**1 General introduction**

Mechanically strong metal composites have attracted interest recently due to green energy requirements. Although aluminum is known as a rust-free light material and is used in car parts and buildings, its use is still limited mainly due to its poor mechanical strength as compared to its iron counterpart. A CNT-based Al composite with enhanced mechanical strength could be utilized to improve the fuel efficiency of vehicles by reducing the vehicle weight. Its applications may be further extended to electronic parts, ships, aircrafts, and satellites. Therefore, the robust formation of CNT-Al composites is desired.

There have been several research studies aimed at improving the mechanical strength of Al by incorporating CNTs. CNTs are not easily mixed with Al due to the large difference of the surface tension between the two materials as the surface tension of Al is 955 mN/m, which is almost 20 times larger than that (45.3 mN/m) of CNTs. One additional technical barrier to formulate CNT-Al composites with high mechanical strength is the high oxidation capability of Al which causes Al particles to be easily oxidized and lose their metal characteristics. Because of these difficulties, the wettability of Al on the CNT surface has been extremely difficult to realize.

Therefore, the issue remains of how to overcome the large difference of surface tension and improve the wettability of Al on the CNT surface, which can be a facile approach to generate CNT-Al composites with high mechanical strength. In this study, we adopted the strategy of forming strong Al-C covalent bonding between Al and the CNT surface. For this, we applied an electroplating method to coat Al nanoparticles on vertically aligned multiwalled CNTs, which eventually enhances the wettability of Al on the CNTs. Strong covalent bonds were formed between Al and the CNT surface during the electrodeposition. This led to an enhanced wet Al powder. Defect-associated nucleation of Al on the CNT surface was observed by Raman spectroscopy and X-ray photoelectron spectroscopy.

**2 Material and methods**

**2.1 Synthesis of vertically aligned carbon nanotubes**

A thin Ni layer of less than 100 nm was deposited onto a TiN/Si (100) substrate using an RF magnetron sputter. The substrate temperature during Ni deposition was maintained by a graphite heater at a pressure of 1 x 10^{-6} Torr. The CNTs were grown on Ni-coated TiN/Si substrates using thermal CVD at 650°C with a gas mixture with C_2H_2 (20%) and Ar (80%).

**2.2 Al electroplating**

The electrolyte was prepared by dissolving 1.17 M anhydrous aluminum chloride into a mixture of two solutions of THF:benzene = 8:2. The electroplating cell consisted of three electrodes: vertically aligned carbon nanotube as a working electrode, Pt mesh as a counter electrode, and Ag/AgCl as a reference electrode.
2.3 Al wetting

Al powder (Samjeon Chemicals, Korea) with a size of 75 μm was placed on top of vertically aligned multiwalled carbon nanotubes which were electroplated by Al as described above. This structure was then heat-treated at 700 °C for 1 hour in a vacuum furnace (10⁻⁵ Torr).

3. Result and Discussion

3.1 Schematic diagram of experimental procedure.

Fig. 1. Schematic diagram of the Al wetting process on a CNT: (a) vertically aligned CNT, (b) Al electroplating, (c) loading of Al powder on top of the vertically aligned CNT, and (d) formation of the Al/CNT composite by heavy Al wetting.

Figure 1 shows a schematic of the experimental procedure used to improve the wettability of additional aluminum powder after electroplating of aluminum on multiwalled carbon nanotubes (MWCNTs) to form Al-CNT covalent bonds. Vertically aligned MWCNTs were decorated with Al nanoparticles by an electroplating method. The synthesized MWCNTs had diameters of 40-50 nm and lengths of 3-5 μm, depending on the growth time. Al nanoparticles were strongly adhered on the outer MWCNT walls due to the formation of strong Al-C covalent bonds. Additional Al powder was then spread on top of the vertically aligned MWCNT film and further annealed at 700 °C for an hour to fully accommodate the wetting of additional Al.

3.2 Plating phenomena and morphology analysis.

Fig. 2. Cyclic voltammetry and current-time transient analysis: (a) CV characteristics of the aluminum plating solution, and (b) CV characteristics without LiAlH₄. (c) the low potential current-time transient for 10 s at -2 V to -5 V vs. Ag/AgCl, and (d) the high potential current-time transient at -1.6 V to -2 V vs. Ag/AgCl.

Figure 2a shows current-voltage (CV) data obtained with the aluminum plating solutions. With a solvent of THF and benzene only, a negligible current (~ 4 μA) along with linear behavior of the CV data (inset of Fig. 2b) was observed, confirming insignificant chemical reaction of solvent with a bias up to -3 V. The conductivity of the solvent is poor and therefore, no active ionic motion is expected, resulting in simple resistor behavior. By adding AlCl₃, the current level increased to the order of mA (Fig. 2b) but still remained low. AlCl₃ was dissolved in the solvent to some degree and Al ions were further adsorbed on the surface upon bias but no apparent reduction peak was observed, as shown in Figure 2b. Actual coating involving reduction of Al ions took place when catalytic LiAlH₄ was added. The current level was increased to 50 mA at -3 V. The reduction of Al ions was clearly observed and began at -1.5 V, as indicated in the inset of Figure 2a.

Figure 2c and 1d show the current-time transient behavior in the early stage of coating. At a low voltage (-1.6 V) still above the reduction voltage, the current profile is composed of three steps: step I involves formation of the electric double layer on the electrode, corresponding to a fast decrease of current, step II represents the reduction reaction of ions in the electrode that gives rise to a gradual increase of current, and step III involves a diffusion-limited current corresponding to saturation of nucleation sites for the reduction of ions.
Figure 3 shows the XRD pattern obtained after electroplating for 5 minutes to confirm the formation of Al crystals. As the voltage increased, Al crystal peaks were clearly observed near 38.5° (111) and 44.7° (200). This clearly confirms Al reduction to form Al crystals.

Figure 4. Morphologies after Al electroplating as examined by SEM and EDS mapping: top views of the (a) pristine MWCNT, and Al-MWCNT by electroplating at (b) -3 V and (c) -5 V for 5 min, (d) side view of the sample electroplated at -3 V, and EDX mapping observations of (e) C and (f) Al.

The SEM morphologies of the Al-coated MWCNTs are shown in Figure 4. The pristine MWCNTs contain carbonaceous particles and nanotubes are entangled on the top part (Fig. 4a). The size of the Al particles at -3 V was around 100 nm (Fig. 4b). At -5 V, the carbon nanotubes were completely covered by Al particles (Fig. 4c). The side view of the Al-coated MWCNTs at -3 V is shown in Figure 4d, demonstrating uniform deposition of Al particles, even at the bottom positions. This was confirmed by the EDX mapping for carbon and aluminum (Fig. 4e-4f). Al particles were uniformly coated over the vertically aligned MWCNTs, independent of the depth.

3.3 Morphology analysis after wetting of additional Al powder.

Fig. 5. Morphology changes after heavy Al wetting: (a-c) the pristine CNT without Al electroplating, (a) top view, (b) side view, and (c) enlarged side view of the white square in (b), and (d-e) the corresponding morphology changes with wetting after Al electroplating at -5 V for 5 min. (g) TEM image after heavy Al wetting, and element mapping of (h) C and (i) Al.

The morphologies of the pristine MWCNT film are shown in Figure 5a-5c. Al powder placed at the top of the pristine MWCNTs remained intact even after the melting of Al. The side view of the MWCNTs clearly shows no wetting of Al on the surface of the MWCNTs. This is expected from the large difference of the surface tensions of both materials and the hydrophobicity of the CNTs. On the other hand, Al powder placed on top of the Al-coated MWCNTs by electrochemical deposition was well melted into the vertically aligned MWCNTs forest. The MWCNTs were cracked and aggregated after wetting, as shown in Figure 5d, where the inset clearly shows a crack formed near the Al wetting area. This phenomenon is ascribed to the volume contraction of melted Al (~22%) during cooling. The side view of the wet area demonstrates that Al was smeared into the side of the MWCNTs forest (Fig. 5e-5f). MWCNTs were embedded into the Al matrix, as shown in the inset of Figure 5f.
MWCNTs scratched from the sample were further sonicated and dropped onto a TEM grid. Al was uniformly coated over all of the MWCNTs, as confirmed by EDX mapping (Fig. 5g-5i). MWCNTs still remained intact even after annealing at 700 °C for an hour.

3.4 Al-C covalent bond analysis by Raman and XPS

![Fig. 6. Al-C covalent bond analysis: (a) Raman spectroscopy analysis in terms of electroplating voltage, (b) D/G intensity ratio (black) and G-band peak shift (blue), (c) Al2p XPS peak after Al electroplating at -5 V for 5 min, and (d) Al2p peak after further heat-treatment at 700 °C for 1 h.](image)

Information for the presence of defects can be found in the Raman spectra. Figure 6a shows a D-band near 1,330 cm⁻¹ and a G-band near 1,590 cm⁻¹ in the pristine sample, which corresponds to contributions from sp³-like defects on the CNT wall or amorphous layers and sp²-like graphitic hexagons, respectively. Interestingly, the intensity of the D-band and the D/G ratio decreased gradually with increasing electroplating bias, as shown in Figure 6b. This implies that the defect density decreased with Al deposition.

The G-band peak was upshifted with increasing bias. This is evidence of electron transfer from the CNTs to Al where Al³⁺ ions are reduced to neutral Al atoms by accepting electrons from the CNTs.⁹

To understand the bonding characteristics, XPS was also performed for the sample obtained at -5 V. Figure 6c shows the Al 2p peak for the Al-coated MWCNTs. This peak was deconvoluted into three peaks: Al metal near 72.8 eV (areal intensity: 5.3%), the Al-C bond near 75.2 eV (39.5%), and the Al-O bond near 75.8 eV (56.2%). The formation of about 40% Al-C bonds is consistent with the large D band intensity in the Raman spectra.

4. Conclusion

In this report, Al-C covalent bonding was formed by electrodeposition of Al and additional Al powder was further wet. Al deposition was confirmed by SEM, EDX mapping, and XRD. Al-C covalent bonds were formed via defects and were confirmed by Raman spectra and XPS. With Al electrochemical deposition, the D-band intensity decreased with increasing deposition voltage, while the G-band peak was upshifted.

References


