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Fabrication and mechanical properties of magnesium matrix composite reinforced with Si coated carbon nanotubes

Yongha Park[a], Kyungmox Cho[a], Ikmin Park[a], Yongho Park[a*]

[a]Department of Materials Science and Engineering, Pusan National University, San 30 Jangjeon-dong, Geumjeong-gu, Busan 609-735, Republic of Korea

Abstract

Multi-walled carbon nanotubes (MWNTs) reinforced Si coatings were prepared using solid reaction method between pure silicon powders and carbon nanotubes (CNTs). And, CNTs reinforced AZ91 metal matrix composites (MMC) were fabricated by the squeeze infiltrated method. The results obtained pave the way for the formation of coated carbon nanotubes for the development of composites with a homogenous microstructure and improved performance. The Si coated MWNTs leads to improvement in the wettability, distribution, bonding strength in the MWNTs matrix composite. The squeeze infiltration technique was a proper method to fabricate magnesium matrix composites reducing casting defects such as pores and matrix/reinforcement interface separation etc. Improved tensile strength were obtained by reinforcing Si coated CNT to magnesium alloys.

Keywords: multi-walled carbon nanotube, magnesium matrix composite, fabrication, mechanical properties

1. Introduction

Many industries such as the automobile, aerospace, and aircraft industries, are expected to develop super materials that are ultra-light and that have high hardness and high strength. In addition, next-generation materials must be environmentally friendly, energy saving, and inexpensive. Since their discovery in 1991 [1], CNTs have been promising reinforcements for nanocomposites, due to the exceptional mechanical and physical properties of these nanotubes, i.e. high strength, high aspect ratio and high fracture strain and superior flexibility. Multi-walled carbon nanotubes (MWNTs) possess unique properties like high stiffness (~970GPa), strength (~63GPa) and the thermal conductivity up to 3000 $W.m^{-1}K^{-1}$ [2]. There are two major parameters for fabrication of CNTs/magnesium matrix composite. First, the uniform dispersion of CNTs in magnesium matrix is a very important factor. CNTs are tangled with each other by Van der Walls force, so the process for CNT dispersion must be applied to fabricate sound composites. Also, the reinforcement and the composite should be produced properly to optimize the effect of CNT

* Corresponding author. Tel.: +82-51-510-2851; fax: +82-51-514-4457.
E-mail address: yhpark@pusan.ac.kr.

Table 1. Properties of various reinforcements

Chemical Composition	ρ (g/cm³)	Dia (μm)	Length (μm)	σ (GPa)	E (GPa)	Shape
CNT	1.3~3.0	0.005~0.02	~10	20~50	600~1,200	fiber
9(Al₂O₃)·2(B₂O₃)	3	0.5~1.0	10~30	7.8	3.92	Whisker
Graphite	2.2	130~180	-	-	-	Particle
Carbon fiber	1.79	6.8	-	3.70	245	Continous fiber

as reinforcement. Inhomogeneities structural in the metal matrix composite result in the degradation of the mechanical properties of the CNT composite materials [3]. Second, the poor interfacial bond strength between reinforcement (CNTs) and the matrix materials leads to a limited stress transfer capability from the matrix to the CNTs [4]. The bond strength of reinforcement with the matrix, and uniform distribution within the matrix are essential structural requirements for the stronger metal matrix composite. This is attributed by many experts to four issues [5] ; (1) the difficulty of dispersing the CNTs in the matrix due to the fact that they tend to stick together, (2) only small amounts of CNTs (1-5wt%) have been used, (3) insufficient bonding at the nanotubes matrix interface given that CNT composites have been observed to fail either fracture at CNT-matrix interface or, in the case of MWNT, pull out of the different layer of MWNT, (4) the difficulty of aligning the nanotubes within the matrix. Chemical methods were acid treatment, surfactant and surface functionalization to change the surface energy of the CNTs. It is improve wetting or adhesion characteristics and reduce tendency to agglomerate in the continuous tube. Some of the processing techniques used in fabrication of CNTs reinforced metal matrix composite (MMC) are electroless plating [6,7], plasma spray forming [8], spark plasma sintering [9,10], mechanical milling [11], and powder metallurgy [12]. Uniform dispersion and alignment of nanotubes within the MMCs is still a challenge. In the present work, we investigated mechanical properties of magnesium alloy and metal matrix composite. The Si-coated MWNTs reinforced magnesium matrix composites were fabricated by squeeze infiltration techniques. The mechanical properties of the AZ91/Si-coated MWNT composites were investigated with a view to industrial applications.

2. Experiment method

Multi-walled nanotubes (MWNTs) used for the present work were purchased from Hanwha nanotech company and produced by arc discharge method. They have a purity higher than 95%, their inner diameter is between 5~10nm and their length between 0.5 and 10μm. Fig. 1 shows schematic images of as-received and different surface treatment MWNTs. In preparing MWNTs, we first prepared pristine MWNTs and Si powders. The pristine MWNTs were refluxed in 3:1 (volume ratio) concentrated H_2SO_4(90%): HNO_3(70%) mixture at 40℃ for 4h [13], washed thoroughly with distilled water to be acid-free, and then finally dried in an oven at 60℃ (Fig 1. (a)). Then, silicon powders and acid treatment MWNTs were physically blended with zirconia balls (diameter 10mm and 1mm) in a container using the same triaxial ball miller with a rolling rate of 1200rpm for 6h in argon (Fig. 1 (b)). The
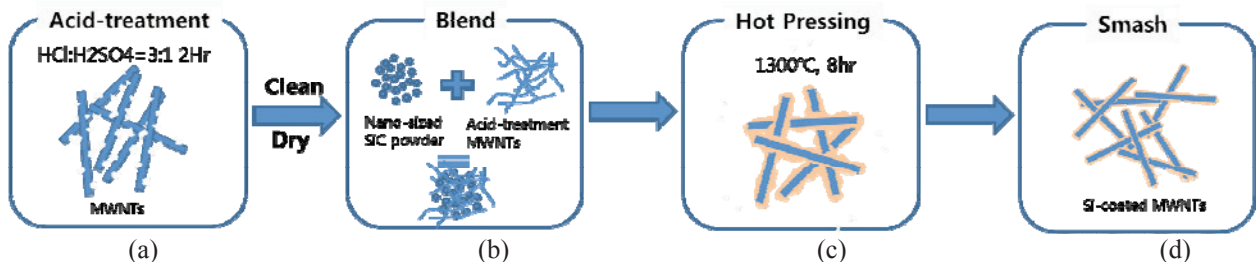

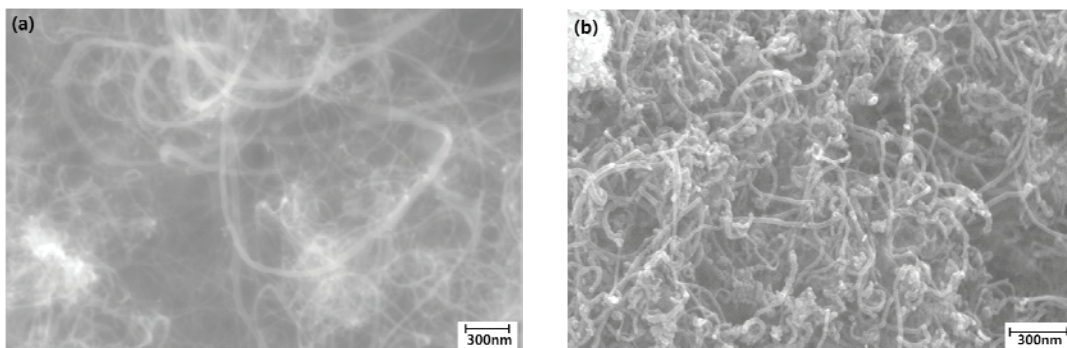Fig. 1 Fabrication procedure for Si-coat MWNT nanocomposites

Fig. 2 SEM micrographs of (a) the pristine MWNTs (b) a MWNTs with Si coating

synthesized Si-CNT powders were hot-pressed in a graphite die in argon atmosphere at a temperature of 1300℃ under a pressure of 40MPa for 8h (Fig. 1(c)). In the case of the carbon nanotubes containing Si powder, the observed aggregated carbon nanotubes are indicative of non-homogeneously distributed carbon nanotubes. Finally, the aggregated Si-MWNT powder was the smash, using zirconia ball with a diameter of 10mm in a triaxial vibrating-type ball miller with a rolling rate of 1200rpm for 12h in argon gas (Fig. 1(d)). To prepare preform, silica colloidal inorganic binder, starch organic binder and polyacrylamide were dispersed in dilute water and a vacuum suction method was used to reduce closed microporosity and to obtain sound preforms. The packing rate of the reinforcement in preform was about 3wt% (MWNT) and it was roughly controlled by the vacuum suction pressure. The molten AZ91 alloy was heated to 700℃, and poured into the preform. The pressure being applied by the punch on the molten metal was 70MPa. The phase structure in the sample (before and after) coating was identified using x-ray diffraction (a Rigaku RINT-2100 made in japan) with monochrometer Cu Kα radiation. The morphology of the coating was investigated with a scanning electron microscope (SEM) and transmission electron microscope (TEM). General metallographic procedure was followed with the etchant of 2% oxalic acid and 98% ethanol mixture. Micro-Vickers hardness and tensile tests were carried out to investigate the mechanical properties of the unreinforced alloy and the composites. Initial engineering strain rate was of 2.0×10^{-4}/min for tensile tests at room temperature

3. Result and discussion

Fig. 2 shows SEM images of the MWNTs preform microstructure. It can be seen that the CNTs were dispersed uniformly in the agglomerate (Fig. 2(b)). Wetting of the CNTs by the binder might be one reason for the good dispersion observed. The differences of the surface morphology between untreated and Si-coated samples are observed. The surfaces of MWNTs before Si-coated treatment are smooth and tidy. However, after Si-coated treatment, the smooth MWNT surface become rough, and the surface defects of treated MWNTs are enhanced, but the integrity of the nanotube patterns is not damaged.
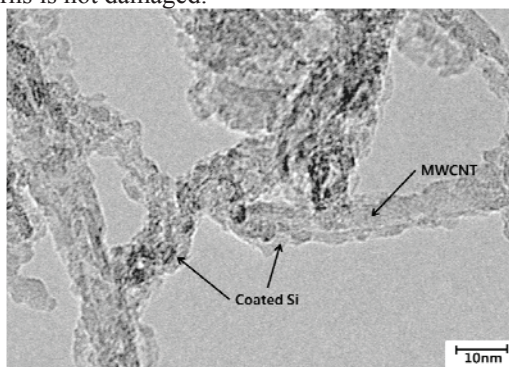

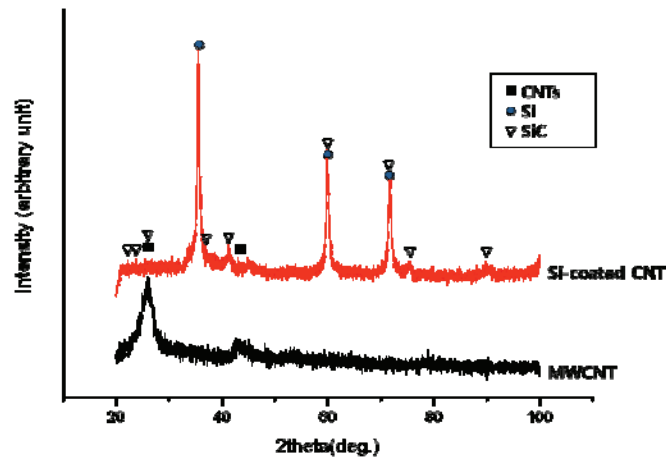Fig. 3 Microstructure of 5wt% AZ91 composite reinforced Si coating MWNT

Fig. 4 XRD pattern of the MWNTs

Fig. 3 shows the TEM image of the Si-coated MWNTs prepared at solid reaction technique. Every nanotube was completely covered by a coating of about 20nm that formed a uniform and conformal core-shell structure. The present method was confirmed as effective for the nano powder substrate and could produce Si-coated nano powder in bulk. Due to the coating mechanism and depending on the oxidative conditions used in acid-treatment step, temperature of Si coating has been obtained. The activated defect sites of acid-treatment MWNT surfaces have many functional groups, such as carbonyl groups, oxygen-hydrogen bond and C-O bonds [14], which greatly promote the combinations between MWNTs and Si, induce the formation of a wettable Si-coated MWNT surface. As MWNTs contain structural vacancies [15] and additional defects on the outer surface of tubes generated by acid treatments, the active defect sites may become the preferred nucleation sites of Si than the defect-free sites on the outer surface of MWNTs. Fig. 4 compares the XRD pattern of the MWNTs materials by Si used in the present study. The first peak at 26° corresponds to the inter-planar spacing of 0.34nm between the sheets of the MWNTs, and is similar to that of graphite. The other peaks are visible at 43° corresponding to the (100) and planes of MWNTs. While the peaks of SiC can be observed from Si-coat MWNTs, and it indicates that the reaction product is between Si coated MWNTs. As can be seen, the characteristic peaks of SiC can be easily indexed as the (111), (200), (220), and (222). In addition, there is only few MWNT reacted with Si powder and transformed into SiC at the outer surface of MWNT. Therefore, the specimen is consisted of most CNT, Si and few SiC composite nanotubes. In the present case, during the solid reaction stage of the interfacial reaction, C atoms break away from the MWNTs surface to react with liquid Si powder [16]. Carbon atoms of MWNTs react with Si atoms to form a very thin layer of SiC on the MWNT surface. Most peaks of MWNTs and silicon coating were still present in the figure. This clearly confirms the protective effect of the coating. The tensile strength of monolithic materials and nanocomposite are listed in Table 3. 0.2% YS and UTS were enhanced in AZ91/Si-coated MWNT compared to monolithic and AZ91/MWNT composite. The increase in tensile strength can be attributed to the overall positive effect derived from lower grain size and well known factors pertaining to reinforcement such as load transfer from matrix to reinforcement. T. Honma et al. [17] provided the advantage in the fabrication techniques may be related to further infiltration of the molten AZ91D alloy into the spacing of the CNF agglomerating regions during the squeeze casting due to the improvement in the wettability of the Si-CNF and shear deformation of the agglomerating regions of the CNF during the squeeze casting.

Table 2. Mechanical properties of MWNT reinforced AZ91 magnesium composite

Material	Tensile strength (MPa)	0.2% proof stress (MPa)	E (%)	Hardness (Hv)
AZ91 alloy	205±5	80±5	5±2	80
5vol% pristine MWNT/AZ91	243±10	210±10	1.0±2	150
5vol% Si coating MWNT/AZ91	296±10	253±10	1.3±2	160

4. Conclusions

A uniform and continuous Si coating was obtained, and the effective fabrication of CNT-reinforced metals depends on the homogenous dispersion of CNTs in the metal matrix and the interfacial adhesion between them. In this study, it is investigate magnesium matrix composites reinforced with multi-wall carbon nanotubes that have been coated with Si in order to improve the wettability. This research has shown that silicon powders can be coated onto carbon nanotubes by a directly heating method. Silicon powder has been effectively coated on the surface of MWNTs and well covered and continuous. The solid reaction method for the Si-coat MWNT nanocomposite has made very simple, inexpensive and high mass. The results obtained pave the way for the formation of coated carbon nanotubes for the development of composites with a homogenous microstructure and improved performance. TEM observations show that the interface between MWNTs and matrix is wettability and in good adhesion. The analysis results of Raman spectroscopy and structure properties of MWNT, SEM images of MWNTs suggest that after solid reaction, the smooth MWNTs surface become rough, and the surface defects of Si-coat MWNTs are enhanced, but the integrity of the MWNTs patterns is not damaged. We believe that the present technique method for preparing Si-MWNT is suitable for fabrication of other CNT reinforced metal composites with high strength properties.

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