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Interface enhancement of carbon nanotube/mesocarbon microbead isotropic composites

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ABSTRACT

Carbon nanotubes (CNTs) are incorporated into mesocarbon microbead (MCMB)-derived isotropic graphite to improve their mechanical properties. CNTs are homogenously distributed on the MCMB surface by acid-treatment and mechanical mixing. The composites are prepared by cold isostatic pressing, carbonization, and graphitization. The mechanical properties and isotropy ratios of the CNT/MCMB composites are determined by four-point bend tests and thermal expansion measurements, respectively. The addition of CNTs improves the flexural strength by *ca.* 20%, while keeps a low isotropy ratio. CNTs dispersed on particle interfaces improve the interfacial strength, this reinforcing mechanism is confirmed by a fracture mode analysis with scanning electron microscope.

1. Introduction

Carbon and graphite materials are characterized by excellent mechanical performance at high temperatures, high electrical and thermal conductivity, and good corrosion resistance. Modern advanced technologies make wide use of polycrystalline graphite in different fields, including graphite electrodes used in electric arc furnaces, graphite cathodes in aluminum electrolysis cells, graphite dies used for continuous casting, fine-grain graphite heaters and crucibles used for single crystal silicon growth, and nuclear-grade graphite moderators in high-temperature reactors [1].

Polycrystalline graphite is usually prepared by two methods [2]. The first one makes use of pulverized coke as a filler and pitch as a binder. The other uses self-sintering carbonaceous mesophase such as mesocarbon microbeads (MCMBs) for binderless forming [3,4]. The strength of MCMB-derived graphite is determined by several factors, including pre-oxidation conditions, the degree of graphitization, as well as particle size distribution.

Pre-oxidation treatment significantly influences the pyrolysis behavior, and change the plasticity of carbonaceous mesophase. Many investigations have been carried out to optimize the pre-oxidation conditions [5] and to investigate the MCMB sintering mechanism [6,7].

The graphitization decreases d_{002} interlayer spacing and induces the growth of graphite layers. In another words, turbostratic structure gradually evolves into graphitic structure. Generally, the carbonized artifacts have much higher strength than the graphitized artifacts. For instance, Wu et al. [8] fabricated carbon blocks by using raw MCMBs with particle sizes of less than 5 μm. The blocks were carbonization at 900 °C and showed a flexural strength of 111 MPa.

The particle size distribution is another important factor that influences mechanical properties of MCMB-derived graphite. The decrease of mean particle size gives rise to higher strength. A remarkably high flexural strength of 100 MPa is available for graphite sample prepared from mesophase pitch powder with a mean particle size of 2.4 μm after graphitization at 2773 K [9]. However, green bodies with small particle sizes are very easy to crack during baking. As a result, it is of great interest to explore new methods that can increase the strength of MCMB-derived graphite while do not reduce the particle size.

In this contribution, MCMBs with a D50 value of 25.0 μm are used as raw material. These MCMBs have been successfully made into graphite blocks with a diameter of 60 mm [6] in our previous work. Here we demonstrate a new approach of using carbon nanotubes (CNTs) to reinforce the MCMB-derived graphite. Many researches have been carried out in order to incorporate CNTs into polymers [10–12], metals [13], and ceramics [14,15] to form

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advanced composites. The reasons we selected CNTs as additives is the excellent mechanical properties of CNTs [16] and its good chemical compatibility with graphite. Wu et al. [8] added CNTs into coal tar pitch to *in situ* produce CNT/MCMB powders, which were subsequently used as the starting material to prepare composite materials. However it is not easy to control the particle morphology and structure during the *in situ* synthesis of CNT/MCMB powder. Song et al. [17] prepared CNT reinforced MCMB based composites by one-step self-sintering, but limited information was reported on the microstructure and reinforcement mechanism. Herein, a similar method was employed to directly disperse CNTs on the outer surface of MCMBs (as illustrated in Fig. 1). The composite powders are pressed and sintered in order to produce a CNT/MCMB isotropic composite, in which CNTs are homogenously deposited at MCMB interface areas. The mechanism of mechanical strength increasing was also investigated in detail.

2. Materials and methods

2.1. Preparation of CNT/MCMB composite powder

MCMBs produced by China Steel Chemical Corporation, Taiwan, were lightly pre-oxidized under optimized conditions, which are not open, and were used as received. The basic information about the MCMBs can be found in our previous publication [6].

Aligned multi-walled carbon nanotubes (MWCNTs) [18,19] were grown on a vermiculite-based catalyst by fluidized bed catalytic chemical vapor deposition. CNTs with an outer diameter in the range of 7–12 nm, a length of *ca.* 10 μm, and a purity of 84.0 wt.% were synthesized. High magnification scanning electron microscopy (SEM) images indicate that the CNTs in the array possess good alignment (Fig. 2), which facilitates the CNT dispersion. The CNT arrays were treated in an acid mixture of 98% H_2SO_4 and 68% HNO_3 with a volume ratio of 3:1 at 90 °C for 20 min, in order to remove impurities and to create oxygen-containing functional groups on the CNT surface [20]. After acid treatment, the purity of CNTs can be increased to 97.5 wt.%. The CNTs were separated by centrifugation, and then ultrasonically dispersed in ethanol for 15 min. Attributed from its low toxicity, ethanol was chosen as solvent. Subsequently, 200 g MCMBs were added into the ethanol. The suspension was continuously ultrasonic-treated and stirred for 60 min and then vacuum dried at 70 °C. The morphology of CNTs on the MCMB surface was observed by SEM. A series of composite powders with various CNT weight contents of 0.0, 0.05, 0.1, 0.25, 0.4, 0.6, and 0.75 wt.% were prepared.

2.2. Cold isostatic pressing, carbonization, and graphitization

Cold isostatic pressing (CIP) was employed to form the green composite body of about 30 mm in diameter and 200 mm in length. Green bodies were carbonized at 1000 °C in N_2 flow. The graphitization was carried out in Ar gas in an intermediate frequency induction heating furnace. The samples were first heated at a constant power of 10 kW to 1000 °C and then heated at a rate of 10 °C/min up to 2800 °C. After holding for 1 h, the furnace chamber was naturally cooled to room temperature.

2.3. Characterization of CNT/MCMB composites

The final bulk density was measured based on Archimedes' principle. X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku D/max 2500 V diffractometer with Cu Kα radiation. The graphitized samples with various CNT contents were machined into specimens of 5 × 10 × 50 mm for four-point bend tests, which were performed in a Shimadzu Servopulser material testing machine. During the test, the crosshead moved at a speed of 1 mm/min, the inner and outer spans were 10 mm and 40 mm, respectively. SEM images of fracture surfaces were recorded and analyzed. The NETZSCH DIL 402 PC thermal dilatometer was used to measure the coefficient of thermal expansion (CTE) in the temperature range of 20–500 °C with a heating rate of 5 °C/min. For the thermal expansion measurements, specimens were machined along both the axial and radial directions, and the isotropy ratio is calculated as the ratio of the CTE along the two orthogonal directions.

3. Results and discussion

3.1. CNT dispersion

The most important factor in the preparation of CNT-reinforced composites is a good CNT dispersion, which indicates the fact that individual CNTs have to be distributed uniformly and well separated from each other. Fig. 3 is SEM images of the composite powders, indicating that CNTs can be homogenously dispersed at relatively low CNT contents, i.e. 0.05, 0.10, 0.25 wt.%. For 0.25 wt.% CNT content (Fig. 3 (d)–(f)), the MCMB surface is covered by a large amount of uniformly distributed CNTs due to physical adsorption. The length of CNTs is shortened to a few microns, and their alignment is also lost. For 0.4 wt.% or higher CNT content, CNT dispersion is no longer homogeneous, the aggregates can be observed in SEM images (Fig. 3(c)). The ethanol is not as well as toluene or DMF solvent to disperse the CNTs. Besides, rather than the bulk homogenous distribution in the whole matrix, the CNTs prefer to be located at the surfaces of graphite particles. Consequently, the CNT content herein is lower than some other reported polymer composites or CNT/carbon composites.

3.2. Mechanical and thermal properties of the composites

The flexural strength upon increasing CNT weight content is presented in Fig. 4(a). The graphite artifact prepared from the original MCMBs, which were not treated in ethanol, shows a flexural strength of 37.05 MPa. CNTs remarkably increase the strength

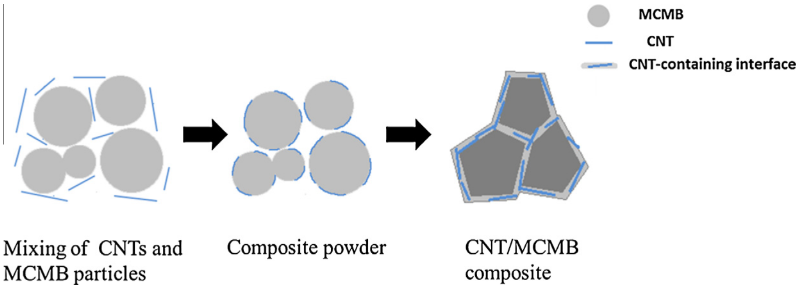

Fig. 1. Schematic of CNT/MCMB composite preparation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)