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Ceramics International 38 (2012) 4105–4110

CERAMICS INTERNATIONAL

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Microstructural evolution of multi-walled carbon nanotubes in the presence of mixture of silicon and silica powders at high temperatures

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Received 14 June 2011; received in revised form 19 December 2011; accepted 25 January 2012
Available online 3 February 2012

Abstract

Microstructural evolution of multi-walled carbon nanotubes (MWCNTs) in the presence of mixture of silicon and silica powders in a coke bed is studied in the temperature range of 1000–1500 °C by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and thermogravimetry–differential scanning calorimetry (TG–DSC). The results showed that a thin amorphous SiO_2 coating was formed on the surface of MWCNTs at the temperature below 1300 °C. With the increase of the treated temperature, the coating became thicker, 3–7 nm in thickness at 1400 °C and a maximum of 10 nm at 1500 °C. Meanwhile, SiC nanowires and SiC nanocrystals around Ni catalyst at the tip of MWCNTs were formed at 1400 °C and 1500 °C, which were related to the vapor–vapor (V–V) and vapor–liquid–solid (V–L–S) reactions between SiO (g) and CO (g) or C (s), respectively. The oxidation resistance of all the treated MWCNTs was better than that of as-received ones. The oxidation peak temperature reached 804.2 °C for the treated MWCNTs, much higher than 652.2 °C for as-received ones.

Keywords: SiC; MWCNTs; Evolution; SiO_2 coating; Oxidation resistance

1. Introduction

Carbon containing refractories have been widely used in the steelmaking industry due to their unique mechanical, thermal and chemical properties in particular to converter, steel treatment ladles or electric arc furnaces, etc., decades ago. As we know, carbon sources play a very important role in improving the thermal shock and slag resistance of this kind of refractories. On the other hand, they also react with Al, Si or SiO_2 additive to form Al_4C_3, SiC, etc., ceramic phases which act as reinforcing and toughening phases to improve their mechanical properties [1,2]. However, with the increasing demand of pure steel production, traditional carbon containing refractories, for example, MgO–C bricks containing about 10–20 wt% graphite flake, can not meet the requirements because of their recarburization into molten steel [3–5]. Therefore, it is necessary to develop low carbon containing refractories that have excellent properties [6,7].

Since carbon nanotubes (CNTs) were discovered by Lijima in 1991 [8], much attention has been paid on their potential application in composite materials due to their excellent mechanical, chemical and physical properties [9–11]. For example, MWCNTs have been widely used as reinforcement to enhance the strength and toughness of ceramic and metallic matrix composites [12–17]. In fact, MWCNTs are one of the most promising carbon source replacing graphite flake to develop low carbon containing refractories with high strength, toughness and excellent thermal shock resistance [18]. Fan et al. [19] added carbon black, graphite flake and phenolic resin into Al_2O_3–C refractory respectively, and observed different morphologies of SiC whisker due to the reaction between silicon-containing vapors like Si (g) or SiO (g) and carbon. Like above-mentioned carbon sources, when MWCNTs are incorporated into carbon containing refractories, they will also suffer from structural transformation by silicon-containing vapors. By now, there are few reports in relation to evolution of MWCNTs surrounded by silicon-containing vapors in the matrixes of carbon containing refractories at high temperatures.

In this paper, microstructural evolution of MWCNTs in the presence of mixture of Si and SiO_2 powders in a coke bed in the temperature range of 1000–1500 °C is investigated, in order to

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0272-8842/$36.00.
doi:10.1016/j.ceramint.2012.01.068

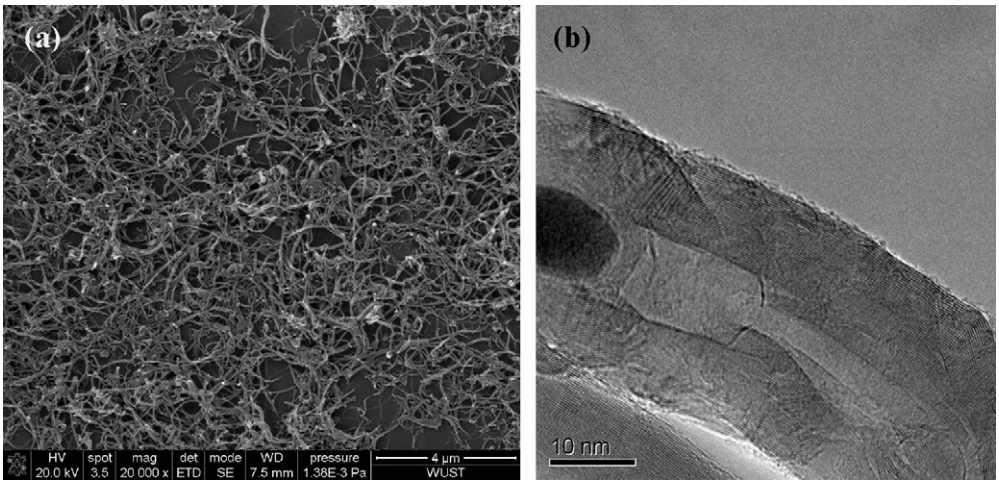

Fig. 1. SEM (a) and HRTEM (b) micrographs of as-received MWCNTs.

make out the reaction mechanisms between silicon-containing vapors and MWCNTs in the matrixes of carbon containing refractories containing Si and SiO_2 as the additives.

2. Experimental

MWCNTs (purity >95%, Alpha Nano Tech. Inc., Chengdu, China) synthesized from hydrocarbon were used as the starting materials. SEM (Fig. 1a) and HRTEM (Fig. 1b) micrographs showed that they had diameters in the range of 20–70 nm and were typically curved and twisted with each other. Some MWCNTs contained metal Ni catalyst grains within the hollow core near the tip. The experiment apparatus was very simple and depicted in detail in Fig. 2. In order to simulate the reactions between silicon-containing vapors and MWCNTs in the matrixes, firstly, Si (<0.045 μm, Zhejiang Kaiyuantong Silicon Co., Ltd., China) and SiO_2 (~0.5 μm, Lianyungang Huacheng Silica Co., Ltd., China) powders with the mole ratio of 1:1 were grinded evenly in a mortar and then set at the bottom of the Al_2O_3 crucible, where MWCNTs were put loosely on its surface. The crucible was covered with an Al_2O_3 lid, then put into an Al_2O_3 sagger fed with carbon black. Subsequently, the sagger was heated in the electric furnace from room temperature to 1000 °C, 1200 °C, 1300 °C, 1400 °C and 1500 °C at a rate of 5 °C/min, then soaked at the final temperature for 3 h respectively. After the experiment, the sagger cooled down naturally to room temperature in the furnace.

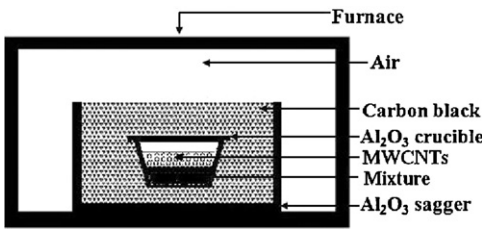

Fig. 2. Illustration of experimental setup.

The phase compositions of as-received and treated MWCNTs were characterized by X-ray diffraction with Cu-Kα radiation (XRD, x'Pert Pro, Philips, Netherlands). Scanning electron microscopy (SEM, Quanta 400, FEI Company, USA) and high-resolution transmission electron microscopy (HRTEM, 2000F, Jeol Ltd., Japan) equipped with energy dispersive X-ray spectroscopy (EDX, Noran 623M-3SUT, Thermo Electron Corporation, Japan) were carried out to examine the surface morphology and the microstructure of as-received and treated MWCNTs. Oxidation resistance of as-received and treated MWCNTs was evaluated by thermogravimetric analysis-differential scanning calorimetry (TG-DSC, STA449, NETZSCH, Germany).

3. Results and discussion

3.1. The phase compositions

XRD patterns of as-received MWCNTs and MWCNTs after treated at 1000–1500 °C are shown in Fig. 3. No new phases were detected in the samples at the treated temperature below

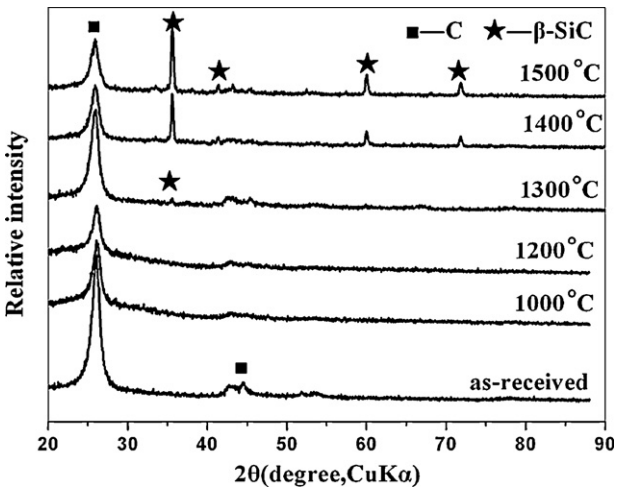

Fig. 3. XRD patterns of as-received and treated MWCNTs.