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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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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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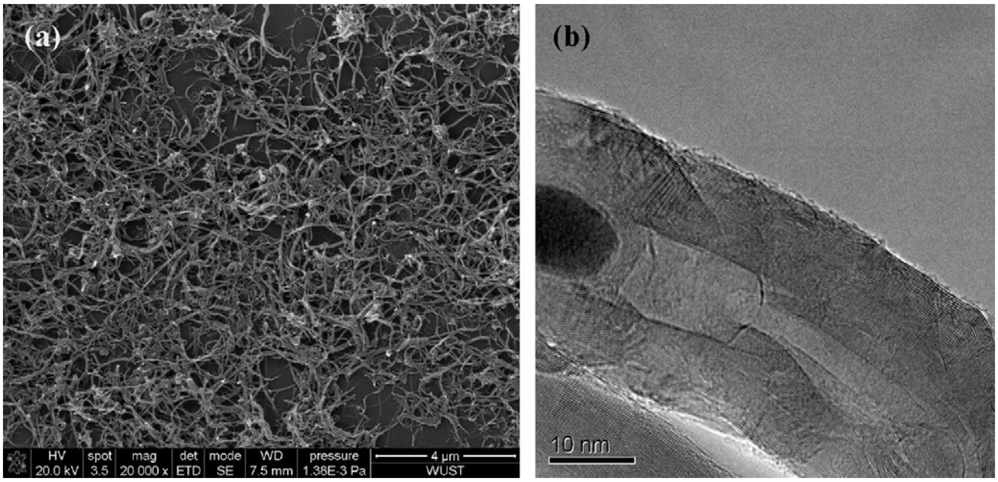

Fig. 1. SEM (a) and HRTEM (b) micrographs of as-received MWCNTs.

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.

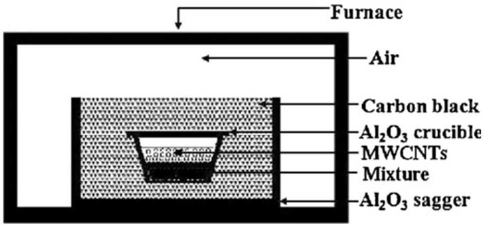

Fig. 2. Illustration of experimental setup.

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

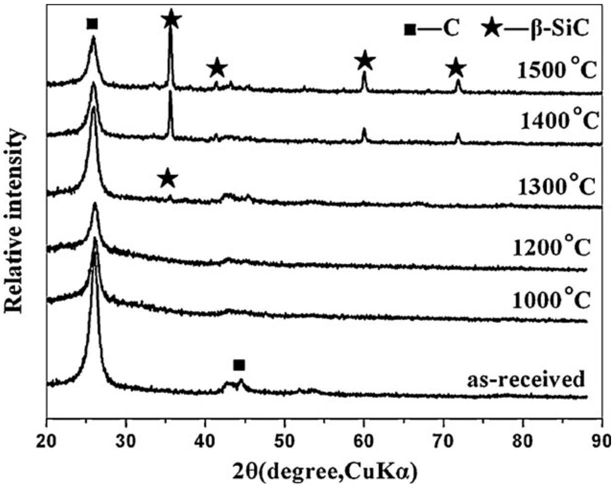

Fig. 3. XRD patterns of as-received and treated MWCNTs.

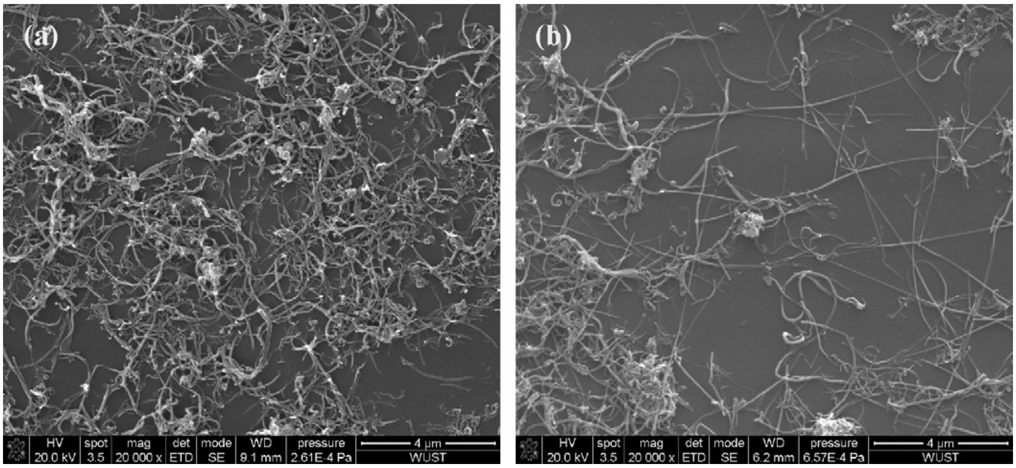

Fig. 4. SEM micrographs of MWCNTs treated at 1300 °C (a) and 1500 °C (b).

1200 °C compared with as-received MWCNTs. Only very weak diffraction peaks of SiC phase could be observed in the samples treated at 1300 °C. The peaks around $2\theta = 35.6^\circ, 41.4^\circ, 60.0^\circ$ and 71.8° corresponded to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of β-SiC, respectively. With the increase of treated temperature, the intensity of SiC phase increased from 1400 °C to 1500 °C.

3.2. The microstructure

All the MWCNTs after treated at different temperatures were examined by SEM analysis. It was found that the morphology of MWCNTs treated below 1300 °C did not change much compared with as-received ones (Fig. 4a). However, besides tangled MWCNTs, straight nanowires with length up to tens of micrometers were observed clearly in the samples treated at 1400 and 1500 °C (Fig. 4b). In addition, the diameters of the nanowires were similar to as-received MWCNTs.

HRTEM analysis was performed to examine the surface morphology and microstructure of the treated MWCNTs, as shown in Fig. 5. A very thin amorphous coating was homogenously formed on the surface of MWCNTs at 1300 °C (Fig. 5a) and the thickness of the coating came up to 3–7 nm at 1400 °C (Fig. 5b). EDX analysis confirmed the coating consisted of Si and O elements and their mol ratio was nearly 1:2, indicating that it was SiO_2 (Point A). For samples treated at 1500 °C, the coating in thickness further increased up to 7–10 nm (Fig. 5c–e). Besides coated MWCNTs, the straight nanowires found in the SEM analysis (Fig. 4b), were confirmed to be crystal SiC (Fig. 5d and f). Fig. 5f displays higher magnification image of the SiC nanowire, in which well-defined fringe separation of 0.26 nm was consistent with the *d*-spacing of (1 1 1) plane, suggesting that the growth direction was [1 1 1]. In addition, SiC nanocrystals were formed at the top of some MWCNTs in the Ni-rich area in the temperature range of 1300–1500 °C (Fig. 5g). A typical EDX spectrum taken from the Ni-rich area, suggested the presence of Si, C and Ni elements (Point B). As well, crystalline planes with *d*-spacing of 0.26 nm corresponded to (1 1 1) planes of β-SiC and 0.36 nm assigned to (0 0 2) planes of graphite domains.

For SiO_2 coated MWCNTs, it was speculated that there was a very thin SiC transition layer existed at the interface between SiO_2 coating and MWCNTs because SiO_2 could react with C atoms at high temperature to form SiC via Eq. (1). However, in our work SiC layer was not clearly observed which might be due to its similar morphology with SiO_2 coating.

$$SiO_2\,(s) + 3C\,(s) = SiC\,(s) + 2CO\,(g) \qquad (1)$$

Fig. 6 shows XRD pattern of MWCNTs treated at 1400 °C after holding at 650 °C for 3 h in air. It was found that as-received MWCNTs were completely oxidized. However, a relatively low peak of MWCNTs still remained for the treated MWCNTs. The intensity of SiC phase increased compared with the sample before test, which was associated with the oxidation of some MWCNTs. Meanwhile, the broad hale from 22° to 24° (2θ) corresponded to amorphous SiO_2, which was not observed in the XRD analysis before test because of its much lower content.

3.3. The oxidation resistance

TG–DSC analysis was adopted to examine the oxidation resistance of as-received and treated MWCNTs, as can be seen in Fig. 7. The experiment was carried out by heating the samples from room temperature to 1000 °C in a static air atmosphere at a heating rate of 10 °C/min. Under this circumstance, SiC could not be oxidized by O_2 (g). Meanwhile, effect of catalyst Ni on the oxidation resistance of different samples was ignored because of its low content in different samples. It is obvious that the starting temperatures (T_s), peak temperatures (T_p) and terminating temperatures (T_t) of exothermic peaks for the treated MWCNTs were much higher than those of as-received ones (Table 1), demonstrating that oxidation resistance of the treated MWCNTs was greatly improved. The peak temperature of as-received MWCNTs was 652.2 °C, while it increased with the increase of treated temperature from 1000 °C (735.8 °C) to 1500 °C (804.2 °C).

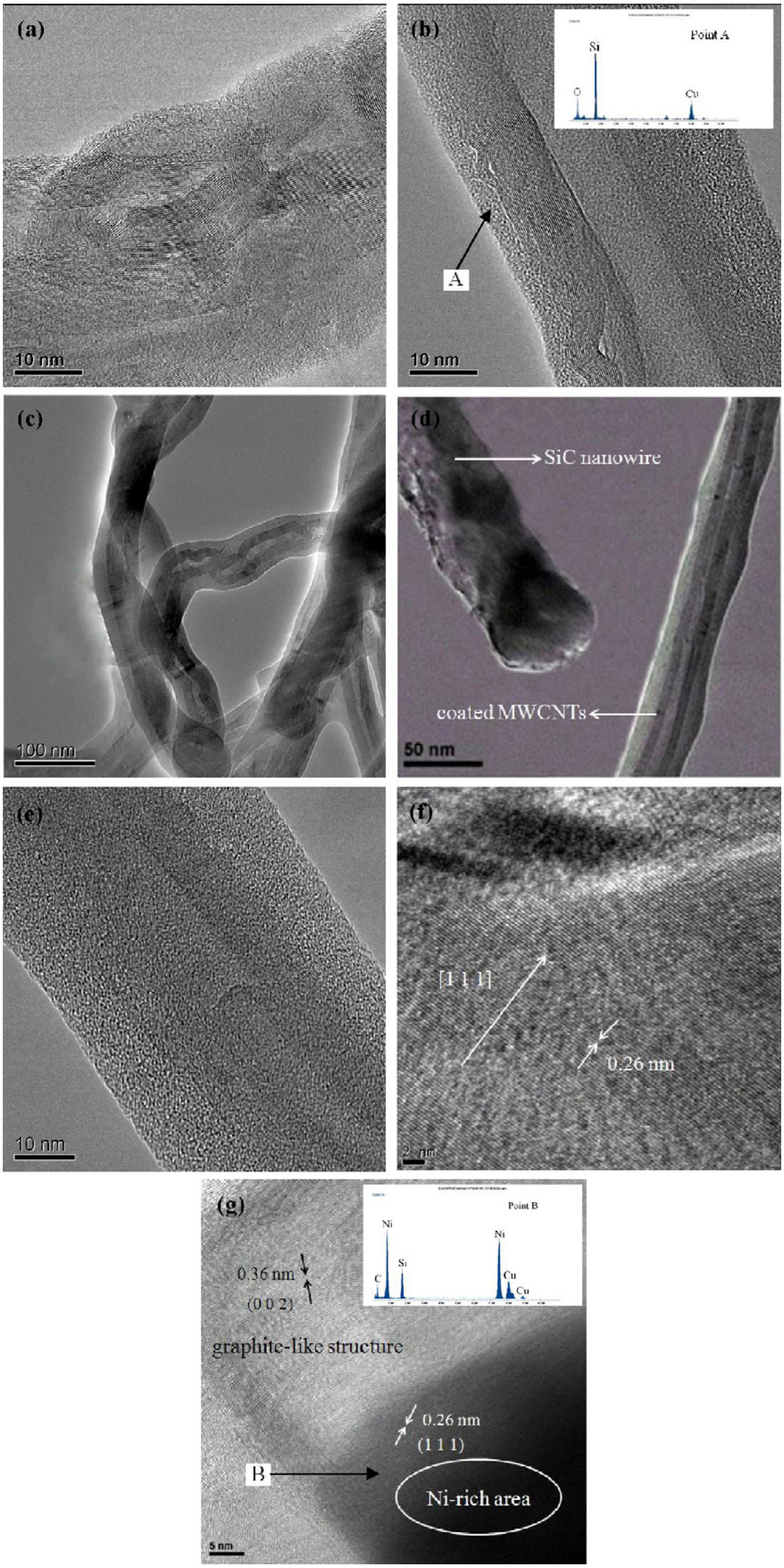

Fig. 5. HRTEM micrographs of the treated MWCNTs: (a) at 1300 °C, (b) at 1400 °C; (c) and (d) at 1500 °C; (e) the higher magnification image of coated MWCNTs at 1500 °C; (f) the higher magnification image of SiC nanowires at 1500 °C; (g) a higher magnification image of a Ni-rich area.

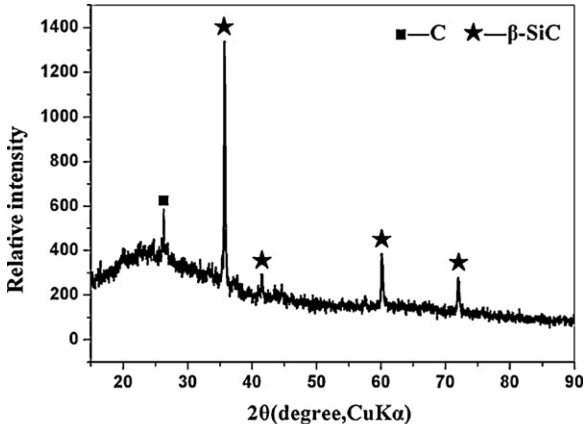

Fig. 6. XRD pattern of MWCNTs treated at 1400 °C after holding at 650 °C for 3 h.

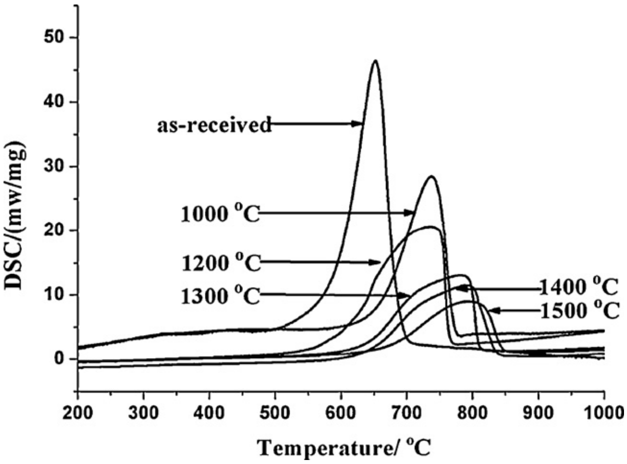

Fig. 7. DSC curves of as-received and treated MWCNTs.

The improved oxidation resistance was associated with the thickness of the protective coating on the surface of MWCNTs. In addition, with the increase of treated temperature, the relative amount of MWCNTs in the samples decreased, so the height of exothermic peak decreased and reached a minimum value for samples treated at 1500 °C.

3.4. The reaction mechanism

Based on the results mentioned above, SiO_2 coated MWCNTs, SiC nanowires and nanocrystals were formed simultaneously during the treatment process. The reaction mechanisms should be different and elucidated as follows.

At high temperatures, the atmosphere in a coke bed contained 3.5×10^4 Pa CO (g) and 6.5×10^4 Pa N_2 (g) in theory. As a matter of fact, a low partial pressure of O_2 (g) still coexisted. SiO (g) could be produced via reaction (2) and Si (g) was formed by phase transformation via Eq. (3), respectively. However, SiO (g) was the main gaseous specie in the crucible and played a dominant role during the reaction process [20,21].

$$\mathrm{Si\,(s,\,l)} + \mathrm{SiO_2\,(s)} = \mathrm{2SiO\,(g)} \tag{2}$$

$$\mathrm{Si\,(s,\,l)} = \mathrm{Si\,(g)} \tag{3}$$

For the formation of SiO_2 coating on MWCNTs, a V–V reaction mechanism is proposed. That is, the generated SiO (g) reacted with O_2 (g) or CO (g) to form SiO_2 coating on MWCNTs via Eqs. (4) and (5). With the increase of treated temperature, the amount of SiO (g) via Eq. (2) increased, leading to the fact that the coating became thicker.

However, in the case of SiC, two different formation mechanisms are proposed here. One is the vapor–vapor (V–V) mechanism for the formation of SiC nanowires. In this process, SiO (g) first reacted with CO (g) to form SiC nanonuclei and then grew SiC nanowires along the [1 1 1] direction. Similar result was also observed by Gao et al. [22]. The other is a metal-catalyzed vapor–liquid–solid (V–L–S) mechanism for the formation of SiC nanocrystals in some MWCNTs [23,24]. Some of the as-received MWCNTs contained residue nickel particles near the tip, while others contained no nickel particles. For some nickel-contained MWCNTs, the nickel particle would melt and provide an energetically favored site for the absorption of SiO (g). Then, SiO (g) reacted with C atoms in this area via Eq. (7) and formed SiC nanocrystals. On the other hand, SiO_2 coating was also deposited on the surface of MWCNTs simultaneously. Compared with reaction (7), (4) and (5) had much lower Gibbs energy from 1000 to 1500 °C, which was more thermodynamically favorable for formation of SiO_2 coating. Once the coating was thick enough, CO (g) could not diffuse through the coating and formation of SiC was stopped, leading to the fact that only SiC nanocrystals were formed while the whole MWCNTs did not transformed into SiC nanowires. The results differed from the reports by Tang et al. [20,21] who used MWCNTs as the templates to synthesize SiC nanowires or nanorods in vacuum or Ar atmosphere, which was attributed to the higher partial pressure of CO (g) and O_2 (g) in our system.

Table 1
Characteristic temperatures of exothermic peaks of as-received and treated MWCNTs.

Temperatures (°C)	As-received	After treated at (°C)				
		1000	1200	1300	1400	1500
T_s	587.3	608.2	610.3	635.8	639.8	650.4
T_p	652.2	735.8	737.4	780.0	789.2	804.2
T_t	693.1	763.0	780.3	808.3	835.6	837.3

$$2SiO\,(g) + O_2\,(g) = 2SiO_2\,(s) \qquad \Delta G^0 = -1,568,842.4 + 490.24T\ (kJ/mol) \tag{4}$$

$$SiO\,(g) + CO\,(g) = SiO_2\,(s) + C\,(s) \qquad \Delta G^0 = -667,484.2 + 329.68T\ (kJ/mol) \tag{5}$$

$$SiO\,(g) + 3CO\,(g) = SiC\,(s) + 2CO_2\,(g) \qquad \Delta G^0 = -404,146.1 + 338.92T\ (kJ/mol) \tag{6}$$

$$SiO\,(g) + 2C\,(s) = SiC\,(s) + CO\,(g) \qquad \Delta G^0 = -78,438.4 + 0.468T\ (kJ/mol) \tag{7}$$

4. Conclusions

Microstructural evolution of MWCNTs in the presence of mixture of silicon and silica powders in a coke bed was studied in the temperature range of 1000–1500 °C. Amorphous SiO_2 coating was formed on the surface of MWCNTs. And its thickness increased with the increase of treated temperature. Meanwhile, SiC nanowires and SiC nanocrystals were formed at the temperature above 1300 °C. The oxidation resistance of the treated MWCNTs improved greatly compared with as-received ones.

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