

## Carbon Nanotube/Aluminium Composites with Uniform Dispersion\*

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Carbon nanotubes (CNTs) are attracting much interest as fibrous materials for reinforcing metal matrix composites due to their remarkable properties such as very high strength, elastic modulus, flexibility and high aspect ratios. However, due to the intricate entanglements of long and fine CNTs and resulting aggregation, disentanglement and uniform dispersion of CNTs in aluminium (Al) matrices have been found quite difficult. In addition, the poor wetting property of carbon for Al has been a great obstacle to forming composites. On a totally new principle, we succeeded in producing nano-scale composites in which carbon nanotubes were uniformly dispersed in Al matrices. We named this method Nano-Scale Dispersion (NSD) method, which can also be employed to disperse various fillers such as whiskers, ceramic fibres, and powders in metal matrices as well as Al. The composites obtained were found to be highly reinforced and not to melt at a temperature far above the melting point of Al. Here we report the procedure of their fabrication and mechanical properties.

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### 1. Introduction

Light metals such as Al and magnesium (Mg) have been studied with much attention as structural materials, though they lack in strength and rigidity compared with iron. CNTs are attractive reinforcement materials for metal matrix composites not only due to their high strength and elastic modulus, but also due to their exceptionally small diameters.<sup>1)</sup> This is because, when the same weight of CNTs is contained in composites, the number of CNTs in a composite increases as the diameter of CNTs becomes smaller. And, when the CNTs are uniformly dispersed in the composites, the respective matrix domains enclosed by the CNTs become extremely small. We expected that this condition might produce a strong effect on the matrix metal and cause a totally new reinforcement system.

In the current process, however, when CNTs are mixed into Al melt, due to the poor wetting properties of CNTs and difference in their densities, CNTs immediately rise to the surface without being mixed. In order to overcome these problems, the mixture of Al powder and CNT aggregates was hot-pressed,<sup>2,3)</sup> but the tensile strength of the non-annealed composites was found to be lower than that of pure Al due to the residual stresses caused by CNTs.<sup>3)</sup> Authors developed NSD method which enabled the fabrication of nano-composites in which CNTs were uniformly dispersed in Al matrices. The process comprises two steps: in the first step, a precursor in which CNTs were uniformly dispersed in an elastomer matrix was prepared; and in the second step, the elastomer matrix was displaced by Al. This method also has the potential to produce new advanced functional materials in which various fillers are uniformly dispersed in various matrices.

### 2. Experimental

In order to examine the dispersion of CNTs in elastomer matrices, prior to the fabrication of CNT/Al composites, CNT/elastomer composites were prepared. CNTs used were multi-wall carbon nanotubes (MWCNTs) with average diameter of 13 nm (ILJIN Nanotech Co.Ltd.). The length of them was reported to be 10-50  $\mu\text{m}$  by the manufacturer. Elastomers used were natural rubber (NR) and ethylene-propylene rubber (EPDM). 20 g of MWCNT powder and 2 g of 1,3-Bis(t-butyl peroxyisopropyl) benzene were gradually added and mixed in succession into 100 g of respective elastomers on a six-inch two-roll mill at a mill opening of 2 mm. With the mixture temporarily removed, the nip was tightened to 0.1 mm. The mixture was then replaced and subjected to 10 passes through the mill. The compounds obtained were cured at 175°C for 20 minutes.

For the fabrication of MWCNT/Al composites, precursors of MWCNT/Al composites were prepared in the first step. 500 g of Al powder (99.85% purity, 28  $\mu\text{m}$  grain size), 10 g of Mg powder (99.8% purity, 45  $\mu\text{m}$  grain size), and a required amount of MWCNT powder were gradually added and mixed in succession into 100 g of NR following fabrication procedure of MWCNT/elastomer composites except that the precursors were not cured. Al powder was mixed in order to cause capillary actions in the second step. MWCNT powder mixed into a precursor was of either 10 g or 20 g, which turned out to be 0.8 vol% or 1.6 vol% of MWCNT/Al composites. The precursors were sheeted into slabs of 2 mm thickness, placed in moulds in several layers, and formed into blocks of 30 mm  $\times$  40 mm  $\times$  20 mm in size by compression moulding at 80°C.

In the second step, on top of a block of each precursor, a plate of pure Al (99.85% purity, 30 mm  $\times$  40 mm  $\times$  10 mm in size) was placed and heated in a furnace in a nitrogen atmosphere. The temperature was gradually raised and kept at 800°C for one hour. The specimens were then gradually cooled, and thus an MWCNT/Al composites were obtained. The morphologies of the MWCNT/elastomer and MWCNT/

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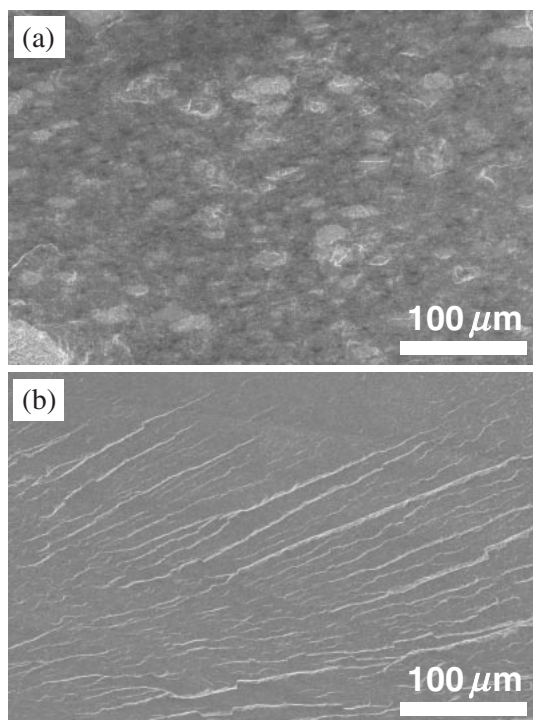


Fig. 1 Scanning electron micrographs of fracture surfaces of MWCNT/elastomer composites demonstrating the dispersion of MWCNTs in (a) EPDM matrix and (b) NR matrix.

Al composites were investigated by an optical microscope (Metal Microscope EIPHOT TME300, Nikon Corporation) and a scanning electron microscope (FE-SEM S-4700, Hitachi Ltd.) under an acceleration voltage of 3 KV. These composites were cut into blocks of 10 mm × 10 mm × 5 mm in size. The stress-strain curves for the MWCNT/Al composites, a specimen whose precursor was prepared without MWCNTs, and pure Al were obtained by compressing the composites at a rate of 0.01 mm/min using a compression tester (AUTOGRAPH AG-1, Shimadzu Corporation).

### 3. Results and Discussion

Figure 1 shows the SEM images of the fracture surfaces of MWCNT/elastomer composites. It is assumed that the poor dispersion of CNT in the EPDM matrix<sup>4,5</sup> exhibited a non-uniform fracture surface (Fig. 1(a)) while there is an uniform fracture surface in the case of CNT dispersed in the NR matrix (Fig. 1(b)) with good dispersion.<sup>4,5</sup>

MWCNT/Al composites obtained through NSD process had metallic lustre on their cross sections, suggesting that elastomer molecules had been thoroughly removed and the composite entirely metallized. Figure 2(a) shows the optical micrograph of the cross section of MWCNT/Al composite. Islands with a lighter colour in the image are Al powders mixed during the preparation of the precursor, and a few black spots are voids in the composite. The sea having a greyish colour is composite matrix, whose colour suggests the dispersion of MWCNTs. The greyish areas in the islands are MWCNTs flowed into the Al powders with Al melt caused by the heating in the second step. Aggregations of MWCNTs were not found. The SEM image of the fracture

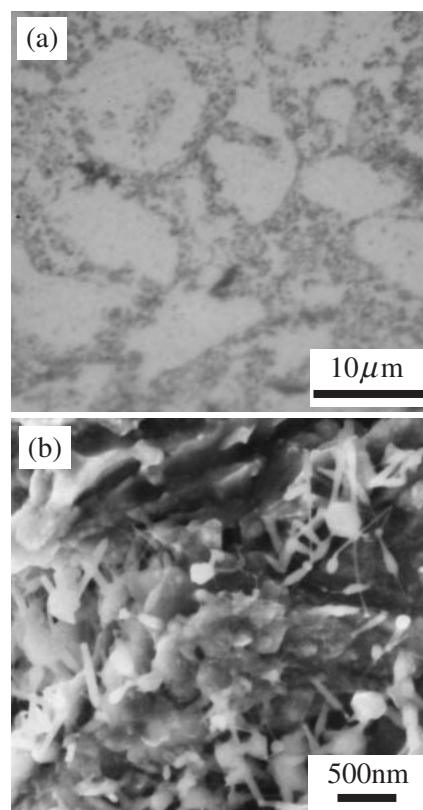


Fig. 2 (a) Optical micrograph of the cross section of MWCNT/Al composite. (b) Scanning electron micrograph of the fracture surface of MWCNT/Al composite.

surface of the composite in Fig. 2(b), which magnifies the matrix area, demonstrates that MWCNTs were well dispersed. From these facts, we assumed that Al melt, by capillarity, permeated the precursor through the capillaries formed by Al powders and MWCNTs, and that, with the temperature rise caused by the approaching Al melt, NR molecules were decomposed and removed in the form of gas. The Al powder mixed into the precursor was originally covered with Al oxide, but the optical micrograph demonstrates that the Al oxide layer on the surface of Al powder was destroyed, and, accompanied by MWCNTs, the permeated Al melt flowed into the Al powder. We assumed that these phenomena were induced by the radicals generated from the decomposed NR molecules, which reduced Al oxide and destroyed the Al oxide layer. The SEM image of the fracture surface displays no traces of holes which would be left if MWCNTs had been pulled out of the matrix, suggesting that MWCNTs were not pulled out but broken when the composite was fractured. The image also shows the adhesion of Al to the surfaces of MWCNTs. These observations suggest that Al and MWCNTs, naturally having poor affinity for each other, showed good wetting in our process. The improvement of wetting property of MWCNTs for Al was considered to have been caused by the above-mentioned radicals resulting from the decomposed NR molecules, which reacted on the MWCNTs and activated the surfaces of them.

Figure 3 shows the stress-strain curves for MWCNT/Al composites obtained through compression tests. For the

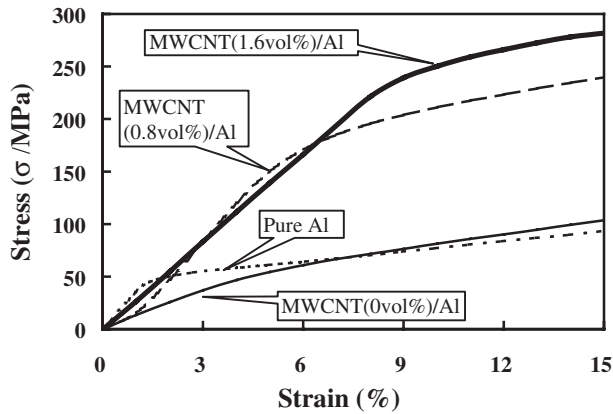


Fig. 3 Stress-strain curves in compression tests for MWCNT/Al composites: (—) composite whose precursor was prepared without MWCNTs, (-----) composite prepared with 0.8 vol% of MWCNTs, (—) with 1.6 vol% of MWCNTs, and (· · · · ·) specimen of pure Al.

composite whose precursor was prepared without MWCNTs, the strain at the elastic limit was increased, but the stress-strain curve showed no great difference from that for pure Al. In contrast, in the cases of MWCNT/Al composites, while the shapes of stress-strain curves were similar to that for Al, the compression stresses were remarkably increased, and the strains at the elastic limits were also multiplied. With the loading of 1.6 vol% of MWCNTs, the proof stress ( $\sigma_{0.2}$ ) was enhanced about sevenfold. In respect of CNT/polymer composites, although a larger number of reports have been made on them compared with those for CNT/metal composites, effective reinforcement caused by CNTs have not been found.<sup>6,7)</sup>

Through NSD method, with the addition of very small amount of MWCNTs, the mechanical properties of the composites were largely enhanced and the melting behaviour

was noticeably changed. We considered that this method is capable of causing uniform dispersion of MWCNTs and improving wetting property of MWCNTs for Al, which will be conducive to the application of nano-composites. The mechanism of reinforcement and changes in melting behaviour, however, cannot be simply explained through the mixing effect. We assumed that these results were caused not only by the extraordinary mechanical properties of MWCNTs, but also, as we mentioned at the beginning, by Al matrix domains having been confined by MWCNTs on nano-scale. The details of these mechanisms will be reported in the next publication.

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