A Review of Key Technologies and Properties for Graphene Cu-Based Composites

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Abstract. Cu-based composites are widely used in mechanical, electrical, communication, transportation and microelectronics industries due to their excellent properties. However, the difficult match between strength and conductivity is the main problem for Cu-based composites. And thermal-mechanical treatment technologies reached the limit to improve and control their comprehensive performance. Graphene is a two-dimensional layered material with carbon atoms hybridized by SP\textsubscript{2} orbital, and has high strength, good electrical conductivity and thermal conductivity. It is expected to solve the contradiction between the strength and conductivity of the composites by introducing graphene into Cu-based composites. In this paper, the commonly used methods for effective dispersion of graphene and interface bonding were introduced, the researches on the strength, toughness, electrical conductivity and thermal conductivity were outlined, lastly the future development of graphene Cu-based composites was prospected.

Keywords: Graphene; Cu-based composite; Effective dispersion; Interface bonding

1. Introduction

Cu-based composites are widely used in mechanical, electrical, communication, transportation and microelectronics industries due to their excellent properties [1-4]. Alloying is a commonly used method to increase the strength of Cu-based composites. This is to increase the strength by mixing one or several alloying elements into Cu matrix. In the previous studies, the selection of metal strengthening phase mostly focused on b.c.c and f.c.c metals. The addition of binary or multi-element metal elements can significantly increase the strength of composites, but it also induces a new thorny problem that the strength and conductivity are difficult to match well [5-7]. Although some thermo-mechanical treatment technologies can be used to alleviate such problem, the optimization and improvement degree is limited. Therefore the comprehensive performance can not be significantly improved.

Graphene is a two-dimensional layered material with carbon atoms hybridized by SP\textsubscript{2} orbital, which has excellent intrinsic properties. Single-layer graphene has high electrical conductivity and thermal conductivity, multi-layer graphene has high strength and ductility. Therefore, graphene is a promising strengthening phase of Cu-based composites [8-15]. In recent years, some important achievements have been achieved in the investigation on graphene strengthening Cu-based composites [16-22]. In this paper, the key technologies and properties of the composites are outlined, and the
existing problems and future research directions are summarized and prospected.

2. Key Technologies

2.1. Effective Dispersion
Graphene is easy to agglomerate as mixed with metal matrix due to its large specific surface area and low stacking density. Moreover, the interface wettability between graphene and Cu matrix is poor, which considerably decreases its performance. At present, the effective dispersion methods of graphene in Cu matrix include ball milling, molecular level mixing, surface modification, electrostatic assembly and ultrasonic assistance. Ball milling has significant influence on the morphology and structural integrity of graphene. It can effectively disperse graphene nanoplatelets (GNPs) in Cu matrix, and increase the mechanical properties of the composites. However, ball milling for too long causes serious damage to GNPs [8]. Molecular level mixing is a commonly used method to prepare graphene Cu-based composites. The graphene oxide (GO) prepared by molecular level mixing has hydroxyl and oxygen-containing functional groups, which can achieve better dispersion of graphene in the matrix [9]. Jiang et al. [10] prepared pristine graphene (PG) by intercalation and exfoliation of graphite, and prepared PG Cu-based composites by surface modification of PG and Cu. Compared with RGO (reduced graphene oxide) Cu-based, PG Cu-based composites obtained by surface modification had higher strength. Gao et al. [11] prepared GO Cu-based composites powder by electrostatic assembly of GO with negative charge and Cu powder with positive charge, which realized the effective dispersion of graphene in Cu matrix, large size and structural integrity of graphene. In addition, ultrasonic assistance can accelerate the reaction speed and prevent the agglomeration of graphene, which can also achieve the effective dispersion of graphene in the matrix [12].

2.2. Interface Bonding
The wettability of the interface between graphene and metal matrix is poor. The interface bonding mode of the composites prepared by traditional technologies is mechanical meshing. The interface usually has defects such as impurities and pores, which decreases the mechanical properties of the composites. At present, the main methods to improve the interface between graphene and Cu matrix include metal particle modification, matrix alloying and oxygen mediated. Zhang et al. [13] prepared Ni-GNPs Cu-based composites by molecular level mixing. The analysis of microstructure showed that there was a transition nickel zone at the interface of the composites, and the chemical bond formed in this zone was the key to obtain high strength. Chu et al. [14] prepared RGO Cu-Ti composites by ball milling. The microstructure showed that the transition zone of Ti$_3$C$_2$S$_2$ formed in situ at the interface of the composites, which played the role of pinning. Compared with the unalloyed RGO Cu-based composite, the tensile strength of RGO Cu-Ti composite increased by 57.7%. Wang et al. [15] prepared high performance graphene Cu-based composites by chemical vapor deposition (CVD) and spark plasma sintering (SPS) technologies using α-naphthol as carbon precursor. α-naphthol hydroxyl group can be chemically adsorbed on Cu powder, which prevents the agglomeration of graphene. In addition, oxygen-containing hydroxyl group can form Cu-O-C at the interface between Cu matrix and graphene during CVD, which improves the interface bonding between graphene and Cu matrix.

3. Properties

3.1. Strength
As reinforcement phase, graphene can effectively increase the strength of composites, which has been proved by previous researches [8-11, 15, 16]. $R$ was defined as the strengthening efficiency index of composite strengthening phase, and its expression was as follows [9, 13, 15, 16]:

$$R = \frac{(\sigma_c - \sigma_m)}{\gamma \sigma_m}$$

where $\sigma_c$ is the yield strength of the composite, $\sigma_m$ is the yield strength of the matrix and $\gamma$ is the
volume fraction of the strengthening phase. Previous researches indicated that the properties of graphene Cu-based composites mainly depended on the dispersion state of graphene in the matrix and the state of interface bonding which were affected by preparation technologies. Table 1 shows the strengthening efficiency index R of the composites prepared by different preparation technologies [15]. Previous researches indicated that the strengthening efficiency index R were mainly influenced by the preparation technologies and the volume fraction of graphene, as showed in figure 1 [16].

**Table 1.** The R values of graphene Cu-based composites fabricated by different methods [15].

| Strengthening          | Method                      | R   |
|------------------------|-----------------------------|-----|
| Reduced Graphene Oxide  | Molecular-Level Mixing      | 32  |
| Graphene Nanoplatelets | Ball Milling                | 14  |
| Multi-layer Graphene   | High-ratio Differential Speed | 28.7 |
| Graphene-Nickel Hybrids| In-situ Chemical Reduction  | 94  |
| Reduced Graphene Oxide  | Impregnation                | 99.8|
| 2D Graphene            | In-situ Reduction           | 88.6|
| 3D-GN                  | In-situ Reduction           | 116.1|

**Figure 1.** Comparison of the strengthening efficiency of graphene Cu-based composites with various preparation methods [16].

The strengthening mechanism of graphene mainly includes dislocation strengthening and load transfer. Dislocation strengthening is achieved by the accumulation of dislocations. Graphene can effectively block the movement of dislocations in Cu matrix and make the dislocations accumulate due to its large specific surface area and elastic modulus, which effectively increased the strength of composites. Load transfer is related to the interface bonding between graphene and Cu matrix, and the strengthening efficiency is mainly determined by the graphene with high stress-bearing capacity. Hwang et al. [9] prepared homogeneously dispersed RGO Cu-based nanocomposite powder by molecular level mixing, and pointed out that the high binding energy between graphene and Cu matrix and the pinning effect of graphene on dislocation jointly determine the high strength of the composite. Cao et al. [17] prepared graphene Cu-based composites with nano-layer structure, and found that the composite with layered orientation structure can transfer and bear load better, which increases the strength of the composites.

3.2. **Toughness**

Toughness is the joint expression of strength and ductility, which reflects the fracture resistance of composites. Graphene has large specific surface area and elastic modulus, which makes it have
significant potential in toughness enhancement. The fracture process of composites mainly includes crack initiation, crack propagation and fracture. The toughening process is mainly explained by shear-lag model and crack deflection model. Crack initiation is mainly carried by Cu grains, crack propagation and fracture are carried by pull-out and fracture of graphene. Toughness characterization is usually obtained by fracture morphology. The toughness of composites usually shows obvious difference due to the different arrangement, volume fraction, transverse dimension and structural integrity of graphene. Cao et al. [17] obtained graphene Cu-based composites powder with layered structure by vacuum filtration technology, and assembled them into graphene Cu-based composite of layered structure and ordered orientation. The fracture morphology showed well-developed dimples and layered structure. The high toughness of the composites is due to the large transverse size and structural integrity of graphene. Xiong et al. [18] successfully prepared nanostructured RGO Cu-based layered composites by preform impregnation process. The reason of toughening is that the multi-layer wrinkled graphene is straightened, which increases the strength and ductility of the composites at the same time.

3.3. Electrical Conductivity
Graphene has higher electrical conductivity than Cu matrix, and it is introduced to exert its synergistic effect with Cu matrix and its inherent conductive advantages. Previous studies have shown that the electrical conductivity of graphene is related to the structural integrity and the dispersion state of graphene, and the density and defects of composites. Li et al. [19] obtained HQG (high quality graphene) Cu-based Composites by ball milling and SPS. Raman spectra shows that HQG has no defects and functional groups. The content of HQG has a obvious influence on the electrical conductivity of the composites. As the content of HQG is too small, the electrical conductivity increment is limited. While the content is too much, the graphene will agglomerate and form a cavity, which decreases the conductivity. Varol et al. [20] prepared MLG (multi-layer graphene) Cu-based composite powder by powder metallurgy technology, and studied the influence of MLG content and the density of composites on the electrical conductivity. The results indicated that MLG agglomerates in Cu matrix at high content, which decreases the conductivity. After sintering, the density of the composite increased, which increased the conductivity of the composites.

3.4. Thermal Conductivity
The high in-plane thermal conductivity of graphene is mainly related to the orientation of graphene. Graphene with high orientation distribution in the matrix can exert the excellent thermal conductivity of graphene to a large extent, and graphene with high volume fraction and ordered orientation can form a continuous thermal conductivity network along the heat transfer direction, which is very effective for improving the thermal conductivity. Wejrzanowski et al. [21] studied the influence of the spatial distribution of graphene on the thermal conductivity of the composites through simulation and experiment, and found that the composites with highly aligned graphene in Cu matrix can obtain higher thermal conductivity. Chu et al. [22] prepared highly aligned GNP Cu-based composites by vacuum filtration and spark plasma sintering, and studied the effects of vacuum filtration and volume fraction of graphene on the thermal conductivity. The results indicated that highly aligned layered structure could be obtained by using vacuum filtration, and long-range highly aligned GNP network was formed in Cu matrix as the volume fraction of graphene was 35 Vol%, which significantly increased the thermal conductivity of the composites.

4. Conclusions
The research about graphene as a strengthening phase of composites has made considerable achievements, and a systematic theory was gradually formed. The high performance of graphene Cu-based composites depends on the effective dispersion of graphene in the matrix and the state of interface bonding. The commonly used methods of effective dispersion of graphene in the matrix include ball milling, molecular level mixing, surface modification, electrostatic assembly and
ultrasonic assistance, and the commonly used methods of interface bonding include metal ion surface modification, metal particle modification, matrix alloying and oxygen mediated. At present, some progress has been made in the research about graphene strengthening Cu-based composites, but most of them are still in the experiment stage. In the future, the related research may mainly focus on the following aspects: (1) To explore the preparation basis of graphene strengthening Cu-based composites and develop new preparation technologies. (2) To study the influencing factors of graphene strengthening Cu-based composites, and establish the preparation theoretical model. (3) To develop a new technology suitable for industrial production by combining the experimental results and theoretical model of graphene strengthening Cu-based composites.

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