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Fabrication and characterization of carbon nanotube reinforced magnesium matrix composites

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ABSTRACT

In the present investigation, Mg chips are recycled to produce Mg–6 wt.% Al reinforced with 0.5, 1, 2 and 4 wt.% nanosized CNTs by mechanical ball milling, cold pressing and subsequently hot extrusion process without sintering step. The microstructure, mechanical properties and corrosion behavior of Mg/Al without CNT (base alloy) and composites were evaluated. The distribution of CNTs was analyzed using a Scanning Electron Microscopy (SEM) equipped with Energy Dispersive Spectroscopy (EDS) analyzer and a Wavelength Dispersive X-Ray Fluorescence spectrometer (WDXRF). Microstructural analysis revealed that the CNTs on the Mg chips were present throughout the extrusion direction and the uniform distribution of CNTs at the chip surface decreased with increase in the CNT content. The results of the mechanical and corrosion test showed that small addition of CNTs (0.5 wt.%) evidently improved the hardness and corrosion resistance of the composite by comparing with the base alloy, while increase in the CNT weight fraction in the initial mixture resulted in a significant decrease of hardness, compression strength, wear rate and corrosion resistance.

1. Introduction

Carbon nanotubes (CNTs) have a potential to be used as reinforcement in metals to improve the composite performance because of their extremely high mechanical property, high chemical and thermal stability as well as good thermal and electrical properties [1]. Mg and its alloys have also drawn interest as the matrix material because they are applied to engineering components in the automotive, material handling and aerospace industries due to their low density, less than 2 g/cm^3, and effective for weight reduction, assisting the improvement of the fuel efficiency [2]. CNTs have attracted attention increasingly as super reinforcements for Mg alloy gradually over the last 5 years and studies have been mainly focused on investigating their contribution to the enhancement of the mechanical performance and corrosion behavior of structure components [3–6]. Despite many interesting studies conducted on composites with CNTs, CNT reinforced Mg matrix composites especially at high CNT concentrations have not seen wide application because of three major difficulties; the CNTs dispersion in the matrix, consolidation with defect-free CNT, and proper bonding at the CNT/matrix interface in order to attain good load transfer between phases. For the stir cast Mg-CNT composites, the distribution of CNTs is always inhomogeneous in a Mg matrix due to the non-wetting nature of CNTs to molten Mg [1,7]. A major challenge in the manufacture of CNT-containing metal matrix composites is distributing the CNTs uniformly. In order to improve the distribution of CNTs, to obtain homogeneous properties and enable the efficient use of the properties, conventional powder metallurgy techniques (compaction and sintering) have been widely preferred and studied [8,9]. However, it is very difficult to distribute CNT in a metal matrix. A two-step process was applied in this study. In the first step, a mechanical ball milling process was performed to pre-disperse CNTs on the Mg chips. Then the chips with the well dispersed CNTs on their surface were mixed with pure Al powder because of the greater plasticity of pure Al. The composite mixture was subsequently consolidated by cold pressing and hot extrusion. The fact that extrusion process is a good way to achieve higher material performance and promote alignment of CNTs in the extrusion direction is remarkable. In this study, Mg/Al-CNT composites were fabricated by the mechanical ball milling, cold pressing and hot extrusion process, and their density, electrical, mechanical, wear and corrosion properties were investigated.

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2. Experimental details

In this study, Mg chips/Al and composite reinforced with 0.5, 1, 2 and 4 wt.% CNT were used. CNTs used were thin multi-wall carbon nanotubes (degree of purity > 90%) synthesized by a catalytic carbon vapor deposition (CCVD) process, purchased from Grafen Chemical Industry, Turkey. According to the supplier, their average diameter and length were 9.5 nm and 1.5 μm, respectively. Before preparation process of composites, as-prepared CNTs were purified by washing with HNO_3/H_2SO_4 (1:1 by volume) for 30 min in an ultrasonic bath at 80 °C. The pretreated CNT was collected and washed to pH 5.0 by doubly distilled water. Afterwards, the pretreated MWCNTs were dried at 100 °C in an oven for 24 h.

The starting Mg chips (purity >99.9%) with sizes of (2–4) × (1) × (0.25) mm were ball-milled under argon atmosphere at 300 rpm for 3 h with a ball to powder weight ratio (BPR) of 32 to coat the surface of Mg chips with the pretreated MWCNTs. The Mg chips were used as a media for observing the CNT's movement during hot extrusion. To obtain good bonding, and as a result improved mechanical properties of the extruded products [10], the present authors used Al powders as a good binder in recycling of Mg chips containing CNTs through hot extrusion process. Commercial materials with low porosity and appreciable high strength can be prepared by hot extrusion after being processed by cold press. Since Al alloy powders can be usually consolidated by extrusion until the full density be reached, the CNT-coated Mg chips were then mixed with Al powder (97.7% pure, 27 μm) at the compositions of Mg–6 wt.% Al–*x* wt.% CNT (*x* = 0.5, 1, 2 and 4). In order to consolidate the prepared mixtures, firstly they were filled into a cylindrical container with a diameter of 30 mm and pressed under 1600 MPa pressure at room temperature. Then, the cold pressed samples were consolidated by hot extrusion at 350 °C with ram speed of 5 mm s^{-1} and extrusion ratio of 9:1, resulting into cylindrical compact products with diameter of 10 ± 0.2 mm. The extrusion was performed without canning, degassing and atmospheric control.

In accordance with the standard metallographic procedure, which includes a grinding process up to 1200 mesh and a polishing process with alumina solution conducted on the base alloy and composites, microstructural characterization studies were conducted on metallographically polished base alloy and composite extruded samples using an Optical Microscopic (OM) and Scanning Electron Microscopy (SEM) examinations, X-Ray Diffraction (XRD) analysis, density and electrical conductivity measurements. The porosity of the samples was calculated by linear intercept method [11]. Electrical conductivities of the samples were measured based on eddy currents on sample surfaces utilizing a Hocking™ AutoSigma 3000 electrical conductivity meter. Prior to measurements, the sample surfaces were grinded with a 1200 mesh emery paper to obtain a flat surface. Mean values of 10 measurements were taken to determine the electrical conductivities of the samples. Furthermore, the degree of CNT distribution in the composites was investigated by the SEM equipped with an EDS analyzer and a Wavelength Dispersive X-Ray Fluorescence spectrometer (WDXRF).

The mechanical properties of the base alloy and composites were evaluated by hardness measurements, compression and wear tests. Hardness measurements were taken on the polished cross-sections of the samples with a Vickers pyramid indenter by utilizing a conventional microhardness tester (Wolpert, HMV2) under indentation load of 200 g. At least 10 successive measurements were performed for the base alloy and composites containing different amounts of CNTs. Round samples were also tested by a Dartec Universal testing machine at a crosshead speed of 1 mm/min to determine the compression properties of the base alloy and composites. The results of the compression tests were compiled by taking average value of three samples. Wear tests were carried out under dry sliding conditions by utilizing a reciprocating wear tester, which was designed according to ASTM G133 standard. A 10 mm diameter steel ball rubs on the surface of the base alloy and composites under normal atmospheric conditions (20 °C and 30% RH). Wear tests were conducted under normal load of 1 N with a constant sliding speed of 0.0128 m/s. Total sliding distance during the experiment was about 40 m. For each CNT content, at least three samples were tested for the reproducibility of data. During wear testing, frictional force data was continuously recorded. After the wear tests, wear tracks were analyzed by using surftest SJ 400 machine manufactured by Mitutoyo Corporation, Japan. Worn surfaces of the wear tracks after dry sliding wear tests were also examined by a SEM.

The corrosion tests were evaluated by both weight loss measurements and accelerated electrochemical tests. Each data point for both weight loss measurement and electrochemical test represents the average of three different measurements. For the weight loss-measuring test, square shape samples with an average size of 2 mm × 2 mm were mechanically polished with SiC as abrasive medium to get the mirror finish and thoroughly rinsed with distilled water and immersed in 3.5% NaCl solution in a Pyrex glass cell exposed to atmospheric air for 12 h. The amount of solution in the container was estimated by taking into account the surface area of the samples as 0.3 ml/mm^2. The samples, which were taken out of the solution at certain intervals during the corrosion experiments, were ultrasonically cleaned in distilled water and alcohol, after which they were weighed using a 0.1 mg-sensitive electronic scale. The normalized weight loss values of the samples were calculated in the unit of g/cm^2 by dividing the weight loss of the each sample by their initial total surface area. The electrochemical corrosion tests were performed utilizing a typical three electrode potentiodynamic polarization test unit in the corroding media of aerated solution of 3.5 wt.% NaCl at room temperature. Before potentiodynamic polarization measurements, an initial delay of 45 min was employed in order to measure the open circuit potential between working and reference electrodes. Potentiodynamic polarization curves were generated by sweeping the potential from cathodic to anodic direction at a scan rate of 1 mV s^{-1}, starting from −0.1 up to +0.4 V. Corrosion potentials (E_{corr}) and corrosion current densities (i_{corr}) were calculated using a Tafel type fit in the software. Finally, the surface images of the corroded samples were examined using a SEM in order to determine the morphology of the developed corrosion.

3. Results and discussions

Fig. 1 presents the SEM images of CNTs at low and high magnifications before and after purification. Fig. 1 indicates that as-prepared CNTs have a large agglomerate of several 100 μm in size that are composed of highly entangled individual CNTs in their as-received state, whereas individual pretreated CNTs in the cluster with ~100 μm size are clearly visible in Fig. 1b. The extent of clustering of CNT was reduced by purification.

The structural evolution of the ball-milled mixtures can be seen from the SEM micrographs shown in Fig. 2. The majority of the Mg chips containing CNT was flake shaped. Compared to the mean size of the Mg chip with 0.5 wt.% CNT, the size of the Mg chip with 4 wt.% CNT was relatively larger. Mg chips with 0.5 and 4 wt.% CNT have been sieved for 15 min using BSS meshes ranging in size from 100 to 350 by Rotap Sieve shaker. Fig. 3 shows the particle size and weight fraction distribution of Mg chips with CNT after 15 min sieving. The results showed that the average particle sizes of the Mg chips with 0.5 and 4 wt.% CNT were found to be 570 μm and 740 μm, respectively. This coarsening of the chips was mainly a result of re-agglomeration of CNTs during the ball milling process.

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