Fabrication Processes and Multi-functional Properties of Carbon Nanotube/Inorganic Nanocomposites

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ABSTRACT

Multi-functional CNT(Carbon Nanotube)/Inorganic nanocomposites were fabricated by Molecular Level Mixing Process. The microstructures and properties of various CNT/Inorganic nanocomposites were reviewed and studies on the relationship between the properties and the microstructures were introduced.

Keywords: carbon nanotube, nanocomposites, fabrication process, molecular level mixing process

1 INTRODUCTION

The critical issues on the development of CNT/Inorganic nanocomposites are homogeneous dispersion of CNTs within an inorganic matrix and interfacial bonding between CNTs and the inorganic matrix. Among the various process for fabrication of CNT/Inorganic nanocomposites, the Molecular Level Mixing Process have shown the most promising results to solve the critical issues. In this study, microstructures and multi-functional properties of CNT/Inorganic nanocomposites fabricated by Molecular Level Mixing Process will be reviewed.

2 EXPERIMENTAL PROCEDURES

The basic concept of the Molecular Level Mixing Process is to functionalize CNTs for dispersion and to mix them with inorganic molecules (ions) in a solution bath[1-4]. In order to oxidize or to reduce the inorganic molecules, various approaches such as calcination, thermal decomposition, reducing by chemical reagents (aldehydes, polyols, hydrazines) and reducing by gases can be adopted. Thus, various processes can be developed on the basis of the Molecular Level Mixing Process in order to obtain designed structures and properties of the CNT/Inorganic nanocomposites in nano scale. In further processes, spark plasma sintering was used for the consolidation of CNT/Inorganic nanocomposite powders. Especially, and spray coating process was developed for fabrication of CNT/Inorganic nanocomposite film for field emission application.

3 RESULTS AND DISCUSSION

3.1 Microstructure of CNT/Inorganic Nano-composite Powders

Various type of the CNT/Inorganic nanocomposite powders fabricated by Molecular Level Mixing Process were shown in Fig. 1. In case of CNT/Cu2O nanocomposite powders, the microstructure shows an implanted type structure in which CNTs are implanted in a Cu2O particle as shown in Fig. 1(a). In case of CNT/Ni nanocomposite powders, the microstructure shows a coated type structure in which CNTs are coated with Ni layer as shown in Fig. 1(b). In case of CNT/Ag nanocomposite powders, the microstructure shows a decorated type structure in which Ag nanoparticles are decorated on the surface of CNT. In case of CNT/Co nanocomposite powders, the microstructure shows a necklace type structure in which Co nanoparticles were threaded by a CNT. The microstructures of CNT/Inorganic nanocomposite powders can be controlled and they can be used for multi-functional applications according to their unique properties based the microstructures.

Fig. 1. Microstructures of various types of CNT/Inorganic nanocomposite powders fabricated by Molecular Level Mixing Process, (a) implanted type CNT/Cu2O, (b) coated type CNT/Ni, (c) decorated type CNT/Ag, (d) necklace type CNT/Co nanocomposite powders.
3.2 Mechanical Properties of CNT/Cu Nano-composites

The mechanical properties of CNT/Cu nanocomposite were characterized by compressive test. The CNT/Cu nanocomposites were sintered by spark plasma sintering after reduction of CNT/Cu$_2$O nanocomposite powders fabricated by Molecular Level Mixing and Controlled Oxidation Process [5]. Compressive stress-strain curves of the Cu and CNT/Cu nanocomposites are shown in Fig. 2. The compressive yield strengths of the Cu and CNT/Cu nanocomposites increased with increasing CNT vol.%. It is notable that the CNT/Cu nanocomposites did not fracture even at a strain level of 60%, while the CNT/Cu nanocomposites fabricated by the molecular-level mixing process fractured before 20% elongation [1]. Such a ductile compressive behavior can be attributed to the reduced oxygen content resulting from the controlled oxidation process. It was reported that CNT/Cu oxide nanocomposite powders obtained by the molecular-level mixing process have a mixed phase of CuO and Cu$_2$O [1]. After reduction, the oxygen contents of the CNT/Cu nanocomposite powders were 1-2 wt.% [7], and the CNT/Cu nanocomposites showed quite brittle fracture even in compression testing [1]. However, the oxygen contents of CNT/Cu nanocomposites fabricated using both the molecular-level mixing and controlled oxidation processes were below 1 wt.% [5].

![Compressive stress-strain curves of CNT/Cu nanocomposites](image1)

Fig. 2. Compressive stress-strain curves of CNT/Cu nanocomposites [5].

The wear properties of CNT/Cu nanocomposite were characterized. The Pin-on-disk type wear tests were performed to evaluate the wear resistance under dry sliding condition. The sintered CNT/Cu nanocomposite has the cylindrical shape of 15mm diameter and 3mm height. Under dry sliding wear condition, the wear rate of CNT/Cu nanocomposites is reduced to about 1/3 compared to those of pure Cu matrix. This result means that this nanocomposite shows three times higher wear resistance by addition of CNTs. In case of pure Cu during the wear process, the worn chips are formed by peeling of Cu grains.

However, in case of CNT/Cu nanocomposite, the Cu grains are not easily peeled from the worn surface by the pinning of homogeneously implanted CNTs across Cu grains. At the same time, the CNTs exposed to the worn surface during wear process can act as a lubricant owing to its low friction coefficient. Therefore, the wear rate of CNT/Cu nanocomposites is remarkably decreased with increasing volume fraction of CNTs due to the reinforcement effect and lubricant effect of CNTs [7]. Thus, it is quite promising to use CNT/Cu nanocomposites for wear resistant material applications.

![Wear rate of CNT/Cu nanocomposites characterized by pin-on-disk](image2)

Fig. 3. Wear rate of CNT/Cu nanocomposites characterized by pin-on-disk [7].

3.3 Field Emission Properties of CNT/Co Nano-composites

CNT/Metal nanocomposite powders can be applied to not only structural material but also functional materials such as field emitter. In order to fabricate the field emitter, the necklace type CNT/Co nanocomposite powders were spray coated on ITO (indium tin oxide) glass. Spray coating requires neither organic binders, which deactivate CNTs, nor a mechanical mixing, which destroys CNTs. Thus, the surface of CNTs can remain clean and maintain a straight shape for field emission without any post-treatment such as taping or rubbing.

The field emission stability over 4 hours was measured under constant electrical field condition. Fig. 4 shows that the spray coated CNT/Co nanocomposite field emitters are more stable than screen printed CNT/Co nanocomposite field emitters.

Mechanisms for current degradation of CNTs are known as field evaporation by resistive heating, detachment by electrostatic charge, ion bombardment. Defective CNTs have relatively high resistivity due to scattering resulting in high resistive heating. Raman spectroscopy is used to determine the relative amount of defects in CNTs after each process step. As a result, it is confirmed that the amount of amorphous carbon of spray coated CNT/Co nanocomposite...
field emitter is much smaller than that of screen printed CNT/Co nanocomposite field emitters.

K. Anazawa et al. reported that defect-free and high purity CNTs can transport current density as high as $10^{11}$ A/m$^2$ while defective CNTs showed electrical breakdown at low current density as small as 8X$10^9$ A/m$^2$.[9] It means that defects of CNTs would suppress the maximum current density, since atomic disordering of CNT walls causes scattering of electric carriers through CNTs. In addition, P. Vincent et al. reported that temperature around CNT tip can reach ~2,000K [10] by resistive heating of CNT. Resistivity of CNTs would increase with increasing amount of defect in CNT walls. These reports are supporting the reason why CNT/Co nanocomposite field emitters with less defects by in-situ spray coating shows better field emission properties than those with more defects by screen printing.

**Fig. 4.** Field emission stability of CNT/Co nanocomposite field emitters [8].

4 CONCLUSIONS

Various types of CNT/Inorganic nanocomposites with homogeneous dispersion of CNTs and strong interfacial bonding were fabricated by using Molecular Level Mixing Process. For structural application, CNT/Cu nanocomposites showed much enhanced mechanical properties such as yield strength and wear resistance with increasing CNT volume percent. For functional application, CNT/Co nanocomposite field emitters were fabricated and field emission stability was increased by using spray coating due to minimized defects of CNTs. It is highly expected that the Molecular Level Mixing Process can contribute not only for development of high strength/modulus structural components but also for development of various functional materials such as field emitters, EMI shielding materials and electrode materials for energy storage and conversion applications.

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