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Microstructures and mechanical properties of Al_2O_3-C refractories with addition of multi-walled carbon nanotubes

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ABSTRACT

Microstructures and mechanical properties of Al_2O_3-C refractories with Al, Si and SiO_2 as the additives fired in the temperature range from 800 to 1400 °C are investigated when multi-walled carbon nanotubes (MWCNTs) were used as the carbon source to partially or totally replace graphite flake in the materials. The results showed that the mechanical properties such as cold modulus of rupture (CMOR), modulus of elasticity (E) of all the specimens increased in the firing temperature range from 800 to 1200 °C, but decreased dramatically at 1400 °C. Compared with specimens with only graphite flake, specimens containing 0.05 wt% MWCNTs possessed better mechanical properties. However, they got deteriorated with the further increase of MWCNTs amount from 0.1 to 1 wt%. The differences in mechanical properties were closely associated with the microstructures of Al_2O_3-C refractories. In comparison with specimens having only graphite flake, the improvement of mechanical properties of specimens containing MWCNTs was attributed to strengthening and toughening mechanism of MWCNTs as well as formation of larger amount of ceramic phases in the matrix at 800 and 1000 °C, respectively. At 1200 and 1400 °C, the improvement was mainly associated with the quantity and morphology of SiC whiskers induced from MWCNTs in the specimens. However, with the increase of MWCNTs amount, the mechanical properties of the materials got deteriorated because of agglomeration of MWCNTs and their influence on the morphology of ceramics phases.

1. Introduction

Carbon containing refractories have been widely used in the steelmaking industry due to their unique mechanical and chemical properties. Incorporation of carbon sources into this kind of refractories, not only endows the materials with excellent thermal shock and erosion resistance, but also improves the strength and toughness due to the formation of ceramic phases such as Al_4C_3, SiC by the reactions between carbon sources and additives like Al, Si or SiO_2 [1–3]. However, with the increasing demand on clean steel production, traditional carbon containing refractories having a relatively high amount of carbon, cannot meet the requirements because of their recarburization into molten steel [4–6]. However, the mechanical properties of carbon containing refractories are bound to get deteriorated by simply decreasing carbon content. Therefore, it is of great importance to develop low carbon containing refractories that have excellent properties [7,8].

Since MWCNTs were first reported in 1991, they have attracted considerable attention due to their excellent physical, chemical and mechanical properties, which makes them potentially useful as a reinforcement to enhance the strength and toughness of ceramic matrix composites [9–16]. For example, Zhu et al. [17] 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. Yamamoto et al. [18] also obtained an enhancement of 25% and 27% in CMOR and K_{IC} with only incorporating 0.9 wt% MWCNTs into Al_2O_3–MWCNTs nanocomposites. 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 [19]. However, it is to be regretted that introduction of MWCNTs into carbon containing refractories has rarely been reported up to now.

In the present work, different amounts of MWCNTs were selected as carbon source to partially or totally replace graphite flake in Al_2O_3-C refractories in order to study the effect of MWCNTs on the microstructures and mechanical properties of this kind of refractories.

2. Experimental

2.1. Raw materials and refractories fabrication

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), white fused alumina (10 μm,

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Table 1
CMOR and *E* of specimens with different amounts of MWCNTs fired at various temperatures.

Temperature	Index	N0	N0.05	N0.1	N0.3	N0.5	N1
800 °C	CMOR (MPa)	4.27	5.76	4.63	4.50	4.44	3.07
	E (MPa)	1000.16	1329.41	1109.59	1045.87	1042.8	772.96
1000 °C	CMOR (MPa)	9.09	12.08	10.66	10.08	9.94	7.77
	E (MPa)	1702.95	2388.14	2026.56	1958.47	1762.02	1605.1
1200 °C	CMOR (MPa)	14.11	23.76	22.51	21.91	18.49	16.88
	E (MPa)	2540.91	3733.36	3596.59	3316.75	3142.68	2992.48
1400 °C	CMOR (MPa)	9.41	14.98	10.57	9.55	9.02	8.9
	E (MPa)	2257.97	2606.00	2488.89	2160.18	2109.00	2038.4

98.6 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 (~0.5 μm, 97.0 wt% SiO_2, Elkem, Norway), graphite flake (200 mesh, 97.5 wt% fixed carbon, Qingdao, China) and MWCNTs (diameter, 20–70 nm; lengthen, ~20 μm; >95.0 wt% C, Chengdu, China) were used as raw materials. In addition, thermosetting phenolic resin (liquid, >40 wt% fixed carbon, Wuhan, China) was added as a binder. The batch composition consisted of 83 wt% tabular alumina, 10 wt% white fused alumina, 2 wt% Al powder, 3 wt% Si powder, 1 wt% microsilica powder and 1 wt% graphite flake as a basis (labeled as N0). In order to figure out the influence of MWCNTs, various amounts of MWCNTs such as 0.05 wt%, 0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt% (labeled as N0.05, N0.1, N0.3, N0.5 and N1, respectively) were used to partially or totally replace graphite flake as the carbon source in the compositions. For trying to obtain the homogenous dispersion of MWCNTs in the mixtures, MWCNTs were firstly mixed with white fused alumina powder in the ball mill using corundum balls as the abrasive media and absolute ethyl alcohol as dispersant at the speed of 250 RPM for 6 h. Then the mixtures were dried at 110 °C for 12 h. 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 prepared by cold pressing at a pressure of 150 MPa and then cured at 180 °C for 24 h. Lastly, as-prepared specimens were put into an alumina crucible fed with fine petroleum coke powder and fired from room temperature to 800, 1000, 1200 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 physical properties such as apparent porosity and bulk density, together with weight changes and linear change of the fired specimens were measured. Mechanical properties including cold modulus of rupture (CMOR) and modulus of elasticity (*E*) were measured by three-point bending test at ambient temperature with a span of 80 mm and a loading rate of 0.5 mm 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. All the preceding measurements were carried out with three samples from each composition. The phase compositions of the coked specimens were analyzed by X-ray diffraction (XRD, x'Pert Pro, Philips, Netherlands). The microstructures of ruptured surfaces of all the coked Al_2O_3-C refractories were observed by scanning electron microscope (SEM, Quanta 400, FEI Company, USA) equipped with energy dispersive X-ray spectroscope (EDS, Noran 623M-3SUT, Thermo Electron Corporation, Japan). Thermogravimetry-differential scanning calorimetry (TG-DSC, STA499, NETZSCH, Germany) was employed to characterize the reactivity of graphite flake and MWCNTs from room temperature to 1000 °C at a heating rate of 10 °C/min in air atmosphere.

3. Results

3.1. Mechanical properties

Mechanical properties including CMOR and *E* of coked specimens were measured by three-point bending test at room temperature, and the results are depicted in Table 1. It is obvious that CMOR and *E* of all the specimens increased simultaneously with the increase of firing temperature from 800 to 1200 °C, then decreased dramatically with the temperature up to 1400 °C. For example, CMOR and *E* of specimen N0 at 800 °C were 4.27 MPa and 1.00 GPa, respectively. Then, they reached a maximum at 1200 °C of 14.11 MPa and 2.54 GPa, but decreased a lot at 1400 °C to 9.41 MPa and 2.26 GPa, respectively. For specimen N0.05, CMOR and *E* were much higher than those of N0 at the same firing temperature. That is to say, they were 5.76 MPa and 1.33 GPa at 800 °C and came up to 23.76 MPa and 3.73 GPa at 1200 °C, but decreased to 14.98 MPa and 2.61 GPa at 1400 °C, respectively. However, with the increase of MWCNTs amount from 0.1 wt% to 1 wt%, both CMOR and *E* decreased continuously.

Fig. 1 shows the force–displacement curves of specimens coked at 800, 1000, 1200 and 1400 °C. It can be clearly seen that the firing temperature and MWCNTs amount had a big influence on the forces and displacements, while their changes had the same trend with CMOR and *E*. Namely, forces and displacements increased with the increase of firing temperature and reach a maximum at 1200 °C, then decreased dramatically at 1400 °C. Meanwhile, the specimens with 0.05 wt% MWCNTs had the highest forces and displacements at various firing temperatures. Likewise, forces and displacements decreased with the increase of MWCNTs amount.

The differences in mechanical properties were closely associated with the physical properties such as apparent porosity, bulk density, weight change and linear change. Fig. 2 illustrates the evolutions of apparent porosity and bulk density of the specimens with different amounts of MWCNTs fired at various temperatures. It is obvious that the apparent porosity decreased with increasing the firing temperature from 800 to 1200 °C, but it increased dramatically at 1400 °C (Fig. 2a). Correspondingly, the bulk density as a function of firing temperature was opposite to that of apparent porosity (Fig. 2b). In addition, it has to be noticed that either N0.05 or N0.1 had the lowest apparent porosity, while it increased with further increasing the MWCNTs amount accordingly no matter what firing temperatures were. As can be seen from the results above, the variation trends of apparent porosity and bulk density were similar with those of mechanical properties. The higher apparent porosity of specimens at 800 and 1000 °C was due to the release of volatile species of the binder, which also resulted in the weight loss and shrinkage of the materials [21], as can be seen in Fig. 3. With the increase of firing temperature to 1200 °C, the enhancement of the mechanical properties as well as the increase of weight change and linear change were considered as a direct consequence of formation of new ceramics phases in the materials, which was discussed in detail in the previous reports [2,21,22]. However, when the firing temperature reached 1400 °C,