Spark plasma sintering of sub-micron copper reinforced with ruthenium–carbon nanotube composites for thermal management applications

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A B S T R A C T

Submicron copper reinforced with carbon nanotubes–ruthenium composites as suitable material for thermal management applications has been fabricated by Spark plasma sintering (SPS). The slurry of CNT–Ru was uniformly dispersed into copper matrix by mechanical stirring process using ethanol as a mixing medium. The composites powders were initially annealed for 30 min at 550 °C with heating rate of 5 °C/min under argon. The annealed powders were then consolidated at sintering temperature of 600 °C and 650 °C with a constant pressure of 50 MPa and the holding time of 5 min. The relative density of 98.15% was obtained for Cu-2 vol%CNT while that of Cu-2 vol%CNT-0.5 vol%Ru was of 97.08%. The Vickers hardness values of Cu-2 vol%CNT-0.5 vol%Ru sintered at 650 °C were found to be 130.4 HV. The coefficient of thermal expansion of 2.3×10^{-6}/°C was measured for copper reinforced with 2 vol% CNT sample at 100 °C. The thermal conductivity of 323 W/mK and 279 W/mK was measured at 100 °C for Cu and Cu-1CNT-0.5 vol%Ru. The X-ray photoelectron spectroscopy was performed on the samples surface in order to determine the effect of additives on the copper surface. XPS revealed that addition of Ru reduced copper oxidation at the surface.

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1. Introduction

As technological development is advancing towards increasing chip performance with continuous downscaling of complementary metal oxide semiconductor (CMOS) devices, the increase in power density has posed challenge for advanced electronic system [1]. The inability of the electronic package to shed this excess heat from the integrated circuit (IC) often results in the failure of the components [2]. Electronic packaging in a variety of microelectronic applications however, involves interconnecting, powering, protecting, and cooling of semiconductor circuits [3]. The purpose of thermal management devices in the electronic packaging is to cool the electronics components and systems and protect it from excessive heat during operation [4]. With the growing concern to achieve optimum performance of smart IC's at high operation temperature without reducing performance [3]; the requirements

of thermal management materials properties are now involving combined properties such as oxidation behaviour [5,6].

The unique engineering properties of copper have made it an outstanding material of choice for thermal management compared to many other materials. Despite the attractive thermal management properties of copper, its traditional properties can however no longer satisfy the recent technological requirement and needs of rapid development of microelectronic technology. Pure copper suffers material compatibility limitations when mounted on the substrate [7]. On the other hand, pure copper and copper-based composites with conventional grain size (micron size) are soft materials [8] [9]. Apart from the fact that Cu has high coefficient of thermal expansion, the widespread application of copper technology has been limited by the oxidation of copper at elevated temperature by forming a non-protective surface scale [10]. Carbon nanotube reinforced Cu matrix composites have emerged as material of interest particularly for thermal management in microelectronic circuits due to the excellent properties such as high thermal conductivity (3000 W/mK) and low CTE of approximate zero [11]. In addition, carbon nanotubes can withstand current density of >10^9 A/cm^2 for >300 h at 250 °C without any sign

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of degradation [12]. However, weak interfacial bonding strength between Cu the matrix and CNTs could lead to formation of pores at interface [13]. The thermal interfacial resistance could also contribute to the scattering of heat carrying phonons at the Cu–CNTs interface which could resulted at low thermal conductivity of the material [14]. Therefore, in order to achieve an optimal performance of Cu–CNTs composite for thermal management, it is important to improve the non-protective surface scale of copper by incorporating suitable materials. Ruthenium is an air-stable transition metal with high melting point (2310 °C) and shows negligible solid solubility with Cu even at 900 °C based on the binary phase diagram [15]. More importantly, ruthenium has good adhesion and is thermodynamically stable with copper; that is why it has been widely used as diffusion barrier as well as in alloy films for barrier-free Cu metallization [16,17]. Ruthenium has also been reported to show significantly stronger Ru—C bonds carbon compared to the Pd—C and Ti—C bonds [18]. Ding et al. [19] reported that the oxidation of Cu was inhibited to an extent with C alloying into the Ru layer. Furthermore, improved density and hardness results were obtained when increasing the Ru volume fraction in copper matrix by up to 2.5 vol% [8]. However, 1 vol% Ru decreased the electrical conductivity of pure Cu due to interfacial resistance and much higher resistivity of Ru ($7.1 \times 10^{-6}\,\Omega$cm) versus ($1.68 \times 10^{-6}\,\Omega$cm) for copper. With this understanding, it was decided that the Ru content be limited to 0.5 vol% in the composite samples.

Several techniques have been employed to synthesis CNT reinforced Cu- matrix composites due to the problem of inhomogeneous distribution of the CNTs in the metal matrix. Carreno-Morelli et al. [20] reported a procedure to incorporate MWCNT into Al and Mg matrix via powder metallurgy technique. A low energy ball milling in a Turbula mixer was employed to homogenize both the matrix and MWCNT composite. Esawi and Morsi [21] found the mechanical alloying mixing method suitable for homogenizing 2 wt% CNT with Al powders. Yamanaka et al. [22] reported on synthesis of carbon nanotube reinforced nickel composites. The colloidal suspension method was employed to distribute CNT homogeneously into the nickel matrix using ethanol as mixing medium. Kim et al. [23] reported on mechanical mixing of a Cu matrix reinforced by nickel-coated single walled CNT. An electroless plating technique was used to coat a layer of nickel on CNT. Cho et al. [24] reported on the dispersion of MWCNT in a copper matrix using mechanical stirring process. Recently, Nie et al. [13] reported a high energy mechanical milling process of Cu–Mo–CNT composite using vibratory miller for 120 min. Due to the level of dispersion reported in these studied, there is need to develop a simple and efficient process of dispersing CNTs into metal matrix without damaging the nanotubes structure.

Besides, there is virtually no reported study available on SPS densification behaviour and the corresponding coefficient of thermal expansion of sub-micron copper powder with irregular and angular shaped particles–shapes detrimental, as it is known, to powder compressibility by the common powder metallurgy compaction method – cold die compaction. The combined effects of CNT–Ru on the mechanical properties of submicron copper for thermal management materials is yet to be reported. Studied on surface oxidation behaviour of Cu–CNT composites produced by spark plasma sintering is also very limited. Spark plasma sintering (SPS) process has been widely used in fabricating Cu and Cu/CNT composites for potential thermal management materials. The accurate control of sintering energy as well as high sintering speed makes SPS a promising technique of producing highly dense materials with control grain growth [25]. An effort is therefore made in this study to fabricate the sample and investigate these properties.

2. Materials and methods

2.1. Feed stock powder and characterization

A commercial copper powder of 99% purity (Alfa Aesar) with particle size of 0.5–1.5 μm and multi-walled carbon nanotube (NC3100 thin MWCNT) with an average diameter of 9.5 nm and an average length of 1.5 μm were used for this study. The carbon nanotubes were supplied by Nanocyl and it was said to contain 95 + %C purity. The powders were mixed at varying compositions as shown in Table 1. The CNTs were ultrasonicated in ethanol for 1 h and vigorously stirred for 5 min using magnetic stirrer. Then Ru powder was added to suspension of CNTs and further ultrasonicated for another 1 h and stirred for 3 min. Copper powder was ultrasonicated in ethanol for 1 h and stirred for 2 min. The respective slurries of Cu and CNT–Ru were then mixed together and ultrasonicated for 1 h and stirred for 3 min. The homogeneous dispersed powder mixtures were then dried using a rotary evaporator and sieved to 75 micron. The dried powders were further blended in a Turbula T2F mixer for 1 h at a speed of 101 revolutions per minute. The mixed powders were annealed for 30 min at 550 °C with a heating rate of 5 °C/min under inert Ar atmosphere to reduce the oxygen content. X-ray powder diffraction was carried out in a Bruker D2 Advance diffractometer using cobalt as anode material at 30 kV and 10 mA. The XRD analysis was done to identify the phases present in the samples. The powders were scanned at a step scan mode of 0.02.

2.2. Consolidation of the composites powders

In this work, the powders were consolidated by spark plasma sintering (HPD5, FCT Systeme GmbH). The powders were loaded into a graphite die 20 mm in diameter, a sintered sample thickness of 5 mm was aimed at. A sheet of graphite foil was placed between the punch and the powders for easy sintered sample removal, thus prolonging tool life. In addition to this, the side walls as well as the top and bottom of the graphite die were coated with fine hBN slurry in order to limit the diffusion of carbon to the compacts. The holding pressure throughout the sintering cycle was kept at 50 MPa. Sintering was done at different temperatures, holding times and heating rates in order to investigate the densification behaviour.

2.3. Characterization of the sintered samples

The densities were measured using the Archimedes's principle process.

The morphological and qualitative analysis of the sintered samples were carried out using SEM with EDS. Samples for analysis were cut in a plane perpendicular to the pressing direction, hot mounted and ground using different sizes of silicon carbide paper up to 4000 grit, then were fine polished using 6 μm, 3 μm and 1 μm diamond suspensions.

Table 1
Consolidation condition for the samples.

No	Sample (vol%)	Sintering profile
1	Cu-1CNT	600 °C, 50 MPa, 80 °C/min, 5 min
2	Cu-2CNT	600 °C, 50 MPa, 80 °C/min, 5 min
3	Cu-0.5CNT-0.5Ru	600 °C, 50 MPa, 80 °C/min, 5 min
4	Cu-1CNT-0.5Ru	600 °C, 50 MPa, 80 °C/min, 5 min
5	Cu-2CNT-0.5Ru	600 °C, 50 MPa, 80 °C/min, 5 min
6	Cu-1CNT-0.5Ru	650 °C, 50 MPa, 80 °C/min, 5 min
7	Cu-2CNT-0.5Ru	650 °C, 50 MPa, 80 °C/min, 5 min