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Effect of reduced graphene oxides decorated by Ag and Ce on mechanical properties and electrical conductivity of copper matrix composites

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Abstract: This work investigated the influence of reduced graphene oxide (rGO) modified with silver (Ag) and cerium (Ce) on mechanical and electrical properties of copper matrix composites. Powders of Ce doped rGO and Ag doped rGO were synthesized using a hydrothermal reduction and an electroless plating (glucose chemical reduction) method, respectively. Then, copper matrix composites with the doped rGO content of 0.25wt% were synthesized using ball milling and spark plasma sintering (SPS). The dispersion of the modified rGO and its bonding with the copper matrix have been signficantly improved. Hardness values of Ce-rGO/Cu and Ag-rGO/Cu composites were 26.3% and 16.4% higher than those of the sintered copper, and 19.4% and 10% higher than that of unmodified rGO/Cu composite. At the same time, the Ce-rGO/Cu and Ag-rGO/Cu composites maintained good conductivity and

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high ductility (with elongations of 26.3% and 25.2%, respectively). Compared with the sintered copper, the tensile strengths of these two types of copper matrix composites were 7.5% and 12% lower, respectively. The increase in hardness by using the the modified rGOs is mainly due to the grain refinement of the matrix, and the lower value of the tensile strength is due to the defects of the modified rGOs and their poor bonding with the copper matrix.

Keywords: Copper matrix composites, Reduced graphene oxides, Powder metallurgy, Spark plasma sintering, Electrical conductivity, Mechanical property

1. Introduction

Copper has excellent conductivity, thermal conductivity and processability, but its mechanical properties limit its wide-range applications for overhead conductors and electrical contact materials [1, 2]. Copper matrix composites are widely used in electrical components, electronic and mechanical manufacture industries, and military [3, 4] because of their excellent electrical, thermal and mechanical properties. Generally fibers, particles, whiskers and other reinforcement materials are added into the copper matrix to improve its mechanical properties, however, the conductivity and thermal conductivity of copper matrix are often affected [5, 6]. Recently carbon nanofibers (CNF) and carbon nanotubes (CNT) are also added into copper matrix. However, due to the fibrous orientation of CNFs, the performance of CNF/Cu composites is often anisotropic, e.g., composites along the length of CNF fibers show larger tensile strength if compared with other directions [7]. Because the CNT is one-dimensional material, it is easy to become agglomerated and hard to disperse uniformly. Moreover, the

production cost of the CNT is high, which limits its applications [8, 9]. Therefore, it is important to employ a suitable strengthening material in copper matrix which can optimize both the mechanical and physical/electrical properties.

Graphene (Gr) with its sp^2 hybrid and honeycomb two-dimensional structure [10], has super-high electrical conductivity (with a carrier mobility of $1.5 \times 10^4 \, cm^2/V \cdot s$) [11] and thermal conductivity ($5 \times 10^3 \, W/m \cdot K$) [12]. Its elastic modulus is as high as 1 TPa and its tensile strength can be as high as 130 GPa [11]. Wang et al. [13] used the chemical adsorption of small aromatic hydrocarbons on the surface of copper powders, followed by spark plasma sintering (SPS) and hot rolling, and prepared 1.4 vol% Gr/Cu composites with a tensile strength of 477 MPa. Hwang et al. [12] used molecular level mixing technology and SPS technology to prepare 2.5 vol% reduced graphene oxide (rGO)/Cu composite, and reported that the tensile strength of the composite material was increased by about 30% compared with that of pure copper. Shao et al. [14] used electrostatic self assembly and SPS technology to prepare 0.2 wt% graphene nanoplates (GNPs)/copper composite, and achieved an increased tensile strength up to 27%.

However, it is often found that graphene is difficult to be dispersed uniformly in metal matrix due to its large surface energy. Due to its agglomeration, its reinforcement effect has been seriously reduced [15]. Also due to the poor wettability of the interface between graphene and copper matrix, the interface bonding between graphene and copper matrix is often very poor [16]. At present, researchers have adopted different methods to solve these problems. For example, Sayyad et al. [17] prepared a 0.8 vol% silver loaded rGO/copper (Ag-rGO/Cu) composite using chemical reduction and spark

plasma sintering (SPS), and reported that its three point bending strength was 65% higher than that of pure copper. However, as the content of Ag-rGO increases, the mechanical properties of the composite were decreased [17]. Mai et al. [6] mixed the graphene nanosheet pre-coated with Ni nanoparticles (Ni@GNS) with copper powder and then sintered using a hot-pressing method to obtain the composite of Ni@GNS/Cu. Wear rate of the obtained copper matrix composite was much lower than that of pure copper as well as 2 wt% GNS/Cu under the same conditions. Wang et al. [18] used lanthanum chloride (LaCl$_3$) and cerium chloride (CeCl$_3$) to modify graphene oxide (GO), and found that coordination bonds between the rare earth elements and the oxygen-containing groups of GO reduce the surface energy of GO and improve the dispersibility. Regulska et al. [19] added rare earth elements to nickel aluminate and found that the addition of rare earth elements refined the original grain size of nickel aluminate. Wu et al. [20] added 0.05wt% rare earth elements to Cu-6wt%Fe composites and found that the average grain size was refined from 32 μm to 20 μm. The above results clearly indicate that adding the chemical elements can effectively improve dispersibility of graphene based materials (including its derivatives such as rGO and GO) and their wettability with copper matrix.

Consolidation technique for composite synthesis using powder technology signficantly influences the microstructure and performance of composite materials. SPS technology is a fast, efficient, and low energy process for preparing composites. Due to its rapid increase in temperature, relaitvely low sintering temperature, and short sintering time, composites with fine grains and dense structure can be easily obtained

[21]. For example, Zhou et al. [22] studied graphene reinforced tungsten-copper composites prepared by infiltration sintering and SPS sintering, and the obtained composite did not show obvious segregation, but with a network skeleton phase of tungsten. Sun et al. [23] obtained a three-dimensional network graphene reinforced copper matrix composites by SPS sintering at 600 ℃, and achieved good mechanical properties. Dong et al. [24] synthesized graphene/titanium composites prepared by SPS technology, which showed high hardness and no obvious cracks in the composites.

The rGO is a relatively low cost reinforcing components compared with graphene, and is also a suitable reinforcing phase for copper-based composites. However, the use of modified rGO to prepare copper matrix composites still has two issues to be solved. The first one is the quality for reducibility of GO, and the other one is the choice of modified metallic particles for the rGO. These metallic particles should increase the dispersion of the rGO in the copper matrix, reduce the overall defects, and obtain a good bonding between rGO and the copper matrix within the composites.

As it is well known, the degree of reduction of rGO is closely linked to the properties of composite materials. If the GO cannot be completely reduced, there will be many structural defects within the rGO. The residual oxygen-containing groups make the state of the sp^2 hybrid orbital of the C atom incomplete, which will cause the decreased electrical and thermal conductivities. Commonly used reduction methods include chemical reduction and thermal reduction ones. The chemical reduction process often uses hydrazine hydrate as a reducing agent, which will pollute the environment due to its toxicity. The conventional thermal reduction has the problem of ineffective

reduction.

For the selection of modified particles for the rGO, most studies have been focused on conventional metal particles (Ag, Ni, etc.), and there are only a few studies to apply the rare earth elements. There was previous study on how rare earth elements can improve the agglomeration of GO [18], but no report on the interface bonding study between rare earth element-modified rGO and the copper matrix. Therefore, in this paper, we will use modified Hummers method to prepare graphene oxide (GO) and use environmentally friendly glucose as a chemical reducing agent to prepare Ag-modified reduced graphene oxide powder (Ag-rGO) using electroless plating. We then prepared the rare earth element Ce-modified rGO (Ce-rGO) using a hydrothermal reduction method. The modified rGO and Cu powders were mechanically milled and sintered using the SPS to obtain 0.25wt% Ce-rGO/Cu and Ag-rGO/Cu composites. Effects of different element-modified rGOs on the microstructure, mechanical properties and electrical conductivity of composites were discussed and compared. As Ag has a similar mechanical and electrical properties with those of Cu, it is expected that Ag-Cu bonds can be formed thus improve the interface strength of composites and also maintain the good conductivity of the matrix. The addition of rare earth element Ce can improve the dispersion of rGO inside the copper matrix.

2. Experiment and method

Graphite flakes (74 μm Nanjing Xianfeng nanotechnology Co., Ltd.), copper powder (5 μm Qinghe Baili Metallurgical Material Co., Ltd.), all the solvents and reagents (H_2SO_4, H_2O_2, HCl, ammonia) were of analytical purity level, and used

without any further treatments.

2.1 Preparation of Ce-rGO and Ag-rGO powders

GO was prepared using an improved Hummers method [25]. Graphite flakes of 4 g were added into 92 ml of 98% H_2SO_4 at a temperature of ~0 ℃ and then 12 g of $KMnO_4$ was added to the solution and magnetically stirred for 120 minutes. The mixed solution was placed in a water bath at 35 ℃ and further stirred for 30 min. Then deionized water of 460 ml was slowly added inside at a temperature of 98 ℃, followed by addition of 5% H_2O_2, until the solution has no any bubbles generated. The suspension was filtered using a centrifuge method, washed with 5% HCl, and then added with deionized water to a pH value of 7. The GO powders were obtained using a freeze-drying method at -70 ℃ after 36 hrs.

To prepare the Ce-rGO powders, GO powder of 640 mg was added into 320 ml of deionized water, which was ultrasonically agitated for 60 min. Then 1.44 g of $CeCl_3·7H_2O$ was slowly added and the solution was ultrasonically dispersed for 3 hours. The formed solution was added into a reaction chamber which was heated at 120 ℃ for 12 hours for the hydrothermal reactions. After cooled down to room temperature, the solution was dialyzed using a dialysis bag, which was added with deionized water until pH=7. The Ce-rGO composite powders were obtained by freeze-drying method at -70 ℃ after 36 hrs.

To prepare Ag-rGO powders, 800 mg of GO powder was added into 400 ml of deionized water, which was ultrasonically dispersed for 60 min to obtain a graphene oxide solution. $AgNO_3$ powders of 849.35 mg were added into 40 ml of deionized water

to obtain a 0.125 mol/L AgNO$_3$ solution, and then 3% ammonia water was slowly added inside dropwisely. When the precipitates in the solution were completely disappeared, the silver ammonia solution was obtained. The graphene oxide dispersion solution was added dropwisely to the silver ammonia solution at a water bath temperature of 50 ℃ and then reacted for 30 minutes. After that, 8 g of glucose was added into 400 ml of deionized water, which was added into the mixed solution of graphene oxide and silver ammonia. The temperature of the water bath was controlled at 95 ℃ under a magnetic stirring for 60 min. After the solution was cooled down naturally, a centrifugal and washing treatment was carried out using a solution of absolute ethanol and deionized water (with a ratio of 1:1) for several times. Finally the Ag-rGO composite powders were obtained using the freeze-drying method at -70 ℃ after 36 hrs.

2.2 Preparation of Ce-rGO/Cu and Ag-rGO/Cu composites

Figure 1 shows a schematic diagram of the preparation process of Ce-rGO/Cu composite and Ag-rGO/Cu composite. Stainless steel balls with diameters of 5 mm, 2 mm and 0.5 mm (mass ratio of 5: 3: 2) were used. Ce-0.25wt% rGO powder and Ag-0.25wt% rGO powder were mixed with Cu powder through a planetary ball mill, with a ball-to-material ratio of 5:1. The rotation speed was 350 r/min, and the ball milling time was 4 hrs. The composite powders were poured into a mold with a diameter of ϕ =15mm, which was then put inside a Labox-235 type plasma sintering equipment. For the SPS process, the sintering pressure was 40 MPa, and the chamber pressure was 3 Pa. The sintering temperature and duration were 800°C and 10 min. Using the same conditions, pure copper samples and 0.25 wt% rGO/Cu composites were also sintered

as the reference materials.

Figure 1 Schematic diagrams of preparation processes for Ce-rGO/Cu composite and Ag-rGO/Cu composite.

2.3 Characterization methods

A scanning electron microscope (SEM, Quanta-450-FEG, USA) attached with an energy dispersive X-ray spectrometer (EDS) was used to characterize the microstructure and constituent elements of composites. A transmission electron microscope (TEM, JEM-3010, Japan) was used to characterize the interfacial microstructures. X-ray diffractometer (XRD, XRD-7000S, Japan) was used to analyze the crystalline structures of composites, where the wavelength of Cu Kα radiation was 1.5418Å. Conductivity value of the composites was directly obtained using a digital conductivity meter (D60K, China), and the unit of the conductivity is the percentage of International Annealing Copper Standard (%IACS). Hardness of the composite was measured using a Vickers hardness tester (HV-120, China), where the indentation load was 5kg and duration was maintained for 10 s. For the tensile tests, the sintered bulk samples were cut and polished, with a dimension of 8 mm × 2 mm × 1 mm. Tensile properties of the composites were characterized using a computer-controlled material testing machine (HT-2402, China) with a tensile speed of 1 mm/min. Archimedes method was used to measure the density of the composite, and the densities of copper and graphene were used to calculate the theoretical density of the composite.

3. Results and discussion

3.1 Microstructures of composite powders

Figure 2 shows a TEM image of the Ce-rGO powder. There are two areas of gray and black colours, and black particles are distributed within the gray matrix. The selected area electron diffraction (SAED) pattern shown in the inset of Figure 2 reveals a shape of hexagonal benzene ring, which indicates that the gray area is rGO. For the black area, its SAED patterns are linked to (111), (200), (220), (311) and (222) planes of CeO_2. Results clearly show that the Ce elements were oxidized by GO and attached on the rGO sheet in the form of CeO_2 nanoparticles.

Figure 2 TEM image of Ce-rGO powder. The inset is the SAED image of the powder in the yellow frame.

The TEM image of Ag-rGO powder (Figure 3(a)) shows that the black elliptical particles of different sizes (20-50 nm) are distributed within a light gray substrate. From the SAED image of area 1 (the inset of Figure 3(a)), the light gray phase is confirmed to be rGO. As shown in Figure 3(a), the rGO presents a typical transparent and thin shape with wrinkled structures. The black Ag nanoparticles are mostly located in the folding region of the rGO. This is because the catalytic activity of these fold regions is high, which easily causes the attachment of Ag particles. The high resolution TEM (HRTEM) image (Figure 3(b)) shows the lattice fringes of the Ag particles on the rGO surface, with a crystal plane spacing d of 0.237 nm, corresponding to the (111) crystal plane of Ag. Moreover, as shown in Figure 3(b), there is no obvious gap in the interfacial area between the rGO and Ag nanoparticles, indicating the formation of a

good bonding structure.

Figure 3 (a) A TEM image of Ag-rGO powder, and the inset is the SAED image of area 1; (b) An HRTEM image of area 2 in (a), and the inset is a lattic structure image.

3.2 Crystalline structures of composites

In order to determine whether there is a phase transition during the recombination of graphene and matrix, the XRD spectra were obtained and the results are shown in Figure 4. The positions of the XRD diffraction peaks of the three composite samples are the same as those of pure copper, which represent the (111), (200), and (220) crystal planes of copper. The reason why the diffraction peaks of rGO and other loaded particles did not appear is that their contents are less than the XRD detection limit [7]. The absence of copper oxide peaks indicates that the Cu matrix was not apparently oxidized during the preparation process. This diffraction result is consistent with that of a Ag-rGO/Cu composite prepared by the hot pressing method reported in Ref. [26]. The positions of the diffraction peaks of all diffraction spectra do not show apparent shifts, and only their intensities are different. Among them, the pure copper has the largest diffraction intensity, which reveal that the addition of rGO helps to refine the crystal grain [27-29].

Figure 4 XRD spectra of graphene copper matrix composites.

In order to investigate the distribution of modified rGO in the copper matrix, we obtained the SEM image of the composite material (Figure 5). The pure copper sample

(Figure 5(a)) has a smooth surface without obvious sintering defects (such as holes and cracks). For the Ce-rGO/Cu composite (Figure 5(b)), the Ce-rGO reinforcement particle is black. The reinforcement particles of Ce-rGO are uniformly distributed inside the copper matrix without obvious cracks. Compared with the rGO/Cu composite material (e.g., without adding any metal particles, see Figure 5(e)), the dispersion has been improved and no apparent defects such as pores are generated. This shows that for the Ce-modified rGO, the self-aggregation of rGO has been restrained which can improve the interface bonding with the copper matrix [30]. These would be beneficial for the good mechanical properties and high electrical conductivities. From the microstructure and Ag-rGO/Cu composite (Figure 5(c)) and the line scan of the aggregated particles (Figure 5(d)), we can confirm that the aggregated particles are Ag-rGO reinforced phases. In general, Ag-rGO is partially aggregated in the matrix. There are a small amount of hole defects, which may cause the decrease of density of the composite. However, if compared with those of rGO-Cu composites (Figure 5(e)), the defects were significantly less and the dispersibility was improved, which would be beneficial for the high conductivities of the composites [31].

Figure 5 SEM images of copper and graphene copper matrix composites. (a) sintered pure copper; (b) Ce-rGO/Cu; (c) Ag-rGO/Cu, where the inset is an enlargement of the agglomerated particles; (d) the line scan of the agglomertaed particel in (c); (e) rGO/Cu and the inset is an enlargement of the aggregate; (f) the line scan of the aggregate in (e).

We believe there are two possible reasons for the agglomeration of the

reinforcement particles. (1) When the Ag nanoparticles are loaded onto the rGO, they do not completely cover the graphene, but are partial agglomerated during the ball milling process. (2) Ag-coated rGO could form an Ag-Ag metallurgical bond. From the SEM of the graphene copper-based composite shown in Figure 5(e), its surface is rough, and there are a large number of hole defects and agglomerates. The graphene oxide agglomeration is mainly due to the large van der Waals forces on its surface. Figure 5(f) shows the line scan of the agglomerate, which proves that it is graphene. The uncoated graphene oxides has a large surface energy and easily agglomerate, which produces many defects in the copper matrix, thus limiting the reinforcement effect.

TEM images of Ce-rGO/Cu composite are shown in Figures 6(a) and 6(b), where the black portion is marked with a lattice spacing of 0.208 nm as shown in Figure 6(c). This lattice spacing corresponds to the (111) crystal plane of copper, indicating that the black structure is the copper matrix [32]. The bright white part is Ce-rGO, which can be confirmed by the SAED pattern of a hexagonal ring in Figure 6(d) [33, 34]. EDS-mapping analysis (shown in Figures 6(b1, b2, b3)) in the yellow box of Figure 6(b) is consistent with the distribution of the Ce element and the C element, which proves the existence of the Ce element. From Figure 6(c), the interfaces between the copper matrix and the Ce-rGO are well bonded, and this good interfacial structure is beneficial for the effective electron migration and load transfer.

Figure 6 (a) Low magnification TEM of Ce-rGO/Cu composite; (b) High magnification TEM; (c) HRTEM of yellow square in (b); (d) SAED patterns in red circle in (b) for

Ce-rGO/Cu composite; EDS-mapping of (b1) Ce element; (b2) Cu element; (b3) C element of which pattern.

Both light gray area and dark gray area can be observed in the TEM image of the Ag-rGO/Cu composite (Figure 7(a)). HRTEM image shown in Figure 7(b) reveal that there are two lattice spacings. The reading of 0.237 nm is similar to the silver (111) interplanar spacing of 0.235 nm, indicating that the dark gray area is Ag-rGO phase. Another reading of lattice spacing 0.210 nm corresponds to the (111) crystal plane of copper, indicating that the light gray part is the copper matrix. Figure 7(a) shows that the dispersion of Ag-rGO is not uniform, and the reinforcement particles are agglomerated, which is consistent with the SEM observation. Figure 7(b) shows that at the composite interface, there is a gap (inside the yellow frame) with poor bonding structures.

Figure 7 TEM images of Ag-rGO/Cu composite. (a) TEM; (b) HRTEM of yellow.

3.3 Properties of composites

The porosity has a significant influence on the mechanical and physical properties of the composite [28]. We used the Archimedes method to obtain the relative density of the composite material, and the results are listed in Table 1. The relative density of pure copper is ~98%. The addition of rGO will cause macro-defects such as holes in the composites, and prevent the good bonding between the Cu powders [7], thus leading to a decrease in the density of the composite material. The relative density readings of the metal modified rGO/copper matrix composites are better than that of unmodified

rGO/copper matrix composite.

The relative density of Ce-rGO/Cu composite is ~ 95.2%, which is better than that of Ag-rGO/Cu composite. This is consistent with the SEM images, indicating that the Ce element can effectively prevent the generation of defects such as holes and restrain the agglomeration of graphene than the Ag element. The results are better than the relative density (90%) of the 0.9 vol% GNPs/Cu composite prepared by powder metallurgy and microwave sintering reported in the literature [3].

Table 1 relative density of composites

Sample	Pure copper	Ce-RGO/Cu	Ag-RGO/Cu	RGO/Cu
Relative density/%	98.0	95.2	93.6	92.7

Figure 8(a) shows the measured hardness values of the composites. Clearly the addition of rGO can be used as an effective reinforcing phase to increase the hardness of the copper matrix. The hardness of Ce-rGO/Cu composite is 69.95 HV, which is about 26.3% higher than that of pure copper (55.4 HV) obtained by the same process, and the hardness of Ag-rGO/Cu composite is about 16.4% higher than that of pure copper. The hardness values of modified rGO/copper matrix composites are higher than that of unmodified rGO/copper matrix composites.

The increase in hardness is mainly due to: (1) Ce and Ag loading can reduce the surface energy of the rGO, which can effectively prevent agglomeration and rapid growth of copper grains during sintering [35]. The Ce-rGO/Cu composite is more effective than the Ag-rGO/Cu composite for preventing formation of these effects, because the rare earth element has high chemical activity, low potential and a special

electronic shell structure, which can purify the composite interface, improve the microstructure, and refine grains. The hardness value of the Ce-rGO/Cu composite obtained in this paper is comparable to those of the graphene copper matrix composites obtained by other methods [7, 36].

Figure 8 Hardness values of graphene copper matrix composites in this study.

Figure 9 shows the conductivity values of the composite material. Apart from the pure copper samples, the best value of conductivity is from the Ce-rGO/Cu composite, which is 92.1% IACS. This value is only 8.1% lower than that of pure copper. Whereas the unmodified rGO/Cu composite conductivity is only 88.7% IACS, which is 11.5% lower than that of pure copper. It is worthwhile to note that the rGO supported by Ce and Ag can play a bridging role at the composite interface, thereby significantly reducing the conductivity of the copper matrix due to the addition of rGO. Although adding rGO enhances the mechanical properties of copper matrix composites, it causes the decreased conductivity of the copper matrix. One reason is that electrons will be scattered through the composite interface, and also free electrons will be reduced [37]. The second reason is that the existence of pores in the powder metallurgy with the sintered sample will decrease the conductivity [38]. The Ce and Ag with a good conductivity will be beneficial for the enhanced conductivities of the modified composites [39]. The conductivity of Ce-rGO/Cu composite is much higher than that of Ag-rGO/Cu composite. This might be due to the relatively high density of Ce-rGO/Cu composite, which reduces the electron scattering effect and maintains a higher

electrical conductivity. Table 2 compares the electrical conductivity values of copper

matrix composites obtained by other methods or reinforcement systems. It can be seen

that the results of this study have shown better values of electrical conductivity.

Figure 9 Conductivity of copper and different rGO-Cu composite materials.

Table 2 Comparison of electrical conductivity between block based composites

prepared by our work and reported Copper Matrix Composites

Sample	Preparation method	Electrical conductivity （%IACS）	Ref.
Ce-0.25wt%RGO/Cu	PM and SPS	92.1	Our work
Ag-0.25wt%RGO/Cu	PM and SPS	90	Our work
0.5wt%Multilayer graphene(MLG)/Cu	PM	78.5	[40]
0.3wt%Primitive graphene(PG)/Cu	PM and SPS	84.2	[37]
Ni-11.8wt%GNPs/Cu	Electrochemical deposition(ED) and Atmosphere sintering	89.2	[32]
0.5wt%CF-0.4wt%Gr/Cu	Wet mixing and Hot press sintering	80.6	[38]
2.5vol%RGO/Cu	Molecular level mixing(MLM)	85	[15]
2.5vol%CNTs-RGO/Cu	MLM	83	[15]
0.5wt%CNTs/Cu	MLM and Microwave sintering	81	[41]
5vol%Al2O3/Cu	High energy mechanical grinding and	80	[42]

	PM		
3wt%Al2O3/Cu	Hot press sintering	47.7	[2]

Table 3 summarizes the results for the obtained tensile properties of the composite materials. The composites maintain the high ductility of the Cu substrate [37]. The stress-strain curve (Figure 10) also shows that the composites have plastic deformation characteristics. The tensile strength values of Ce-rGO/Cu composite and Ag-rGO/Cu composite are 185 MPa and 176 MPa, respectively, which are about 8.8% and 3.5% higher than that of unmodified rGO/Cu composite (170 MPa). However, this enhancement effect is obviously not significant. The reason might be that the composite material prepared by SPS is not fully densified. There are some macro-defects such as pores, and the defect concentration of rGO itself is relatively large. For all the composite materials, their tensile strength values are lower than that of sintered pure copper. A similar phenomenon was reported in the literature [43], in which tensile strength of rGO/Al composites produced by ball milling, hot isostatic pressing, and hot extrusion techniques is lower than that of pure aluminum under the same process. The authors claimed that the rGO itself had high-density defects and surface folds, and also the interface product such as Al_4C_3 causes weak binding in the composite. This phenomenon was also reported in Ref. [37], in which the authors explained that the rGO contained a large number of defects and the uneven dispersion of graphene in the matrix led to a decrease in the tensile strength of the copper matrix. Similar results were reported in Refs. [44] and [45]. In this study, we attributed the reduced tensile strength to the facts that the composite has a relatively higher density of defects and folds of

rGO, which could be the weak points of the composite material when tensile stress is applied. Formation of cracks causes stress concentration until the cracking and fracture release the stress. Also the dispersibility of rGO is not good enough, thus limiting its enhancement effect. The density of the composite material prepared by the powder metallurgy is also not high, and there are defects such as holes in the composite material. Although the loading of metal ions improves the bonding of rGO and coppe matrix, the metal ions do not completely cover the whole structure of rGO, thus resulting in poor bonding of rGO and the matrix (Figure 7(b)).

Figure 10 Tensile stress-strain curve of pure copper and different rGO/Cu composites.

Table 3 Tensile properties of composites

Sample	Elongation/ %	Standard deviation/ %	Tensile strength/MPa	Standard deviation/MPa	Young's modulus/GPa	Standard deviation/GPa
Pure copper	30.2	0.5	200	0.43	181.73	4.45
Ce-RGO/Cu	26.3	0.2	185	0.13	25.90	0.02
Ag-RGO/Cu	25.2	0.3	176	0.10	35.09	0.03
RGO/Cu	26.8	0.3	170	0.12	43.03	0.05

Figure 11 shows the SEM image of the tensile fracture surfaces of the composites.

As shown in Figure 11(a), there are a large number of small dimples on the tensile fracture surfaces of pure copper, indicating that pure copper shows a typical ductile fracture [13]. For the copper marix composites after adding the rGO, the fracture characteristics are the combination of ductile fracture and brittle fracture. The ductile fracture has the obvious dimples, and the brittle fracture occurs along the grain boundary or interfaces of the composite [37]. The fracture morphology of the Ce-rGO/Cu composite is shown in Figure 11(b), in which some small holes are obseved. Only a very small amount of graphene-like sheets are found to break on the fracture surface, and the rest of the graphene are found to be pulled out, leaving large pits on the fracture surface. This indicates that most of the rGOs are agglomerated and easily pulled out. Figure 11(c) is an SEM image of the fracture surface of Ag-rGO/Cu composite. Compared with Figure 11(b), agglomeration of the Ag-modified RGO is quite severe (e.g., forming a thicker rGO layer), preventing the good contacts among copper particles, and ralso esulting in limited connectivity of the metal substrate. Therefore, the tensile strength of the composite material is reduced. From the fracture surfaces, the number of dimples for the Ag-rGO/Cu composites is much less, which is corresponding to its lower elongation if compared with that of Ce-rGO/Cu composites. Figure 11(d) shows the fracture morphology of the rGO/Cu composite. Compared with Figure 11(b) and (c), the agglomeration phenomenon of graphene is quite severe, forming spherical particles.

Figure 11 SEM images of tensile fracture surfaces of copper matrix composites. (a)

pure copper; (b) Ce-rGO/Cu; (c) Ag-rGO/Cu; (d) rGO/Cu.

A schematic diagram of the stretching process of the composite material is shown in Figure 12. In Figure 12(a), there are holes and cracks in the composite material made by powder metallurgy. The tensile strength of the composites is lower than that of sintered pure copper, because the graphene and the copper matrix are only mechanically bonded without forming a chemical bond. During the fracture, the rGOs can be easily pulled out (Figure 12(b)), and the large hole defects are left after their pulling out. This shows that the bonding interfaces between the rGO sheet and the copper matrix are very weak, and the high-density defects along the composite interface under the external stress promote the stress to initiate cracking and fracture [44]. At the same time, it can also be found that only rGOs parallel to the loading direction can be effective to prevent the facture of composite, whereas the rGOs perpendicular to the load direction are not effective.

Figure 12 Schematic diagrams of rGO/Cu composite stretching process. (a) composites before deformation; (b) fractured composites showing the fracture and pull-out of rGOs.

4 Conclusion

In summary, the Ce-loaded rGO powders were prepared using the hydrothermal reduction method, and the Ag-loaded rGO powders were made using the electroless plating method and glucose chemical reduction. The Ce-rGO/Cu composite and Ag-rGO/Cu composite with the rGO content of 0.25wt% were prepared using the SPS technology. Results show that the hardness values of Ce-rGO/Cu composite and Ag-

rGO/Cu composite are increased by 26.3% and 16.4% respectively compared with pure copper. The electrical properties of Ce-rGO/Cu composite are also improved and its conductivity reaches 92.1% IACS. The rGO loaded with Ag or Ce particles can prevent the significant coarsening of Cu grains during the sintering process and increase the hardness of the composite material. At the same time, due to the ultra-high conductivity of Ag, the excellent conductivity of Ce and the ability to purify the interface, the conductivity of the composite material can also maintain a high value. The modified rGO promotes the dispersion of graphene and enhances the bonding with the copper matrix than the original rGO. Therefore, the relative density, hardness, electrical conductivity and tensile strength of rGO/Cu and Ag-rGO/Cu composites are much better than those of rGO/Cu composites. However, the tensile strength values of all composites are lower than that of the sintered copper. The fracture mechanism of the composites is changed from the ductile fracture of pure copper to a mixed mechanism of ductile fracture and brittle fracture. The rGOs become agglomerated into thicker layers, and the bonding among these agglomerates is very poor. The defects of rGO and the weak bonding interfaces with the copper matrix are the main factors that cause the decrease of tensile strength.

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