Carbon nanotube reinforced aluminum matrix composites by novel powder metallurgical process

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1 Introduction

Carbon nanotubes (CNTs) are now well known to possess an extremely high strength, high elastic modulus, and low weight, exceeding that of conventional fibers [1]. Therefore, CNT–metal matrix composites [2] are expected to assume the role of structural materials in the next generation. However, CNT–metal matrix composites are currently falling behind in bulk fabrication due to the difficulty of dispersing the CNTs, as compared to polymer– and ceramic–CNT composites [3–4]. In the cases of polymer and ceramic matrices, some reports have demonstrated that agglomerated CNTs with a huge cohesive force could be broken up and homogeneously mixed in a matrix by utilizing their electrokinetic potential, and the resultant composites exhibited the expected performances [5]. However, most of these approaches are unavailable for CNT dispersion in metals because of the low controllability of the zeta potential of metal particles and the large density gap between the metal and CNT.

This study examined the feasibility of fabricating bulk Al–CNT composites with regularly oriented CNTs from a nanoscale dispersed powder by combining the processes of spark plasma sintering (SPS) and hot extrusion [6,7]. The SPS underwent a uniaxial pressing carried out to densify the Al–CNT mixed powder, and then the orientation in the sintered compact powder was enhanced by hot extrusion. The microstructure and mechanical properties of the Al–CNT composites were then characterized.

2 Experimental procedure

A precursor was prepared by the NSD method with the goal of dispersing the CNTs in the aluminum powder [3]. This precursor consisted of commercial gas atomized Al powder (average particle size 14.82 μm), multi-walled carbon nanotubes (MWCNTs) (purity 99.5%, diameter 20 nm, length 15–50 μm), and natural rubber (NR). The powder composition was adjusted for 5 vol% CNT–Al powder. The precursor was heat-treated at 500 °C for 2 h in an argon atmosphere (1 l/min) to evaporate the NR. The obtained Al–CNT mixture powder was sintered in a carbon mold using a spark plasma sintering. The sintering conditions were a maximum temperature of 600 °C, holding time of 20 min, heating rate of 40 °C/min, and pressure of 50 MPa. The sintered compact had a diameter of 15 mm and a length of 30 mm.

The sintered compact was extruded in a 60° conical die at 400 °C with a pressure of 500 kN. The microstructures of the samples after every step were observed with an optical microscope, field-emission scanning electron microscope and high-resolution transmission electron microscope (HR-TEM), using energy-dispersive spectrometry (EDS) and selected-area diffraction patterns (SAD). To evaluate the tensile strength, the extruded bulks were machined into test pieces with 3 mm diameters in accordance with ICS 59.100.01. The tensile strength was measured by a universal testing machine.

3. Results and discussion

The MWCNTs had a curled shape and a bamboo-like structure. There were many disordered regions, and some amorphous carbons were absolved on their surface. No remaining NR was found by observation, which indicates the perfect removal of the NR. The Al particles almost retained their spherical shape, even though they were subjected to kneading and heat treatment. The relative density of the sintered compact was 96.1%.

Fig.1 shows the true stress versus true strain curve of the extruded Al–CNT composite, compared with the extruded pure Al. The true tensile strength of the extruded Al–CNT composite was 194 MPa, which is twice that of pure Al. Moreover, the composite maintained good ductility, with an elongation of 10.1%. Here, the true tensile strength of pure Al is generally reported to be about 100–110 MPa, whereas the obtained true tensile strength of the extruded pure Al bulk in this study was a lower value of 85 MPa. This disagreement arose from differences in fabrication processing and testing conditions. In any case, a strength enhancement of more than double was outstanding in comparison with other reports.

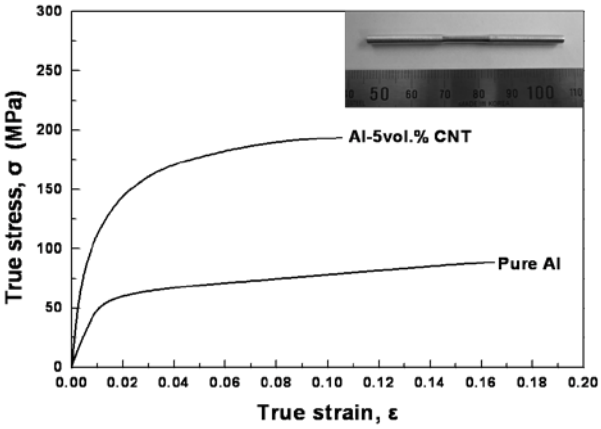

Fig.1. True stress-true strain curve of the extruded Al-CNT composites. [6]

Fig. 2 shows micrographs of the longitudinal cross sections of the extruded Al–CNT composite. The microstructure of the Al–CNT composite was extended parallel to the extrusion direction and the grain size was reduced to around 1 μm along the minor axis. The occasional pores can be identified as etch grooves derived from the agglomeration of CNTs, because they were not seen before the etching. Additionally, the grain boundaries have only a few CNTs in the thickness direction as a result of the rearrangement of the bundled CNTs in the sintered compact . This microstructure was formed through the flowing of CNTs with a large plastic deformation of the soft Al matrix by the high extrusion pressure. The observations so far demonstrated that the present method for the production of Al–CNT composites is capable of providing a uniform CNT dispersion and a higher degree of CNT orientation, as well as a dense and fine microstructure. Such a microstructure is expected to be very helpful in increasing the mechanical properties of Al–CNT composites.

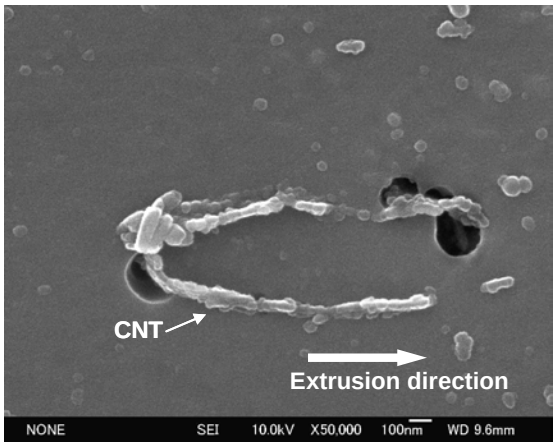

Fig.2. Well aligned CNT in the extrusion direction [7]

The observation revealed that the grain boundary of the sintered compact was definitely filled with several phases[7]. These phases were identified by EDS, the SAD pattern, and HR-

TEM as the CNTs, amorphous carbon, Al oxide, graphite, and a small quantity of aluminum carbide. The alumina phases, which were determined to have an amorphous structure by the SAD, were derived from the oxide scale on the raw Al particles, because they surround the Al grains, as seen in Fig. 5(b). In addition, broken alumina layers were occasionally found The presence of aluminum carbide between the Al and CNTs is a particularly important fact to emphasize. The formation of carbide will be helpful for a strong bonding between the Al matrix and CNTs. However, the surface of an ideal CNT with a perfect graphene structure is known to be chemically inert with the Al liquid phase. Thus, this formation of aluminum carbide means that the CNTs exposed their reactive prism planes, i.e. structural defects, at the sintering stage. Therefore, the following possibilities for forming the aluminum carbide (Al_4C_3) can be suggested [16]: the molten aluminum and the open ends of the CNT tips react with the Al_4C_3. Otherwise, the Al_4C_3 results from the reaction between the molten Al and the amorphous carbon or the defect region of the graphite sheet on the CNTs. In either case,

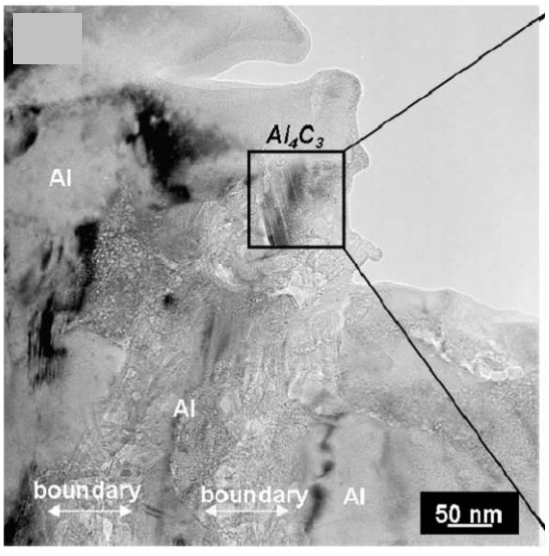

Fig.3. Al carbide formation on a CNT.[7]

it must be assumed that molten Al was generated between the surfaces of the particles in spite of the solid state sintering.

As shown in Fig.3, the formation of carbide will be helpful for a strong bonding between the Al matrix and CNTs. As proven above, the extruded bulk does not include work hardening. Therefore, the enhancement in strength came primarily from the reinforcement effect of the CNTs. In particular, the aluminum carbide phases are supposed to bring out the reinforcement effect. The aluminum carbide that was generated during the sintering process was implanted into the aluminum matrix in the extrusion process, as seen in Fig. 3. Such controlled present interfaces could allow ideal load transfers from the matrices to the CNTs.

The fractographies of the composite after the tensile test are shown in Fig. 4 The fracture surface had a lot of dimples associated with ductile fracture as shown in Fig. 4 (a). The appearance of dimples means that the interfaces between the Al particles were very strongly metal-metal bonded. The bridgings were obviously formed by the CNTs wrapped in the matrix (see black arrow in Fig. 4 (a)). Furthermore, there were no pulled-out CNTs observed, but broken CNTs after tensile tests (see white arrow in Fig.4 (b)). It is implied that stress was transferred effectively through carbides.

The prepared Al-CNT composite containing a highly optimized tensile strength and elongation despite a slight 5vol. % CNT addition indicates that the present Al-CNT composite under stress is not easily affected from a plastic deformation due to difficulty of rearrangement of dislocation. This phenomenon increases under micro-ordered structures dramatically due to little generated dislocation (meaning limited movement of dislocation) [8]. CNTs in our composite were distributed selectively around the boundary zone in nanoscale. This may be one of the reasons why our composite was highly optimized in tensile strength and

elongation. As a result, the remarkable enhancement in tensile strength and no decrease of elongation of Al-CNT composite were able to be possible simultaneously. In addition, the extrusion pressure would give an enhancement on adhesion between CNTs and matrices.

Summary

Aluminum (Al)/carbon nanotube (CNT) composites were fabricated by combined process of SPS pre-sintering and hot extrusion. The CNTs were well dispersed onto the Al particles by a nanoscale dispersion method. The pre-sintered CNT composites prepared by spark plasma sintering were used for subsequent hot extrusion.

Microstructural observations by optical, field-emission scanning electron, and high-resolution transmission electron microscope confirmed that the sintered Al/CNT compact and extruded bulk material had a good dispersion of oriented CNTs. Raman spectroscopy showed that the processing did little damage to the CNTs.

It is found that the Al-CNT composite showed no decrease in elongation despite highly enhanced tensile strength compared to that of pure Al as shown in Fig.1.

It is thought that the thickness of boundary layer could be controlled by the amount of CNT which leads to well aligned CNT in the extrusion direction (Fig.2) and also good adhesion between matrix and CNT due to generated aluminum carbide in Al-CNT composite (Fig.3).

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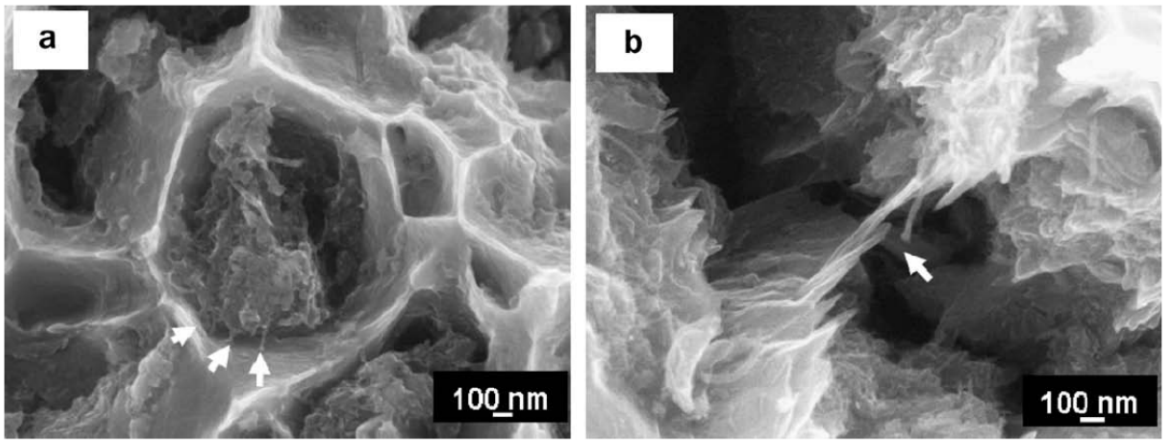

Fig.4. Al carbide formation on a CNT.[6]