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TiC-modified carbon nanotubes, TiC nanotubes and TiC nanorods: Synthesis and characterization

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ABSTRACT

In the present study, single-phase TiC nanotubes and nanorods were synthesized by a novel pressureless spark plasma sintering (SPS) technique using carbon nanotubes (CNTs) and titanium powders at 1050 °C for 5 min. Moreover, formation mechanism of the resultant nanomaterials was clarified in detail. X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) patterns and Raman spectroscopy were conducted to study the microstructure and nature of the produced samples. XRD patterns indicated that all powders reacted to form TiC after applying 1050 °C. In addition, according to the TGA results, a significant increment in thermal properties was achieved compared to the pristine CNTs.

1. Introduction

Discovery of carbon nanotubes (CNTs) has been widely attributed to Iijima in 1991 [1]. However, this finding has been debated because several other researchers had previously stated carbon structures similar to those reported by Iijima, such as: Radushkevich et al. [2] in 1952, Bacon in 1960 [3], and Oberlin et al. [4] in 1976. Discovery of CNTs has excited interest in producing advanced nanomaterials such as nanotubes, nanorod, nanowhiskers and so on for many applications, because of their remarkable properties [5–12]. CNTs have been used as a template to prepare many kinds of nanocarbides, such as TiC, NbC, SiC nanostructures [13–15]. Carbide ceramics, especially TiC, have high melting points, good resistance to corrosion and oxidation in harsh environments, and significant mechanical properties such as ultrahigh hardness and high elastic modulus [16,17]. Owing to the attractive properties of titanium carbide, it can be applied as a nanostructural reinforcement for polymer, metal and ceramic matrix composites with a potential application in catalysis, microelectronics and industry [18]. TiC has better thermal stability and wettability to the metal matrices when compared with pure CNTs [19]. Many studies have been carried out to prepare new one-dimensional (1-D) nanostructured advanced materials such as nanotubes, nanowires, nanorods and nanowhiskers for potential applications. In particular, ceramic nanotubes/nanorods represent an interesting and important class of nanomaterials with wide applications such as nanoelectronics or quantum devices and drug delivery due to their singular shape and properties. Carbide nanorods and nanotubes with a high aspect ratio (like CNTs) would be promising reinforcements for next-generation materials [20,21]. For the mentioned reasons, synthesizing these types of ceramics is of interest. However, there have been few reports about synthesis of carbide ceramic nanotubes. Some researchers have reported the synthesis of carbide nanowires and nanotubes [13,22,23]. Taguchi et al. synthesized TiC nanotubes by heating CNTs and Ti powders at 1300 °C in a vacuum for 30 h [21]. In addition, they also produced SiC-CNTs hybrid structures in which carbon nanotubes were sheathed with a SiC layer by heating the materials in crucible at 1200 °C for 100 h [5]. Moreover, MWCNTs were coated with SiC by heating nanotubes with Si powder at 1200 °C for 5 h in a vacuum ($\sim 10^{-3}$ Pa) [24]. In order to overcome the problems of the mentioned techniques with long durations and frustrating stages, spark plasma sintering (SPS) was used in this study. SPS process is a pulsed current field assisted sintering technique based on electrical spark discharge phenomenon and can be used as a remarkable method for synthesizing and consolidating a large variety of materials [19]. The main advantage of this method is preventing grain growth in nanostructured materials [25]. The presence of the electric field accelerates diffusion due to the enhanced ion migration speed. Modification or synthesizing process can be done rapidly through SPS and, therefore, it can be employed to control grain growth by using sintering time shorter than those typical of conventional processes [17]. There are few studies regarding pressureless spark plasma sintering (SPS) just for porous materials [17,26]. However, to the best of our knowledge, nobody has reported the simultaneous synthesis of TiC nanorods and nanotubes, as well as TiC coated-CNTs, through a rapid pressureless SPS at 1050 °C for just 5 min. The objective of the present study is,

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therefore, to synthesize TiC nanotubes by a solid-state reaction between Ti and CNTs through a three-stage method. Characterization and microstructural observation of the resultant nanomaterials were carried out by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy. In addition, formation mechanism of these simultaneously produced nanomaterials was also elucidated.

2. Experimental procedure

MWCNTs (Shenzhen Nanotech Port Co. Ltd., China), as a template material, and Ti powder (Xingye Metallic Materials Co. Ltd., China) were used in this study. At the first stage, 1:1 at. ratio of Ti and CNTs (4 g) were mixed through ultrasonication method followed by wet milling (QM-3SP2). Afterwards, an additional amount of CNTs (2 g) was added to the mixture by ultrasonication and wet milling (stage two). Then, at stage three, the mixture transferred to the SPS furnace and heated at 1050 °C for just 5 min [19]. Structure and morphology of the treated-CNTs were characterized by XRD (Bruker D8, Cu kα radiation) and TEM (HRTEM, Tecnai, FEI). In order to evaluate the structural integrity of CNTs, Raman spectroscopy (Thermo Scientific DXR) was carried out by using a 532 nm argon laser. Thermo-gravimetric and differential scanning calorimetric analysis (TGA/DSC, Netzsch) were performed in an air condition for the treated and raw-CNTs.

3. Results and discussion

Fig. 1a and b shows TEM and high-resolution TEM (HRTEM) micrographs of the carbon nanotube templates, respectively. The interplanar spacing, provided in the inset image of Fig. 1b, is 0.34 nm, corresponding to the (002) planes of CNTs. In addition, the presence of impurity is observed at very limited sites (As shown by the arrow and the marked area in Fig. 1a and c). According to the interplanar spacing measurement in HRTEM image of Fig. 1d and selected area diffraction pattern (SAED; provided as an inset in Fig. 1d), it can be found that the impurity is Fe catalyst. Based on the manufacturer data sheet, the amount of impurity in the as-received CNTs is reported to be less than 3 wt%.

In order to achieve pressureless conditions during SPS process (used here), some modifications are made to the conventional die assembly. To better understanding the differences between SPS and pressureless-SPS methods, schematic of these processes are provided in Fig. 2. Based on Fig. 2a, T-shaped punches were fabricated from the same graphite material used for the die. There is a working space above the sample which can produce no external load condition during processing. The working space was filled by several graphite foils between the sample and upper punch of the graphite mold to ensure the pulsed current can pass through the powders. A minimum pressure was applied in order to provide sufficient contact resistance through the punch exterior and die wall interior. In the case of pressureless-SPS, the temperature was measured by a Pyrometer focusing on the bottom of the central borehole in the upper graphite punch, as can be seen in Fig. 2a. For a comparison, Fig. 2b shows a configuration of the die assembly for the conventional SPS (i.e. SPS with pressure). For measuring the temperature in SPS, two types of instruments are used; thermocouple (Fig. 2b) for sintering temperatures below 1000 °C and pyrometer (Fig. 2a) for sintering temperatures in excess of 1000 °C [27]. As mentioned before, pressureless-SPS was used to synthesis powder materials such as TiC nanotubes and nanorods, while the conventional SPS with the pressure

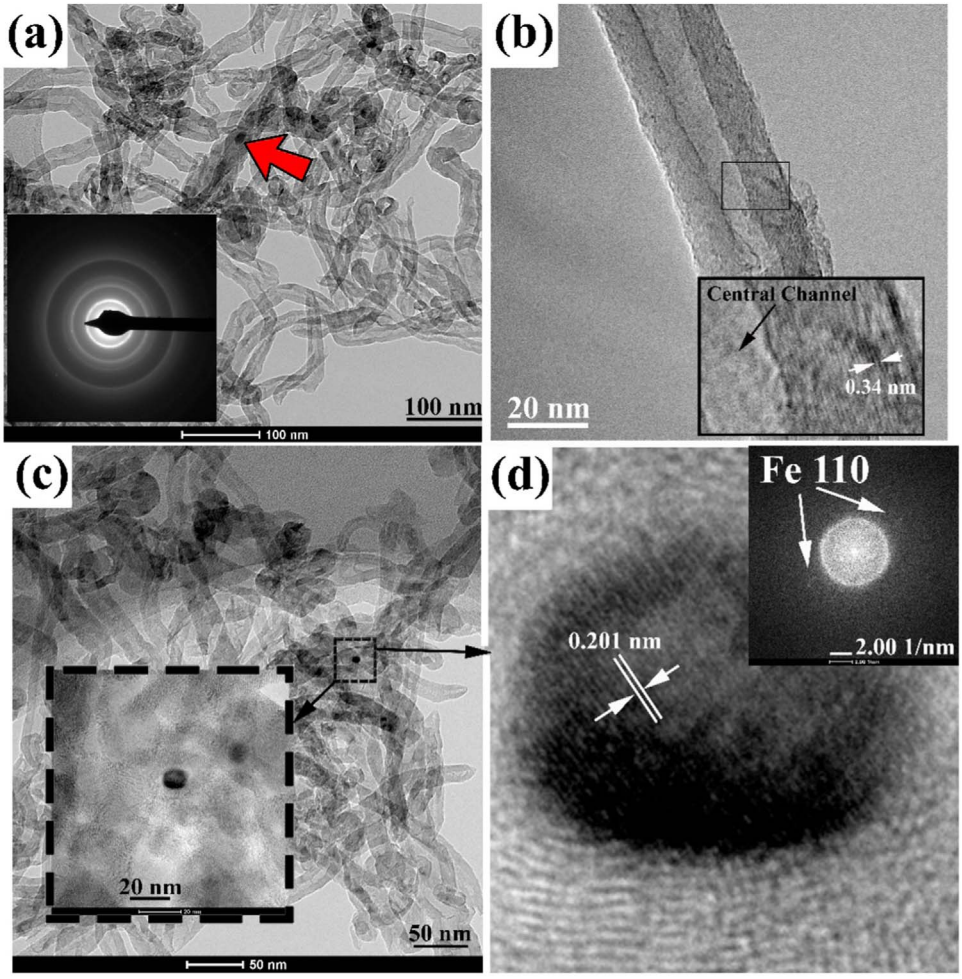

Fig. 1. (a-c) TEM observations of the raw-CNTs, (d) HRTEM image of the marked area in section (c) showing the presence of Fe catalyst. SAED analysis result is provided in the inset of (d) corresponding to (110) planes of Fe. Red arrow in section (a) indicate the location of Fe catalyst. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).