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Feature article

Fracture behavior of low carbon MgO–C refractories using the wedge splitting test

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ABSTRACT

The fracture behavior of low carbon MgO–C refractories containing various carbon sources were investigated by means of the wedge splitting test and microscopic fractographic analysis to evaluate quantitatively their thermal shock resistance in the present work. The results showed that the addition of various nanocarbons in MgO–C specimens can lead to more tortuous crack propagation path during the wedge splitting test and much better thermal shock resistance compared to the specimen with flaky graphite as carbon source; particularly, the specimen containing carbon nanotubes had the most outstanding thermal shock resistance. Also, it was suggested from the correlation analysis that the increase of the specific fracture energy and interface crack propagation as well as the decrease of the modulus of elasticity, coefficient of thermal expansion and transgranular crack propagation can contribute to an improvement of thermal shock resistance of MgO–C refractories.

1. Introduction

Since 1970s MgO–C refractories have been widely used in steelmaking industry for their excellent corrosion resistance and thermal shock resistance [1,2]. Generally, they contain relatively high carbon contents (10–20 wt%) and cannot meet such requirements for low carbon and ultra–low carbon steelmaking technology because of carbon pick–up in molten steel. Also, there is a call for CO_2 emission reducing and energy–saving in steelmaking process [3,4]. So it is imperative to develop low carbon MgO–C refractories (8 wt% carbon content, even lower than 3 wt% one) with high performance. In that case nano–sized carbon sources such as carbon black (CB) [3–6], carbon nanotubes (CNTs) [7] and graphene oxide nanosheets (GONs) [8] are expecting to replace natural flaky graphite partly to produce nano–structured matrix for such refractories with outstanding mechanical and thermomechanical properties. More recently, expanded graphite, viewed as a three dimensional network composed of numerous GONs, is also incorporated into low carbon MgO–C refractories to improve their comprehensive properties [9–11]. On one hand, they are not only easier to fill among the tiny spaces between coarse, medium and fine particle in specimens, but also to fill among interior pores and gaps, which contribute to reduced porosity, increased densification as well as enhanced strength and slag corrosion resistance. On the other hand, these kinds of nano–sized carbons with different morphologies can absorb the thermal stress and promote the in-situ formed ceramic phases (e.g., Al_4C_3, AlN and SiC) to improve the thermal shock resistance. However, as for the thermal shock resistance of the refractories, it is often evaluated only by measuring the residual strength and calculating the residual strength ratio after different thermal shock cycles [12–14]. In fact, the method is rather time-consuming and the data error is also well apparent; meanwhile, it can only characterize qualitatively the thermal shock resistance of such refractories. Hence, Harmuth et al. [15,16] firstly introduced the characteristic length (l_{ch}, proportional to the R‴′ parameter and inversely proportional to a brittleness number) to evaluate the resistance of the refractories against to crack initiation and propagation due to thermal shock; the l_{ch} value can be calculated by utilizing the results from the wedge splitting test according to Tschegg [17,18]. Also, the fracture behavior of the refractories is determined by this test. In the past decades, this approach has been widely used to investigate the fracture behavior of refractory products (including magnesia bricks, magnesia–spinel bricks, Al_2O_3–MgO castables, etc.) and to further assess their thermal shock resistance [19–23].

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In the present work, the fracture behavior and crack propagation of low carbon MgO–C refractories containing various carbon sources were studied with the aid of the wedge splitting test and microscopic fractographic analysis to evaluate quantitatively their thermal shock resistance. Also, the correlations between the microstructure and thermal shock resistance were further revealed with the aim to provide some proper approaches for improving the thermal shock resistance of low carbon MgO–C refractories.

2. Experimental

2.1. Preparation of MgO–C refractory specimens

In order to distribute carbon sources homogeneously in magnesia powders (~45 μm, 98 wt%, Dashiqiao, China), different MgO/C composite powders were prepared firstly, in which carbon sources used for the work included carbon black (CB, 20–30 nm, 99.5 wt% fixed carbon, SSA (111 m^2/g), N220, Wuhan, China), multi-walled carbon nanotubes (CNTs, diameter of 20–70 nm, length of ~20 μm, 95 wt% fixed carbon, Chengdu, China) as well as expandable graphite (50 mesh, 96 wt% fixed carbon, Qingdao, China) for the preparation of expanded graphite (EGs) and graphite oxide nanosheets (GONs). Their prepared methods were similar to our previous work [7]. Only difference lay in the fact that the mass ratio of various carbon sources and MgO powders is 1:26. The composite powders containing EGs, GONs, CNTs and CB were designated as MgO-EGs, MgO-GONs, MgO-CNTs and MgO-CB, respectively.

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, Wuhan, China) and one in powder form (55 wt% carbon yield, Wuhan, China) were used as binder. Different MgO–C compositions were formulated by varying carbon sources. The investigated MgO–C compositions are presented in Table 1. All the compositions were mixed for 15 min in an Eirich mixer with a rotating speed of 900 r/min. After kneading, the specimens (230 mm × 114 mm × 75 mm) were compacted under a pressure of 630 t and then cured at 200 °C for 24 h. Subsequently, MgO–C specimens with different sizes were cut and processed according to the requirements of various performance tests. For instance, bar shaped specimens (25 mm × 25 mm × 140 mm) were for the three-point bending and modulus of elasticity tests, and columnar specimens (Φ10 mm × 50 mm) were used for the determination of coefficient of thermal expansion. Also, the specimens for the wedge splitting test (75 mm × 100 mm × 100 mm) were obtained, whose specific geometry can be seen in other work [23]. Finally, the as-obtained specimens were treated at a heating rate of 5 °C/min to 800 °C and 1400 °C for 3 h in a sagger filled with coke grit, respectively.

Table 1
Investigated MgO–C compositions.

Raw materials	Compositions (wt%)				
	S-G1	S-CB	S-CNTs	S-EG1	S-GON1
Fused magnesia aggregate	70	70	70	70	70
Magnesia powders	26	–	–	–	–
Flaky Graphite	1	–	–	–	–
MgO–CB	–	27	–	–	–
MgO–CNTs	–	–	27	–	–
MgO–EGs	–	–	–	27	–
MgO–GONs	–	–	–	–	27
Si powder	1	1	1	1	1
Metallic Al	2	2	2	2	2
Phenolic resin powder	+1	+1	+1	+1	+1
Liquid phenolic resin	+4	+4	+4	+4	+4

2.2. Testing and characterization methods

The bulk density (BD) and apparent porosity (AP) of MgO–C specimens obtained were measured according to Archimedes' Principle with kerosene as medium. Cold modulus of rupture (CMOR) was measured by the three-point bending test at room 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). Modulus of elasticity (E) was measured by Resonance Frequency and Damping Analyzer (RFDA, IMCE in Belgium) at room temperature. Also, the thermal shock behavior of MgO–C specimens after coking at 1400 °C was determined by oil quenching method for five thermal shock cycles. The specific description of the thermal shock test was referred to our previous work [8]. Furthermore, the coefficient of thermal expansion (α, room temperature to 1400 °C) of the specimens after treating at 1400 °C was measured via a thermal dilatometer (Unitherm™ model 1161 dilatometer system, Anter Corp., Pittsburgh, PA); the measurement was made in an atmosphere of N_2 (99.9% N_2) to prevent oxidation of the specimens after treating at 1400 °C. All the above properties measured for each composition were average values from three test pieces.

In addition, the wedge splitting test according to Tschegg was used for the determination of the specific fracture energy of MgO–C specimens due to the stable crack propagation in the specimen with sufficiently large dimension [24]; meanwhile, the presence of a notch in the specimen allowed to investigate the formation of a macrocrack, and the damage was supposed to be mainly concentrated in the cross section below the notch. The schematic illustration of this test is shown in Fig. 1(a). During the test, a load transmission equipment situated in a specimen groove transformed the vertical force (F_V) into horizontal force (F_H) with the help of a wedge (the wedge angle [β] of 8° for this work), two roles and two load transmission pieces [25–27]. So, F_H can be calculated by the following equation: $F_H = F_V/2\tan(\beta/2)$. Also, the load/displacement curve of each specimen was achieved (Fig. 1(b)). The specific fracture energy (G_f), nominal notch tensile strength (σ_{NT}), and characteristic length (l_{ch}) can be further obtained by calculating the following formulas:

$$G_f = \frac{1}{A}\int_0^{\delta_{ult}} F_H d\delta \quad (1)$$

$$\sigma_{NT} = \frac{F_{H,max}}{b \cdot h}\left(1 + \frac{6y}{h}\right) \quad (2)$$

$$l_{ch} = \frac{G_f \cdot E}{\sigma_{NT}^2} \quad (3)$$

Where $\delta_{\mu lt}$ is the ultimate displacement and A is the area of the projection of the fracture surface. In the present study, as usually done for the wedge splitting test, the G_f was not calculated until total failure but until 15% of the maximum force in the post-peak region. b and h are the width and height of the fracture surface area, respectively, and y is the vertical distance of the center of gravity of the fracture surface from the horizontal force. E is the modulus of elasticity. The data for each composition were averaged with three test pieces.

As for the thermal shock resistance parameters, R'''' and R_{st} were proposed firstly by Hasselman [28,29], depended on the surface fracture energy (γ_s). Later, the work of fracture (γ_{WOF}) was used to replace γ_s for the calculation of R'''' and R_{st} [30,31]. Similarly, it can be proposed here to calculate these parameters from G_f instead of γ_s [see the formulas (4) and (5)]. Note that G_f obtained from the wedge splitting test did not include the factor ½ normally

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