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Electrical and mechanical properties of carbon nanotube reinforced copper nanocomposites fabricated by electroless deposition process

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ABSTRACT

Multiwalled carbon nanotube/copper (CNT/Cu) nanocomposite powders with different CNTs volume fractions were prepared by electroless Cu deposition on the CNTs. The CNTs underwent acid treatment, sensitization and electroless copper deposition on their surface respectively. The microstructure of the prepared CNT/Cu nanocomposites was investigated by SEM and HRTEM as well as by XRD analysis. Copper was deposited in a form of a layer on the CNTs surface. The CNT/Cu nanocomposite powders were sintered by spark plasma sintering. The microstructure of the sintered materials were investigated by SEM indicating that the CNTs were homogenous distributed in the copper matrix with good sinterability and porosity content lower than unity in case of 5 and 10 vol.% of CNT/Cu nanocomposites and 2.9 and 3.5% respectively for 15 and 20 vol.% CNT/Cu nanocomposites. The electrical conductivity, hardness and the tensile properties were measured for evaluating the sintered CNT/Cu nanocomposites. The electrical conductivity decreased by increasing CNTs volume fraction in copper matrix, but the hardness was increased by increasing CNTs volume fraction. The Young's modulus was increased and the elongation was decreased by increasing the volume fraction of CNTs in copper matrix. In addition, the yield strength of the sintered materials was increased by increasing CNTs volume fraction except in case of 20 vol.% CNT/Cu composite the material was fractured before yielding.

1. Introduction

Carbon nanotube is the most typical one dimensional nanomaterial in the order of micrometers in length and nanometers in diameter. Although discovered first, multi-walled carbon nanotubes (MWNTs) have not been studied as thoroughly as single-walled carbon nanotubes (SWNTs). This could partly be due to the higher specific stiffness and strength of a SWNT as compared to those MWNTs. However, in certain applications, MWNTs offer superior properties over SWNTs. For example, MWNTs are expected to have higher resistance to bending and buckling than a SWNTs. Also, MWNTs are easier to manufacture and are, therefore, less expensive than SWNTs. It was founded that that Young's modulus varied from 0.27 to 4.15 TPa with an average value of 1.8 TPa, while MWNTs grown by the arc discharge method have Young's modulus of 1 TPa, and Young's modulus of those grown by the catalytic decomposition of hydrocarbons is one to two orders of magnitude lower. Thus only highly ordered and well-graphitized MWNTs having strong carbon–carbon bonds within each layer have Young's modulus comparable to that of graphite [1–5]. Because CNTs have outstanding mechanical, thermal, and electrical properties CNTs have been used as reinforcement for a variety of composite materials [6]. Therefore, the composite properties can be enhanced by placing nanotubes into appropriate matrices, such as in metal matrix materials, enhancing in this way the mechanical properties.

CNTs as integrated molecules, have high chemical stability due to the covalent bond between the carbon atoms is connected with sp^2 hybrid. It has been confirmed that CNTs have much less chemical activity than carbon fiber and graphite [7]. It has been proved that CNTs had properties like graphite such as the low wetability to metals. Therefore the properties of their surfaces, which do not have catalytic effect [8,9]. Authors have studied the wetting of carbon nanotubes in detail and reported that the determining factor for wetting was surface tension, with a cut-off limit between 100 and 200 mN/m. This limit implied that typical pure metals, such as: aluminum (surface tension of 865 mN/m), copper (1270 mN/m), iron (1700 mN/m) [10], would not be easily wetted on the surface of MWNTs. This means, if CNTs are used as reinforcing fibers for metal–matrix composites without any surface treatments, it will be difficult to achieve high-strength interfacial adhesion. In previous works we developed CNT/Cu nanocomposites, by

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mechanical milling and molecular level methods, which show remarkable enhancement of the mechanical properties specially hardness and tensile strength [11–13].

Composite coatings improved properties of composites heavily depend on the nature and content of reinforcements in the coatings. The most important point is to obtain continuous, uniformly distributed and dense coated metal layer. Otherwise, the layer with voids or gaps may weaken; even destroy the integration between CNTs and metal matrix, lowering the expected advantages of metal–matrix reinforced by CNTs. There are several reports on the electrochemical composite coating CNTs, but unfortunately CNTs as one dimension nanoscale material are easily to agglomerate in solution decreasing the electroplating efficiency process [14–17].

Electroless metal coating technique has been widely used to prepare the composite coatings. As the advancement of electroless powder coatings, in which particles are used as reinforcing phase and the coated metal as a matrix. But up to now, it is described rarely about electroless nanometer composite coatings. Electroless plating with catalytic metals was an effective way for necessary surface treatments [18], after which the coated layers can serve as medium for adhesion and transferring loads. Previous studies proceeded with coating CNTs by metals with sensitization by stannous chloride followed by activations with palladium chloride and after that coating of the activated CNTs surface with Ni–P layer followed by mixing this composite powders with Cu power and underwent powder metallurgy processing of these composites [19,20].

It is expected that the metal matrix composites reinforced by nanotubes would have high strength [21]. In general, the mechanical properties of composites are often affected by microstructures in the composites [22–24]. Recently, the tribological properties of CNTs reinforced copper composites fabricated by a powder metallurgy technique were investigated. While the composites with high volume fraction of CNTs exhibited high porosity, the wear resistance of the composites decreased under high load conditions [25,26].

The present work aims to improve the interfacial bonding strength between Cu and CNTs by acid treatment and electroless copper coating of MWNTs to produce CNT/Cu nanocomposite powder with different CNTs volume fraction. The produced composite powders were sintered using spark plasma technique. The prepared sintered materials were underwent microstructure investigations, physical and mechanical properties measurements to evaluate each nanocomposite.

2. Experimental

Multiwalls carbon nanotube grade of 10–50 μm length and 15–10 nm diameter with BET surface areas about 200 m/g was supplied from Iljin Nanotech Co., Ltd. concentrated hydrochloric, nitric, sulphoric acids, were provided from Junsei Chemical Co., Ltd. and were used for CNTs surface cleaning and acid treatment. The concentrated hydrochloric acid was used for dissolving any metallic contaminants in the CNTs powder by sonication of CNTs in hydrochloric acid for 5 h followed by soaking for 12 h and then filtration and drying in vacuum dryer for 2 h at 80 °C. The produced CNTs powder undergoes further acid treatment by sonication in nitric acid and sulphoric acid mixture of the ratio (1:3) for 10 h followed by soaking for 12 h and then filtered and dried in vacuum dryer at 80 °C for 2 h and stored in vacuum chamber under 10^{-1} Torr.

The sensitization and electroless copper deposition bath was composed of highly pure chemicals were supplied from Aldrich Co (Germany) consisting of stannous chloride dihydrate, copper sulphate penta hydrate, trisodium citrate dihydrate and formaldehyde. Stannous chloride dihydrate was used for sensitizations of CNTs by stirring the acid treated CNTs in solution consists of 2 wt.% stannous chloride in water and the pH was adjusted between 1 and 3 by the addition of hydrochloric acid. The sensitization time was optimized 2 h, the sensitized CNTs underwent washing with distilled water, centrifugation and filtration. The sensitized CNTs followed by catalytic treatment of the sensitized CNTs with stirring it in copper sulphate penta hydrate solution for 2 h. Previous studies were occurred for the electroless copper bath included 70 g/l copper sulphate as a source of copper, 170 g/l trisodium citrate dihydrate as a complexing agent of the copper ions and 100 ml/l formaldehyde as a reducing agent of the copper ions [27,28]. The pH of the solution was adjusted at 11.5 and the temperature at room temperature. After completion of the electroless copper deposition reaction the coated CNTs underwent washing with distilled water and acetone, filtration and drying in vacuum dryer for 2 h at 80 °C. The complete process of fabrication of CNT/Cu nanocomposites was illustrated in Fig. 1. This process was used for preparing four different CNT/Cu composite powders of 5, 10, 15, 20 vol.% of CNTs. Also a comparative pure copper powder was prepared by the same electroless deposition method as mentioned before. The prepared composite powders underwent elemental analysis for determining the carbon content for each composite powder using Elemental analyzer (EA1110-FISONS) and a C/S analyzer (ELTRA CS800). The prepared powders were characterized using high resolution scanning electron microscopy (HRSEM), transmission electron microscopy (TEM) and X-ray diffractometer.

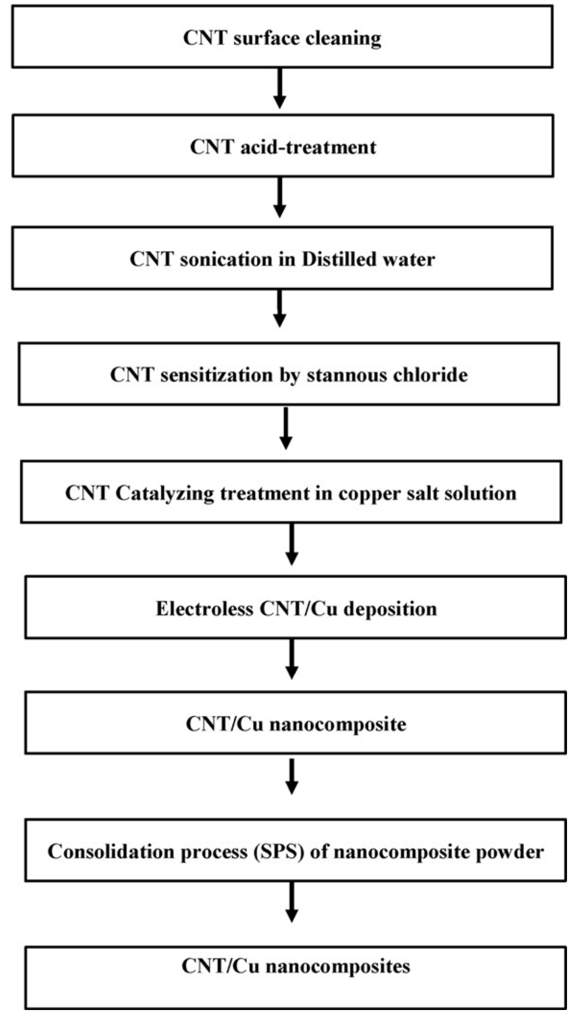

Fig. 1. Schematic fabrication process steps for electroless preparations of CNT/Cu nanocomposites.

Each composition of CNT/Cu composite powder underwent spark plasma sintering by using Spark Plasma Sintering System of model Dr. SINTER.LAB at compaction pressure of 50 MPa for 1 min