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Deposition of boehmite on carbon nanofibers using aluminum alkoxide and its thermal transformation

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Abstract

We attempted to prepare carbon nanofibers (CNFs) bonded chemically with alumina particles using acid-treated CNFs and aluminum sec-butoxide. The structure and morphology of the boehmite deposited on the CNFs, the boundary between the CNFs and the deposited boehmite, and the thermal transformation of the deposited boehmite were investigated using Raman spectroscopy, X-ray diffraction (XRD) analysis, field-emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The boehmite deposited not only particulately on the CNFs but also in a film-like manner on parts of the CNFs. In addition, the boehmite could deposit not only on the disordered inner walls of the CNFs but also on the ordered inner walls. By heating at 1200 °C, the boehmite on the CNFs was transformed into α-alumina and θ-alumina. At this time, some alumina particles, particularly those formed on the ordered inner walls of CNFs, fell out of the CNFs, and only those alumina particles which might chemically bond with CNFs remained on the CNFs. Finally, CNFs dotted with alumina particles with a size of < 50 nm were obtained.

Keywords: A. Sol–gel processes; B. Nanocomposites; Alumina; Carbon nanotube

1. Introduction

Carbon nanotubes (CNTs) have not only a high aspect ratio but also incredible mechanical properties, such as high tensile strength and high elasticity [1–8], so CNTs are regarded as attractive candidates for the reinforcement of ceramic materials. Many studies have reported on ceramics combined with CNTs, for example CNT/Al_2O_3, CNT/ZrO_2, CNT/Si_3N_4 and CNT/SiC composites, and so on. However, significantly higher performance based on CNTs has not always been obtained.

In our previous papers [9–11], we reported on combined alumina ceramics with carbon nanofibers (CNFs), which were a type of multi-walled carbon nanotube, and we have shown that the fracture toughness of the obtained CNF/alumina composites increased with a decrease in the average alumina grain size of the composites. This improvement was caused by the bridging and/or pull-out of bent CNFs along the alumina grain boundaries. In other words, straight CNFs in the composites almost did not perform the reinforcement, because hydrophobic CNFs were very easily pulled out from hydrophilic alumina matrices. Therefore, if a strong chemical bond is formed between CNFs and alumina matrices, even such straight CNFs will contribute to the improvement of fracture toughness. Such chemical bonding may be realized by combining alumina ceramics with CNFs, the surfaces of which are coated with alumina by chemical bonding.

There have been some reports on the alumina coating of CNTs. Hernadi et al. prepared alumina, titania and silica coatings on CNTs using organometallic compounds as raw materials, and a homogenous alumina coating, accompanied by needle crystals, was obtained on CNTs using aluminum isopropoxide and no solvent [12]. They also reported that a homogenous amorphous alumina coating was prepared on CNTs with adsorbed sodium dodecyl sulfate as surfactant, using aluminum trichloride in 2-propanol [13]. Yang et al. reported

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that a continuous alumina coating, which was a γ-Al_2O_3 layer with a thickness of 1–3 nm, was successfully prepared on CNTs modified with polyvinyl alcohol [14]. However, the boundaries and bonding between the coating and the CNTs have not been observed in detail, and the thermal transformation of the coating has not been investigated.

Therefore, in this study, we tried to prepare CNFs chemically bonded with alumina particles using acid-treated CNFs and aluminum sec-butoxide. We believed that chemical bonding between CNFs and alumina would be achieved through a dehydration reaction between the hydrophilic functional groups, such as the carboxylic (–COOH) and hydroxyl (–OH) groups, formed on the CNFs by acid-treating the CNFs and the alumina precursors formed by the hydrolysis of aluminum sec-butoxide. The structure and morphology of the alumina precursors deposited on the CNFs, the boundary between the CNFs and the deposited alumina precursors, and the thermal transformation of the alumina precursors were investigated.

2. Experimental procedure

The CNFs (VGCF-S; diameter: 100 nm, length: 10–20 μm; Showa Denko, Japan) used in this study were first soaked in an acid mixture (conc. H_2SO_4:conc. HNO_3 = 3:1 v/v) for 0.5 and 5 h under ultrasonic conditions. The acid-treated CNFs were separated from the acid mixture by filtration, rinsed with distilled water, and then freeze-dried. In this paper, the CNFs soaked in the acid mixture for 0.5 and 5 h are described as AT05-CNFs and AT5-CNFs, respectively.

Under ultrasonic conditions, 0.05 g of AT05-CNFs or AT5-CNFs was dispersed in 200 mL of water. The obtained AT05-CNF and AT5-CNF suspensions were then heated to 100 °C and 0.05 g of aluminum sec-butoxide was added to them. These suspensions were refluxed at 100 °C for 18 h, cooled to room temperature, and then kept still for 3 days to sediment the CNF bundles, CNF agglomerates, and large alumina precursors into the bottom layer of the suspensions. Then, these suspensions were elutriated; namely, only the upper layers of these suspensions, where the CNFs would be well dispersed, were extracted from these suspensions. The extracted upper layers were filtered, and the separated AT05-CNFs and AT5-CNFs were rinsed with distilled water and freeze-dried. Alumina precursor was deposited on the separated and rinsed AT05-CNFs and AT5-CNFs. And these AT05-CNFs and AT5-CNFs are described as alumina precursor-deposited AT05-CNFs and AT5-CNFs, respectively. Finally, they were heated at 1200 °C for 1 h under vacuum.

The prepared specimens were evaluated using Raman spectroscopy, X-ray diffraction (XRD) analysis, field-

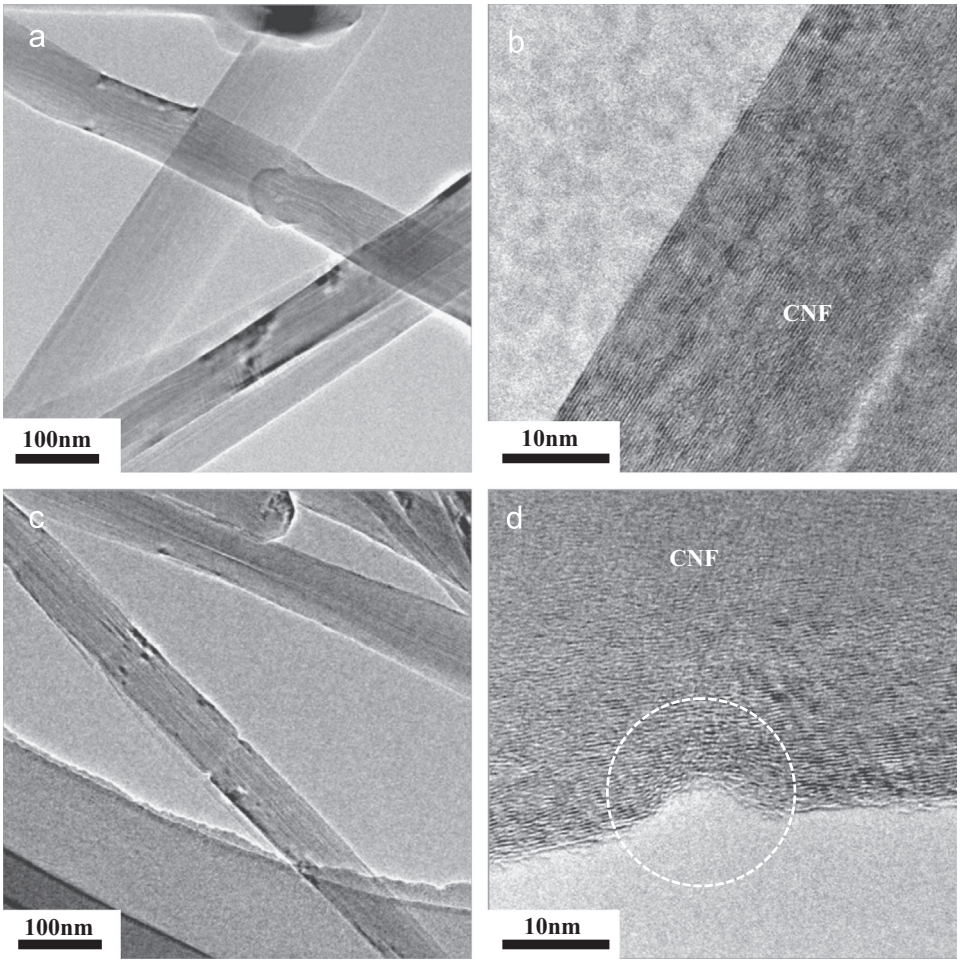

Fig. 1. TEM images of (a and b) pristine CNFs and (c and d) AT5-CNFs. (a and c) low magnification; (b and d) high magnification.