Preparation of Carbon Nanotube Encapsulated Copper Nanowires and Their Use as a Reinforcement for Y–Ba–Cu–O Superconductors

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Copper nanowires with multiwall carbon nanotubes (MWNTs) encapsulated inside were prepared via surface modification of MWNTs followed by chemical deposition of copper on surfaces. These MWNTs-encapsulated copper nanowires were investigated as a reinforcement to improve the mechanical strength of the Y–Ba–Cu–O superconductor. TEM and SEM reveal that MWNTs are uniformly coated by copper and the diameters of the prepared MWNTs-encapsulated Cu nanowires range from 50 to 150 nm and the lengths are up to several micrometers. These MWNTs-containing Cu nanowires could effectively improve the hardness of the Y–Ba–Cu–O without sacrificing its superconductivity. The Vicker’s hardness of the Y–Ba–Cu–O is reinforced by ~20% after 5 wt % of MWNTs incorporation. This study presents the first result that demonstrates the feasibility of the reinforcement of brittle YBaCuO superconductor by using MWNTs.

Introduction

Since Iijima discovered multiwall carbon nanotubes (MWNTs) in 1991,1 MWNTs have drawn much research attention to their application potentials. MWNTs have many uncommon physical properties, such as high mechanical strength and toughness, and are thus suggested to be a promising reinforcement additive for composite materials.2–4 To be used effectively as a reinforcement for composite materials, MWNTs should be homogeneously dispersed in the composite matrix and the interfacial adhesion between MWNTs and the matrix should be strong.5 Unlike some other reinforcements, MWNTs are not soluble in solvents that can help disperse MWNTs in the matrix, and thus MWNTs tend to form bundles or aggregate together during the preparation of the composite. In addition, those liquids with surface tensions higher than 100–200 mN/m do not wet MWNTs.6 This excludes the use of most metal elements as a wetting agent for MWNTs to be dispersed homogeneously in a ceramic matrix7 and to increase the adhesion (or compatibility) between MWNTs and the matrix.8 It has been found that some metal elements such as Ti and Ni having many or few d-vacancies were able to effectively deposit on the single-wall nanotubes (SWNTs) while other metal elements such as Au and Al having no d-vacancies were not.8,9 This was attributed to the existence of strong interaction between Ti (and Ni) and SWNTs leading to partial covalent bonding between the metals and carbon atoms. Au and Al with negligible affinity for carbon interact weakly with SWNTs through van der Waals forces, resulting in an ineffective deposition on SWNTs. Cu chosen as a compatibilizer in this study has no d-vacancy and is not expected to have a strong interaction with carbon according to previous work.9,10 To serve as an effective compatibilizer, thus, Cu needs a different way of depositing on the outer surfaces of MWNTs. Our approach now is to deposit Cu on MWNTs11 through a chemical reaction to address the bonding and wetting issues.

The Y–Ba–Cu–O compound system having a high superconducting temperature (Tc) at 93 K was first discovered by Chu and Wu and co-workers in 1987.12,13 This superconductor, however, is hard but brittle, and its applications are restricted. To improve the mechanical strength of the compound and develop its applications, reinforcement additives may be applied. The

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preparation of Y–Ba–Cu–O superconductor is similar to other advanced ceramics by compressing and sintering certain oxide powders. Incorporation of thermally unstable organic fibers as a reinforcement for the Y–Ba–Cu–O ceramic is limited to poor compatibility and dispersion, may lead to decomposition during sintering, and result in an ineffective reinforcing effect. The superconductivity of the Y–Ba–Cu–O ceramic may thus be destroyed. Therefore, organic fibers are not an effective reinforcement for Y–Ba–Cu–O ceramic materials.

This work is to prepare thermally stable surface-treated MWNTs by depositing Cu on their surfaces as a reinforcement for the Y–Ba–Cu–O ceramics. These surface-treated MWNTs can be well-dispersed in Y–Ba–Cu–O through the compatibilization (or wetting) of Cu, which is expected to be able to diffuse into and interact with the Y–Ba–Cu–O to form strong bondings. In addition, MWNTs can be avoided from thermal decompositions during sintering under air through the protection of metal oxides on their surfaces. Addition of these surface-treated MWNTs can thus lead to an effective reinforcing effect for the Y–Ba–Cu–O ceramic without sacrificing its superconductivity as demonstrated in this study.

Experimental Section

MWNTs were prepared by the arc-discharge method under an argon atmosphere and dc electric field.14,15 The inner core of the deposits on the cathode obtained from the arc discharge of carbon electrodes contains 40–60 wt % MWNTs, which was then purified and functionalized by refluxing with H2SO4/HNO3 (32/ by volume) for 3 h.5,16,17 Carboxylic acid groups were generated on the surface of MWNTs during the purification by the mixture of the strong acids. The carboxyl-functionalized MWNTs were then subjected to surface treatments by depositing Cu on their surface through chemical reactions. In a typical experiment, 8 mg of functionalized MWNTs was suspended in 40 mL of deionized water into the copper nitrate (Cu(NO3)2·3H2O, Showa) was then added until 1.5 mM in concentration. The pH of the resulting mixture was then adjusted by adding triethylamine (N(Et)3), Merck) to the value of ~9.0. The mixture was stirred for 10 min at room temperature, 10 mL of 1 equiv (relative to Cu2+) ion of hydroquinone (Lancaster) was slowly added drop by drop in a period of ~1 h. The precipitated products were changed in color from blue to dark green and finally to yellowish brown. These precipitates, that is, Cu(NO3)2·N(Et)3-treated functionalized MWNTs, were washed by distilled water several times followed by drying. Under a scanning electron microscope (SEM), these yellowish brown precipitated powders exhibit a rodlike shape with diameters in nanometers and lengths in micrometers. These MWNTs-containing Cu nanowires were then calcined in air at 400 °C for 8 h to form CuO on the nanowire surfaces, which exhibit black in color.

The Y–Ba–Cu–O compounds were prepared with nominal compositions represented by YBa2Cu3O7−δ, where δ = 0 or 1 (vide infra), through solid-state reaction of appropriate amounts of yttrium oxide (99.9% Y2O3, Sigma), barium carbonate (99.9% BaCO3, Showa), and copper oxide (99.9% CuO, Showa) powders in a fashion similar to that previously reported.18 To prepare the Y–Ba–Cu–O/MWNTs composites, the CuO powder was premixed via repeated grinding with a certain amount of the black CuO-coated MWNTs-containing Cu nanowires before mixing with Y2O3 and BaCO3. The mixture was ground and then heated in air at 930 °C for 24 h. The grinding and heating procedures were repeated to obtain a thoroughly reacted mixture, which was then compressed into a disk by a high pressure of 1000 kg/cm2 followed by sintering in air at 930 °C for 24 h. The hardness of the prepared composite disks was measured by using a Vicker’s hardness meter (model MV-1, Matsuzawa Seiki Co., Ltd.) at a load of 5 kg. The superconductivity of the Y–Ba–Cu–O/MWNTs composites was measured by using a superconducting quantum interference device (SQUID, Quantum Design, model MPMS5) magnetometer. A transmission electron microscope (TEM) measurements were carried out in a Hitachi 2000FX TEM spectrometer.

Results and Discussion

During purification of MWNTs by H2SO4/HNO3, oxidations of MWNTs can take place at the tip and on the outer shell of the tubes. These oxidations can give MWNTs functional groups, such as carboxyl, hydroxyl, or carbonyl groups (~COOH, ~OH, ~C=O), on the surface of the MWNTs.5,16,17 In this study, the outer shell of MWNTs was oxidized to give carboxylate groups (e.g., MWNTs–COOH) with a concentration of the carboxylate groups on the MWNTs being 0.5 μmol/mg as determined by adjusting the pH value to 11 using 0.01 M NaOH followed by titration using HCl (data not shown). MWNTs–COOH was then subjected to surface treatments by depositing Cu on its surface through chemical reactions. MWNTs–COOH was mixed with copper nitrate (Cu(NO3)2) and triethylamine (N(Et)3) to form copper complex [Cu2(C2O4−(CNT–COO))2] on the MWNT surface19–21 (Scheme 1). The resulted precipitates were blue in color. The adsorbed copper complex was then reduced to copper atoms by 1 equiv of hydroquinone. The reduced copper atoms at the carboxylate sites serve as nucleation sites for the adsorption of subsequently reduced Cu atoms and the growth of copper nanowires. The color of the precipitates was found to change from blue to dark green and finally to yellowish brown.

The prepared yellowish brown products were examined by scanning electron microscopy (SEM). As shown in Figure 1a, the diameter of MWNTs-containing Cu nanowires ranges from 50 to 150 nm and the length can be up to several micrometers. The transmission electron microscope (TEM) image in Figure 1b shows that MWNTs were uniformly coated with copper. EDX measurement of the Cu–CNT nanowires on a nickel
grid shows that the major components of the nanowires are Cu and C (see Supporting Information, Figure S1). To reveal the internal structure of the MWNTs-containing Cu nanowires, the sample was embedded in epoxy resin and cut into thin slices by an ultramicrotome. The TEM image in Figure 1c for the sample slice shows that one Cu nanorod contains several roughly parallel-oriented MWNTs. This indicates that the MWNTs-containing Cu nanowires tend to aggregate and align parallel to each other to form a large diameter of MWNT-containing Cu nanowires. These MWNTs-containing Cu nanowires were then oxidized in air at 400°C for 8 h to form CuO on the surface of MWNTs. This oxidation treatment causes the Cu nanowires to change to black in color.

The solid-state reaction method was applied to prepare the Y-Ba-Cu-O/MWNTs composites. A certain amount of the black CuO-coated MWNTs-containing Cu nanowires were premixed with various amounts of CuO powder and then mixed with appropriate amounts of Y2O3 and BaCO3 powders. The mixture was then ground followed by heat treatments as described previously. MWNTs can be thus well dispersed in the Y-Ba-Cu-O compounds. The dc magnetizations of the so obtained Y-Ba-Cu-O/MWNTs composite and the pristine Y-Ba-Cu-O were measured by a dc superconducting quantum interference device (SQUID) magnetometer. In Figure 2, the temperature dependence of the magnetization was shown as measured with a SQUID magnetometer under an applied magnetic field of 50 G. As can be seen in Figure 2, although the resulting diamagnetic signals are slightly different, the onset temperature (Tc) of superconductivity for the Y-Ba-Cu-O/MWNTs composites is almost the same as that for the pristine Y-Ba-Cu-O compound with a Tc near 93 K. This result indicates that the incorporation of MWNTs insignificantly affects the superconductivity of the Y-Ba-Cu-O composites. X-ray diffraction (XRD) measurements of the Y-Ba-Cu-O composites with and without MWNTs are very similar to each other, and both contain the peaks for orthorhombic YBa2Cu3O7 and tetragonal YBa2Cu3O6 phases (see Supporting Information, Figure S2).
As described previously, the YBa2Cu3O7−δ/MWNTs composites were prepared by sintering at 930 °C in air for 24 h. To reveal if MWNTs were intact in the composites after sintering at such a high temperature, the Y−Ba−Cu−O/MWNTs composites were dissolved in an 8 N HNO3 solution. The residual black precipitate, that is, MWNTs, was then subjected to TEM analysis. As can be seen in Figure 3, oxidative damages were present on the tube walls of some MWNTs, and some nanoparticles were present. It is known that MWNTs without any protection will be completely oxidized to CO2 under air at a temperature above 700 °C.24 Apparently from Figure 3, the CuO-coated MWNTs prepared in this study demonstrate an insignificant decomposition during sintering at high temperature under air. The protection for MWNTs might come from metal oxides that were coated on the surface of MWNTs. The oxygen atoms in metal oxides are in the reduced form (with −2 charges). The reduced form of oxygen dianions does not have the oxidation ability. It is the zero-charged oxygen atoms that have the ability to oxidize carbon nanotubes. Via the protection of metal oxides coatings, the direct contact of MWNTs with molecular oxygen from air can be prevented and MWNTs are able to survive severe oxidation, and thus provide reinforcement for the Y−Ba−Cu−O composites (see results below).

The hardness of Y−Ba−Cu−O/MWNTs composite disks was examined by using a Vicker’s hardness meter. Figure 4 shows the plots of Vicker’s hardness as a function of the content (wt %) of the MWNTs-containing Cu nanowires in Y−Ba−Cu−O composites. The hardness of Y−Ba−Cu−O/MWNTs composite disks was found to increase with increasing content of the MWNTs-containing Cu nanowires in Y−Ba−Cu−O composites. As compared with the unfilled Y−Ba−Cu−O composite, the hardness could be increased by ~20% for 5 wt % of filling of the MWNTs in Y−Ba−Cu−O. To elucidate how

![Figure 3](image-url) TEM image of the residual black precipitate obtained from the dissolution of the Y−Ba−Cu−O/MWNTs composites in an 8 N HNO3 solution.

![Figure 4](image-url) Vicker’s hardness of the Y−Ba−Cu−O/MWNTs composites as a function of the content (wt %) of the MWNTs-containing Cu nanowires in Y−Ba−Cu−O. The error bar is ca. ±8%, as determined by five hardness measurements.

![Figure 5](image-url) SEM images of the fractured Y−Ba−Cu−O/MWNTs composite disk. (a) Some rods were seen to protrude from the fracture surface. (b) Some rods were bridging between two sides of microcracks on the surface of the Y−Ba−Cu−O/MWNTs composites disk.

MWNTs-containing Cu nanowires enhanced the hardness of Y−Ba−Cu−O, the fracture surface of the
composite disk was examined by SEM. As shown in Figure 5a, some rods were found to protrude from the fracture surface. By investigating the microcrack on the surface of the Y-Ba-Cu-O/MWNTs composite disk, it was found that some CuO nanowires bridged between two sides of the cracks (see white arrows in Figure 5b). The incorporation of MWNTs-containing Cu nanowires within the Y-Ba-Cu-O matrix can thus prevent the propagation of the cracking process. The higher content of the added MWNTs-containing Cu nanowires, the higher probability that the extensive cracking can be prevented, and therefore the higher mechanical strength resulted. As a result, MWNTs after surface treatment can be an effective enforcement for the Y-Ba-Cu-O superconductor.

Conclusions

Copper nanowires can be prepared by using surface-modified multiwalled nanotubes as templates. These MWNTs-encapsulated copper nanowires could be an effective reinforcement for the brittle Y-Ba-Cu-O superconductor without sacrificing its superconductivity. Through the protection of metal oxides, the MWNTs were prevented from decomposition during sintering of the Y-Ba-Cu-O/MWNTs composite at 930 °C under air for 24 h. Reinforcement effects were demonstrated by Vicker’s hardness. The hardness of Y-Ba-Cu-O/MWNTs composite disks increases with increasing content of the MWNTs-containing Cu nanowires in Y-Ba-Cu-O with ~20% increase after 5 wt% addition of the MWNTs-containing Cu nanowires in Y-Ba-Cu-O, as compared with the pristine Y-Ba-Cu-O.

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Supporting Information Available: Figures of an EDX spectrum and X-ray diffraction spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. CM020747J