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Microstructure and mechanical properties of multi-walled carbon nanotubes containing Al_2O_3–C refractories with addition of polycarbosilane

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Abstract

Carbon nanotubes (CNTs) are a promising reinforcement for fabricating Al_2O_3–C refractories. However, CNTs are prone to agglomerate or react with antioxidants or reactive gaseous phases such as Al (g), Si (g) and SiO (g), etc. at high temperatures. To overcome the problems above, polycarbosilane (PCS) and multi-walled carbon nanotubes (MWCNTs) were firstly mixed with micro-alumina powder in a liquid medium and then incorporated into Al_2O_3–C refractories. Then the microstructure and mechanical properties of Al_2O_3–C refractories fired in the temperature range from 800 °C to 1400 °C were investigated in this work. The results showed that the MWCNTs were well dispersed in the specimens with addition of PCS in contrast to the specimens without PCS due to the PCS adsorption on the surface of MWCNTs during the mixing process. And the mechanical properties, such as cold modulus of rupture (CMOR), flexural modulus (FM), forces and displacements of Al_2O_3–C refractories with PCS were much higher than those without PCS, which was attributed to more homogeneous dispersion of MWCNTs, more residual MWCNTs as well as different morphologies of ceramic whiskers. Meanwhile, the oxidation resistance of Al_2O_3–C refractories with PCS was improved greatly, which was supposed that the in situ formed SiC_xO_y coating prevented the oxidation of MWCNTs to some extent.

Keywords: C. Mechanical properties; Al_2O_3–C refractories; MWCNTs; Polycarbosilane

1. Introduction

Al_2O_3–C refractories have been widely used as high-duty and functional materials in the continuous casting of steelmaking industry like slide gates, submerged entry nozzles and monobloc stoppers, due to their excellent mechanical, thermal and chemical properties [1]. For the most effective productivity of the steel plant, this kind of refractories are required to have excellent thermal spalling resistance, mechanical properties as well as oxidation resistance. An optimization and enhancement of the above properties can be achieved by designing their micro-/nano- structures [2,3].

Since CNTs were discovered by Lijima 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 as well as high fracture toughness [4–11]. For example, Zhu et al. [10] reported that addition of 1.5 wt% MWCNTs into Al_2O_3–MWCNTs nanocomposites could result in an increase of 67% and 119% in cold modulus of rupture (CMOR) and fracture toughness (K_{IC}), respectively. However, MWCNTs could be easily oxidized or transform into other phases at high temperatures owing to high partial pressure of oxygen and presence of metals or other reactants in the materials [12–14]. For instance, if MWCNTs were treated in the presence of silicon powder or mixture of silicon and silica powders at high temperatures, various kinds of ceramic composite coating formed on the surface of MWCNTs and some MWCNTs also transformed into ceramic nanomaterials due to different partial pressures of Si (g) and SiO (g) in the systems [15–17]. As well, when MWCNTs were incorporated into

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MWCNTs–Al matrix composites, MWCNTs reacted with Al and transformed into Al_4C_3 and AlC_2 phases [18]. Likewise, most of MWCNTs transformed into SiC phase with increasing the sintering temperature although the strength and toughness increased with addition of a small amount of MWCNTs in the Si_3N_4 ceramics [19]. On the other hand, the homogeneous dispersion of MWCNTs in the matrix is another problem to be encountered. Zhang et al. [20] reported that the Young's modulus and flexural strength of CNTs–Al_2O_3 composites increased greatly with only addition of 1 wt% MWCNTs. However, with further increasing the amount of MWCNTs from 3 wt% to 5 wt%, the mechanical properties became deteriorated continuously due to the agglomeration of MWCNTs. Similar phenomenon also happened to MWCNTs reinforced Al_2O_3 nanocomposites [21]. Our previous work also indicated that high amount of MWCNTs such as 1 wt% MWCNTs, resulted in severe agglomeration in the matrix and caused the deterioration of the mechanical properties of Al_2O_3–C refractories. In addition, most of MWCNTs were consumed due to oxidation or transformation into ceramic whiskers during the firing process [22]. By now, the surface treatment technology has been successfully employed to solve the dispersion and structural transformation of MWCNTs in the composites [23–27]. For example, SiC coated MWCNTs substituting for as-received ones were added into polymer or ceramic matrix composites to prevent the agglomeration and structural transformation, respectively. Furthermore, the mechanical properties of the composites containing coated MWCNTs were improved greatly compared with as-received ones. However, the method for the fabrication of coated MWCNTs, based on a relatively complicated and time-consuming producer, was not always practical and cost-efficient.

We have developed a new and simple process to produce the SiC_xO_y coating on the surface of MWCNTs using PCS as the precursor. The coating resulted from the in situ pyrolysis products of PCS which adsorbed on the surface of MWCNTs during the mixing process [28]. In this work, PCS and MWCNTs were directly mixed with micro-sized alumina in a liquid medium and then incorporated into Al_2O_3–C refractories. The microstructure including MWCNTs dispersion, structural transformation as well as whiskers formation and mechanical properties of Al_2O_3–C refractories with or without addition of PCS were investigated after firing in the temperature range from 800 °C to 1400 °C.

2. Experimental

2.1. Raw materials and refractories fabrication

MWCNTs (purity $>95\%$, Alpha Nano Tech. Inc., Chengdu, China) synthesized from a hydrocarbon precursor were used as starting materials and shown in Fig. 1a (SEM) and b (TEM). They were typically curved and twisted with the diameters in the range of 20–70 nm. MWCNTs and micro-sized alumina powder (CL370, 5 μm, 98.6 wt% Al_2O_3, Almatis) without or with 2 wt% commercial PCS were mixed in a ball mill using corundum balls as the abrasive media and absolute ethyl alcohol as dispersant at a speed of 250 rpm for 6 h. The mass ratio of CL370 to MWCNTs and PCS were 10:1:0 and 10:1:2, which were defined as M1 and M1-PCS, respectively. All the mixtures above were dried at 110 °C for 12 h.

Al_2O_3–C refractories were prepared using tabular alumina (2–1 mm, 1–0.5 mm, 0.6–0.2 mm, <75 μm and <20 μm, 98.5 wt% Al_2O_3, Almatis), silicon powder (<45 μm, 98.4 wt% Si, Anyang, China), aluminum powder (<45 μm, 98.3 wt% Al, Xinxiang, China), microsilica powder ($\sim$0.5 μm, 97.0 wt% SiO_2, Elkem, Norway), and pre-prepared mixtures as raw materials and thermosetting phenolic resin (liquid, >40 wt% fixed carbon, Wuhan, China) as binder. The batch compositions consisted of 83 wt% tabular alumina, 2 wt% aluminum powder, 3 wt% silicon powder, 1 wt% silica powder, pre-prepared mixture M1 or M1-PCS and additional 4 wt% thermosetting phenolic resin, which was labeled as M1 and M1-PCS, respectively. Finally, all the raw materials were mixed for 30 min in a mixer with the rotating speed of 80–100 rpm. After kneading, specimens of 25 mm in width, 25 mm in height and 100 mm in length were compacted under a pressure of 150 MPa and then cured at 180 °C for 24 h. Specimens were fired in an

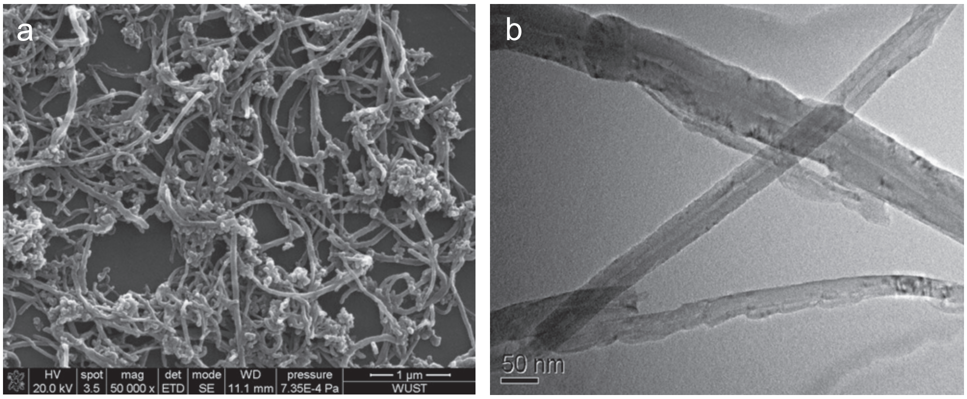

Fig. 1. SEM (a) and TEM (b) micrographs of as-received MWCNTs.

Al_2O_3 sagger fed with fine petroleum coke powder in an electric furnace from room temperature to 800 °C, 1000 °C, 1200 °C and 1400 °C using a heating rate of 5 °C/min and a holding time of 3 h, respectively.

2.2. Tests and characterization methods

The phase compositions of all the Al_2O_3–C refractories fired at different temperatures were analyzed by X-ray diffraction (XRD, X'Pert Pro, Philips, Netherlands). The microstructure of ruptured surfaces of coked Al_2O_3–C refractories was observed by scanning electron microscopy (Nova 400 Nano FESEM, FEI Co., Philips, Eindhoven, The Netherlands) equipped with energy dispersive X-ray spectroscopy (EDS, Phoenix, Philips, Eindhoven, The Netherlands). The transmission electron microscopy (TEM, 2000F, Jeol Ltd., Japan) was used to examine the morphology and microstructure of as-received and coated MWCNTs. The mechanical properties including cold modulus of rupture (CMOR) and flexural modulus (FM, which means Young's modulus determined by a bending test) were measured by three-point bending test at ambient temperature with a span of 80 mm and a loading rate of 0.5 mm/s by means of electronic digital control system (EDC 120, DOLI Company, Germany). The force–displacement curve of each refractory specimen was recorded simultaneously during the test. The oxidation resistance of Al_2O_3–C refractories was carried out by heating the cured specimens from room temperature to 1400 °C at 5 °C/min and a holding time of 3 h in air.

3. Results and discussion

3.1. Phase compositions of Al_2O_3–C refractories

In order to study the effect of PCS on the phase compositions in Al_2O_3–C refractories, XRD patterns of specimens M1 and M1-PCS coked from 800 °C to 1400 °C were shown in Fig. 2. As for specimen M1 (Fig. 2a), only Al_2O_3, Al, Si and MWCNTs (graphite structure) were detected at 800 °C. At 1000 °C, Al phase disappeared whereas AlN, Al_4C_3, cristobalite phases together with a little amount of SiC phase formed [29–31]. With the firing temperature of 1200 °C, AlN and Al_4C_3 phases disappeared and the peaks of Si phase disappeared instead of the formation of more SiC phase. At 1400 °C, the peak intensity of SiC phase decreased a bit while a little amount of mullite was detected at the same time [32,33]. In contrast to specimen M1, the graphite phase still existed in all the specimens of M1-PCS fired from 800 °C to 1400 °C (Fig. 2b). Additionally, the peak intensity of AlN and Al_4C_3 phases was little lower in the specimen M1-PCS fired at 1000 °C. Up to 1200 °C, Si phase still existed while SiC phase appeared and its amount was lower than that in specimen M1. The peak intensity of SiC phase increased a lot with increasing the temperature to 1400 °C.

The difference in phase compositions between specimen M1 and M1-PCS suggested that PCS addition could protect MWCNTs from being oxidized and transforming into ceramic phases, which could be explained by in situ formed SiC_xO_y coating on the surface of MWCNTs as shown in Fig. 3 [28]. During the mixing process of pre-prepared powder, PCS adsorbed on the surface of MWCNTs and then pyrolyzed into SiC_xO_y ceramic

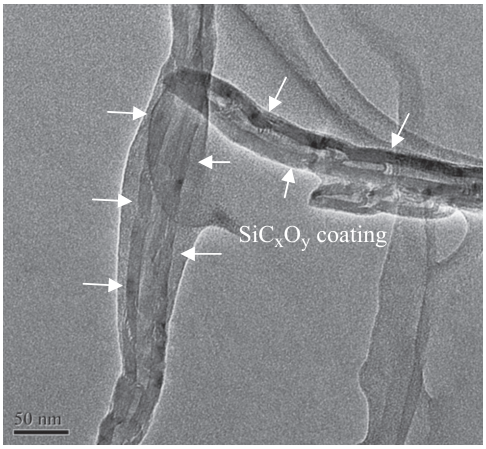

Fig. 3. TEM micrograph of SiC_xO_y coated MWCNTs.

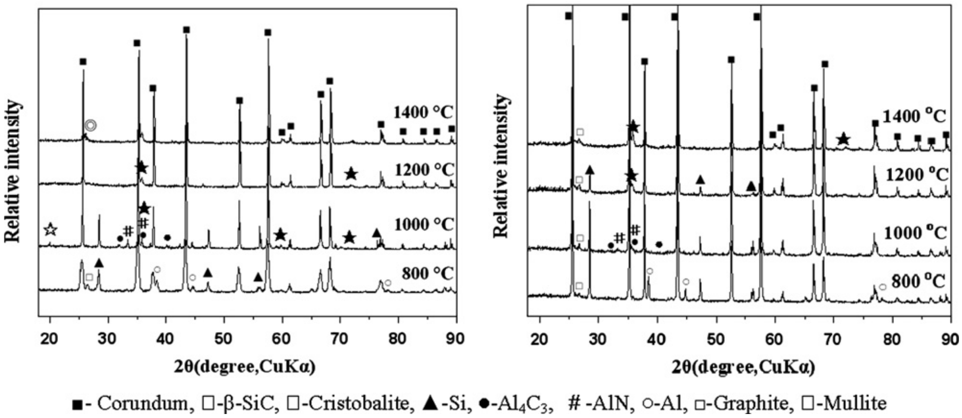

Fig. 2. XRD patterns of specimens M1 (a) and M1-PCS (b) fired at different temperatures.

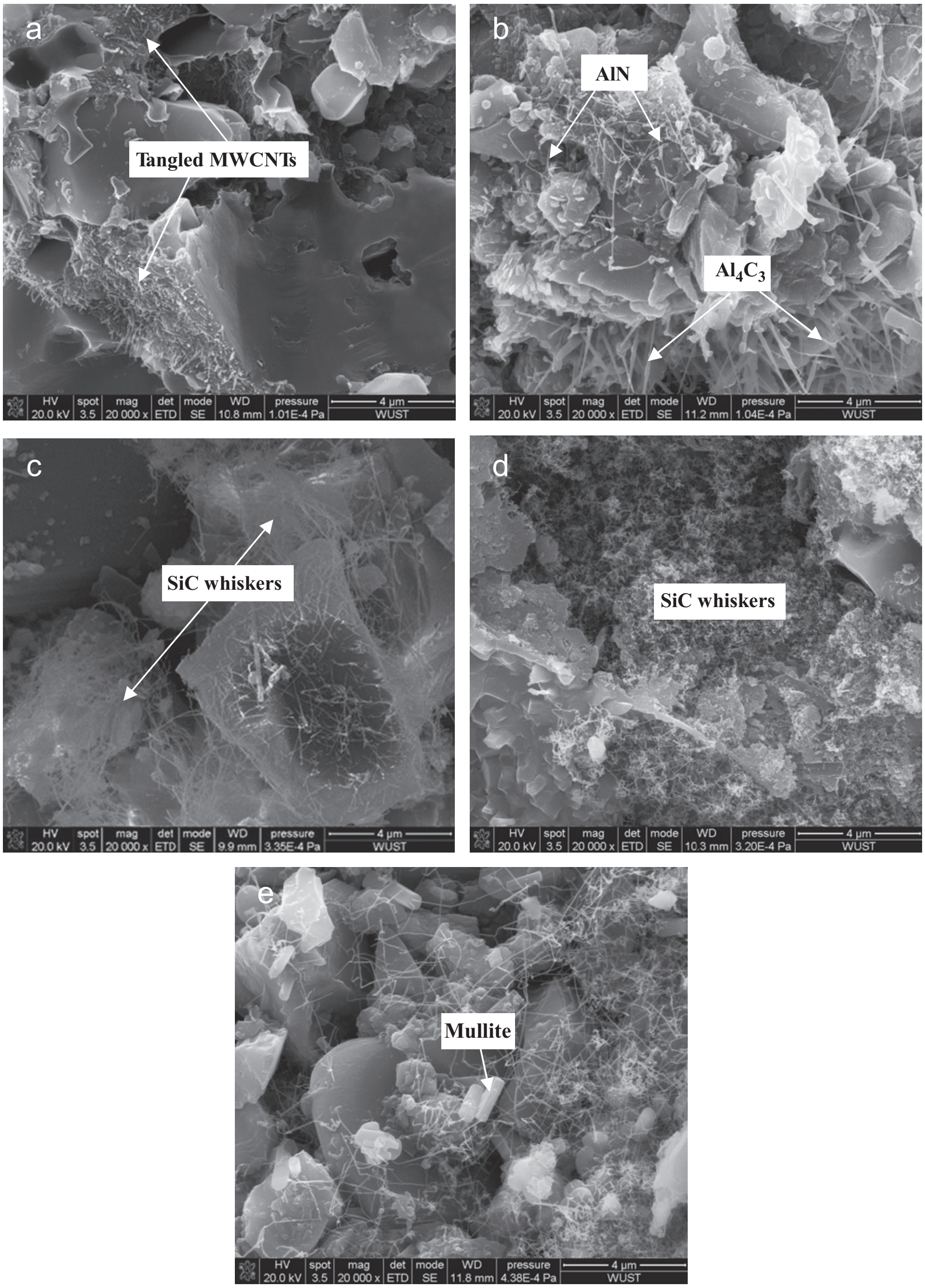

Fig. 4. SEM micrographs of specimen M1 fired at 800 °C (a), 1000 °C (b), (c), 1200 °C (d) and 1400 °C (e).

coating on MWCNTs when Al_2O_3–C refractories were fired at different temperatures [28]. The coating, on the one hand, protected MWCNTs from being oxidized into CO (g). On the other hand, it also hindered the reactions between Al (l, g), Si (s, g) and MWCNTs as well as CO (g), thus decreasing the amount of formed ceramic phases at high temperatures.

3.2. Microstructure of Al_2O_3–C refractories

SEM micrographs of ruptured surfaces of specimens M1 and M1-PCS coked from 800 °C to 1400 °C are shown in Figs. 4 and 5, respectively. As for specimen M1 fired at 800 °C, no ceramic whiskers formed and MWCNTs tangled with each other seriously in the matrix (Fig. 4a). At 1000 °C, striated AlN, regular columnar or plate-shaped Al_4C_3 together with long and fine SiC whiskers were observed as identified by EDS combining with XRD analysis (Fig. 4b and c). In contrast, many SiC whiskers with nanosize in diameter and microsize in length formed in the samples fired at 1200 °C (Fig. 4d). However, SiC whiskers became coarser and locally formed in the matrix, while mullite formed simultaneously with increasing the temperature to 1400 °C (Fig. 4e).

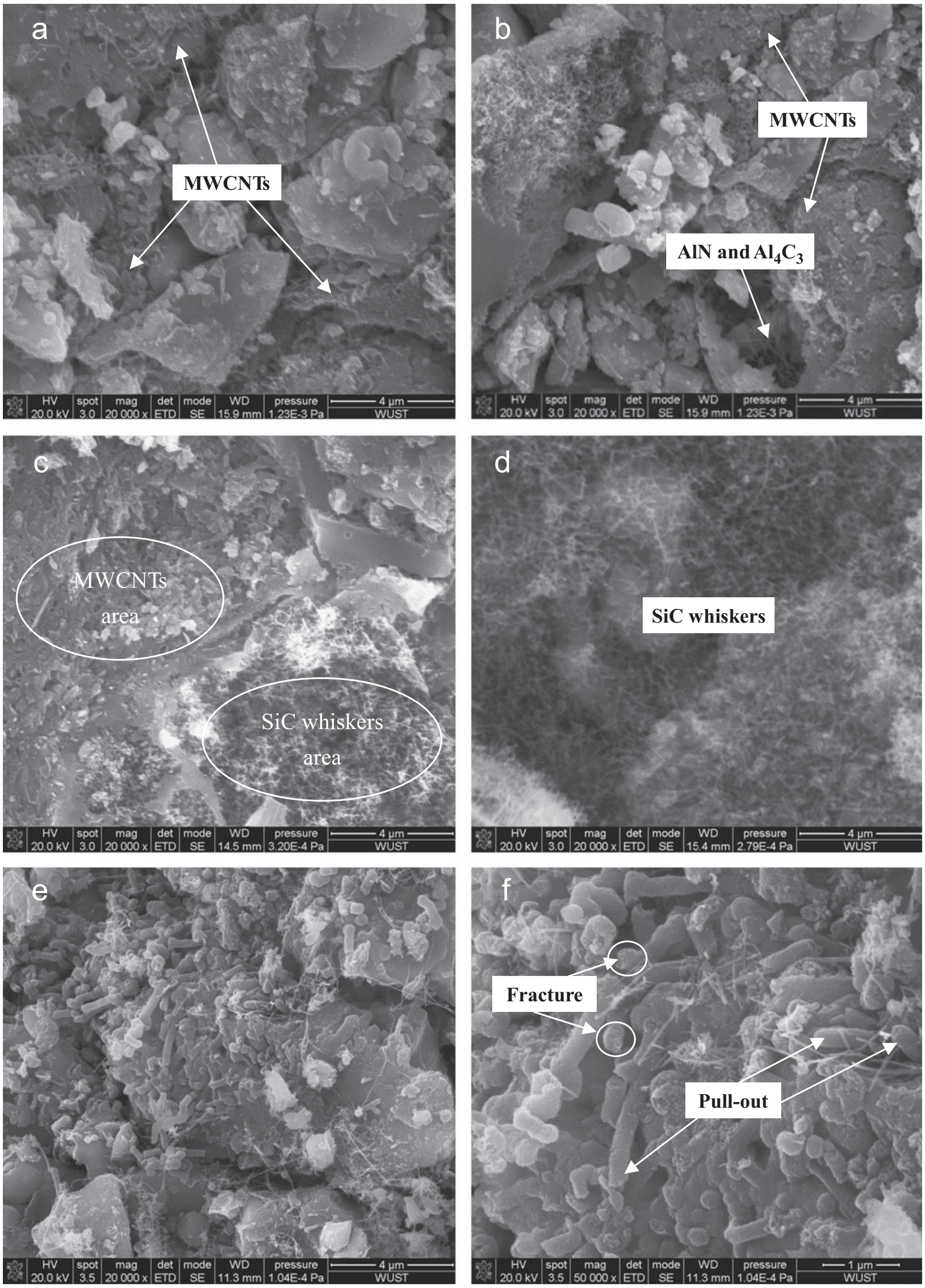

Fig. 5. SEM micrographs of specimen M1-PCS fired at 800 °C (a), 1000 °C (b), 1200 °C (c) and 1400 °C (d)–(f).

In contrast to specimen M1, MWCNTs dispersed more homogeneously in the specimen M1-PCS at 800 °C (Fig. 5a), which was due to the adsorbed PCS molecules on the surface of MWCNTs that reduced the Van der Walls force between MWCNTs (the major driving force of the formation of agglomeration of as-received MWCNTs). This reduction of Van der Walls force between MWCNTs using organic molecules was largely reported in MWCNTs–polymer composites [23–26]. At 1000 °C, less AlN and Al_4C_3 whiskers formed in the matrix while SiC whiskers were not detected, which was in accordance with XRD analysis (Fig. 5b). Up to 1200 °C, much less SiC whiskers formed and located partially in the pores. Moreover, residual MWCNTs were clearly observed in some parts of the matrix (Fig. 5c). More amount of SiC whiskers with much thinner diameter formed with increasing the temperature to 1400 °C, which was different from those in specimen M1 at the same firing temperature (Fig. 5d). In addition, some residual MWCNTs were observed and it is obvious that the diameters of them were much thicker than as-received MWCNTs, which was attributed to the in situ formed SiC_xO_y coating on MWCNTs (Fig. 5e and f). Furthermore, it is noteworthy that some residual MWCNTs were broken but others still intact in the fracture surface, which indicated their fracture and pull-out mechanisms as the reinforcement in the refractories [34–37].

3.3. Mechanical properties of Al_2O_3–C refractories

Mechanical properties including CMOR and FM of the coked specimens M1 and M1-PCS were measured using three-point bending method at room temperature and listed in Table 1. CMOR and FM of all the specimens increased simultaneously with the temperature from 800 °C to 1200 °C, but decreased a lot at 1400 °C, which depended on the ratio of Al and Si added in the refractories [22,38]. With addition of PCS, specimen M1-PCS possessed higher CMOR and FM than M1 after firing at different temperatures. The improvement of the mechanical properties was attributed to more homogeneous dispersion of MWCNTs as well as to higher amounts of residual MWCNTs, which could exhibit full scope to reinforcing effect in the specimens [34–37]. As well, the SiC_xO_y coating could greatly strengthen the interfacial bond between MWCNTs and matrix, which also gave a benefit to the mechanical properties, as it was largely reported in MWCNTs–polymer or ceramic matrix composites [39–41].

Table 1
CMOR and FM of specimens M1 and M1-PCS fired at various temperatures.

Specimens	Index	After firing at (ºC)			
		800	1000	1200	1400
M1	CMOR (MPa)	6.17	9.56	13.51	12.57
	FM (GPa)	1.55	1.68	2.36	2.22
M1-PCS	CMOR (MPa)	9.91	15.58	19.98	14.26
	FM (GPa)	2.55	2.37	3.08	2.36

Fig. 6 shows the force–displacement curves of specimens M1 and M1-PCS after firing at different temperatures. It can be seen that the changes of forces and displacements had the same trend with CMOR and FM. The forces and displacements of all the specimens first increased and reached a maximum at 1200 °C, then decreased at 1400 °C. In contrast with M1, the specimen M1-PCS

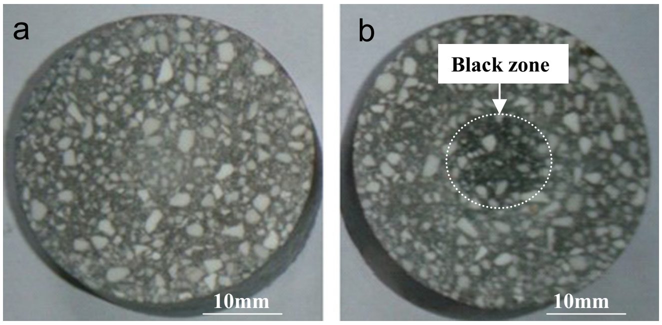

Fig. 7. Cross-section photographs of specimens M1 (a) and M1-PCS (b) after oxidation test.

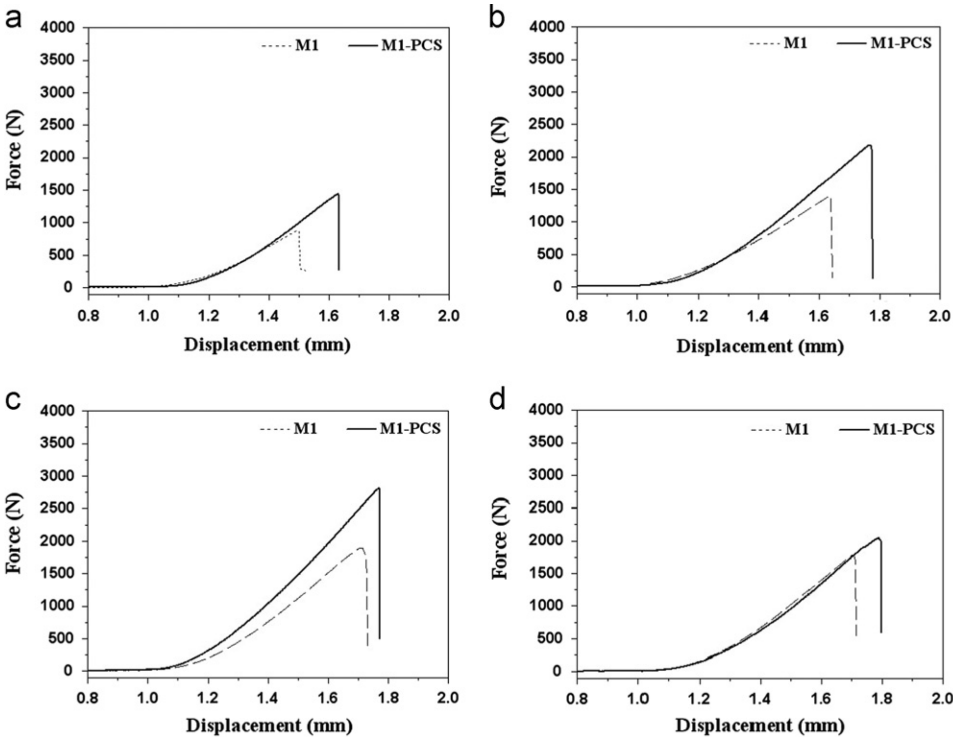

Fig. 6. Force–displacement curves of specimens M1 and M1-PCS fired at 800 °C (a), 1000 °C (b), 1200 °C (c) and 1400 °C (d).

exhibited higher forces and displacements for all coking temperatures.

3.4. Oxidation resistance of Al_2O_3–C refractories

The photographs of the cross section of specimens M1 and M1-PCS after oxidation test are shown in Fig. 7. No central black zone in the specimen M1 could be observed after oxidation test (Fig. 6a). In contrast, the specimen M1-PCS still exhibited a considerable black core, indicating that PCS addition could improve the oxidation resistance of Al_2O_3–C refractories greatly. The improvement of oxidation resistance was attributed to the in situ formed SiC_xO_y coating which protected MWCNTs from oxidation to some extent.

4. Conclusions

This paper offers a new way to solve the problems of MWCNTs agglomeration and structural transformation in Al_2O_3–C refractories in one step by using a common ball mixing method and in situ coating technology using PCS as the precursor. The following conclusions can be drawn by studying the phase compositions, microstructure, mechanical properties and oxidation resistance of MWCNTs containing Al_2O_3–C refractories without or with addition of PCS after firing from 800 °C to 1400 °C.

(1). PCS addition promoted the homogenous dispersion of MWCNTs, and protected MWCNTs from being oxidized or transforming into ceramic whiskers in the matrix of Al_2O_3–C refractories.
(2). The mechanical properties of Al_2O_3–C refractories were improved greatly with addition of PCS due to the more homogenous dispersion of MWCNTs as well as more residual MWCNTs.
(3). The oxidation resistance of Al_2O_3–C refractories with addition of PCS was much better than those without PCS because of the protection of in situ formed SiC_xO_y coating on the surface of MWCNTs.

Acknowledgments

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