Carbon Nanotubes: Application in Carbon Containing Refractories

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Carbon nanotubes (CNTs) possess many unique mechanical properties and are considered as a new carbon source to develop high-performance carbon containing refractories. However, the problems with CNTs are involved in that they can easily transform into ceramic phases or be oxidized at high temperatures and difficult to homogeneously disperse in the matrix when they are incorporated into carbon containing refractories. Some research work has been carried out to solve the problems mentioned above in the present paper. Firstly, the microstructural evolution of multi-walled carbon nanotubes (MWCNTs) in the presence of different silicon sources such as silicon powder (Si), mixture of aluminium and silica powders (Al+SiO₂) and mixture of silicon and silica powders (Si+SiO₂) was studied in a coke bed in the temperature range from 1000–1500 °C. Secondly, the coating technology was adopted to form ceramic phases on the surface of MWCNTs using polycarbosilane (PCS) as precursor in order to improve their oxidation resistance. Thirdly, in-situ formation of CNTs in the Al₂O₃-C matrixes by the pyrolysis of phenolic resin was studied to make them homogeneous dispersion in the matrix. Finally, the influence of in-situ formed CNTs and ceramic whiskers on the mechanical properties of Al₂O₃-C refractories was studied after coking from 800 to 1400 °C.

1 Introduction

Since carbon nanotubes (CNTs) were discovered by Iijima in 1991, much attention has been paid on their potential application in ceramic matrix composites due to their excellent mechanical properties such as high elastic modulus, high tensile and bending strength and high fracture toughness [1–8]. For example, Zhu, et al. [9] reported that addition of 1.5 mass-% MWCNTs into Al₂O₃ nanocomposites could lead to an increase of 67 % and 119 % in cold modulus of rupture (CMOR) and fracture toughness (KIC), respectively. However, MWCNTs could be easily oxidized or transform into other phases at high temperature owing to high partial pressure of oxygen and presence of metal or other reactants in the materials [10–12]. For instance, MWCNTs could react with Al and transform into Al₄C₃ and AlC₃ phases in the MWCNTs-Al matrix composites [13]. Also, most of MWCNTs transformed into SiC phase with increasing the sintering temperature although the addition of a small amount of MWCNTs in the Si₃N₄ ceramics could obtain a sharp enhancement of strength and toughness [14]. On the other hand, the homogeneous dispersion of CNTs-Al₂O₃ composites were greatly improved with only addition of 1 mass-% MWCNTs. However, with further increasing the amount of MWCNTs from 3 mass-% to 5 mass-%, the mechanical properties became deteriorated continuously due to the agglomeration of MWCNTs. Similar phenomena happened while MWCNTs were used to reinforce Al₂O₃ nanocomposites [16]. Like ceramic matrix composites, CNTs can also be a new carbon source as reinforcement to enhance the strength and toughness of carbon containing refractories [17]. Actually, MWCNTs in carbon containing refractories also have the same problems like those in the ceramic matrix composites. Therefore, it is necessary to study the above-mentioned problems of MWCNTs in carbon containing refractories and figure out their influence on the microstructures and mechanical properties of this kind of materials.

2 Microstructural evolution

Aluminum, silicon and silica are considered as the mainstream additives in carbon containing refractories. At high temperatures, the vapors such as Si(g), SiO(g) and Al(g) originated from the additives could react with carbon sources like graphite flake or carbon black to form ceramic phases [18]. Similarly, when CNTs are incorporated into carbon containing refractories, they also suffer from structural transformation at high tempera-
In this work, microstructural evolution of MWCNTs in the presence of different silicon sources such as silicon powder (Si), mixture of aluminium and silica powders (Al+SiO₂) and mixture of silicon and silica powders (Si+SiO₂) was studied in a coke bed in the temperature range from 1000–1500 °C. The experimental processes and setups were illustrated in detail in previous papers [19–21].

Fig. 1 shows XRD patterns of as-received MWCNTs and MWCNTs after treated using different silicon sources. No new phases were detected at the temperature below 1300 °C in all the samples. As for Si as silicon source, only very weak diffraction peaks of SiC phase were observed at 1400 °C. The intensity of SiC peaks became much stronger while for MWCNTs, it became much weaker after they were treated at 1500 °C (Fig. 1a).

With regard to Al+SiO₂ as silicon source, SiC peaks did not appear until the temperature was up to 1500 °C (Fig. 1b). However, in the case of Si+SiO₂, SiC peaks appeared at 1300 °C and their intensity increased a lot at 1400 °C. With further increasing the temperature to 1500 °C, the intensity of SiC peaks did not change much (Fig. 1c).

HRTEM micrographs of treated MWCNTs using different silicon sources at various temperatures. Fig. 1 shows XRD patterns of as-received MWCNTs and MWCNTs after treated using different silicon sources.
temperatures were shown in Fig. 2. As for Si as silicon source, a very thin SiC coating formed on the surface of MWCNTs at 1400 °C (Fig. 2a). With the increase of temperature to 1500 °C, almost all the MWCNTs changed into SiC solid nanowires with about 200 nm in diameter as identified by only presence of Si and C elements in the EDS analysis together with 0.26 nm involved in (1 1 1) planes of β-SiC (Fig. 2b–c). A similar coating with smaller thickness was also observed on MWCNTs after treated using Al+SiO2 at 1500 °C (Fig. 2d). With regard to Si+SiO2, a very thin amorphous coating homogeneously formed on the surface of MWCNTs at 1300 °C and the thickness of the coating came up to 3–7 nm at 1400 °C. For samples treated at 1500 °C, the coating in thickness further increased up to 7–10 nm. EDS analysis confirmed the coating consisted of Si and O elements and their molar ratio was nearly 1:2, indicating that it was SiO2 (Fig. 2e). In addition, SiC nanocrystals also formed at the top of some MWCNTs in the Ni-rich area in the temperature range of 1300–1500 °C. A typical EDS spectrum taken from the Ni-rich area suggested the presence of Si, C and Ni elements. As well, crystalline planes with d-spacing of 0.26 nm corresponded to (1 1 1) planes of β-SiC and c-graphite domains, with spacing of 0.36 nm assigned to their (0 0 2) planes (Fig. 2f). The difference in microstructural evolution of MWCNTs was due to different partial pressures of Si (g) and SiO (g) in the system using various silicon sources [19].

Fig (3) reveals the gaseous compositions in the systems calculated by thermodynamic analysis software (FactSage 5.5). It can be seen that at different temperatures, Si (g) partial pressure in the system is highest for Si silicon source, and SiO (g) partial pressure is the highest for Si+SiO2 silicon source. In the case of Al+SiO2, Si (g) and SiO (g) partial pressures are both the lowest.

3 Coating formation on MWCNTs

In order to improve the oxidation resistance of MWCNTs, a simple and effective way was offered to coat MWCNTs with ceramic phase using polycarbosilane (PCS) as precursor. The experimental processes and setups were indicated in the previous report [22]. XRD pattern of cured PCS treated at 1500 °C is shown in Fig. 4a. It can be seen that the broad halos from 22 to 24° (2θ) corresponded to amorphous SiC, SiO2, while the low and broad diffraction peak at 35.6° associated with β-SiC phase. FESEM micrograph (Fig. 4b) of the pyrolyzed PCS powder showed that many vitreous grains as well as balls with several micrometers in diameter coexisted with each other. Besides these, a small amount of nanowhiskers were embedded in the balls and others were located on the surface of vitreous grains. According to XRD and EDS analysis, the grains, balls and whiskers were confirmed to be SiC, SiO2 and SiC respectively.

HRTEM micrographs of MWCNTs after treated with PCS are shown in Fig. 5. A SiC coating with about 5~10 nm in thickness was clearly observed on the surface of MWCNTs as identified by XRD and EDS analysis (Fig. 5a–b). The formation of SiC coating was attributed to the absorption of PCS on MWCNTs and its pyrolysis at high temperature [22]. The oxidation resistance of the coated MWCNTs including as-received ones was evaluated in Fig. 6. According to DSC curves, it is obvious that the peak tempera-

![Fig. 3 Gaseous compositions in the systems using different silicon sources at 1500 °C](image-url)

![Fig. 4 XRD, FESEM micrograph and EDS analysis of the pyrolyzed PCS at 1500 °C](image-url)
tures of the exothermic peaks for the coated MWCNTs was much higher than that of as-received MWCNTs, demonstrating that the oxidation of coated MWCNTs was delayed and their oxidation resistance was greatly improved.

4 In-situ formation of CNTs and ceramic whiskers

In order to solve the problem of dispersion, in-situ formation of CNTs in the Al₂O₃-C matrix specimens was designed and the compositions are indicated in Tab. 1. Addition of Ni(NO₃)₂·6H₂O into the specimens M-AN and M-SN was carried out as follows. Firstly, white fused alumina powder (45 µm, 98,6 mass-% Al₂O₃, Almatis) and Ni(NO₃)₂·6H₂O (98+%, analytical, reagent, sigma-Aldrich) were mixed evenly using ethanol as the organic solvent. Then the slurry was dried at 110 °C for 4 h followed by grinding into fine powder. Finally, the as-prepared powder or white fused powder was mixed with resin powder (solid, >40 mass-% fixed carbon, Wuhan, China) and Al or Si powder according to each composition, then cold pressed to specimens with 20 mm in diameter and 20 mm in height under a pressure of 31.8 MPa. Subsequently, the samples were fired in a coke bed from room temperature to 800 °C, 1000 °C, 1200 °C and 1400 °C using a heating rate of 5 K/min and a dwell time of 3 h, respectively.

4.1 Al₂O₃-Al-C matrix specimens

XRD patterns obtained from specimens M-A and M-AN coked from 800 °C to 1400 °C were shown in Fig. 7. As for specimen M-A, only Al₂O₃ and Al phases were detected after fired at 800 °C. At 1000 °C, Al₄C₃ and AlN phases were detected, and their peaks intensity increased a little with increasing the temperature to 1200 °C. When the temperature was up to 1400 °C, Al₃O₃C and Al₂CON phases were detected while AlN,
\( \text{Al}_2\text{C}_3 \text{ and } \text{Al} \text{ phases disappeared on the contrary (Fig. 7a).} \) Compared with specimen M-A, the diffraction peak of \( 26,5^\circ \) involved in \((0 0 2)\) plane of graphite structure was observed in the specimen M-AN from 1000 °C to 1400 °C. On the other hand, the intensity of \( \text{Al}_2\text{C}_3 \text{ and } \text{AlN} \text{ phases was a little higher than that in specimen M-A at 1000 °C and 1200 °C, while catalyst } \text{Ni} \text{ was also detected (Fig. 7b).}\)

SEM micrographs of ruptured surface of specimens M-A and M-AN coked from 800 °C to 1400 °C were shown in Fig. 8. In the specimen M-A, no whiskers could be observed in the temperature range from 800–1200 °C (Fig. 8a–c). However, a number of whiskers such as \( \text{Al}_2\text{O}_4\text{C}, \text{Al}_3\text{CON} \text{ and } \text{AlN} \text{ as identified by XRD and EDS analysis formed in the pores with increasing the temperature to 1400 °C (Fig. 8d).} \) In the case of specimen M-AN, numbers of nanostructure substance deposited in the matrix at 800 °C and their diameters and lengths became larger with the increase of temperature to 1000 °C (Fig. 8e–f). HRTEM micrographs further confirmed that they were tabular MWNTs with about 20 nm in diameter and 0.5 µm in length which implanted and bounded well with the \( \text{Al}_2\text{O}_3 \text{ powder (Fig. 9a–b).} \)

With the increase of temperature to 1200 °C, a large amount of AlN and \( \text{Al}_2\text{C}_3 \text{ whiskers were observed in the texture and their amount increased a lot and the diameter of some got coarser at 1400 °C (Fig. 8g–h).} \)

4.2 \( \text{Al}_2\text{O}_3\text{-Si-C matrix specimens} \)

Fig. 10 shows XRD patterns of specimens M-S and M-SN coked from 800–1400 °C. In the specimen M-S, only \( \text{Al}_2\text{O}_3 \text{ and } \text{Si} \text{ phases were detected from 800–1200 °C. At 1400 °C, } \text{Si phase disappeared while } \text{SiC} \text{ and } \text{SiO}_2 \text{ phases formed on the contrary (Fig. 10a).} \) With regard to specimen M-SN, the same results were also observed at 800–1000 °C except for the formation of graphite structure and catalyst Ni. At

![Fig. 8 SEM micrographs of Al₂O₃-C matrix specimens M-A and M-AN coked at different temperatures](image-url)
1200 °C, the peak intensity of Si phase decreased a lot, while a large number of SiC phase formed on the contrary. With further increasing the temperature to 1400 °C, Si phase disappeared while the peak intensity of SiC phase increased a lot, together with the formation of a little amount of SiO₂ phase (Fig. 10b).

SEM micrographs of ruptured surface of specimens M-S and M-SN coked from 800–1400 °C were shown in Fig. 11. No whiskers formed in the specimen M-S from 800–1200 °C (Fig. 11a–c). In contrast, many SiC whiskers with nanosize in diameter and micrometer size in length formed in the matrix at 1400 °C (Fig. 11d). In the case of specimen M-SN, a large amount of CNTs knitting into net-like structure homogeneously formed in the pores or on the surface of Al₂O₃ particles at 800 °C and 1000 °C (Fig. 11e–f). At 1200 °C, both MWCNTs and SiC whiskers could be observed in the matrix (Fig. 11g). With further increasing the temperature to 1400 °C, more amount of SiC whisker with smaller diameter formed and bonded with each other compared with M-S (Fig. 11h). In addition, a higher magnification confirmed that catalyst Ni droplets were encapsulated at the tip of some SiC whiskers, indicating a typical vapor-liquid-solid (V-L-S) growth mechanism (Fig. 11i).

Differences in microstructure and morphology of Al₂O₃-C matrix specimens were attributed to different formation mechanisms with or without catalyst. It is well-known that transition metals, such as iron, cobalt and nickel can work as catalysts to accelerate the formation of ceramics whiskers (AlN, Al₄C₃, SiC, etc.) via V-L-S growth mechanism, which was confirmed by the fact that the amount of whiskers in the specimens M-AN and M-SN was much larger and their formation temperature was also much lower than the specimens M-A and M-S [25–27].

5 Mechanical properties of Al₂O₃-C refractory specimens

The raw materials, preparation and characterization methods of the investigated Al₂O₃-C refractory specimens were presented in the previous work [28]. In order to investigate the influence of catalyst, the Al₂O₃-C refractory specimens with or without Ni(NO₃)₂·6H₂O were defined as S-R and S-RNi respectively.

Fig. 12 shows mechanical properties including CMOR and E of coked Al₂O₃-C refractory specimens measured by three-point bending test at room temperature. It is obvious that the CMOR and E increased simultaneously with the increase of firing temperature from 800–1200 °C, and then decreased dramatically with the temperature up to 1400 °C. Compared with S-R, specimen S-RNi had a much higher CMOR and E in all temperature range.

Fig. 13 shows the force-displacement curves of Al₂O₃-C refractory specimens after coked at different temperatures. It can be seen that the changes of forces and displacements had the same trend with CMOR and E.
Fig. 11 SEM micrographs of Al₂O₃-C matrix specimens M-S and M-SN coked at different temperatures

Fig. 12 CMOR and E of Al₂O₃-C refractory specimens coked at different temperatures
Namely, forces and displacements increased with the increase of firing temperature and reach a maximum at 1200 °C, then decreased dramatically at 1400 °C. Like CMOR and E, specimens S-RNi had the higher forces and displacements than S-R in all temperature range.

The differences in mechanical properties were greatly influenced by the microstructure of Al₂O₃-C refractory specimens. In comparison with specimen S-R, the improvement of mechanical properties of specimen S-RNi, on the one hand, was attributed to the strengthening and toughening actions of in situ formed CNTs like crack deflection, bridging, fracture and pulling-out [29–32]. On the other hand, residual CNTs as well as more amount and better interlocked ceramic whiskers also endowed specimens S-RNi with better mechanical properties. The reason why the mechanical properties of all the specimens get deteriorated from 1200–1400 °C was attributed to the volume expansion of the specimens as discussed in detail in the precious work [33].

6 Conclusions

The following conclusions can be drawn on the basis of study of microstructural evolution of MWCNTs, coating formation, in situ formation of CNTs and ceramic whiskers and the mechanical properties of Al₂O₃-C refractories:

1) Microstructural evolution of MWCNTs was of great difference using different silicon sources at different temperatures, which was attributed to the different partial pressures of Si(g) and SiO(g) in the systems.

2) SiCₓOᵧ coating formed on the surface of MWCNTs using PCS as precursor and the oxidation resistance the coated MWCNTs was greatly improved compared with as-received ones.

3) CNTs were in situ formed in the matrix using nickel nitrate as catalyst by pyrolysis of phenolic resin. Meanwhile, catalyst also promoted the formation of ceramic whiskers and decreased their formation temperatures.

4) The mechanical properties of Al₂O₃-C refractories with addition of nickel nitrate were greatly improved, which was attributed to the in situ formed CNTs and more amount of ceramic whiskers.

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Reference


