Synergistic Strengthening Effect of Ultrafine-Grained Metals Reinforced with Carbon Nanotubes**

Yong J. Jeong, Seung I. Cha, Kyung T. Kim, Kyong H. Lee, Chan B. Mo, and Soon H. Hong*

The recent application of nanotechnology to structural materials is a promising way to produce new strong materials that exceed current limitations. Grain-size refinement is considered as one of the most effective strengthening methods of materials,[1–5] At the same time, the addition of carbon nanotubes (CNTs)[6–9] in a material is known to be more effective than conventional reinforcements. Here, CNT/Co nanocomposites were fabricated by reinforcing the CNTs in ultrafine-grained Co matrix via a modified molecular-level mixing process. The CNT/Co nanopowders have a structure resembling a pearl necklace, consisting of Co nanoparticles penetrated by CNTs and were fabricated and then consolidated into CNT/Co nanocomposites using spark plasma sintering. The microstructure of the CNT/Co nanocomposite consisted of a three-dimensional (3D) network of CNTs in ultrafine-grained Co matrix with an average grain size of 300 nm. The CNT/Co nanocomposite showed an outstanding yield strength of 1.5 GPa. This indicates that the synergistic strengthening mechanism of homogeneously dispersed CNTs in an ultrafine-grained metal matrix could improve the mechanical properties of materials.

Since the strength is the most important property for structural metals, many attempts have been made throughout history to fabricate stronger metals. Advances in physics and chemistry have been applied continuously to overcome the limitations on the mechanical performance of metals. The recent emergence of nanotechnology has also contributed to the development of strong structural metals. Grain-size refinement to fabricate ultrafine-grained or nanocrystalline metals[1–5] and reinforcement with CNTs[6–9] are known to be one of the most promising methods to strengthen the metals through nanotechnology. Among these, grain-size refinement has characteristic features.[1] The strength of metals increases with decreasing grain size according to the well-known Hall–Petch relationship. When the grain size of metals reaches a submicrometer- and nanoscale,[1–5] very high strengths can be obtained compared to coarse-grained metals with the same chemical composition and phase constitution. There are several ways to fabricate ultrafine-grained or nanocrystalline metals, including the sintering of nanoparticles and the severe deformation of bulk metals.[1–5] Compared to refinement of metal grain size into ultrafine-grained or nanocrystalline ranges, it is difficult to add CNTs to a metal matrix due to the strong aggregation of CNTs and the weak interfacial strength between the metal matrix and the CNTs.[6–8] There is therefore some doubt about the strengthening ability of CNTs in a metal matrix. However, with the development of the molecular-level mixing process,[9] in which CNTs are mixed with a metal matrix in the disperse state in a solvent to form CNT-implanted composite powders, it has been observed that the strengthening efficiency of CNTs in a Cu matrix is extraordinarily high. The CNTs have a strengthening efficiency eight times that of SiC particles and three times that of SiC whiskers.[9] However, despite the considerable strengthening efficiency of CNTs in Cu, the resulting mechanical properties are not impressive; the compound has a yield strength of about 500 MPa, which is similar to values for Al-based alloys. This results from the low yield strength of the matrix, in this case the pure Cu, which has a yield strength of around 100 MPa.[9]

Our strategy to produce a strong metal was to reinforce the ultrafine-grained Co with CNTs, fabricating a CNT/Co nanocomposite in which the metal matrix did not undergo any changes in chemical composition or constituent phase except for the addition of CNTs as reinforcement. To fabricate CNT/Co nanocomposites with an ultrafine-grained Co matrix, we modified the molecular-level mixing process, which was introduced as a unique method of fabricating CNT/metal nanocomposites, to incorporate the concept of nanocrystal fabrication.[10–12] First, the CNTs are functionalized with carboxyl and hydroxyl groups by acid treatment to provide an active site for reacting with metal ions.[13–16] Then, the functionalized CNTs are dispersed within oleylamine by sonication, and Co(II) acetylacetonate is added to this mixture. It has been reported that the transient metal salts are decomposed in oleylamine during refluxing to form oxide nanocrystals.[17] On refluxing in an Ar atmosphere, CNT/CoO composite powders are fabricated in which cube-shaped CoO nanoparticles about 50 nm in size are threaded by CNTs, as shown in Figure 1. For comparison, CoO nanopowders were fabricated under the same conditions without CNTs.

As shown in Figure 1a, and b, the size and shape of the CoO nanocrystals were similar regardless of the addition of CNTs. The X-ray diffraction (XRD) analysis verified the
CoO phase, as shown in Figure 1d. The penetration of CNTs into CoO nanocrystals can be seen in transmission electron microscopy (TEM) images shown in Figure 1c. This penetration is a characteristic feature of powders prepared using molecular-level mixing and enables the homogeneous distribution of CNTs. However, compared to material prepared using the previous molecular-level mixing process, the oxide particles are much finer. In mixtures of CuO and Cu₂O penetrated by CNTs prepared using the previous molecular-level mixing process, the oxide size ranged from several micrometers to tens of micrometers. In contrast, the average particle size of CoO penetrated by CNTs prepared using our modified molecular-level mixing process was about 50 nm, with a narrow size distribution (see Supporting Information for low-magnification TEM micrographs). This improvement arises mainly from the modification of the oxide formation process. In our modified molecular-level mixing process, the CNT/CoO nanopowders are fabricated based on the nanocrystal-fabrication process. Note that the morphology of the CNT/CoO nanopowders is similar to that reported for CNT/Co pearl-necklace-structured composite powders,[18] except that the particles are oxide. However, in CNT/Co pearl-necklace-structured composite powders, the Co nanoparticles move along the CNTs during the sintering process.[19] Although this phenomenon is applied to exposing CNTs on the surface of the Co layer for field-emission display panel, it shows the possibilities of separating CNTs from metal nanoparticles during the sintering process. However, it has been reported that oxide formation on CNTs induces chemical bonding between the functional groups on the CNTs and the oxides, which prevents the movement of nanoparticles on the CNTs and results in a strong interface.[19] The formation of a strong interface is supported by the morphology of the CNT/Co nanopowders, which is obtained by reducing CNT/CoO nanopowders in a H₂ atmosphere at 410 °C, as shown in Figure 2. The morphologies of the reduced Co nanopowders and CNT/Co nanopowders are similar, as shown in Figure 2a and b. Remarkably, the CNTs are not separated from the Co nanoparticles, but penetrate the Co powders in the CNT/Co nanopowders after reduction at 410 °C, where the Co moves along the CNTs if the CNT/Co nanopowders are fabricated directly without oxide formation on the CNTs, as shown in Figure 2c. However, the size of the Co particles increases during the reduction process up to an average of 100 nm and some neck formation between Co particles is observed. The phase of the Co is identified as a face-centered-cubic (fcc) structure based on the XRD analysis in Figure 2(d), which is common in micrometer-sized Co powders. The CNT/Co nanocomposites with an ultrafine-grained matrix and ultrafine-grained Co are fabricated using spark plasma sintering. Although the principles and applications of the spark plasma sintering process are well known, recall that the high heating rate and surface activation that promote the sintering process inhibit grain growth. The microstructures of CNT/Co composites containing 7 vol.% CNTs and ultrafine-grained Co are presented in Figure 3. As shown in Figure 3a and b, the grain size of Co in the CNT/Co composite, about 310 nm, is similar to that of ultrafine-grained Co (350 nm). The scanning electron microscopy (SEM) micrograph in Figure 3c illustrates that the CNTs are dispersed homogeneously in the Co matrix. Furthermore, the high-resolution TEM micrograph in Figure 3d shows that the CNTs are located within Co grains.

CNT/Co nanocomposites with an ultrafine-grained matrix are fabricated using a modified molecular-level mixing process. The CNT/Co nanopowders are fabricated using a nanocrystal-fabrication process, which leads to the formation of an ultrafine-grained Co matrix, in which the CNTs are embedded homogeneously to form a 3D network. The mechanical properties of the CNT/Co nanocomposites...
are shown in Table 1. For comparison, microcrystalline Co specimens were fabricated using both spark plasma sintering and conventional sintering using micrometer-sized Co powders. The compressive yield strength of the microcrystalline Co prepared by spark plasma sintering of micrometer-sized powders is 700 MPa and the average grain size is 2 μm. When the grain size of the Co increases to 15 μm using conventional pressureless sintering, the yield strength decreases to 550 MPa. Conversely, when the Co grain size is reduced to 350 nm using spark plasma sintering of Co nanopowders, the yield strength increases to 970 MPa. Furthermore, when 7 vol. % CNTs are added to the ultrafine-grained Co matrix, the yield strength increases to 1500 MPa, which is comparable to that of ceramics rather than metals. Simultaneously, the elastic modulus increases from 175 to 206 GPa with the addition of 7 vol. % CNTs (the elastic moduli are given in the Supporting Information.) These results clearly prove that the CNT/metal nanocomposite designed using a combination of grain-size refinement of the matrix and the addition of CNTs to the matrix improves the mechanical properties beyond the current limitations of metals.

The enhanced mechanical performance of the CNT/Co nanocomposite with an ultrafine-grained matrix can be seen more clearly in Figure 4. The stress–strain relationship during the compressive test in Figure 4a shows that the strength of the CNT/Co nanocomposites with an ultrafine-grained matrix is vastly superior to that of Co. In addition, the yield strength of Co increases with decreasing grain size. Furthermore, the strain-hardening exponent of the CNT/Co composites with an ultrafine-grained matrix shows, even a little plastic deformation due to 1% porosity after sintering results in a higher yield strength and compressive strength compared to those of Co. However, the increase in yield strength does not have to be connected to an increase in compressive strength, as shown in Figure 4a. Due to the low strain-hardening rate of ultrafine-grained Co, the maximum compressive strength of the ultrafine-grained Co is lower than that with a grain size of 2 μm at strains over 0.13. Furthermore, it is lower than that for a grain size of 15 μm at strains over 0.25, indicating that the ultrafine-grained Co is harder, but not stronger, than microcrystallines. The low strain hardening of ultrafine-grained or nanocrystalline metal has been previously reported,[20,21] but its origin is not clear. As the CNT/Co composite with an ultrafine-grained matrix shows, even a little plastic deformation due to 1% porosity after sintering results in a higher yield strength and compressive strength compared to those of microcrystalline Co.

The hardening with the addition of CNTs is clearly demonstrated in Figure 4b. For Co without CNTs, the yield strength increases with decreasing grain size according to the Hall–Petch relationship, but the yield strength of the CNT/Co composite with an ultrafine-grained matrix is much higher than the value predicted from the Hall–Petch relationship. Considering the increase in both the elastic modulus and yield strength with the addition of CNTs, the strengthening or hardening mechanism should occur due to the load transfer from the Co matrix to the CNTs. However, the calculated strengthening efficiency of the reinforcement is almost 8, which is much lower than the value for CNT/Cu composites with a coarse Cu grain.[9] This originates from the finite strength of CNTs. By applying a shear-lag model, the load shared to one CNT during loading can be calculated as follows under the assumption of perfect bonding at the CNT/metal interface:

\[ \sigma_{\text{CNT}} = \frac{S}{2\pi} \sigma_{\text{matrix}} \]  

where \( \sigma_{\text{CNT}} \) is the stress at the CNT, \( S \) is the aspect ratio of the CNT, and \( \sigma_{\text{matrix}} \) is the stress at the metal matrix.[22]
When the composite yields, $\sigma_{\text{matrix}}$ becomes the yield strength of the matrix. Applying the yield strength of ultrafine Co, that is, 970 MPa, and the observed aspect ratio of 100, the calculated stress on each CNT is almost 50 GPa, which cannot be supported by a single CNT. Therefore, before macroscopic yielding of the composite occurs, it is likely that the interface is debonded or the CNTs are broken into CNTs with a smaller aspect ratio, so that the strengthening efficiency drops. Despite this, the CNT/Co composites with an ultrafine-grained matrix show outstanding mechanical performance in various features beyond the limitations of current structural materials.

In summary, two promising strengthening mechanisms, grain-size refinement of a metal matrix and reinforcement with homogeneously dispersed CNTs, were combined to fabricate strong CNT/Co nanocomposites. Co nanoparticles penetrated by CNTs were fabricated using a modified molecular-level mixing process, and a CNT/Co composite with a nanocrystalline matrix could be fabricated using spark plasma sintering. The CNT/Co nanocomposites with an ultrafine-grained Co matrix and homogeneously dispersed CNTs show synergistic strengthening effects and their mechanical performances are beyond those of conventional metallic materials and are comparable to those of ceramics, rather than metallic materials. In addition, we expect that other metallurgical treatments, including precipitation and adding a solid solution to the matrix, can be used with our product to enhance performance.

### Experimental Section

**Fabrication of CNT/Co nanopowders:** Multi-walled (MW) CNTs, supplied by Iljin Nanotech, with diameters of 10 to 40 nm,
Ultrafine-Grained Co (300 nm) Composite
Reinforced by 7 vol % CNT

Ultrafine-Grained Co (300 nm)

Microcrystalline Co (15 μm)

Microcrystalline Co (2 μm)

Ultrafine-Grained Co (300 nm)

Reinforced by 7 vol % CNT

(a) Stress–strain curves of Co with various grain sizes and CNT/Co composite with an ultrafine-grained matrix during the compression test and (b) the resulting Hall–Petch relationship.

Figure 4.

... were purified and functionalized by acid treatment using HF, H₂SO₄, and HNO₃. The CNTs were stirred for 24 h in HF and then cleansed with a mixed solution of H₂SO₄/HNO₃ in a ratio of 3:1. Then, 9.6 mg of functionalized MWCNTs were added to 80 ml of oleylamine (Aldrich, Tech-Grade 70%) in a reaction chamber and sonicated for 3 h. To this, 8 mmol (2.1216 g) of cobalt(II) acetylatedone (Co(acac)₂, Aldrich) were added and the mixture was sealed in an Ar atmosphere. The mixture was heated to 120°C, maintained for 30 min, and then refluxed for 2 h at 250°C by heating the reaction chamber at a uniform heating rate of 10°C/min⁻¹. After slow cooling to room temperature, the CNT/CoO nanopowders were washed with ethanol and hexane and were separated by centrifugation at 10000 rpm for 10 min. The CNT/CoO nanopowders were dried at 80°C in a vacuum and were reduced by holding for 2 h at 410°C under a hydrogen atmosphere.

Consolidation of CNT/Co nanopowders: The CNT/Co nanopowders were precompacted in a graphite mold under a pressure of 10 MPa. The precompacted powders were consolidated by spark plasma sintering at 650°C for 1 min in a vacuum with an applied pressure of 50 MPa. After spark plasma sintering, the consolidated CNT/Co nanocomposite was 10 mm in diameter and 2.5 mm thick.

Characterization of CNT/Co nanopowders and nanocomposites: Microstructure observation of the CNT/Co nanopowders and CNT/Co nanocomposites was carried out using optical microscopy (LEICA DC200), SEM (Philips XL-30S), TEM, and high-resolution TEM (Tecnai 20F). The volume fraction of CNTs was determined by analyzing the carbon content using an elemental analyzer (Fisons EA1110) and a C/S analyzer (ELTRA CS800). Compressive tests were performed using an Instron 5583 with a crosshead speed of 0.2 mm min⁻¹ using cylindrical disk-shaped specimens 2.5 mm thick and 2 mm in diameter.

Keywords:
carbon nanotubes · mechanical properties · metallic materials · nanocomposites