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Grain refinement assisted strengthening of carbon nanotube reinforced copper matrix nanocomposites

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Carbon nanotube reinforced copper matrix (CNT/Cu) nanocomposites were fabricated by the modified molecular-level mixing process, which produces a homogeneous dispersion of CNTs in a fine grained metal matrix. These nanocomposites, consisting of 1.5 μm Cu matrix grains and 5 vol % of multiwall CNTs, show a high strengthening capability; enhancing the yield strength of unreinforced Cu by 2.3 times. The enhanced yield strength stems from the reinforcing effect of CNTs and additional hardening of the Cu matrix by grain refinement. The results reveal that the metallurgical treatment of the matrix is important for the development of high-strength CNT/metal nanocomposites. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2899939]

The fabrication of carbon nanotube (CNT)/metal nanocomposites is attractive for high-strength structural applications since CNTs are considered as promising reinforcements to enhance the mechanical performance of monolithic metals due to their remarkable strength, modulus, and high aspect ratio.[1,2] There are several representative results showing enhanced properties of CNT/metal nanocomposites processed by conventional powder metallurgy (PM) methods. For example, Kuzumaki *et al.*[3] reported an increase of tensile strength of CNT/Al composites compared to pure Al. Deng *et al.*[4] have also observed enhanced tensile strengths and Young's modulus for 1 wt % CNT addition to an Al matrix. Our previous result[5] also shows interesting tensile properties and improved yield strength of CNT/Cu composites with increasing volume fraction of CNTs.

However, the property improvement by CNTs in these CNT/metal composites fabricated by PM techniques has not reached up to the expected values. The reason originates from the fact that the critical problem of an inhomogeneous dispersion of CNTs has not been perfectly solved in order to synthesize CNT/metal nanocomposites with minimized aggregation of CNTs. Recently, strengthening of metals by homogeneously dispersed CNTs in the matrix has been achieved by applying molecular-level mixing[6] between the functionalized CNT surface and metal ions. The CNT/Cu nanocomposites fabricated by this process showed that CNTs can play a role as the most effective reinforcing agents as long as they are homogeneously dispersed and mixed in the Cu matrix.[6]

As a result of the above described previous research, the origin for the strengthening of CNT/metal nanocomposites has been described from the viewpoint of the reinforcing effect of CNTs as extensively proven in CNT/polymer composites,[7,8] even though metals themselves have a large strengthening potential as George *et al.*[9] suggested. Thus, it is still not clear whether strengthening of the metal matrix through strengthening mechanisms based on dislocation motion in the matrix can also contribute to the strength of CNT/metal nanocomposites. In fact, refining grains may effectively strengthen a material, as the well-known Hall–Petch (HP) relation reveals that the strength increases linearly with $d^{-1/2}$ (where d is the grain size). Extremely high strength and hardness have been observed in various metals and alloys.[10,11] However, there have been surprisingly little trials applying the technique of matrix grain size refinement to strengthen CNT/metal nanocomposites.[12]

In this letter, we report that matrix grain size refinement provides additional strengthening besides the effect of CNT addition for CNT/Cu nanocomposites processed by the modified molecular-level mixing process. The synthesis route used in this study is a unique method to fabricate ultrafine grained metal matrix composites reinforced with homogeneously dispersed CNTs, resulting from consolidation of nanosized CNT/metal composite powder (for further details, see Ref. 12).

Multiwall CNTs (MWCNT) (Iljin Nanotechnology Co. Ltd.) with diameters of 20–40 nm synthesized by thermal chemical vapor deposition were stirred for 24 h in hydrofluoric acid and then cleansed in a mixed solution of H_2SO_4/HNO_3 (3:1 ratio) for attaching functional groups such as carboxyl. A mass of 10.5 mg of functionalized MWCNT was added to 100 ml of oleylamine (Aldrich, Tech-Grade 70%) in a 250 ml flask and dispersed in an ultrasonic bath for 3 h. 15 mmol (3.0 g) of copper(II) acetate monohydrate [Cu(ac) H_2O, Aldrich] were added into that flask and then the mixture was sealed and purged with argon for 1 h. The mixture was heated to 523 K and maintained at this temperature for 10 min through heating the flask in a heating mantle with a uniform heating rate of 10 K/min. After slow cooling to room temperature, CNT/Cu-oxide composite powders consisting of CuO and Cu_2O were obtained from the reaction of heterogeneously nucleated Cu oxides on the CNT surface. Then, the CNT/Cu-oxide composite powders were reduced at 573 K for 2 h under hydrogen atmosphere. The obtained CNT/Cu composite powders were precompacted in a graphite mold with 15 mm in inner diameter, followed by spark plasma sintering at 823 K for 1 min in a vacuum of 0.13 Pa with an applied pressure of 50 MPa. The heating rate up to the sintering temperature was 100 K/min. The nanosized Cu powder fabricated by the same process except CNT addition was consolidated into fine grained Cu by spark

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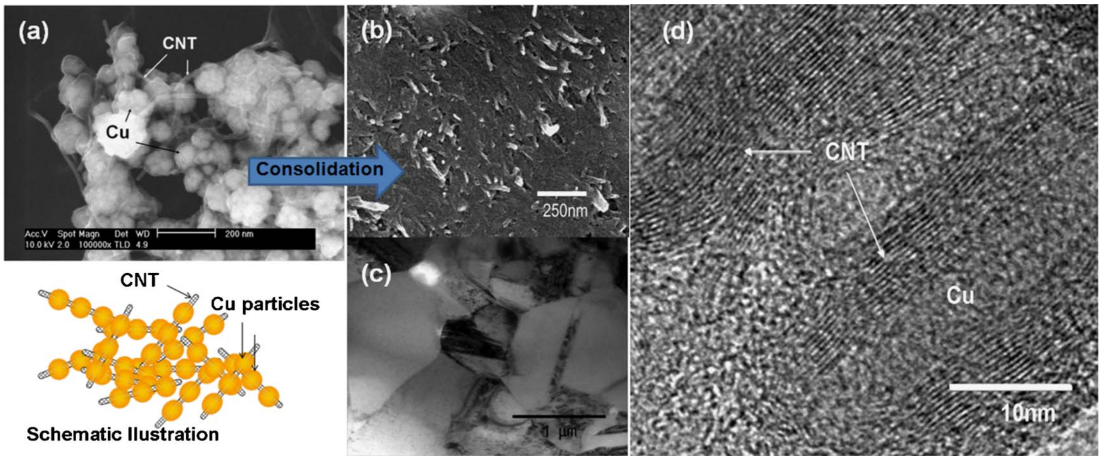

FIG. 1. (Color online) 5 vol % CNT/Cu nanocomposite powder with pearl-necklace-like structure, as shown in the schematic illustration, (a) SEM image, (b) cross-sectional SEM image after consolidation and mechanical polishing, (c) low-magnification TEM image of the nanocomposite showing the grain size of the matrix, and (d) high resolution TEM image revealing the embedded CNTs in the Cu matrix.

plasma sintering. The weight percent of CNTs obtained from elemental analysis (EA1110-FISONS) was converted into volume percent by using the density of 1.8 g/cm^3 of multiwall CNTs (Ref. 6) and the density of 8.9 g/cm^3 of Cu. Here, the weight percent of CNTs is 1.0 wt % for a 5 vol % CNT/Cu nanocomposite. In order to investigate the effect of the matrix grain size, we also fabricated unreinforced Cu and CNT/Cu nanocomposites with large matrix grains of about 4 μm by sintering micrometer-sized composite powder obtained from the molecular-level mixing (see the detailed experimental procedures in Ref. 6).

The room temperature mechanical strength of unreinforced Cu and the CNT/Cu nanocomposite was characterized under compression by using an INSTRON 4206 testing machine with a crosshead speed of 0.2 mm/min. The tested samples had a cylindrical disk shape of 2 mm height and 1.5 mm diameter. The microstructures were analyzed by field emission scanning electron microscopy (SEM) (XL30SFEG), and high resolution transmission electron microscopy (TEM) (JEM-3010, 300 kV) was used for the observation of the embedded CNTs, as well as for evaluating the grain size of the samples. Chemical etching of the Cu and CNT/Cu nanocomposites with large grained matrix was performed by using a mixed solution of 75 ml water with 25 ml HCl and 5 g $Fe(NO_2)_2$ for 15 and 1 s, respectively.[13]

The SEM image of CNT/Cu composite powder with addition of 5 vol % CNTs is shown in Fig. 1(a) together with a schematic illustration depicting the structure of the composite. Similar to the previously observed CNT/Co nanopowders,[12] the composite powders have a pearl-necklace structure where several Cu particles are threaded by a CNT. The cross-sectional SEM image of the fabricated 5 vol % CNT/Cu nanocomposite in Fig. 1(b) shows that the CNTs are homogeneously dispersed and mixed in the Cu matrix. The TEM image in Fig. 1(c) reveals an average grain size of approximately 1.5 μm for the Cu matrix. Moreover, the high resolution TEM image in Fig. 1(d) shows that the CNTs are embedded within the Cu grains. It was already reported that CNT/Cu nanocomposites processed by molecular-level mixing have a strong interface due to the presence of interfacial oxygen atoms supplied from the process.[12,13] The average grain size of the unreinforced Cu (1.5 μm for Cu-1) is very similar to that (1.5 μm for CNT/Cu-1) of the Cu matrix in the nanocomposite (Table I).

The compressive stress-strain curves of unreinforced Cu and CNT/Cu nanocomposites with different matrix grain size, resulting from the size difference of the starting powders, are displayed in Fig. 2(a). As previously suggested, the yield strength of metal matrix composites (σ_c) can be expressed on the basis of the following equation generalized from theoretical models using the load transfer concept[6,14]

$$\sigma_c = \sigma_m(1 + V_f R), \tag{1}$$

where R is the strengthening efficiency of the reinforcement, V_f is the volume fraction of reinforcement, and σ_m is the yield strength of the matrix. The strengthening capability of composites by reinforcements is limited by their volume fraction and the R value defined as $(\sigma_c - \sigma_m)/V_f\sigma_m$ and also limited by the kind of reinforcing agents, such as SiC, carbon fibers, and CNTs.[6] Using more and stronger reinforcements produces a higher yield strength of the composite. The equation reveals that the strengthening of composites by reinforcements occurs parallel to other strengthening mechanisms stemming from hardening of the matrix.

In fact, the yield strength of the CNT/Cu nanocomposites is enhanced by 27% from 360 to 460 MPa when the matrix strength increases from 150 to 190 MPa as the grain size drops from 4 to 1.5 μm. The yield strength of 460 MPa for the 5 vol % CNT/Cu nanocomposite is comparable to the value of 455 MPa obtained for composites with 10 vol % CNT addition and a Cu matrix grain size of 4.5 μm.[13] Apparently, hardening of the matrix by grain refinement without more addition of CNTs causes additional strengthening of the composite. Because we used CNTs of the same purification process and size supplied from the

TABLE I. Comparison of grain sizes, yield strengths, and R values; d_m, average grain size; $\sigma_{0.2}$, 0.2% offset yield strength; and R, strengthening efficiency per unit volume fraction of reinforcement $(\sigma_{c,y} - \sigma_m)/V_f\sigma_m$, (Ref. 6).

Samples	d_m (μm)	$\sigma_{0.2}$ (MPa)	R	Vol % of CNTs
Cu-1	1.5	195	⋯	⋯
Cu-2	4.5	150	⋯	⋯
CNT/Cu-1	1.5	460	27	5
CNT/Cu-2	4.2	360	28	5

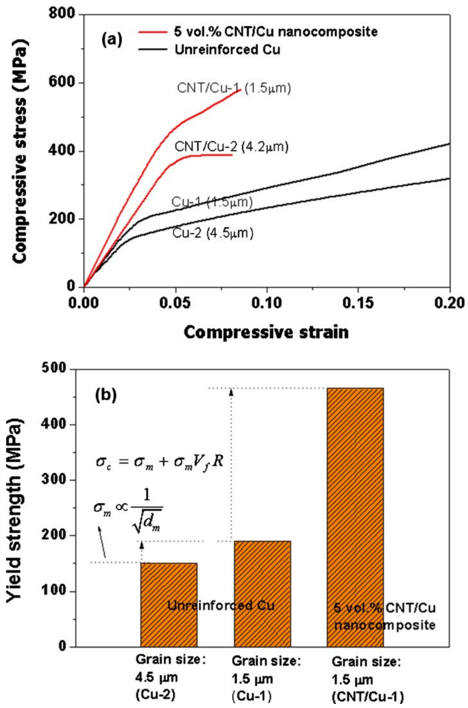

FIG. 2. (Color online) (a) Compressive stress-strain curves for 5 vol % CNT/Cu nanocomposites and unreinforced Cu with different grain sizes. (b) Comparison of the yield strength of unreinforced Cu and 5 vol % CNT/Cu nanocomposites with different Cu matrix grain sizes.

same company in order to study the effect of the matrix, we can corroborate that this strengthening originates from the grain refinement of the matrix. Figure 2(b) reveals that the increase of yield strength occurring for unreinforced Cu originates from grain refinement. The 5 vol % CNT/Cu nanocomposite with fine matrix is additionally hardened by the CNTs besides the strengthening effect of the fine grained metal matrix. Furthermore, it must be considered that the strengthening efficiency of CNTs in CNT/Cu nanocomposites with 1.5 and 4.2 μm grain size, corresponding to CNT/Cu-1 and CNT/Cu-2 in Table I, is calculated to be 27 and 28, respectively. These similar values regardless of the matrix grain size reveal that the hardening of the matrix directly correlates with the increase of the compressive strength of the composite when CNTs are homogeneously dispersed and well bonded with the Cu matrix.

This explanation is clearly proven by Fig. 3, which shows the hardening of Cu materials according to the HP relation $\sigma_m = \sigma_0 + k(1/d_m)^{1/2}$, where σ_m is the yield strength of the matrix, σ_0 is the frictional stress, k is a constant, and d_m is the mean grain size of matrix. Considering the region of nanosized Cu shown at the right hand side in Fig. 3, implies that if the Cu matrix consists of nanosized grains obtained by nanoscale twins[15] and solid solution,[16] a strength of several gigapascals can be achieved for CNT/metal nanocomposites. Furthermore, it is possible to obtain additional strengthening by work hardening of the matrix and alignment of CNTs[17] when rolling, extrusion or severe plastic deformation[18] processes are applied to CNT/metal nanocomposites.

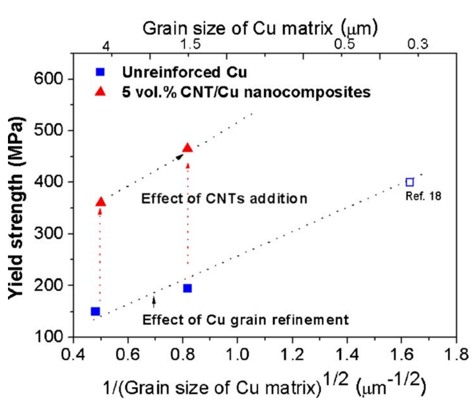

FIG. 3. (Color online) Relationship between yield strength and grain size of the matrix for 5 vol % CNT/Cu nanocomposites showing both strengthening effects by CNT addition and grain refinement.

In summary, we fabricated CNT/Cu nanocomposites by using the modified molecular-level mixing process. The nanocomposites exhibit Cu matrix grains of 1.5 μm in size and significantly enhanced yield strength compared to unreinforced Cu. The strengthening of the CNT/Cu nanocomposites mainly stems from the homogeneously dispersed CNTs within the Cu matrix but also synergistically comes from the effect of refining the matrix grain size. These findings suggest that applying matrix grain size refinement is very effective to obtain high-strength CNT/metal nanocomposites while simultaneously maintaining the strengthening efficiency of dispersed CNTs in a metal matrix.

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