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Tribological studies on microwave sintered copper–carbon nanotube composites

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ABSTRACT

Multiwall carbon nanotubes were coated with copper using an electroless two-step sensitization–activation method in order to improve the interfacial strength of the metal matrix. Copper-coated carbon nanotubes (5–20 vol.%) were mixed with copper metal powder and microwave heating was used to sinter them. The composites were subjected to pin-on-disc testing to study their tribological characteristics. Their mechanical and tribological properties were comparable to those of conventional and spark plasma sintered ones. The improvement in properties was limited to 15 vol.% due to the agglomeration of carbon nanotubes. The composites exhibited a lower coefficient of friction and a lower wear rate compared to unreinforced copper, because of the formation of a carbonaceous film at the contact surface. The self lubricating effect of carbon nanotubes reduces the frictional heating. The wear mechanism for low carbon nanotube concentrations was plastic deformation, whereas at high concentrations it was flake formation/spalling.

1. Introduction

The discovery of carbon nanotubes (CNT) revolutionizes several fields of materials and technology. Many researchers have endeavored to fabricate advanced composites to exploit the unique properties of CNT. Owing to their improved mechanical, physical, electrical and electronic properties, carbon nanotubes are used as reinforcements in polymer, ceramic and metal matrices. Copper and copper alloys are widely used in the electrical applications and bearing materials, due to their excellent electrical and thermal conductivities [1]. The CNT reinforced copper composite is a novel material having higher potential for electrical sliding contact applications like brushes for electric motors [2]. Copper and CNT were mixed at molecular level and copper–CNT composites were consolidated through spark plasma sintering. They exhibited increased compressive strength [3]. Inhomogeneous distribution of CNT in matrix led them to exhibit two step yielding behavior [4]. Moreover, the effects of interfacial bonding on mechanical properties of hot pressed single wall carbon nanotube (SWCNT)/copper composites were investigated and the importance of metallic coating on nanotubes was emphasized [5]. Electroless copper coated CNT/Cu composites were sintered by spark plasma sintering [6].

Microwave processing is a newer method evolved to cater the demands of better properties, potentially at a lower cost [7]. In conventional heat-treating processes, energy is transferred to the material from the surface of the material where as in microwave heating, the energy is directly delivered to the material through the molecular interaction with the electromagnetic field [8]. Recent research studies on microwave processing of metal powders elucidated the improved properties of materials through a finer grain size, and smaller number of rounded and uniformly distributed pores [9]. The unique heating property of microwave irradiation on CNT is applied in fabrication of a new architecture of two-dimensional metallic nanobowl array in thermoplastic substrate [10]. The selective interaction of CNT with microwaves confirmed the potential of microwave sintering of CNT composites.

Isostatically processed copper–CNT (0–25 vol.%) composites were subjected to tribological tests under dry condition using block-on-ring apparatus. Coefficient of friction was reported to be decreasing with the increase in volume fraction of CNT. Deeper grooves and flake like wear debris were formed due to adhesive wear [2]. Composites with high volume fraction CNT exhibited higher porosity, lower hardness and poor wear performance [11]. The experimental results showed that the tribological properties of spark plasma sintered composites were enhanced by three times compared to those of unreinforced copper matrix. The enhancement in tribological property is attributed to the effect of homogeneous distribution of CNT in copper matrix, good bonding at CNT/Cu interfaces and high relative density of composites [12]. Spark plasma sintering is an expensive process, and hence there is a need for a low cost technology. Microwave processing is offering better properties with reduced cost by way of reduc-

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tion in the processing time. Literature on tribological studies of copper–CNT composites is scarce even for the conventionally fabricated copper–CNT composites. Present work aims to fabricate copper/CNT composites through microwave sintering. Tribological characteristics of copper/CNT composites are also studied.

2. Experimental procedure

2.1. Electroless coating of CNT

Commercially available electrolytic copper powder (99.98% purity, average particle size 12 μm) was used as the matrix material. Commercially supplied multiwall CNT with diameter of 24–76 nm and with a length of a few micrometers was used as a reinforcement. CNT was purified and oxidized using nitric acid treatment by sonication for 10 min at 60 °C to remove the catalytic particles on the surface of CNT. To improve the interfacial bonding of copper matrix and CNT reinforcement, CNT were coated with a layer of copper by electroless plating using the established two-step sensitization–activation method. Prior to electroless plating, the purified CNTs were pretreated in a sensitization solution (0.1 M $SnCl_2$–0.1 M HCl) and activation solution (0.0014 M $PdCl_2$–0.25 M HCl) for 30 min each. The activated CNTs were introduced into the electroless copper bath having composition of 4.75 g/l $CuSO_4 \cdot 5H_2O$, 12.5 g/l $KNa(C_4H_4O_6) \cdot 4H_2O$, 1% formaldehyde and 2 g/l NaOH. The solution was stirred for 30 min using ultrasonicator. The pH was maintained at 12 during the electroless coating process.

Transmission electron microscope (TEM) was used to observe the coating on CNT. A drop of copper coated CNT dispersed in diluted ethanol was then deposited on a copper grid covered by a very thin carbon film for TEM sample preparation.

2.2. Microwave sintering of composites

Powder metallurgy technique was used to fabricate the copper coated CNT–copper composites with varying CNT volume fraction (5, 10, 15 and 20%). Coated CNTs were dispersed in ethanol with vigorous sonication for 10 min. Then copper powder was introduced in ethanol solution where CNTs were suspended. Solution was stirred and dried at 120 °C allowing ethanol to evaporate. Dried copper powder with CNT was well mixed in electric agate pestle mortar for 2 h. The mixed powder was uniaxialy compacted in a hydraulic press, in order to obtain green disc like pellets having dimension of 15 mm diameter and 10 mm height. Hybrid heating setup was built inside the microwave furnace (3.2 kW, 2.45 GHz) in such a way that outer layer was transparent to microwave (Alumina wool) and the inner one was absorber of microwaves (Silicon Carbide fencing) around the graphite crucible for uniform heating. Silicon Carbide fencing not only provides hybrid heating facility to green pellets but also reduces the thermal gradient to promote the fabrication of crack free components. The green pellets were heated to 800 °C with the soaking time of 5 min. Sintered specimens were then cooled in the furnace itself. The ramp rate was controlled to 12 °C per minute for entire sintering operation.

2.3. Characterizations of composites

Microwave sintered copper–CNT samples were studied through Scanning Electron Microscope with Energy-dispersive X-ray spectroscopy (SEM with EDX). Sintered density of the samples was determined by Archimedes' principle. The sinterability of the sample was evaluated through relative density. The hardness of the composites was evaluated by Vickers's hardness tester with 10 kg indenting load.

2.4. Tribological performance testing

Tribological performance of the copper–CNT composites was evaluated through a pin-on-disc test set-up operating in dry condition. The samples were machined to have the form of cylindrical pins of 15 mm diameter and 10 mm height. The samples were ground and finished with 800-grit silicon carbide paper and cleaned with acetone. The loads were vertically applied onto pin sample against EN30 steel disc hardened to 62 HRC. The hardened disc was also polished prior to each test to an average surface roughness (Ra) of 5.48 μm. The loads applied on the sample ranged from 12 to 60 N while the sliding speed and sliding distance were maintained at 2.77 m/s and 12,330 m respectively through out wear test. The pin sample was weighed prior to and after each wear test to determine the mass loss and mass loss was then converted into volumetric wear rate. Thermal history during testing was monitored using 'Rt' type thermocouple, embedded to pin's periphery. The worn surfaces at the end of tests were examined and analyzed using SEM.

3. Results and discussion

3.1. Characterization of microwave sintered composites

HRTEM image of multiwall CNT is shown in Fig. 1a and TEM images of non-coated and copper coated multiwall CNT are shown in Fig. 1b and c respectively. In the activation process, palladium could not be attached in some occasional sites on the surface of CNT, which turned into voids or gaps where the absence of growth of copper could be observed. The coating thickness was observed to be around 40–50 nm and well adherence of coating to the CNTs surface also could be observed.

Typical SEM micrographs of microwave sintered copper coated CNT composites are shown in Fig. 2(a–c). Homogenous distribution of CNT in copper matrix is observed. SEM micrograph of Cu–CNT (5% and 15%) composites, shown in Fig. 2(a and b) reveals not only the homogenous distribution of CNT in copper matrix but also the lower number of porous sites. It is also understood that the CNTs are not broken by the applied pressure during the compaction and they are very intact with the matrix material. Agglomeration and comparatively more amount of porous sites are observed in the Cu–20 vol.% CNT composite, as seen in Fig. 2c. A good interfacial strength can be observed due to the bonding of copper particle with the copper coated CNT. Typical SEM with EDAX at the interface is shown in Fig. 2d. High intensity peak of carbon and low intensity of peak of copper was observed and its quantified elemental value also embedded in this same figure. Absence of other elements like oxygen and interfacial reaction products confirms the intact.

Fig. 3 shows the peaks of carbon, copper and oxygen elements observed from the EDX analysis of microwave processed composites. Presence of oxygen peak is attributed to the oxidation of CNT which occurred during nitric acid treatment.

The variation of sintered density and relative density of sintered composites with the CNT volume fraction is presented Fig. 4. For each type of composition, five compacts were evaluated for density and their average was reported. From Fig. 4, it is observed that sintered density of composites decreases with the increase in the volume fraction of CNT. It is due to the reinforcement of lower density CNT in the copper matrix. As per the rule of mixture, theoretical density reduces with the increase in volume fraction of CNT in copper matrix.

In microwave sintering, the fine copper particles can couple with microwave radiation and then volumetrically heated. The heating of copper particles takes place through joule effect caused by microwave induced electrical current loss in the particles. The