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

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A B S T R A C T
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.

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1. Introduction
Carbon nanotube is the most typical one dimensional nano-material 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 found 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 sp² 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
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 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 m2/g was supplied from Iljin Nanotech Co., Ltd. concentrated hydrochloric, nitric, sulphuric 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 sonication 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 sulphuric acid mixture of the ratio (1:3) for 10 h followed by sonication for 12 h and then filtered and dried in vacuum dryer at 80 °C for 2 h and stored in vacuum chamber under 10−6 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 pentahydrate, 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 pentahydrate 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.

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.
and temperature of 550°C under $10^{-3}$ Torr vacuum conditions by heating rate up to the sintering temperature was maintained at 100 K/min. The sintering process was occurred in different sizes uniaxial graphite molds of 10, 15 and 20 mm diameter to produce a 3 mm thickness sample for each CNT/Cu nanocomposite. Microstructure characterization of pure copper sample and the related CNT/Cu nanocomposites was carried out using high resolution scanning electron microscopy (HRSEM).

The electrical conductivity for the prepared materials were measured relative to the international annealing copper standard (IACS %) using ohmmeter of the model Autosigma 3000. Hardness tester of the model Mitutuyo Hardness testing system HM were used for measuring Vickers hardness for the pure copper sample and the related CNT/Cu nanocomposites. The load was selected at 50 gf for testing. The test were repeated for 5 times at different points in each sample. Tensile tests were performed using INSTRON 4206 under a crosshead speed of 0.2 mm/min. Dog-bone shape sub-size specimens with gage length of 9 mm and width of 2.5 mm based on the ASTM E8M were used for tensile test.

3. Results and discussion

3.1. Electroless CNT/copper deposition

The electroless Cu bath was used for preparing both the pure copper powder and the coated CNT/Cu nanocomposite powder. Fig. 2a shows SEM micrograph of the electroless deposited copper powder has spheroid particle shape with size of 100–200 nm. The CNTs were functionalized by acid treatment with sonication to modify the surface of the graphene structure by introducing functional groups such as carboxylic, carbonyl and hydroxyl groups on the CNTs surfaces. This process enhance the shortening of the CNTs length as well as the functionalized CNTs can be suspended in the solution. Fig. 2b and c shows two TEM micrographs for the as received CNTs and the acid treated CNTs respectively. The as received CNTs have the shape of agglomerated filaments but after the acid treatment and sonication these agglomerated filaments were destroyed and the CNTs length was descended by shortening of the CNTs chains.
The acid-treated CNTs underwent sensitizations by stannous chloride. The sensitized tin particles were deposited on the surface of CNTs as shown from TEM micrograph in Fig. 2d. These sensitized particles have spherical particle shape with about 3–5 nm particle size. The sensitized CNTs were soaked in the electroless bath followed by electroless Cu deposition on the sensitized CNTs. The electroless copper deposition reaction was finished within about 1 h after all the copper salt content in the solution was reduced to metallic copper and all the blue color of the copper salt in the solution was disappeared. The most important feature of the process is the coating of CNTs with Cu metal. Figs. 2e shows SEM micrographs for the coated CNTs by copper metal. Also the prepared CNT/Cu nanocomposites were investigated by HRTEM as shown in Fig. 2f. It was observed from these microstructures, the copper was deposited on the CNT surface in coated type morphology. The XRD pattern in Fig. 3a indicates one kind of peaks of the copper metal phase only. From the XRD data as shown in Fig. 3b there is one low intensity peaks for the graphene structure of CNTs were detected due to the amorphous behavior of the graphene structure of the acid-treated CNTs. The produced CNT/Cu nanocomposite powder was analyzed by XRD as shown in Fig. 3c. Two kinds of peaks one for pure copper metal and the other for CNTs.

3.2. Microstructure of sintered CNT/Cu nanocomposites

The fabricated CNT/Cu nanocomposite powders as well as the pure copper powder were consolidated into bulk by spark plasma sintering, which enable the powders to be sintered by joule heat and spark plasma generated by high pulsed electric current applied through the compact. Prelimiarly experiments were carried out to select the optimum conditions of the spark plasma sintering technique. The observations indicated that the shrinkage of the CNT/Cu stopped after 1 min at 550 °C under 50 MPa pressure and 10−3 Torr vacuum condition [11–13]. The cross-section surface morphology in the transverse direction to the uniaxial pressing direction of etched CNT/Cu nanocomposites with different CNTs volume fraction is shown in Fig. 4. The microstructure of consolidated CNT/Cu nanocomposites with low CNTs volume fraction shows homogeneous distribution with no segregation of the CNTs from the copper matrix with a fine microstructure preventing grain coarsening. But by increasing the CNTs volume fraction to 20 vol.% there were some large pores created in the copper matrix due to some agglomerations of CNTs at the grain boundaries of the copper matrix. These pores are the origin of the dropping in some physical and mechanical properties of 20 vol.% CNT/Cu nanocomposite as we can see in the next section. Fig. 4b–d shows SEM microstructures for 5 vol.% CNT/Cu, 15 vol.% CNT/Cu and 20 vol.% CNT/Cu. It was observed from these microstructure there are a black open pores located...
in the copper matrix and these black pores increased by increasing the CNTs volume fraction. In comparing these microstructures with pure copper it was found that the CNTs were dispersed in the copper matrix but still some agglomerations located in the copper grain boundaries of 15 vol.% CNT/Cu. Also by increasing the CNTs content in the copper matrix the CNT volume fraction was increased as shown in the high resolution SEM micrographs of the cross-section surface morphology in the transverse direction to the uniaxial pressing direction of CNT/Cu nanocomposites in Fig. 5. In addition, it was found that the sintered CNT/Cu nanocomposites included content of tin resulted from the sensitization process and the tin content increased up to 3.2 wt.% in case of 20 vol.% CNT/Cu nanocomposite. This tin content can interact with copper matrix to produce some intermetallics particles which could affect on the properties of the produced composite.

3.3. Physical and mechanical properties of CNT/Cu nanocomposites

The relative density of CNT/Cu nanocomposites was calculated by the ratio of the measured Archimedes density relative to the calculated densities of the nanocomposite by the rule of mixtures. It was observed that the relative densities of the prepared CNT/Cu nanocomposites were decreased by increasing the CNTs volume fraction. The relative densities were 99.7 in case of 5 vol.% CNT/Cu, 99.1 in case of 10 vol.% CNT/Cu, 97.1 in case of 15 vol.% and 96.51 in case of 20 vol.% CNT/Cu. The relative density of CNT/Cu was lower than pure Cu due to agglomerations of CNTs at grain boundaries of the copper matrix which is the origin of the pores formation. These agglomerations increased by increase the CNTs volume fraction.

Fig. 6 shows the electrical conductivity values according to international annealing copper standard (IACS %) which were decreased...
by increasing the CNTs volume fraction in the copper nanocomposite. Because CNTs have resistivity of the order $10^{-3}$ $\Omega$ cm [29–31] but copper in the order $10^{-6}$ $\Omega$ cm, CNTs have 0.001 conductivity relative to the pure copper metal which decrease the conductivity of copper in the CNT/Cu composites linearly with the CNTs volume fraction up to 15 vol.% CNTs but in case of 20 vol.% CNT/Cu the conductivity was dropped down because of three reasons. The first reason is due to the agglomeration of some CNTs at the copper grain boundaries, they can form a kind of grain boundary phase which will increase the scattering of the charge carrier at grain boundary, hence reducing the conductivity. The second reason is due to the higher porosity value of 20 vol.% CNT/Cu than the other CNT/Cu nanocomposites. But the third reason is the tin content resulted from the sensitization process of CNTs which included in the prepared nanocomposites. Because tin can react with copper and form intermetallics have lower conductivity than copper and it decrease the total electrical conductivity values of the produced nanocomposites.

The hardness of the CNT/Cu nanocomposites as well as the pure copper was measured by Vickers hardness test. Fig. 7 shows the effect of the CNTs volume fraction on the hardness of the prepared CNT/Cu nanocomposites. The hardness increases with increasing the CNTs volume fraction up to 20 vol.% when the CNTs are reinforced, the hardness of CNT/Cu nanocomposites is 1.4 GPa, which is about 2.1 times higher than that of Cu without CNTs. We compare these results with our previous results for CNT/Cu fabricated by molecular level process [12]. It was observed that the CNT/Cu nanocomposites fabricated by electroless coating method shows lower hardness values than those were fabricated by the molecular level mixing process. Because the CNT/Cu nanocomposites fabricated by electroless coating of the CNTs with copper shows some agglomeration of CNTs in copper matrix than that prepared by the molecular level method. Therefore, it is confirmed that enhancement of hardness by CNTs reinforcement is originated from the high interfacial strength at CNT/Cu interface and homogeneous distribution of CNTs within Cu matrix.

The stress–strain curves as shown in Fig. 8 are obtained from the tensile test of CNT/Cu nanocomposites as well as the pure copper. The direction of the load is parallel to the compaction direction of the samples. The yield strength and the Young’s modulus were calculated from the stress–strain curves for the tensile test of the investigated samples. Fig. 9 shows yield strengths and Young’s modulus of the produced CNT/Cu nanocomposites with different CNTs volume fraction. In general the yield strengths and Young’s modulus of CNT/Cu nanocomposites are increased with increasing the CNTs volume fraction until the CNTs volume fraction increased to 15%. But in case of 20 vol.% CNT/Cu the sample was fractured before yielding due to agglomerations of CNTs in the grain boundaries. In addition, the presence of the copper–tin intermetallics in the CNT/Cu nanocomposite decrease the tensile properties of the fabricated CNT/Cu nanocomposites. The yield strength of CNT/Cu nanocomposite with 15 vol.% CNT is measured as 341.2 MPa, which is approximately 2.85 times higher than that of unreinforced Cu fabricated by spark plasma sintering. This tensile result of the CNT/Cu nanocomposites fabricated by electroless method shows higher elongation with lower tensile strength than that fabricated by molecular level method [13].
The Young’s modulus of CNT/Cu nanocomposite with 20 vol.% CNTs is measured as 105.9 GPa, which is almost 2 times higher than that of pure Cu, which is measured as 51.6 GPa. The higher values of Young’s modulus and yield strengths indicates that the CNT/Cu nanocomposites are successfully fabricated by electroless copper deposition on the surface of CNTs and spark plasma sintering process. Also by measuring the elongations of each CNT/Cu nanocomposites. The results observed that the elongation decreased by increasing the CNTs volume fraction. In case of pure copper 19.2% which was decreased to 10.2 vol.% and 2.5% in case of 5 vol.% CNT/Cu. This means the elastic properties of the copper were decreased by increasing the CNTs in CNT/Cu and 2.5% in case of 5 vol.% CNT/Cu. This means the elastic copper was decreased to 10.2 vol.% in case of 5 vol.% CNT/Cu composite the nanocomposite was fractured before yielding due to the decreasing in the elastic properties of the investigated materials by increasing of the CNTs volume fraction more than 10 vol.%. However, these compositions contain CNTs volume fraction up to 10 vol.% the materials has high ductility. By increasing the CNTs volume fraction as in the composition 15 vol.% CNT/Cu the elongation were decreased to 1.2%. But in case of 20 vol.% CNT/Cu the sample was fractured before yielding due to the decreasing in the elastic properties of the investigated materials by increasing of the CNTs volume fraction more than 10 vol.%.

4. Summary

CNT/Cu nanocomposites have been fabricated by spark plasma sintering of acid-treated and electroless coated MWCNTs by copper. These results confirm that the homogeneous distribution of CNTs in metal matrix is the most critical issues to enhance the physical and mechanical properties of CNT/Cu nanocomposites. By using electroless copper deposition process on the CNTs surface the homogeneity between CNTs and copper can be increased and the agglomerations of CNTs at the copper grain boundaries were decreased. The density and the electrical conductivity were decreased by increasing the CNTs volume fraction but the hardness and Young’s modulus were increased by increasing the CNTs volume fraction. The yield strength of the produced sintered materials were increased by increasing the CNTs volume fraction except in case of 20 vol.% CNT/Cu composite the nanocomposite was fractured at lower strength value.

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