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Copper matrix composites enhanced by silver/reduced graphene oxide hybrids

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ABSTRACT

Silver/reduced graphene oxide (Ag-rGO) has been employed as reinforcements to prepare the copper matrix composites via ball milling and hot-pressed sintering at different pressure. The micro-hardness increased with the pressure and reached 89.1 HV at 60 MPa, 27.3% higher than the pure copper. The electrical and thermal conductivity had the maximum at 50 MPa and reached 56.8 m/Ω mm^2 and 343.5 W/m k, respectively. The excellent mechanical, thermal and electrical properties of the Ag-RGO/Cu composites indicated that Ag-RGO hybrid was an effective reinforcement to fabricate Cu matrix composites.

1. Introduction

Graphene, a two dimensional carbon atoms layer, has attracted tremendous attention owing to its outstanding properties, such as extraordinary mechanical strength [1], remarkable electron mobility (200000 $cm^2\,V^{-1}\,s^{-1}$) [2], excellent thermal conductivity (5000 W mK^{-1}) [3] and large surface area (2600 $m^2\,g^{-1}$) [4]. All these properties make graphene have broad application prospects in various field, such as energy storage [5], biological engineering [6] and electronics [7]. Another possible application to harnessing these properties would be to incorporate graphene sheets in a composite material.

As reinforcement, graphene is hoping to further improve the mechanical, electrical and thermal performance of the matrix. However, the agglomeration of graphene during fabrication process and the poor binding ability with the matrix such as copper matrix limit its further application and development as reinforcement [8]. So lots of effort has been devoted to investigating the effective integration of graphene flakes and the matrix. [9–12].

In this work, reduced oxide graphene modified by silver nanoparticles (Ag-RGO) has been used as reinforcement to prepare Cu matrix composites. The wetting and bonding capacity between the matrix and RGO were enhanced due to the existence of silver nanoparticle acting as a bridge. The mechanical, thermal and electrical performances of the composites were further studied. The result indicated that Ag-RGO hybrid was an effective reinforcement to fabricate Cu matrix composites.

2. Experimental details

The reinforcement Ag-RGO was prepared from graphene oxide and silver nitrate through one-step reduction method [13]. Then 23 mg Ag-RGO were mixed with 15 g copper powders (~150 nm, 99.99%), and the mixture was treated by ball milling at 500 rpm for 5 h by using different diameter balls for the purpose of producing the graphene-coated copper powders. Subsequently, the composite powders were processed at 800 °C and 30, 40, 50, 60 MPa for 45 min by vacuum uniaxial hot-pressing sintering method, named sample #1, sample #2, sample #3, sample #4. The pure Cu specimens named sample #5 were also fabricated at 60 MPa for comparison.

The crystal phase of the samples was characterized X-ray diffraction (XRD, Aolong DX-2700). The morphology and microstructure were observed by Scanning Electron Microscopy (SEM, Nova NanoSEM 430) and Transmission Electron Microscopy (TEM, FEI tecnai G2 F20). The density of composites was measured by Archimedes' principle. The hardness measurement was performed using a Micro-Vivtorinox hardness tester (HVS-1000). The electrical resistivity of the composites was measured by the four-probe method contact (Low DC Resistance Tester, JK2516). The thermal conductivity were measured by the FLASHL INE 5000 laser flash thermal diffusivity analyzer and the specific heat was measured by differential scanning calorimetry (DSC200F3, Shanghai).

3. Results and discussion

As shown in Fig. 1(a), the XRD patterns of Ag-RGO composites showed four primary peaks at 2θ = 38.1°, 44.3°, 64.4° and 77.4°, corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystallographic plane

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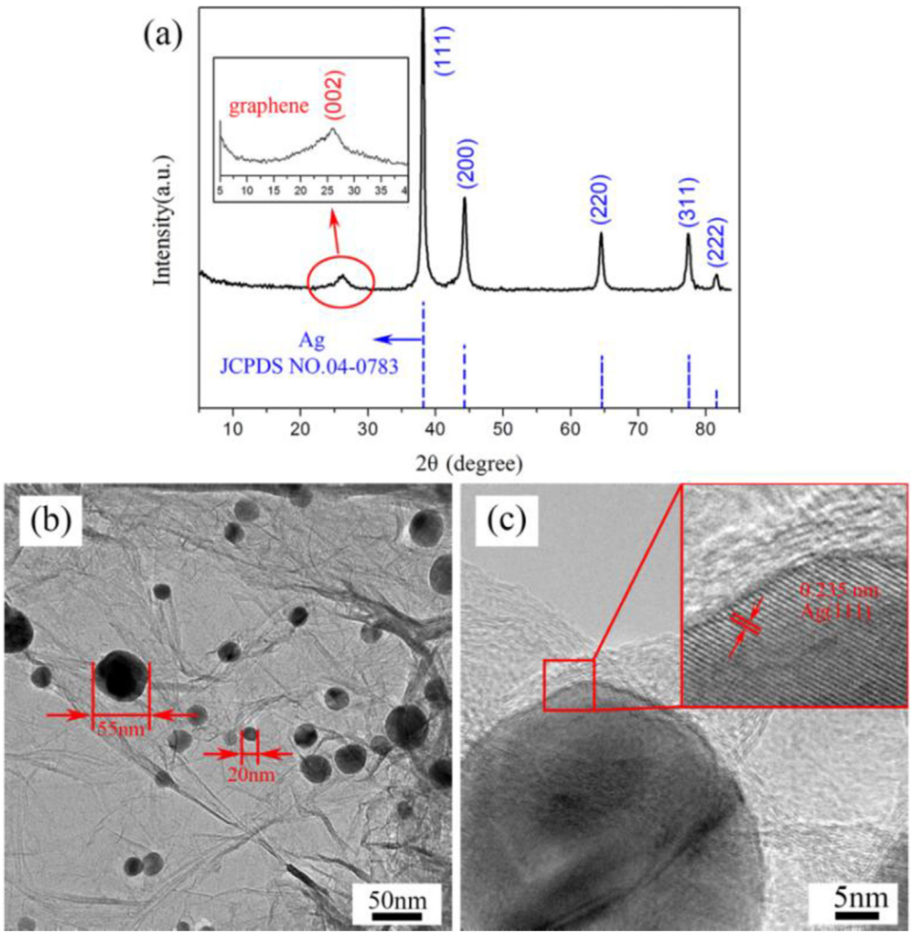

Fig. 1. (a) XRD patterns; (b) TEM and (b) HR-TEM images of Ag-RGO composites.

of sliver-3C (JCPDS NO. 04-0783) [14], respectively. Furthermore, the Ag-RGO composites also showed a typical diffraction peak at 2θ = 25°, corresponding to the (002) diffraction peak of RGO [15]. Obviously, this diffraction peak was diminished greatly owing to the low scattering length of carbon compared to metal atoms [16].

To further clarify the micro details of the Ag-RGO composites, we investigated the TEM and HR-TEM images. It can be found in Fig. 1(b) that the RGO exhibited the typical transparent film morphology, and a lot of dark irregular spherical particles were uniformly dispersed on the surface with the diameter of 20–55 nm. The fringes distance shown in Fig. 1(c) was 0.235 nm, corresponding to the (111) lattice planes of cubic Ag. The Ag nanoparticles bonded with RGO nanosheets could act as spacers to prevent the agglomeration of RGO nanosheets while RGO nanosheets could in turn prevent the aggregation of these active nanoparticles with high surface energy [17].

The SEM micrographs of Ag-RGO/Cu composite powders were shown in Fig. 2(a). It can be found that, the RGO nanosheets were successfully embedded into the Cu powders. It was worth noting that in Fig. 2(b), some tiny spherical particles were observed on the surface of RGO nanosheets, and the EDS result indicated that these spherical particles were Ag nanoparticles. All of these results proved that the Ag-RGO reinforcement still remained the original form even after the ball milling process for several hours.

The mixed copper matrix composite powders were then sintered at temperature 800 °C for 45 min under different pressures. As shown in Fig. 2(c), a group of diffraction peaks appeared at 2θ = 43.2°, 50.4°, 74.1°, corresponding to the (111), (200), and (220) crystallographic plane of Cu (JCPDS NO. 04-0836), respectively. Additionally, the diffraction peaks appeared at 2θ = 29.6°, 36.4°, 42.3°, 61.3° and 73.5° were well corresponded to the (110), (111), (200), (220) and (311) crystallographic plane of $Cu_{2+1}O$ (JCPDS NO. 05-0667), respectively. As reported, the $Cu_{2+1}O$ were reduced from copper oxide during the sintering process under anoxic condition [18], and they can improve the mechanical properties of the composites just like other reinforcement [19]. Moreover, no diffraction peaks of RGO or Ag were detected and this could be explained by the small loading of RGO or Ag-RGO in these samples [20].

Hardness entails the comprehensive performance of several mechanical properties, such as abrasion resistance, stiffness, strength, etc [21]. As shown in Fig. 3(a), The Vickers microhardness of the composites increased from 81.3 HV to 89.1 HV with the increase of the sintering pressure up to 60 MPa, 29.3% higher than the pure copper. The remarkable enhancement of hardness could be attributed to the effect of Ag-RGO [11].

As reported in the previous study, the reinforcement might degrade the conductivity performance of composites [22]. As shown in Fig. 3 (b), the electronic conductivity of the samples increased with the increasing sintering pressure from 30 MPa to 50 MPa, and reached a maximum 56.8 m/Ω mm^2 at 50 MPa, 18.6% higher than that of the pure Cu. The changing trend of the thermal conductivity was similar to the electronic conductivity, and reached a maximum 343.5 W/cm k at 50 MPa, 21.8% higher than that of the pure Cu.

Fig. 3(c) and (d) showed the SEM images of the sample #3 sintered at 50 MPa. It can be found that black filaments were uniformly distributed in the grey matrix, and the EDS results confirmed that grey phase was copper matrix and the dark phase was the reinforcement Ag-RGO.

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