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Processing of copper–carbon nanotube composites by vacuum hot pressing technique

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ABSTRACT

Copper (Cu) matrix composites reinforced with 0.2, 5 and 10 vol% single wall carbon nanotubes (SWCNT) and 5 and 10 vol% multi-wall carbon nanotubes (MWCNT) were processed by high energy milling of pure copper powder with carbon nanotubes (CNTs) and subsequent consolidation by vacuum hot pressing. Microstructural observations of the sintered composites revealed equiaxed twinned microstructure for 0.2 vol% SWCNT composite and elongated grain structure, with CNT layers in between, in composites having higher CNTs content. The porosity in the composites was associated with CNT layers. The distribution of CNTs was found to be different in axial and transverse directions. Significant improvement in hardness of Cu–SWCNT composite was observed with increase in CNTs content. Whereas, in case of MWCNT composite, hardness reduced for 10 vol% CNT composites. Compression strength of the SWCNT samples was found to be higher than the MWCNT reinforced samples.

1. Introduction

Carbon nanotubes (CNTs) have been suggested as an excellent reinforcement to improve the mechanical performance of metallic materials due to their high elastic modulus, strength and aspect ratio [1]. Novel composites have been developed by incorporating CNTs into polymer, ceramic and metal matrices via various routes to realize composites with outstanding properties over conventional composite materials [2–8]. Uniform dispersion of CNTs in the matrix is the most important requirement to achieve uniform properties in these composites. The ease of CNT dispersion in the polymer matrix has resulted in considerably huge amount of research in polymer–matrix composites (PMCs) in order to improve their electrical conductivity along with the enhancement of mechanical properties [9–11]. However, work on metal matrix composites has been relatively scarce primarily due to difficulties in achieving homogeneous dispersion of CNTs with in metal matrices especially at high CNT loading [12–15] and lack of suitable synthesis techniques. Mechanical alloying and molecular level mixing [16] have been the best dispersion techniques and have received the maximum [17–19]. In order to obtain excellent mechanical and physical properties, several fabrication routes namely thermal spraying [20], hot-pressing [21], hot extrusion [22], spark plasma sintering [23] and electro-less deposition [24] have been used to synthesize metal–CNT composites.

Copper, due to its very high thermal and electrical conductivity, has always been a natural choice for the applications where high thermal and electrical conductivity is required such as welding electrode, high-voltage switches to more advanced active-cooling applications, such as first wall-and-diverter interactive components in fission, magnetic confinement fusion reactors, thrust chamber liners for reusable launch vehicle (RLV) engines and rocket nozzle liners. However, pure copper has very low strength and thus limits its usability. The effort to improve the mechanical properties of the copper by alloying or dispersing with second phase leads to lower thermal and electrical properties. The use of CNT as a reinforcement phase is expected to improve the mechanical properties without harming the thermal and electrical properties.

Several methods have been devised to synthesize Cu–CNT composites. Cha et al. have devised new method called molecular level mixing for synthesizing Cu–CNT powders from aqueous solution of copper salts containing dispersed CNTs [16]. It was shown that the presence of oxygen at the Cu–CNT interface resulted in good load transfer affecting high degree of strengthening [25] in compacts obtained by spark plasma sintering. Another technique used for improving dispersion is by attaching CNTs to Cu flakes produced by ball milling by means of a binder [26]. Roll bonding

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has also been used for dispersing CNTs between thin Cu foils [27]. Ball milling has been used by several authors for Cu–CNT composites [28–31]. Consolidation of the ball milled powders has been reported by high pressure torsion [31] and SPS [32].

There are only a few reports on synthesis of Cu–CNT composites by hot pressing which is a very versatile technique. Bulk composites for real life applications can be produced by hot pressing. Therefore, the purpose of the present investigation was (a) to synthesize Cu–CNT composites by mechanical alloying and consolidate them through hot pressing; (b) to study the effect of type of CNT on the microstructure and properties and (c) to study effect of CNT content on the mechanical properties. In order to achieve the above objectives, Cu–CNT composite powders were processed by high energy milling of pure copper with 0.2, 5 and 10 vol% SWCNTs and 5 and 10 vol% MWCNTs. The composite powders were sintered by vacuum hot pressing technique. The hot pressed composites have been characterized using optical microscopy, SEM, XRD and bulk hardness testing. The results obtained are discussed in the paper.

2. Experimental procedures

Copper (99.9% pure, −140 mesh) and CVD grown multi walled carbon nanotubes (MWCNT) (approximately 15 ± 5 nm in diameter and 5–20 μm in length, having purity more than 90% supplied by Nanolab Inc, USA) and CVD grown single walled carbon nanotubes (SWCNT) (approximately less than 2 nm in dia., supplied by Thomas Swan & Co. LTD., UK), were used in the present experimental study. No functionalization of the nanotubes was carried out prior to mixing. Fig. 1 shows the SEM images of the starting feed stock. Measured amounts of CNTs to achieve a volume percent (vol%) of 0.2, 5 and 10 in case of Cu–SWCNT and 5 and 10 in case of Cu–MWCNT were mixed with copper powder in stainless steel mixing jar containing stainless steel balls of 10 mm diameter (giving initial ball to powder ratio (BPR)=5:1).The density of MWCNT used in this study as quoted by the manufacturer was 1.8 g/cm^3 and that of SWCNT was 1.2 g/cm^3. While calculating the relative density of the composite powders, the density of the pure copper was considered as 8.9 g/cm^3; for the MWCNT reinforced Cu composites, the weight percentage of CNT is 1.06 for 5 vol% of Cu–CNT composite while it is 2.25 for 10 vol% Cu–CNT composite. On the other hand, for the SWCNT reinforced Cu composites, the weight percentage of CNTs is 0.71 for 5 vol% of Cu–CNT composite while it is 1.5 for 10 vol% Cu–CNT composite. The jar was filled with argon and agitated in an Attritor mill (Szegvari make) at 200 rpm for milling time of 20 h. Changes in the size and shape of the particles on milling was studied using SEM. The composite powder was hot mounted and polished and observed with SEM to reveal the cross section of a milled powder particle and elucidate the dispersion of CNTs.

The composite powders were hot pressed in a graphite die using 30 MPa uniaxial stress under high vacuum (10^{-5} mbar) in a 250 T capacity/2000 °C rated Industrial Vacuum Hot Press. Sintering temperature of 700 °C and soaking time of 30 min was used for hot pressing Cu–CNT composite. The compacts produced underwent delamination in the center on cooling and were repressed at a temperature of 725 °C under identical conditions. This leads to a defect free bulk composite. Fig. 2 shows the profile of temperature versus time of vacuum hot pressing operation. A constant stress of 30 MPa was applied for the entire hot pressing cycle until the initiation of the cooling cycle. For repressed samples this stress was maintained until cooling up to 500 °C.

The microstructure of the sintered samples of 65 mm diameter and 5 mm height were characterized using optical microscopy, SEM and Raman spectroscopy. Density of the compacts was measured using the water immersion technique. The metallographic samples were etched with ($FeCl_3$+HCl+H_2O) solution for revealing microstructure of the hot pressed composites. SEM was used to evaluate the distribution of the nanotubes in the powder as well as the matrix. Elemental analysis of the composite materials was carried using EDAX attached to ESEM. Raman spectroscopy was carried out to study the changes undergone by CNTs during the fabrication process.

Brinell hardness of the composite was measured using 2.54 mm dia. steel ball as indenter with 31.25 kgf load. The compression tests were performed using an Instron 3367 table top tester with a 30 kN

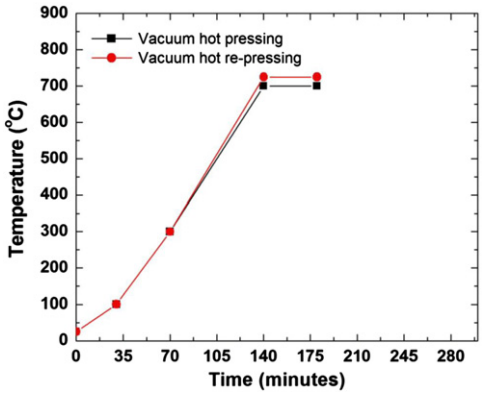

Fig. 2. Temperature cycle used during the processing of the samples.

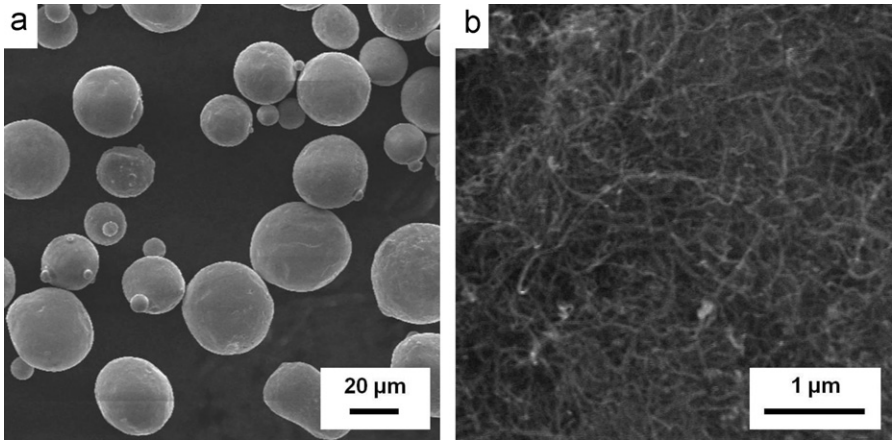

Fig. 1. SEM images of (a) Cu powder and (b) MWCNT used in the study.