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Thermal Conductivity and Microhardness of MWCNTs/Copper Nanocomposites

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Abstract

The effects of dispersion states of carbon nanotubes on thermal conductivity and Micro-hardness of Multi-walled carbon nanotube (MWCNT) reinforced copper nanocomposites were investigated. The nanocomposites were fabricated in a novel method. It involves the synthesis of MWCNT-implanted copper composite spheres and the preparation of the MWCNT/copper bulk materials using vacuum hot pressing and hot rolling. The thermal conductivity of the composites with different concentration of MWCNTs were measured. Although the coefficient of thermal conductivity decreases with the increase of the MWCNT content, it is still high enough to be used as electronic packaging materials even the concentration of MWCNTS in the composite is up to 5 wt%. Furthermore, the microhardness of the nanocomposites are much higher than that of pure copper, which is ascribed to the good dispersion of the MWCNTs in matrix.

INTRODUCTION

Electronic packaging involves interconnecting, powering, protecting and cooling of semiconductor circuits for use in a variety of microelectronic application. For microelectronic circuits, the main type of failure is thermal fatigue, owing to the different thermal expansion coefficient of semiconductor chips and packaging materials. In addition, because the power density increases rapidly, the ability to dissipate heat becomes a very important factor. Therefore, effective thermal management is a key issue for packaging of high performance semiconductors. The ideal material working as heat sink and heat spreader should have a coefficient of thermal expansion (CTE) of (4-8)$\times10^{-6}$ /K and a high conductivity, especially, in recent years, the packaging materials with low density is becoming increasingly important owing to the continuous progress of miniaturization for electronic devices. Copper tungsten or copper molybdenum is one of the most important materials for thermal and electronic applications. It has a thermal conductivity of 150-220W/Mk with a CTE of 4-8$\times10^{-6}$ /K[1] but offer a high density and poor machinability. SiC combines a thermal conductivity of about 200-300W/mK with a CTE of 4.5$\times10^{-6}$ /K[2], and offer a good availability, but poor solderability. Diamond has exceptional thermal properties along with a low CTE of 1.0$\times10^{-6}$ /K. The thermal conductivity of synthetic diamonds of Ib type can be estimated in the range of 1500-2000 W/mk[3]. Therefore, the use of diamonds particles as reinforcement in copper based composites is considered very attractive to meet the increasing demands for high performance heat sink materials and packages. Unfortunately, an introduction of the diamond makes the composites poor machinability.

Among the strategies to improve the overall performance of composites , in particular to increase their mechanical strength and thermal conductivity, incorporation of carbon nanotubes (CNTs) is highly promising, due to their outstanding mechanical and thermal properties. The CNTs are characterized not only by a very high thermal conductivity (>2000 mK) and ability to increase the toughness of intrinsically brittle materials, probably through “bridging” and “pull-out” toughening mechanism, but also by a relatively high thermal stability in non-oxiding atmospheres. The potential benefit of CNTs in ceramic matrix composites which arises from their tubular three-dimensional structure, has prompted significant research in the field, with CNTs and CNT-reinforced materials being among the most studied materials within the last decade[4-10]. Multi-walled carbon nanotubes (MWCNTs) with their one-dimensional structure, high aspect ratio, and superior thermal conductivity (3000 W/mK for an individual MWCNT and 2000W/mK for bulk MWCNTs at room temperature)[11] have attracted

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much attention as good nanofiller candidates to form heat conductive pathways and considerably improve the thermal conductivity of composites with low loadings.

The unique structural, electronic, mechanical and other properties of carbon nanotubes promise their use in a wide spectrum of advanced applications in nanotechnology and electronic nanodevices. Compared with polymer, metal or ceramic is usually solid and incompatible with CNTs. Thus, it is easy to lead clustering of CNTs and phase separation in the mixing stage. Recently, researchers have attempted to remedy these problems by means of traditional powder-metallurgy processes molecular level mixing which consist of mixing CNTs with matrix powders followed by sintering or hot-pressing. However, these attempts have failed to fabricate CNTs/metal composites with homogeneously disperse due to aggregation of CNTs and differences in density between CNTs and metal. Another issue that requires attention is that nonuniformity and segregation of CNTs in composites are inevitable because of the addition of a low density solid (CNTs) in a comparatively high density solid (metal). This issue suggests us that we should exploit an effective method to “lock” CNTs into the matrix in advance. Furthermore, the most important issue is wear interfacial strength between the carbon nanotubes and the matrix because of their chemical inertness. To obtain fully dense nanocomposites, advanced sintering methods are used, such as spark-plasma sintering (SPS) technique and pulsed -electric-current sintering (PCS) technique. Zhan et al. have fabricated the Al_2O_3 nanocomposites containing 10 vol. % single-walled carbon nanotubes by SPS. SEM observation revealed that carbon nanotubes were distributed along grain boundaries. A loose network with a lack of interfacial contact can be noted.. Chu et al. reported a processing to fabricate CNTs/Cu composites by particles-compositing method followed by SPS technique. The addition of CNTs showed enough high in thermal conductivity of the composites for electronic packaging applications, but no significant reduction in CTE compared with neat copper. This is due to the combined effects of unfavorable factors induced by the presence of CNT cluster, i.e.large porosity, low effective conductivity of CNT clusters themselves. Unmatching CTE to chip limits application of CNT/Cu composites in electronic packaging.

In this paper, we propose a unique method to overcome the above problems by synthesis of MWCNT-implanted cuprous oxide composite spheres based on molecular level combination. These spheres were reduced to MWCNT/Cu composite spheres at hydrogen atmosphere. The resulting Cu-based spheres incorporate CNTs within the matrix rather than on their surfaces. This unique spherical structure rather than large random shaped aggregates will be very beneficial to fabricating fully dense composites of CNTs with a metal matrix.

2. Fabrication of MWCNT-reinforced copper composite

The synthesis of MWCNT-implanted cuprous oxide spheres as shown in Figure 1 is reported in a previous paper[12]. In brief, the method involves Cu ions combining with functionalized MWCNTs at molecular level and formation of spheres after reduction, nucleation and growth of Cu ions attaching to the surface of MWCNTs. The MWCNT-implanted composite spheres allow MWCNTs to avoid being damaged and effectively bond to the matrix. These spheres were reduced to MWCNT/Cu composite spheres at 400 ^{o}C for 3 h under a hydrogen atmosphere. Vacuum hot-pressing were adapted to fabricate MWCNT/Cu composite bulks. Disk-shaped specimens were hot-pressed in a graphite mold by uniaxial pressurization in a vacuum of 10^{-3} Torr to prevent oxidization of the powders. The diameter of the specimen was 15mm and the thickness was 0.8mm. To obtain fully dence nanocompoxites, hot rolling technique was used. Hot rolling is a three-dimensional flow process for plastic forming of metal plates, bars and profiles. In hot rolling a preheated work piece material is brought into a gap between two rolls. The hot-rolling experiments were carried out at 850 ^{o}C using an experimental rolling mill with a single two-high rolling stand, with a thickness reduction of 65%. An electrically heated tubular furnace with air-atmosphere situated next to the rolling mill was used for heating the work piece bars before the rolling. As a comparison, another MWCNT/Cu composite bulk

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with mechanically mixing of copper powders and CNTs was prepared in the same vacuum hot pressing condition. 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 conductivity of the composite were carried out on hardness-testing device (401MVDTM) and laser thermal conductivity-analyzing instrument (LFA427) respectively.

3. Results and discussion

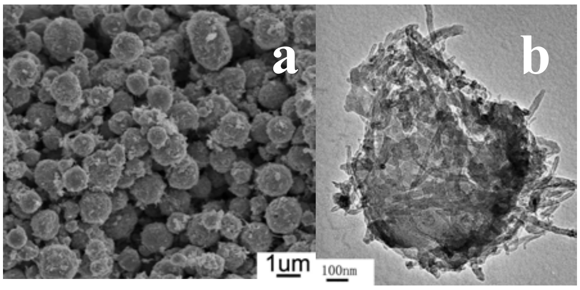

Fig. 1 (a) SEM image of the MWCNT/Cu_2O composite spheres. (b) TEM image of the MWCNT/Cu_2O

Figure 1 shows the SEM image and TEM image of the MWCNT/Cu_2o composite spheres. An important feature as shown in the SEM images is that the MWCNTs were homogenously implanted within the spheres rather than on their surfaces. TEM image（Fig. 1b）confirms that interior structure of the sphere is composed of a network of tubes. Apparently, the MWCNTs are locked inside the spheres and avoided moving freely to form large aggregates during the following mixing stage. It is inferred that the sphere shaped particles have a good flowability and compressibility, which can enhance the density of the composite.

Fig. 2 shows the microstructure of the fracture surfaces of MWCNTs/Cu composite bulks during the different processing stages. The microstructure of consolidated CNT/Cu nanocomposites fabricated by vacuum hot pressing shows that, although some content of the particle shape is retained, the carbon nanotubes are fairly homogenously dispersed in the matrix. No agglomeration was observed. In figure 2a, although different units which may come from different composite spheres can be distinguished, the MWCNTs keep 'locked' inside every unit instead of forming large aggregates. In particular, the MWCNTs are well bonded with the matrix as

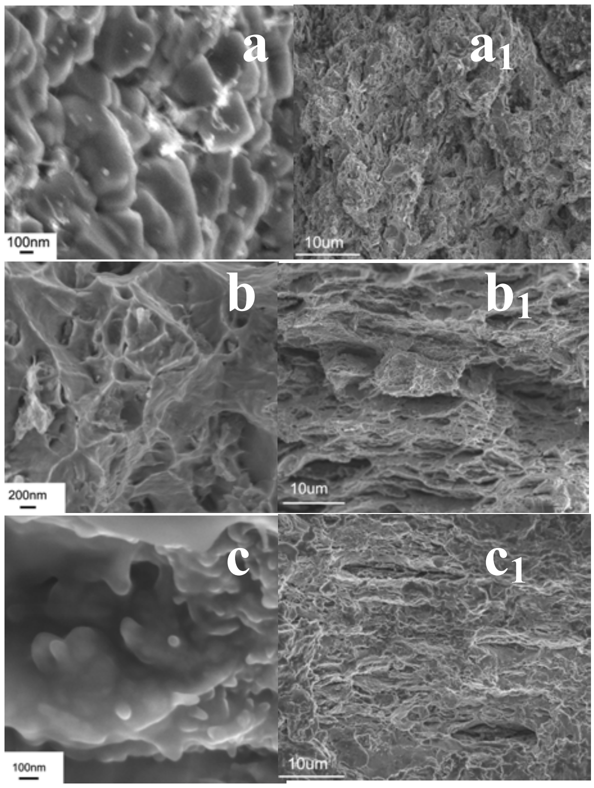

Fig. 2 SEM of the fracture surfaces MWCNTs/Cu composites (1 wt % of MWCNTs). (a),(a1) Vacuum hot pressing. (b), (b1) hot rolling, (c), (c1) annealing after hot rolling.

shown in figure 2. This status is required for effective load transfer from the reinforcement to matrix. Low-resolution SEM a1, b1,c1, show an obvious improvement of density with hot rolling and annealing. After hot rolling for hot pressed composite, the particle-shaped is disappeared, but lots of pores in the composite can be seen. In addition, traces of deformation bands are evident after hot rolling, and many shallow pits within the matrix can be observed. In contrast, after annealing for hot rolled composite, the shallow pits disappeared. Therefore, it is in great need to perform annealing to make the composite denser because the pores and pits will heavily decrease the thermal conductivity of the composite. The SEM images (Fig.2 c, c_1) show a significant improvement of the densification. It is not apparent that CNTs were pulled out of the ruptured surface. The typical extending length of nanotubes was less than 300 nm, which strongly suggested that were cut during the deformation process due to the efficient load transfer from matrix. No pores and gaps are evident. As a comparison, the morphology

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of the fracture surfaces for MWCNTs/Cu composite bulks with mechanically mixing of MWCNTs is also given in figure 3. It is apparent that the CNTs appear in the formation of bundles within the matrix. The Cu matrix is completely free of CNT, indicating fully dense material can not be obtained. This confirms that the mean grain size of Cu is virtually unchanged indicating that there is no grain growth during the sintering process. It shows more clustering phenomena and bad bonding between Cu and MWCNTs.

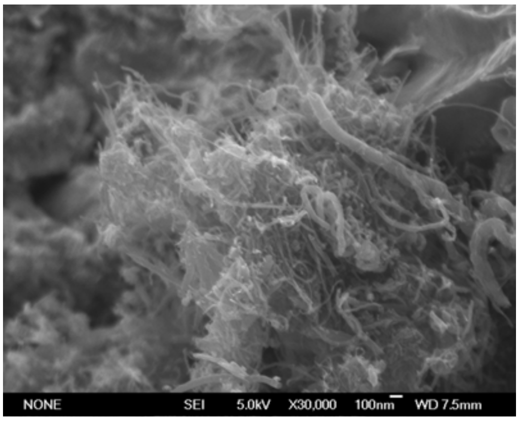

Fig.3 SEM of the fracture surfaces of MWCNTs/Cu composite (mechanically mixing)

Table 1 Microhardness of the composites

Concentration (wt%)	0	1	2	5	1 (mechanicaly mixing)
Microhardness after Vacuum hot pressing (HV)	69	124	94	104	58
Microhardness after hot rolling and Vacuum annealing (HV)	68	110	99	112	none

The variation of hardness of hot rolled composites is shown in table 1. For comparison, the hardness values of hot pressed composites are also presented in the same table. The hardness of the composites formed from composite spheres was much higher than that of unreinforced pure sintered copper. The composite with mechanically mixed CNTs has the lowest hardness value. It is also observed that there is a decrease in hardness for 0wt% and 1wt% composites and an increase in hardness for 2wt% and 5wt% after hot rolling and annealing. This phenomenon is attributed to the following reason. The second forming of the composite may lead to an improvement on the relative density, which can be confirmed in Fig.2, especially for the composite with high concentration of CNTs. The improved mechanical properties confirm the potential usage of CNT as a reinforcement in metal matrix.

Table 2 Thermal conductivity of the specimens

Parameter	0wt%	1wt%	2wt%	5wt%
Conductivity after Vacuum hot pressing ($Wm^{-1}K^{-1}$)	295.6	216.0	180.7	56.4
Conductivity after hot rolling and Vacuum annealing ($Wm^{-1}K^{-1}$)	301.3	205.7	185.2	132.8

Table 2 gives the thermal conductivity of the composite with the CNT concentration for materials processed by hot pressing and hot rolling respectively. Though the thermal conductivity is not very high, it is still high enough to be used as electronic packaging materials even the concentration of MWCNTS in the composite is up to 5 wt%. It is found that the thermal conductivity of the composite decreases with the increase of the CNT concentration. This can be attributed to the following possible reasons. The modification of the MWCNTs with some groups and the coupling interactions between the MWCNTs and copper may have an obvious effect on decrease of thermal expansion and increase the mechincal properties, they also lead to the enhancement of phonon scattering and decrease of the mean free path of phonons, which will heavily decrease the thermal conductivity of the MWCNTs themselves. The second possible reason can be related to the following unfavorable factors, namely the interface thermal resistance between the metal–matrix and CNT reinforcement, porosity, inhomogeneous distribution or clustering of CNTs and incomplete consolidation processing. It is also observed that there is a large improvement on the conductivity with the 5wt% after hot rolling and vacuum annealing, which is possibly ascribed to the decrease of the pores and increase of the density.

Because CNT has ultra-high conductivity along the tube direction but very low conductivity in

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radial direction, the random distribution of CNTs with various tube orientations would disturb this unidirectional heat transfer mechanism and, to some extent, reduce the effective conductivity of individual CNTs. Therefore, if we rearrange all the tubes along a heat transfer direction in the matrix, thermal conductivity could be greatly enhanced. However, the fabrication of not only highly aligned, but also well dispersed CNT/metal composites is still a critical challenge and will be left for future work.

Conclusions

Multi-walled carbon nanotube (MWCNT) reinforced copper nanocomposites were prepared using a unique spherical composite powders. The MWCNTs are homogenously 'locked' in the composite and tightly bonded to the matrix, which makes them play excellent reinforcement role on the microhardness compared with the unreinforced pure sintered copper. Alhough the thermal conductivity is not very high; it is still high enough to be used as electronic packaging materials even the concentration of MWCNTS in the composite is up to 5 wt%.

Acknowledgments

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