Effect of Flake Graphite Size on the Thermal Conductivity of Blast Furnace Carbon Refractories

Y.W. Li, X. Chen, S. Ge, B. Qiang, W. Zhang

Five kinds of flake graphite are used to investigate the thermal conductivity of carbon refractories for a blast furnace with the aid of X-ray diffraction (XRD), scanning electron microscopy (SEM), mercury porosimetry, and a laser thermal conductivity meter. The results indicated that the thermal conductivity of carbon samples increased with increasing flake graphite size, especially in the direction perpendicular to the shaping direction, and its anisotropy degree between the directions perpendicular and parallel to the shaping direction became larger. The composite graphite can increase the thermal conductivity of the specimen compared to single graphite in the direction parallel to the shaping direction and reduce the anisotropy degree between the directions parallel and perpendicular to the shaping direction.

1 Introduction

It has been of established consensus that the life of blast furnaces (BF) is mainly determined by the erosion and corrosion rates of hearth and bottom carbon refractories [1–3].

Nowadays, one of the main developmental trends of carbon refractories for BF is high thermal conductivity due to the reason that high thermal conductivity can sustain the risk of high thermal loads and high temperature gradients [2]. Commonly there are two routes towards increasing the thermal conductivity of carbon refractories, namely, adding a component with high thermal conductivity and increasing its density [4, 5].

Flake graphite is an attractive material for high temperature applications due to its high modulus, excellent thermal conductivity and thermal shock resistance, etc. [6]. Nevertheless, flake graphite exhibits considerable the anisotropy of its thermal conductivity due to its hexagonal and layer structure, which results in the anisotropy for thermal conductivity of flake graphite containing materials [7], and exhibits anisotropy in both physical and chemical properties. Up to date, few reports can be found in the literature regarding the effect of flake graphite size on the thermal conductivity of carbon refractories for BF.

In the present work five kinds of flake graphite are used to address the size effect on thermal conductivity and its anisotropy of carbon samples, which aims to establish a theoretical basis for the development and production of super-high quality carbon refractories for BF.

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2 Experimental

Commercially electro-calcined anthracite aggregates (C > 90 %, Al_2O_3 < 2,5 %, SiO_2 < 6,2 %, volatiles < 1,3 %, *Lanzhou Fangda Carbon Co., Ltd.*, China), flake graphite (100 mesh, 200 mesh, 325 mesh, 600 mesh and 1000 mesh, respectively, > 97 %, *Qingdao Tiansheng Graphite Co., Ltd.*, China), silicon powder (Si > 98 %, *Zhejiang Kaihua Yuantong Silicon Co., Ltd.*, China) and activated alumina powder (Al_2O_3 > 99 %, *Jiangdu Jinghui Special Refractory Material Co., Ltd.*, China) were used as raw materials to prepare carbon refractories. Two batches of samples were designed, one batch was carbon brick samples containing 66 mass-% electro-calcined anthracite aggregates, 20 mass-% flake graphite with the above mentioned various sizes, 8 mass-% silicon and 6 mass-% activated alumina.

For the samples containing composite graphite, the mass percentage of two kinds of graphite was 10 %, respectively. The other batch was only the corresponding matrix powders of carbon brick samples with various flake graphite sizes. Using thermosetting phenolic resin as a binder, the above mixtures of samples were kneaded following the fixed standard procedure. After kneading, cylindrical carbon brick specimens of 50 mm in diameter and 50 mm in height and cylindrical matrix powder specimens of 36 mm in diameter and 36 mm in height were pressed with a pressure of 100 MPa and 50 MPa, respectively. Then, the specimens were cured following the standard temperature-time curve up to 200 °C, embedded in carbon powder and heated to 1400 °C for 3 h.

The properties of the fired specimens were characterized by weight change (WC), diameter change (DC), bulk density (BD), apparent porosity (AP) and cold crushing strength (CCS). Specimens (6 × 6 × 6 mm³) were ex-

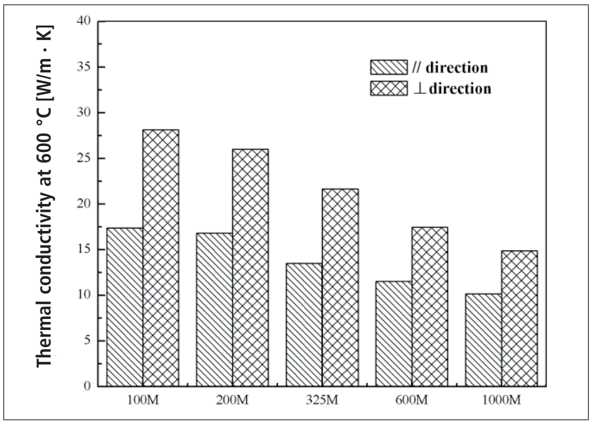

Fig. 1 Thermal conductivity of matrix powder samples at 600 °C

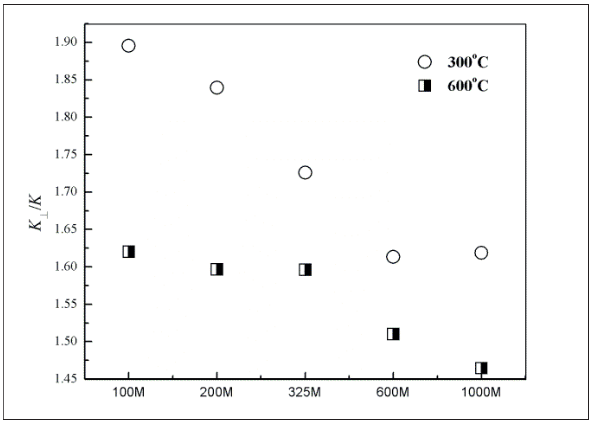

Fig. 2 The anisotropy for thermal conductivity of matrix powder samples

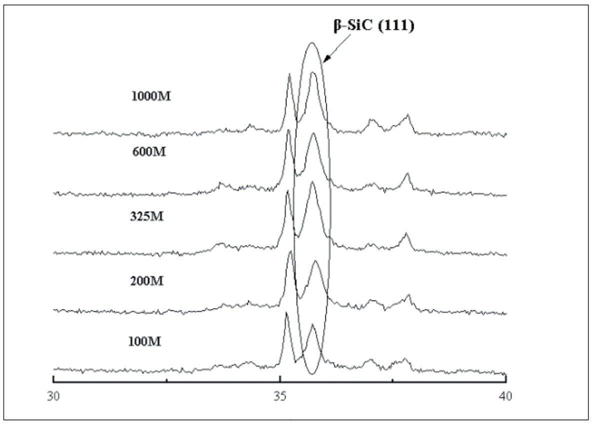

Fig. 3 XRD patterns of matrix powder samples

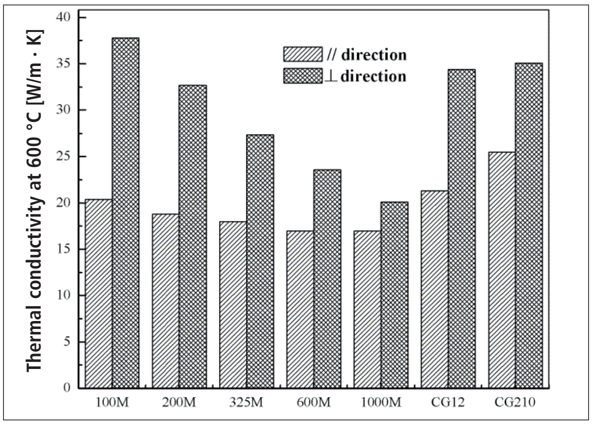

Fig. 4 Thermal conductivity of carbon brick samples at 600 °C

amined by mercury porosimetry (Autopore IV9500, *Micromeritics Instrument Corp.*, USA), then the mean pore diameter (MPD) and < 1 µm pore volume (PV) of open pores were calculated.

Also, the thermal conductivity (TC) of the specimens (12,5 mm Ø × 3 mm) were measured at 300 °C and 600 °C with a Laser Thermal Conductivity Meter (Flashline 5000, *Anter Corp.*, USA) in directions parallel and perpendicular to the shaping direction.

The phase composition of all specimens was analyzed by X-ray diffraction (XRD, *Philips*, X'Pert Pro, using Ni-filter, CuK_{α} radiation at a scanning speed of 2°/min of 16 °C) and the micro-structural features were observed by scanning electron microscopy (Nova400 NanoSEM, *Philips*, Netherlands).

3 Results

3.1 Matrix powder samples

The thermal conductivities of the matrix powder samples at 600 °C are illustrated in Fig. 1. The conductivities decreased with the size reduction of flake graphite used, and thermal conductivity of each specimen perpendicular to the shaping direction ($K_{\perp}$) was greater than that parallel to the shaping direction ($K_{//}$), which is related to the intrinsic anisotropy of graphite.

Meanwhile, the flake graphite size can damp the anisotropy for thermal conductivity of matrix powder samples. The degree of anisotropy for the materials can be defined as $K_{\perp}/K_{//}$ [9], as shown in Fig. 2. As can be seen, the trend of $K_{\perp}/K_{//}$ for thermal conductivity at 300 °C and 600 °C decreased against the decrease in graphite size. The $K_{\perp}/K_{//}$ at 300 °C was larger than that at 600 °C due to the fact that the thermal conductivity of graphite decreases with increasing temperature.

The other properties of the matrix powder samples are presented in Tab. 1. The bulk density of samples decreased and their apparent porosity went up as the size of the added graphite became smaller, which is in agreement with thermal conductivity of the samples. Meanwhile, the weight change of samples indicated that much more gaseous matters such as $SiO_{(g)}$, $Si_{(g)}$ volatilize in samples with higher porosity at high temperature.

Among all the samples, it is found that the cold crushing strength of 25,2 MPa was highest while the mean pore diameter of 0,101 m in size was lowest for the 325-mesh flake graphite containing sample, which could be associated with the in-situ formation of SiC [8].

From Fig. 3, it can be seen that the 325-mesh flake graphite containing sample owed the highest SiC main peak intensity, indicating the formation amount of SiC was highest compared with other samples.

3.2 Carbon brick specimens

The thermal conductivity of the carbon brick specimens at 600 °C are illustrated in Fig. 4, whose results are similar to those of the matrix powder samples.

However, it was found that the thermal conductivity of specimens with composite graphite sizes was higher than those with single graphite size in the direction parallel to the shaping direction, decreased or increased in the direction perpendicular to the shaping direction. This means that addition of composite graphite into specimens can modify the thermal conductivity of the carbon brick specimens in different directions.
The similar result was also found in MgO-C refractories [10], which was explained by the reason that the composite graphite could improve the densification of the specimens and optimize the packing structure of graphite in specimens. The degree of anisotropy for the carbon brick specimens is illustrated in Fig. 5.
It seemed that the degree of anisotropy for thermal conductivity of specimens decreased by adding composite graphite sizes compared with specimens where only single coarse graphite was added.
The other properties of the carbon brick specimens after firing at 1400 °C are shown in Tab. 2. As can be seen, the change trends of properties being the same as those of the matrix powder samples.
Interestingly the properties of specimens with composite graphite surpassed those of specimens with single graphite, which is attributed to the structural optimization of samples.

Tab. 1 **Properties of the matrix powder samples**

Mesh	BD	AP	WC	DC	CCS	MPD	PV	TC			
	[g · cm^{-3}]	[%]	[%]	[%]	[MPa]	[m]	[%]	[W · m^{-1} · K^{-1}]			
								300 °C (//)	300 °C (⊥)	600 °C (//)	600 °C (⊥)
-100	1,82	26,2	4,2	0,3	17,7	0,22	94,2	19,5	36,9	17,4	28,2
-200	1,79	28,3	3,2	0,2	19,3	0,147	95,3	17,7	32,5	16,8	26
-325	1,77	28,7	2,4	-0,2	25,2	0,101	98,6	15,4	26,7	13,5	21,7
-600	1,75	30,3	2	-0,3	23,8	0,11	98,7	13,4	21,4	11,5	17,4
-1000	1,66	33,1	1,2	-0,7	16,1	0,225	94,7	10,3	16,9	10,1	14,9

Tab. 2 **Properties of the carbon brick samples***

Mesh	BD	AP	WC	DC	CCS	MPD	PV	TC			
	[g · cm^{-3}]	[%]	[%]	[%]	[MPa]	[m]	[%]	[W · m^{-1} · K^{-1}]			
								300 °C (//)	300 °C (⊥)	600 °C (//)	600 °C (⊥)
-100	1,72	12,5	-0,5	-0,1	27,5	0,352	76,7	22,7	44,2	20,4	37,8
-200	1,71	13,3	-0,9	-0,2	30,3	0,26	84,4	18,5	38,3	18,8	32,7
-325	1,71	13,4	-1,1	-0,2	37,6	0,203	88,9	18,1	32,3	18	27,4
-600	1,71	13,5	-1,2	-0,5	35,1	0,181	87,5	17,1	25,3	17	23,6
-1000	1,7	13,6	-1,4	-0,7	32,2	0,167	75,8	17	22,8	16,8	20,5
CG12	1,73	12,7	-0,5	-0,2	34,4	0,283	86,4	20,4	36,7	21,3	34,4
CG210	1,72	12,3	-0,3	-0,4	36,7	0,194	89,6	23,8	33,3	25,6	35,1

***CG12: 10 % -100 mesh plus 10 % -200 mesh, CG210: 10 % -200 mesh plus 10 % -1000 mesh**

4 Discussions

On basis of the above experimental results, the thermal conductivity of carbon brick specimens was actually associated with the size and array of flake graphite.
It is well known that flake graphite has the anisotropy in thermal conductivity with the characterization of layer structure, which results in different array of flake graphite in specimens depending on the graphite size.
For the sample containing graphite with larger size, the flake graphite easily spread along the direction perpendicular to the shaping direction (Fig. 6a) and that was vertical in the shaping direction (Fig. 6b).
In the specimen with finer graphite added, it was found that the flake graphite distributed in disorder no matter which direction is perpendicular or not (Fig. 6c, 6d). It seemed that the disorder degree increased with the decrease in flake graphite size, which may be used to explain the phenomenon that the degree of anisotropy for thermal conductivity of specimens decreased as the size of the used flake graphite became smaller.
In the experiment the specimen containing the finer flake graphite has the lower thermal conductivity (Fig. 1 and 4). It is suggested that the thermal conductivity is associated with the number of grain boundaries in the heat flow path [11].
The specimen containing finer graphite has less heat flow path than that with coarser graphite in the same amount in the specimen.
However, for the specimen containing composite graphite, adding coarser and finer together, the thermal conductivity takes place remarkably. This means the composite graphite can increase the heat flow path, especially in the direction parallel to the shaping direction.
Also, the graphite size effect of the thermal conductivity performance can be characterized by electric resistance. The electric resistance measurement was conducted by using 1,5 g different graphite under the same conditions (Fig. 7). As can be seen that the finer the flake graphite

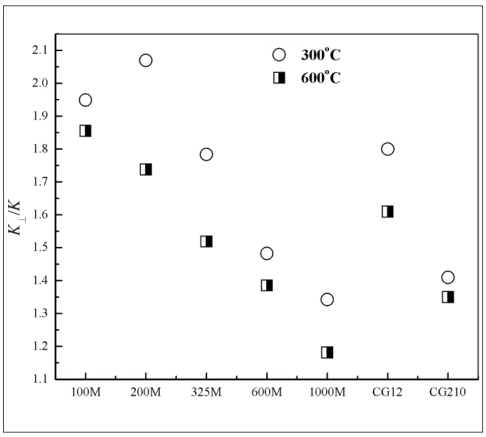

Fig. 5 **The anisotropy for thermal conductivity of carbon samples**

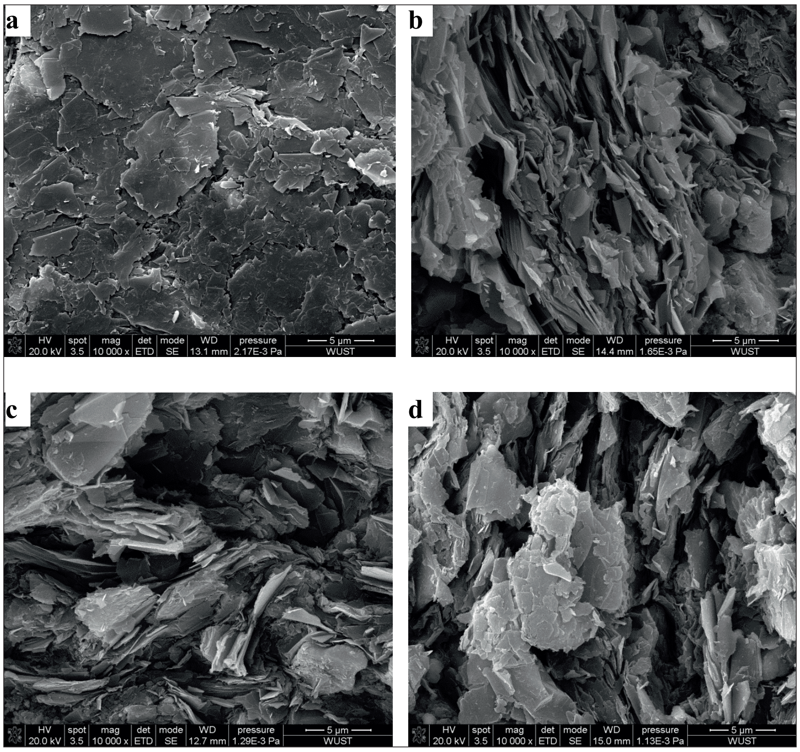

Fig. 6 SEM micrographs of matrix powder samples; a -100 mesh, //; b -100 mesh, ⊥; c -1000 mesh, //; d -1000 mesh, ⊥

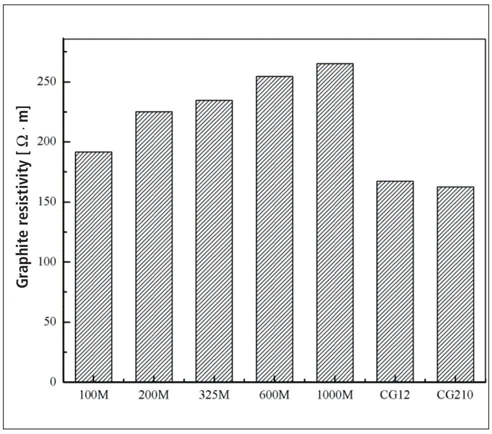

Fig. 7 The resistivity of flake graphite

the higher the electric resistance and composite graphite has less resistivity than single graphite.

5 Conclusions

The following conclusions can be made on the basis of the study of the effect of flake graphite size on the thermal conductivity of carbon refractories for blast furnaces.

- With the increase of flake graphite size, the thermal conductivity of carbon specimens increase, especially in the direction perpendicular to the shaping direction, and its anisotropy degree between the directions perpendicular and parallel to the shaping direction became larger.
- The carbon specimen containing composite graphite has higher thermal conductivity than that of the carbon specimen containing only single graphite in the direction parallel to the shaping direction and reduce the anisotropy degree between the directions parallel and perpendicular to the shaping direction. It is supposed that adding composite graphite into carbon specimens can be adopted to improve the thermal conductivity of carbon specimens in all directions.

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