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ScienceDirect

Ceramics International 40 (2014) 4333–4340

CERAMICS INTERNATIONAL

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Effect of nanocarbon sources on microstructure and mechanical properties of MgO–C refractories

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Received 7 August 2013; received in revised form 22 August 2013; accepted 22 August 2013
Available online 8 September 2013

Abstract

A study of microstructural evolution, mechanical and thermo-mechanical properties of MgO–C refractories, based on graphite oxide nanosheets (GONs), carbon nanotubes (CNTs) and carbon black (CB), was carried out by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS), three-point bending and thermal shock tests. Meanwhile, these results were compared to the conventional MgO–C refractory containing 10 wt% flaky graphite prepared under the same conditions. The results showed that higher cold modulus of rupture was obtained for the composition containing GONs, and the composition containing CNTs exhibited larger displacement after coking at 1000 °C and 1400 °C. Also, the addition of nanocarbons led to an improvement of the thermal shock resistance; in particular, both compositions containing CNTs and CB had higher residual strength ratio, approaching the thermal shock resistance of the reference composition containing 10 wt% flaky graphite, as it was associated with the presence of nanocarbons and *in-situ* formation of ceramic phases in the matrix.

Keywords: C. Mechanical properties; C. Thermal shock resistance; Nanocarbons; MgO–C refractories

1. Introduction

Thanks to their excellent thermal, chemical and mechanical properties, MgO–C refractories are widely applied in steel-making equipment and components, for instance, converters, electric arc furnaces, RH vacuum degassers and slide gates for the flow control of Ca-treated steel [1–3]. However, conventional MgO–C refractories comprise a high amount of carbon up to 12–18 wt% and thus they are sensitive to the oxidation. Furthermore, high carbon pick-up in molten steel is encountered as well as the high energy loss and emission of CO_x when they are in service [4–6]. In order to satisfy the requirements of advanced steel-making technology and environmental protection, many efforts have been made to develop the low carbon containing refractories recently. The application of nanocarbons in the form of nano-carbon black (CB), carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene or graphite oxide nanosheets (GONs) shows great potential in developing low carbon containing refractories with enhanced properties. The literature [6–16] reported that developed low carbon MgO–C refractories using CB exhibited better mechanical and thermo-mechanical properties than conventional high carbon MgO–C refractories. Also, Luo et al. [17] found that the addition of CNTs benefited *in-situ* formation of SiC whiskers in the matrix and consequently the mechanical properties of Al_2O_3–C refractories were improved. It was also reported that adding 0.4 wt% CNFs in the MgO–C refractories enhanced the flexural strength by 2.2 times compared to that of specimens without CNFs [18]. In our previous work, GONs were incorporated into MgO–C and Al_2O_3–C refractories, and superior properties were obtained, due to the combination effects of the relatively homogeneous distribution of GONs and *in-situ* formation of ceramic phases interlocked with each other [19–21].

Although the addition of nanocarbons in carbon containing refractories shows improvement on the mechanical properties, the complete replacement of flaky graphite by nanocarbons is a very tough task because the nanocarbons are more prone to oxidation than the flaky graphite. Also, the extensive research is limited on MgO–C refractories utilizing single nanocarbon

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http://dx.doi.org/10.1016/j.ceramint.2013.08.101

source, and the effects of various nanocarbon sources on the microstructure and mechanical properties of MgO–C refractories still need to be further explored. Out of the reasons, the present work makes a comparative study of MgO–C refractories using three kinds of nanocarbon sources, respectively. The results are also compared with conventional MgO–C refractory containing 10 wt% flaky graphite (without any nanocarbon) prepared under the same conditions.

2. Experimental

2.1. Preparation of MgO/C composite powders

In order to distribute nanocarbons homogeneously in magnesia powders (~45 μm, 98 wt%, Dashiqiao, China), different MgO/C composite powders were prepared firstly. The preparation method of MgO-GONs was shown in Refs. [19,20]. The MgO-CNTs and MgO-CB composite powders were prepared in the following manner: the as-obtained CNTs (diameter, 20–70 nm; length, ~20 μm; >95.0 wt% fixed carbon; Chengdu, China) or CB (~30 nm, >99.0 wt% fixed carbon, Pingdingshan, China) and MgO powders (~45 μm, 98 wt%, Dashiqiao, China) were mixed manually in a mass ratio of 2:100 respectively and then wet-milled using absolute alcohol as the disperse media at room temperature for 7 h in a planetary ball mill (corundum balls as the abrasive media) with the rotating speed of 400 r/min, in which the ratio of corundum balls to the powder mixtures was 1:1. Afterwards, the composite powders were dried at 60 °C for 48 h followed by grinding.

2.2. Preparation of MgO–C refractory specimens

Fused magnesia (3–1 mm, 1–0.5 mm, 0.5–0 mm and <45 μm, 98 wt% MgO, Dashiqiao, China), metallic aluminum (<45 μm, 98 wt% Al, Xinxiang, China), silicon powder (<45 μm, 98 wt% Si, Anyang, China), flaky graphite (FG, <74 μm, 97.5 wt% fixed carbon, Qingdao, China), and different MgO/C composite powders were used as raw materials. Thermosetting phenolic resins, one in liquid form (36 wt% of carbon yield, Zibo, China) and one in powder form (55 wt% carbon yield, Zibo, China) were used as binder. Different MgO–C compositions were formulated by varying nanocarbon sources. Conventionally used MgO–C refractory (composition Ref. 2), containing 10 wt% flaky graphite as carbon source, has also been prepared under the same conditions. The investigated MgO–C compositions are presented in Table 1. All the compositions were mixed for 30 min in a mixer with a rotating speed of 80–100 r/min. After kneading, bar shaped specimens (25 × 25 × 140 mm^3) were compacted under a pressure of 150 MPa and then cured at 200 °C for 24 h. Finally, the as-prepared specimens were treated at a heating rate of 5 °C/min to 1000 °C and 1400 °C for 3 h in a sagger filled with coke grit, respectively.

2.3. Testing and characterization methods

Cold modulus of rupture (CMOR), flexural modulus (FM) and displacement were measured by the three-point bending test at ambient temperature with a span of 100 mm and a loading rate of 0.5 mm/min using an electronic digital control system (EDC 120, DOLI Company, Germany). The force–displacement curve of each specimen was recorded simultaneously during the test. Also, the thermal shock behavior of MgO–C specimens after coking at 1400 °C was determined. The specific method of the thermal shock test was referred to Refs. [19,20].

Table 1
Investigated MgO–C compositions.

Raw materials	Compositions (wt%)				
	GN	CT	CB	Ref. 1	Ref. 2
Fused magnesia aggregate	70	70	70	70	70
Magnesia powders	12	12	12	22	17
Flaky graphite	4.8	4.8	4.8	5	10
MgO-GONs	10.2				
MgO-CNTs		10.2			
MgO-CB			10.2		
Silicon powder	1	1	1	1	1
Metallic aluminum	2	2	2	2	2
Phenolic resin powder	+1	+1	+1	+1	+1
Liquid phenolic resin	+4	+4	+4	+4	+4

The crystallographic phases of the coked samples were determined via X-ray diffractometry (XRD) (X'Pert Pro, Philips, Eindhoven, The Netherlands; using Ni filtered, Cu K_α radiation at a scanning rate of 2 deg/min and a temperature of 16 °C). The microstructural evaluation was carried out by means of field emission scanning electron microscopy (FSEM) (Nova 400 Nano FESEM, FEI Co., Philips, Eindhoven, The Netherlands) coupled with energy dispersive X-ray spectroscopy (EDS) (EDAX, Phoenix, Philips, Eindhoven, The Netherlands).

3. Results and discussion

3.1. SEM images of different MgO/C composite powders

Fig. 1 shows the SEM images of various MgO/C composite powders. Obviously, FG was an irregular and laminated structure (Fig. 1a), and nanocarbons (GONs, CNTs and CB) were distributed rather homogeneously in MgO powders, as shown in Fig. 1b–d, respectively.

3.2. Phase composition and microstructure of MgO–C compositions

XRD analysis of the investigated MgO–C compositions after coking at 1000 °C identified the main phases as periclase, graphite, spinel ($MgAl_2O_4$) and silicon, which were in agreement with those reported by the previous study [19,20,22,23]. The SEM micrographs of the MgO–C compositions after coking at 1000 °C are shown in Fig. 2. All the investigated compositions presented a similar microstructure. Next to the typical *in-situ* formation of $MgAl_2O_4$ grains (Fig. 2a–e), the *in-situ* formed whiskers of Al carbides were also evident