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Thermal expansion of MWCNT-reinforced copper composite

XU Long-shan(许龙山), CHEN Xiao-hua(陈小华), PAN Wei-ying(潘伟英), LI Wen-hua(李文华),
YANG Zhi(杨　植), PU Yu-xing(蒲玉兴), YI Guo-jun (易国军) , YI Bin(易　斌), ZHANG Ke(张　科)

College of Materials Science and Engineering, Hunan University, Changsha 410082, China

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Abstract: Multi-walled carbon nanotube (MWCNT)-reinforced copper composite was fabricated by a novel method, which involves solution phase synthesis of MWCNT-implanted cuprous oxide composite spheres, formation of MWCNT/ copper composite spheres after reduction in H_2 atmosphere and preparation of the MWCNT/copper bulk with vacuum hot pressing. The SEM images of the fracture surfaces indicate that MWCNTs are homogeneously dispersed in the composite and bonded to the matrix. In addition, the thermal expansion of the composites with various MWCNT contents (0%, 1% and 5%, mass fraction) were investigated. The coefficient of thermal expansion (CTE) decreases with increasing MWCNT content, which are all much lower than that of pure copper.

Key words: carbon nanotubes; copper; composite; thermal expansion

1 Introduction

As a good electronic packaging material, it should have high thermal conductivity to dissipate the heat generated during the operation of many current electronic systems, and low thermal expansion (CTE) to decrease the strains caused by the CTE mismatch among the devices. Copper has high thermal conductivities, while copper and its alloys have not been used popularly as matrix materials in electronic packaging due to their high thermal expansion and density. The copper matrix-carbon fibre (C_f) composite may fulfill some requirements for the negative axial CTE and low density of C_f [1−3]. However, the hardness, especially the thermal conductivity of the Cu-C_f composite were always decreased a lot. Therefore, another good additive is in dire need of solving the problems.

With the outstanding mechanical properties, especially extraordinarily low thermal expansion (CTE≈ 0) and high thermal conductivity (3 000 W/(m·K)) [4−8], carbon nanotubes (CNTs) are attractive reinforcing agent to lower CTE of the copper packaging material. However, the fabrication of a uniform CNT reinforced copper composite is quite challenging because of the addition of a low density of solid (CNTs) in a comparatively high density of solid (copper), which is also incompatible with CNTs. Thus, it is easy to lead to clustering of CNTs and phase separation in the mixing stage[9−12]. Recently, researchers have attempted to remedy these problems by solvent-assisted mixing or treating the sidewalls of the CNTs at molecular level in a fashion that promotes their dispersion and interaction with the matrix materials[13−15]. In this study, a special technical process for preparation of multi-walled carbon nanotube (MWCNT)-reinforced copper composite is reported. It involves distribution of carbon nanotubes in MWCNT/Cu composite spheres in advance and preparation of the MWCNT/copper bulk with vacuum hot pressing.

2 Experimental

2.1 Preparation and purification of MWCNTs

Multi-walled carbon nanotubes (MWCNTs) were synthesized by the chemical vapor deposition (CVD) of acetylene. Then, concentrated acids ($c(H_2SO_4)$:$c(HNO_3)$ =3:1) were used to purify the MWCNTs and modify their surface with some hydrophilic groups, such as —COOH, —OH.

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Corresponding author: CHEN Xiao-hua; Fax: +86-731-8821483; E-mail: hudacxh62@yahoo.com.cn

2.2 Fabrication of MWCNT-reinforced copper composite

The fabrication of MWCNT-reinforced copper composite spheres is reported in another paper. In brief, first, acid treated MWCNTs were wrapped with gelatin in the solution for the electrostatic attraction, then 0.2 mol/L $CuSO_4$ and 0.1 mol/L glucose were added in order. The gelatin acts as ligand to catch Cu^{2+} ions to form copper complex around the surface of MWCNTs. Because glucose is a weak reducing agent, only in a strong basicity solution can the Cu^{2+} be reduced to Cu^{+}. Therefore, NaOH solution was added into the mixture drop by drop under stirring. When the pH reached 11, and the temperature reached 70 ℃, the MWCNTs/cuprous oxide spheres were obtained. After dried at 80 ℃ in vacuum, these spheres were reduced to MWCNT/Cu composite spheres at 400 ℃ for 3 h under a hydrogen atmosphere. The MWCNT/Cu composite bulks, which were named composite A, were fabricated from the composite spheres with vacuum hot pressing at 850 ℃, 80 MPa for 2 h. As a comparison, another MWCNT/Cu composite bulk (named as composite B) was prepared under the same condition by pressing the powders in which the MWCNTs were added in a method of ball milling. The characterization of composite spheres and the fracture of the bulks were carried out by powder X-ray diffraction (XRD, D5000), scanning electron microscopy (SEM, JSM-6700F) and transmission electron microscopy (TEM, JEM-3010). The microhardness and the thermal expansion of the composite were carried out on hardness-testing device (401MVDTM) and thermal dilatometer (DIL 402PC) respectively.

3 Results and discussion

3.1 Microstructures of composite spheres

Figs.1(a) and (b) show the typical SEM image of MWCNTs/Cu_2O composite particles, in which the particles are uniform in size with a spherical shape. The most important feature one can see is that MWCNTs are homogenously implanted within spheres rather than on their surface. Examining the sphere by TEM (Fig.1(c)) reveals that interior structure of the sphere is composed of a network of tubes that possessed dimensions similar to those in the nanotube mats. Obviously, this type of microstructure makes MWCNTs combine strongly with the matrix. The SEM images of the reduced particles are shown in Fig.1(d). We found that the reduction of the particles with H_2 at 400 ℃ brings about a slight change

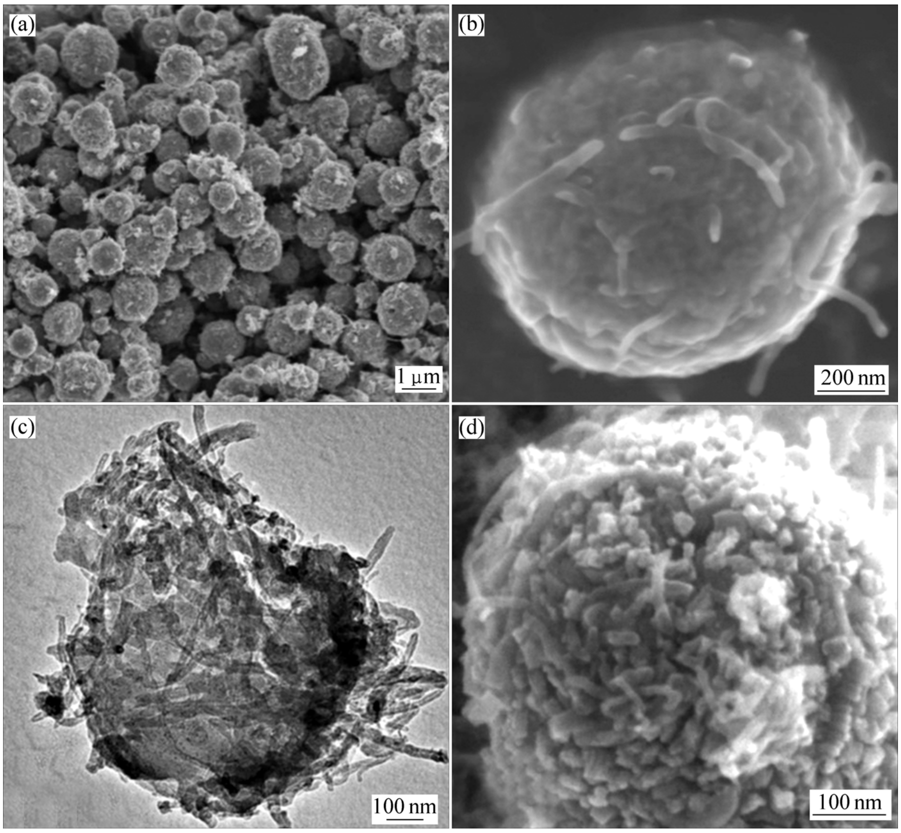

Fig.1 Morphologies of MWCNT/Cu_2O and MWCNT/Cu composite spheres: (a), (b) SEM images of MWCNT/Cu_2O composite spheres; (c) TEM image of MWCNT/Cu_2O composite spheres; (d) SEM image of MWCNT/Cu composite spheres

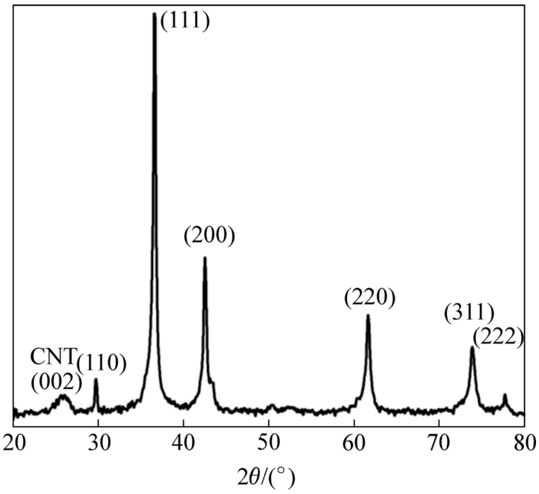

Fig.2 XRD pattern of MWCNT/Cu_2O composite spheres

on the surface of sphere. The microspheres retain their structural integrality and MWCNTs are still locked within the spheres, although some shallow pits on the surface take place.

3.2 XRD and EDS analysis of composite spheres

Fig.2 shows XRD pattern of the specimen. The XRD taken from as-prepared particles indicates that there are seven peaks with 2θ values of 25.80°, 29.71°, 36.58°, 42.50°, 61.66°, 73.90° and 77.72°. The peak at 25.80° is attributed to the characteristic peak of MWCNTs. The peaks at 29.71°, 36.58°, 42.50°, 61.66°, 73.90° and 77.72° correspond well with the reported values of Cu_2O(JCPDS 5-667). These peaks can be assigned to ⟨110⟩, ⟨111⟩, ⟨200⟩, ⟨220⟩, ⟨311⟩ and ⟨222⟩ crystal planes of Cu_2O, respectively. The EDX spectrum of MWCNT/Cu composite spheres has been carried out, as shown in Fig.3. It seems that no impurity peaks are detected but the C and Cu peaks. Therefore, the purity of the MWCNT/Cu composite powders can meet the needs of the MWCNT/Cu composite.

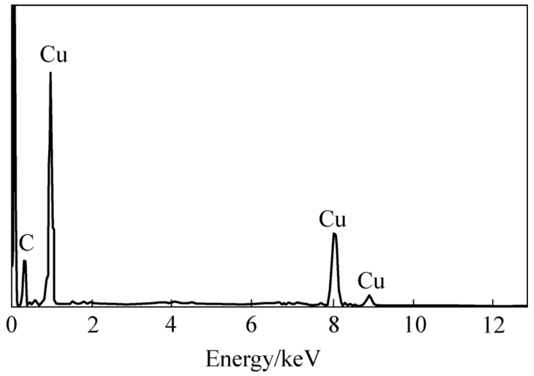

Fig. 3 EDS spectrum of MWCNT/Cu composite spheres

3.3 Microstructures of MWCNT/Cu composite

Microstructures of the consolidated MWCNT/Cu composite are shown in Fig.4 and Fig.5. It can be seen from Fig.4 that composite A appears a homogenous dispersion of MWCNTs within the Cu matrix. Another important feature one can see is that lots of MWCNTs are broken in the tensile failure rather than pulled out, which indicates that MWCNTs are bonded tightly with the matrix. This status is required in order to achieve effective load transfer from the matrix to the reinforcement. While in Fig.5, composite B appears more clustering phenomena and bad bonding between Cu and MWCNTs. The proposed mechanism for explaining the different phenomena is as shown in Fig.6.

3.4 Density and microhardness of MWCNT/Cu composite

Table 1 shows the density and microhardnesss of the pure copper and three kinds of the MWCNT/Cu composites. It is seen that the density of the MWCNT/Cu

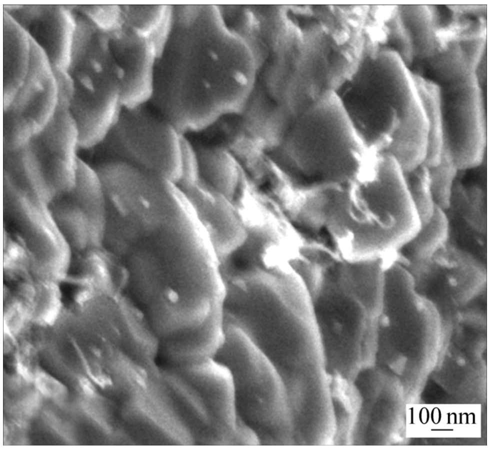

Fig. 4 SEM image of fracture of MWCNT/Cu composite A

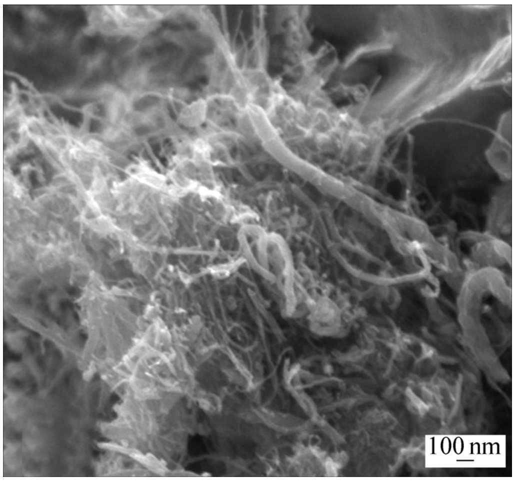

Fig. 5 SEM image of fracture of MWCNT/Cu composite B

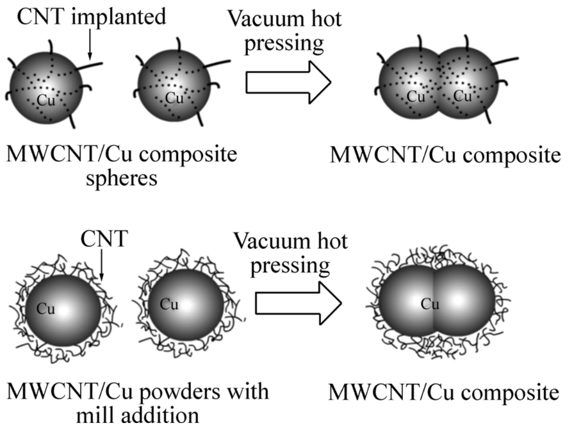

Fig. 6 Proposed scheme of forming processes of composites

composite is lower than that of pure copper due to the existence of MWCNTs. However, the microhardness of the composite A is much higher than those of the specimen without MWCNTs and composite B. The microhardness of composite B also is the lowest among them. It indicates that the uniformity and compatibility of MWCNTs in composite play good reinforcement role within the matrix, while the clustering of MWCNTs in the composite plays no reinforcement role on the microhardness. Table 1 also shows that the content of MWCNTs might affect the microhardness of the composite.

Table 1 Density and microhardness of composites (mass fraction, %)

w(MWCNT)/%	ρ/(g·cm^{-3})	HV
0	8.82	68.7
1	7.88	124
5	6.35	103.9
1$^{1)}$	7.62	57.7

1) Milling addition

3.5 Thermal expansion of MWCNT/Cu composite

Fig.7 shows a thousandth linear change versus temperature plots of the four kinds of specimens. It can be concluded from the slope of the curve that the average CTE of the MWCNT/Cu composite is much lower than that of the pure copper. Moreover, the average CTE of composite A decreases with the increase of the mass fraction of MWCNTs, which is also lower than that of MWCNT/Cu composite B at the same content. According to Fig.7, the variation of CTEs with temperature for the specimens is shown in Table 2. It can be seen that the CTE of the 5% MWCNT/Cu composite decreases to 5.76×10^{-6} K^{-1} at 120 ℃, which is about one-fourth of that of the pure copper. This indicates that MWCNTs are a promising filler to lower the CTE of electronic packaging materials.

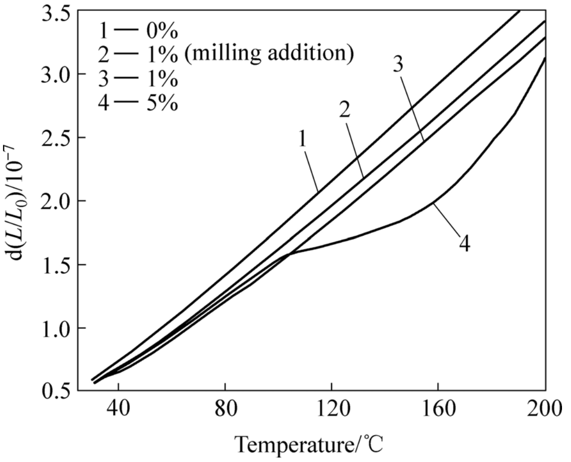

Fig.7 Plots of thousandth length change versus temperature of pure copper and MWCNT/Cu composite

Table 2 CTE of specimens with different molar fractions of MWCNT (10^{-6} K^{-1})

Temperatrure/ ℃	0	1%	5%	1%$^{1)}$
40	15.31	7.66	8.72	10.14
80	18.08	14.65	14.78	16.36
120	19.03	17.19	5.76	17.45
160	19.04	17.85	16.6	18.18

1) Milling addition

4 Conclusions

1) MWCNT/Cu composite was prepared with a unique method.

2) MWCNTs are homogenously ‘locked’ in the composite and tightly bonded to the matrix, which makes them play excellent reinforcement role on the microhardness and CTE of the composite.

3) The CTE of the 5% MWCNT/Cu composite decreases to 5.76×10^{-6} K^{-1} at 120 ℃, which is about one-fourth of that of the pure copper.

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