MICROSTRUCTURE AND MECHANICAL PROPERTIES OF CARBON NANOTUBE REINFORCED ALUMINUM

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ABSTRACT Carbon nanotube reinforced aluminum (Al) composites were produced by hot-press and hot-extrusion methods. Microstructure of the composite was examined by transmission electron microscope (TEM) and the mechanical properties were measured by tensile test. TEM observations have shown that the nanotubes in the composites are free from damage during the composite preparation and that no reaction products at the nanotube/Al interface are visible after annealing for 24h at 983K. The strength of the composites is little affected by time of annealing at 873K, while that of the pure Al produced in a similar powder metallurgy process decreases significantly with the time. Some irregularity is observed on the fractured surface of the heat-treated composites. TEM observations have revealed that nanotubes are embedded in Al matrix and the rupture occurs along the embedded nanotubes. The studies are considered to yield experimental bases to produce high performance composites.

Keywords: *carbon nanotube, aluminum, composite, extrusion, interface reaction, transmission electron microscope, tensile test*

1. INTRODUCTION

The engineering application of the carbon nanotube as a new fiber material has been expected because the material exhibits a extremely high elastic modulus[1-3]. Recently, we have found that the nanotube is not brittle but deforms plastically under bending stress at room temperature[4-7]. Owing to these mechanical properties, nanotube is an ideal fiber for the composite reinforcement. In conventional carbon fiber/Aluminum (Al) composites, Al carbide (Al_4C_3) grow on the prism plane of the carbon fiber. The reaction is serious because the formation of a sharp notch on the fiber by attack of growing Al_4C_3 needles results in a drastic decrease of the composite strength[8]. The Al_4C_3 may decompose by subsequent hydrolysis and oxidation into more brittle phase, further reducing of structural integrity of the composite. In contrast to that, however, it is expected that the nanotube/Al system is free from such a chemical reaction problem and can be produced by plastic working process.

In this study, we try to produce the nanotube reinforced Al composite by a powder metallurgy process in order to demonstrate a possibility of the application of the nanotube to an engineering material, focusing on microstructure and mechanical properties of the composites.

2. PROCEDURE

2.1 Processing of the composite

Nanotubes were synthesized by carbon DC arc-discharge[9]. A cathodic debris formed on a graphite block contained both nanotubes and other concomitants such as graphitic particles or amorphous carbons. Nanotubes were purified by ultrasonic processor and centrifugation in a disperse medium from the fibrous masses taken from the debris. Nanotubes of 90% purity were obtained in bundles by the process. The density of nanotube was assumed to be $2.0 Mg/m^3$. Al powders (99.99% purity, 40 μ m in grain size) mixed with 5 or 10 vol% nanotube (5 or 10% composite) were encapsulated in Al case. The cases were preheated for 1.5h at 873K in a vacuum of 5.3×10^{-1}Pa and then compressed with 30MPa in carbon dies for 60 min. The obtained composites were extruded at 773K to rod with 7mm in diameter (extrusion ratio 25:1).

The relative density of the composites were measured by the Archimedes method. Tensile test pieces with dimensions of a gauge length in 15mm and a diameter in 3mm were machined from the composites at three processing stages; as-extruded, 50h and 100h heat-treated at 873K at 1.3Pa. The tensile tests were carried out with Instron-type tensile testing machine (Autograph AGS-D Type-3, Shimadzu) at room temperature with a cross-head speed of 0.5mm/min.

Microstructure of the composites were observed by SEM (S-4200, Hitachi) and TEM (JEM-200CX, JEOL). The specimens for TEM observation were mechanically thinned to approximately 40 μ m, and then fractured by tensile stress.

3. RESULTS

3.1 Mechanical properties

The density of a pure Al specimen produced as a reference is close to the intrinsic density of Al, whereas the densities of the composites are lower by 4～6% in comparison with theoretical ones.

The tensile strengths are presented in Fig.1. In the as-extruded state, every specimen shows comparable strength. After the heat-treatment, however, the strengths of the composites are little affected by time of annealing at 873K, while that of the pure Al decreases significantly with time. The elongation of the pure Al tends to increase with annealing time at 873K due to recrystallization and coarsening of the grain as shown in Fig.2. Mechanical properties of the composites reinforced with nanotubes are more thermally stable than pure Al.

3.2 Micro structure

Figure 3 a) shows a tip of a composite specimen. Although some Al beads are observed on the nanotubes, no contrast corresponding to the reaction product is found at the present interface (Fig.3b)) which was heat-treated for 24h at 983K. Nor observed is any chemical reaction even at the interface between bent segments of the nanotubes and Al matrix.

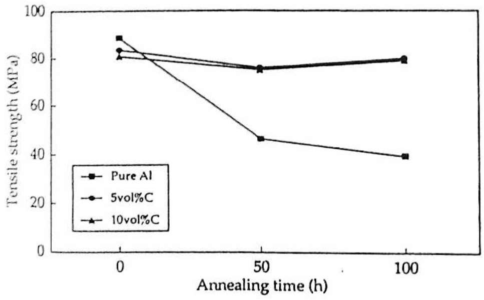

Fig.1 Tensile strength of the specimens as a function of annealing time at 873K

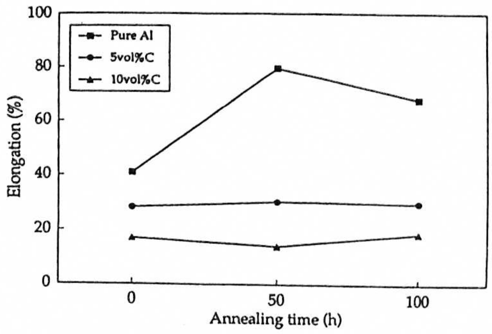

Fig.2 Elongation of the specimens as a function of annealing time at 873K

Figure 4 a) and b) show the fractured surfaces. In the composite specimen, the inhomogeneous structure which is made of coalescence of carbon powders is observed. After heat-treatment, the irregularity of the fractured surface tends to increase and the nanotubes are scarcely observed in the Al matrix. TEM observations, however, revealed that the nanotubes are embedded in Al matrix and the ruptures in the heat-treated composite occur along the embedded nanotubes as shown in Fig.5. It was inferred that the irregularity of the fractured surfaces are possibly caused by embedded nanotubes in Al matrix.

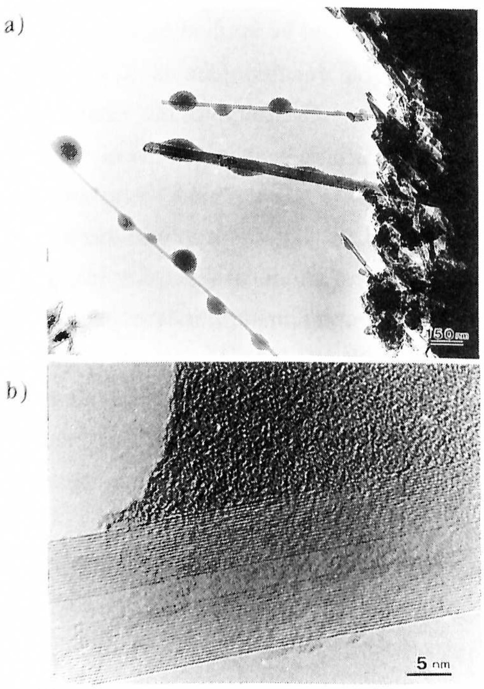

Fig.3 TEM image of a) a tip of the 10% composite heat-treated for 24h and 983K and b) high resolution TEM image of the interfacial structure.

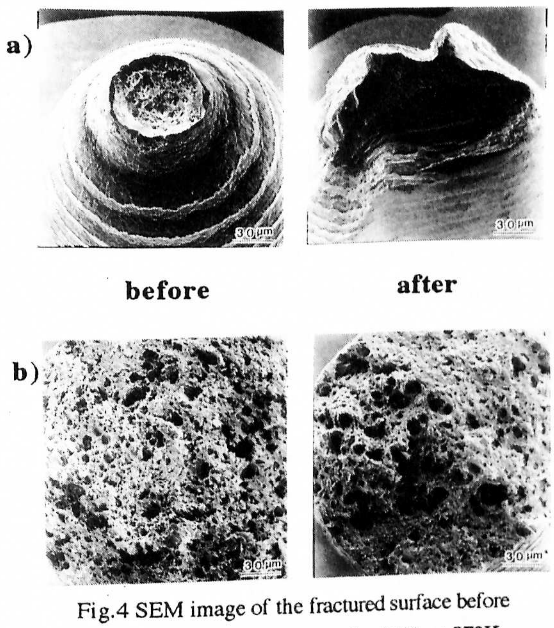

Fig.4 SEM image of the fractured surface before and after heat-treatment for 100h at 873K a) pure Al, b) 10% composite.

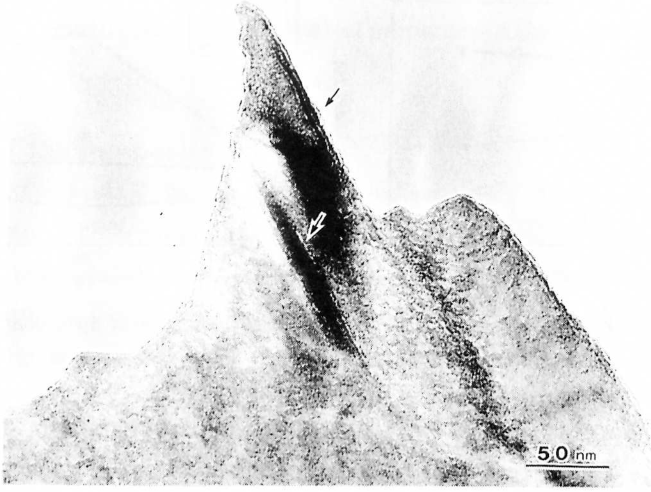

Fig.5 TEM image of the fractured surface of the 10% composite.
Arrows show the embedded nanotubes in Al matrix.

4. DISCUSSION

An important issue of this study is whether or not the nanotubes can be applied to Al matrix as a reinforcement. The experiments have exhibited some remarkable results. One is a stability of nanotubes in Al matrix when processed by powder metallurgy. Contrary to the conventional carbon fiber/Al composites, TEM observation shows that the Al carbide is absent at the nanotube/Al interface. In the conventional case, the carbide grow epitaxially on the prism planes of carbon fiber. Surface free energy of the prism planes ($4.8 Jm^{-2}$) is larger than that of graphitic basal plane ($0.14 Jm^{-2}$)[10] and it has been reported that there is an anisotropy of chemical reactivity in graphite crystal[11]. Therefore, unless the nanotube is fractured by external stress, nanotube is expected to be chemically stable due to its cylindrical structure made of graphitic basal plane. In fact, nanotubes are not damaged during the composite preparations, nanotube is hence suitable for the Al matrix composite. A further detailed investigation will be required to examine an effect of distorted π-electronic structures caused by the cylindrical structure of the nanotubes on the bonding interaction in the nanotube/Al interface.

The theoretical strength σ_c of the composite for the volume fraction of the nanotube can be estimated by Kelly-Tyson's formula[12]

$$\sigma_c = \sigma_f V_f\left(1-\frac{l_c}{2l}\right)+\sigma'_m(1-V_f)$$

$$= 2331V_f + 40$$

where σ_f is a tensile strength of nanotube estimated by commercial high modulus carbon fiber(=3GPa), V_f is a volume fraction of nanotubes, l_c is a critical length of a nanotube in Al matrix (= 0.85 μ m), l is an average length of nanotubes used in this experiment (=2 μ m) and σ'_m is a tensile strength of Al matrix (= 40MPa). The strength of the 10% composite is estimated about 270MPa. The experimentally obtained strengths are much lower than the theoretical one. A possible cause of the disagreement is the inhomogeneous dispersion of the carbon powder in the Al matrix. The little difference of the mechanical properties between 5% and 10% composites is possibly caused by the same reason. A high purity refinement of the nanotubes and the homogeneous dispersion method are important factor to produce the nanotube reinforced composite.

The roll of nanotubes as a reinforcement in Al matrix has been successfully observed by TEM. The fracture in the heat-treated composite proceeded along the embedded nanotube in the Al matrix. During the cooling of the composites after heat-treatment, nanotubes in the matrix are compressively stressed in the radial direction due to volume contraction of Al matrix caused by difference of thermal expansion coefficients between nanotube and Al matrix. The nanotube/Al system, however, is not chemically strong bonded at the interface. Therefore when the cracks propagate vertically to the nanotube/Al interface, debonding of the interface will occur along the longitudinal direction of the nanotube. The irregular shape of the fractured surface is possibly caused by the fracture mechanism. The nanotubes in the composite play an effective roll in the crack deflection.

CONCLUSION

Nanotube/Al composites have been prepared by hot-press and hot-extrusion. Contrary to the conventional carbon fiber/Al system, no carbide is observed at the interface in the nanotube/Al composite even after heat-treatment for 24h at 983K. The mechanical properties of the composites are little affected by the annealing time at 873K differently from the pure Al. TEM observation has revealed that nanotubes play the roll of crack deflection in Al matrix. Higher purification of the nanotubes and more homogeneous dispersion are yet necessary to produce an advanced composite reinforced with nanotubes.

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