig.4 illustrates the main strategies for regulating the graphene/copper interface, and by controlling the interface, the bonding between graphene and copper can be improved, significantly enhancing the mechanical properties of the composite. One approach is to modify graphene nanosheets into graphene oxide, introducing numerous active oxygen-containing groups. These groups promote the formation of covalent interactions with copper, allowing for better dispersion in solution systems and ultimately increasing the interfacial bonding strength [10]. Another strategy involves unrolling the outer structure of multi-walled carbon nanotubes to form oleander leaf-shaped hybrids shown in Fig.5. This promotes the formation of covalent bonds at the graphene/copper matrix interface, thus strengthening the interfacial bonding [9].

In copper-based composites prepared through oxidation, reduction, ball milling, and sintering of flake graphite, Ag nanoparticles inhibit the agglomeration of reduced graphene oxide, facilitating tight interfacial bonding with copper. Data shows that the yield strength and tensile strength of these composites reach 332 MPa and 478 MPa respectively, which are 98% and 93% higher than pure copper [9]. Moreover, in copper-based composites prepared using the NaCl template method and molecular-level mixing, copper nanoparticles and graphene-like networks act to connect the interfaces and refine the grains, resulting in high strength and elongation. Experiments show that the yield strength and fracture elongation of these composites are improved by 126% and 41% respectively, compared to pure copper [9].

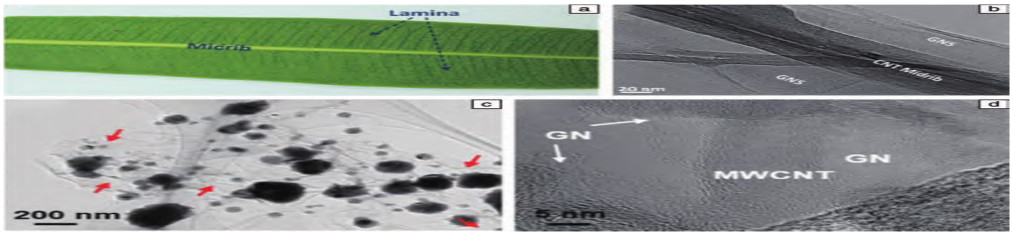

Fig. 5 Morphology of C-C hybrid reinforcements: (a) image of Nerium indicum Mill leaf, (b) HRTEM image of leaf-like CNT-GNR hybrids [9]

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4. Technical Challenges and Solving Methods

4.1 Dispersion

Graphene has a large specific surface area and high surface energy, making it prone to agglomeration in solution, which hinders its reinforcing effect and negatively impacts the overall performance of the composite. In order to solve this problem, the good hydrophilicity of oxygen-containing group graphene oxide can be used to improve its dispersion in solution. Wet mixing can also be used to make graphene evenly distributed at the grain boundaries of the matrix, causing grain refinement and improving the agglomeration of the material. In addition, nickel particles can be added to the reinforcement to act as spacers to hinder the agglomeration of graphene, or the solution system can be subjected to ultrasonic treatment, and the graphene can be dispersed by the shock wave generated by the ultrasonic cavitation effect.

4.2 Interfacial Bonding

Graphene has poor wettability with copper, making it difficult to form strong interfacial bonding. This weakens the effect of load transfer strengthening, as the interface may crack under the load, leading to discontinuity in the internal structure and a decline in the composite's overall performance. In this regard, 0.2% chromium can be added to the copper matrix to form an interlayer of Cr_7C_3 at the interface to improve the load transfer efficiency and enhance the pinning effect of graphene [1]. Graphene can also be treated by plasma to produce holes with a diameter of 5nm-10 nm on the surface. During sintering, copper oxides will be formed at the holes [1], thereby improving the interface bonding between graphene and copper matrix and improving the mechanical properties of the composites.

5. Conclusion

This paper reviews the fabrication processes of graphene/copper composites and their respective characteristics. It focuses on the enhancement mechanisms of these composites, analyzing methods to improve their mechanical and physical properties, such as the structural modification of the reinforcement and the configuration design of the composites. Additionally, strategies for interface regulation to enhance the material's performance are discussed. Finally, the paper proposes feasible solutions to address the technical challenges faced by these composites, aiming to let them better serve the manufacturing industry. Currently, there are numerous research findings in the field of graphene/copper composites. Due to their excellent mechanical properties and electrical and thermal conductivity, they have been widely used in the production of tough materials and high-performance copper foils. With their unique performance advantages, graphene/copper composites hold great potential for applications in aerospace, military, and power industries.

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