

IMPROVED OXIDATION RESISTANCE AND MECHANICAL PROPERTIES OF $\text{Al}_2\text{O}_3\text{-C}$ REFRACTORIES WITH ADDITION OF BORON-DOPED EXPANDED GRAPHITE

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ABSTRACT

Boron (B)-doped expanded graphite (EG) has been synthesized by annealing the synthetics, which were obtained from the suspensions of EG and boric acid. Afterward, the B-doped EG were introduced into $\text{Al}_2\text{O}_3\text{-C}$ refractories to partially replace graphite flake. Boron atoms were introduced into the skeleton via different B-C bonding, such as B_4C , B-sub-C and BC_2O . The B-doped EG appeared better oxidation resistance and lower reactivity in comparison with as-received EG. With addition of 0.5 wt% B-doped EG into $\text{Al}_2\text{O}_3\text{-C}$ specimens, mechanical properties such as modulus of rupture (CMOR), flexural modulus (FM) were improved in comparison with specimens containing graphite flake or EG. Besides, the $\text{Al}_2\text{O}_3\text{-C}$ specimens appeared significantly better oxidation resistance due to addition of B-doped EG.

1 INTRODUCTION

Expanded graphite (EG) is a vermicular-shaped carbon source composed of parallel graphene nanosheets, which possess high elastic modulus and tensile strength. In recent years, it has been introduced into carbon containing refractories to partially replace traditional graphite flake to enhance their mechanical properties [1-2]. However, in comparison with graphite flake, there are much more fractured $\text{C}=\text{C}$ defects in the carbon skeleton of EG, which results in the worse oxidation resistance [3]. Besides, the fractured $\text{C}=\text{C}$ bonds acted as active sites and preferentially react with gaseous phases such as $\text{Al}(\text{g})$, $\text{Si}(\text{g})$ or $\text{SiO}(\text{g})$, which usually lead to the structure collapse of EG. Therefore, it's imperative to repair these fractured $\text{C}=\text{C}$ defects of EG to adjust its oxidation resistance and reactivity at high temperature. It's reported that the graphene containing defects can be repaired by incorporating B atom into carbon honeycomb lattice without changing the crystal lattice significantly [4]. Similarly, to repair the carbon network of EG, the boron atom can be applied to form different B-C covalent bonding. According to the thermodynamics calculation, the boron atom would react preferentially with oxygen compared with carbon atom, which may improve the oxidation resistance of B-doped EG. Besides, it's deemed that the reactivity of B-doped EG could be controlled due to the decrease of active sites via B-C

bonding. So, it may remain the relative structure integrity of B-doped EG in carbon containing refractories at high temperature.

In the present work, the B-doped EG was synthesized using hydrothermal method. Meanwhile, the B-C bonding types were evaluated as well as the oxidation resistance and reactivity of B-doped EG. After that, the B-doped EG was used as carbon source to partially replace the graphite flake in $\text{Al}_2\text{O}_3\text{-C}$ refractories. The effect of the B-doped EG addition on the microstructure, mechanical properties and oxidation resistance was elucidated.

2 EXPERIMENTAL

2.1 Synthesis of B-doped EG

The B-doped EG was synthesized by hydrothermal method using boric acid as the chemical dopant. Namely, the EG was added into boric acid aqueous solution and the mixture was stirred for 1 h. Next, the mixture was placed in a vacuum atmosphere (-0.1 MPa) and heated to 60 °C for 30 min. After that, the black solids were filtered, and then were heated to 700 °C and 1000 °C in Ar atmosphere for 2 h (labeled as BG700 and BG1000, respectively). Lastly, the collected powder was washed with excess deionized water.

2.2 Preparation of $\text{Al}_2\text{O}_3\text{-C}$ specimens

Commercially tabular alumina (8-14 mesh, 14-28 mesh, 28 mesh, 325 mesh and 20 μm , 99.5 wt% Al_2O_3), $\alpha\text{-Al}_2\text{O}_3$ (2 μm , 99% Al_2O_3), aluminum powder (45 μm , 99 wt% Al), silicon powder (45 μm , 98.47 wt% Si), microsilica powder (0.5 μm , 97 wt% SiO_2), graphite flake (200 mesh, 97.58 wt% fixed carbon, China), expanded graphite (EG) and the synthesized BG1000 were used as raw materials to fabricate $\text{Al}_2\text{O}_3\text{-C}$ specimens. The thermosetting phenolic resin (liquid, >40 % fixed carbon,) was added as the binder. Three batches compositions with different carbon source are listed in Table 1. Bar shaped specimens (with 25 mm in width, 25 mm in height and 140 mm in length) and cylindrical specimens (with 36 mm in diameter and 36 mm in height) were fabricated by cold pressing at 150 MPa and cured at 160 °C for 24 h. The as-received specimens were placed inside a corundum sagger filled with petroleum coke powder. Finally, the whole crucible was heated to 1200 °C and 1400 °C

at a heating rate of 5 °C/min and held for 3 h before cooling to room temperature.

Table 1 Three batches of Al₂O₃-C refractories

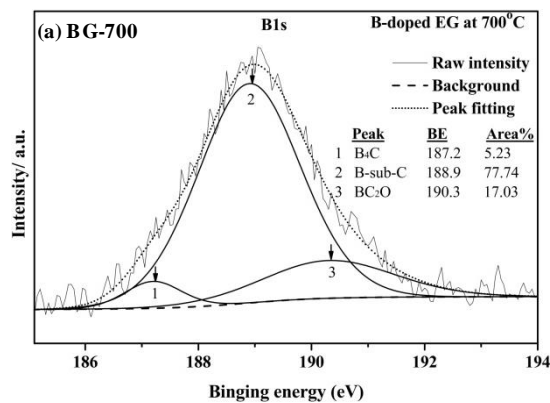
Ingredient (wt%)	F1	E5	EB
Alumina	93	93	93
Aluminium	2	2	2
Silicon	3	3	3
Microsilica	1	1	1
Graphite flake	1	0.5	0.5
EG	0	0.5	0
B-doped EG	0	0	0.5

2.3 Tests and characterization methods

X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG Multilab 2000 apparatus. Thermogravimetry-differential scanning calorimetry (TG-DSC, STA499, NETZSCH, Germany) was employed to evaluate characteristic temperatures (°C) of exothermic peaks of carbon sources. The experiment was carried out by heating the samples from room temperature to 1200°C in a static air atmosphere at a rate of 10°C/min. The microstructure of Al₂O₃-C specimens was observed by scanning electron microscope (SEM, Quanta 400, FEI Company, US) linked with an energy dispersive spectroscope (EDS, EDAX, Phoenix, US). Mechanical properties including cold modulus of rupture (CMOR) and flexural modulus (FM) were measured by using the three-point bending test at ambient temperature by means of electronic digital control system (EDC 120, DOLI Company, Germany). The oxidation resistance of all the Al₂O₃-C specimens was evaluated via their mass change rate by firing cylindrical specimens from 200 °C to 1300 °C in air.

3 RESULTS AND DISCUSSION

3.1 Characterization of boron-doped EG



The atomic percentage (at.%) of each element (C, B and O) was calculated from the survey spectra, and the result was summarized in Table 1. The original EG was composed of only 92.75 at.% C and 7.25 at.% O elements. With the doping of boron on EG, 1.21 at.% and 1.33 at.% B atoms were observed in sample BG-700 and BG-1000, respectively. Meanwhile, the content of oxygen (O) atoms of B-doped EG significantly reduced compared with original EG due to the effective thermal reduction. It's worth noting that the B atomic content increased with the firing temperature from 700 °C to 1000 °C.

Table 2 Atomic concentration of C, B and O of EG, BG-700 and BG-1000

Sample	Element content/At.%		
	C	B	O
EG	92.75	-	7.25
BG-700	92.46	1.21	6.33
BG-1000	94.2	1.33	4.47

In order to ascertain the specific bonding patterns of B atoms, high resolution B 1s XPS spectrums of B-doped EG are shown in Fig. 1. The Gaussian deconvolution analysis indicated that the spectrum can be divided into three peaks with various intensities, which are centered at 187.2, 188.9 and 190.3 eV. The peaks at 187.2 and 188.9 eV can be assigned to the B-C bonding in B₄C and B-sub-C [4], respectively. In fact, the B-sub-C bonding refers to the state in which a C atom is substituted by a B atom in a graphite crystal structure. Moreover, the peak at 190.3 eV can be attributed to the B-C bonds in planar BC₃ nanodomains and/or the B-O bond in BC₂O [5]. Therefore, the presence of the B-C bonding in the B 1s signals clearly provides evidence for the replacement of C atoms within the graphite sheet by highly coordinated B atoms. These doped B atoms in graphitic structure of EG may have positive effect on the oxidation resistance.

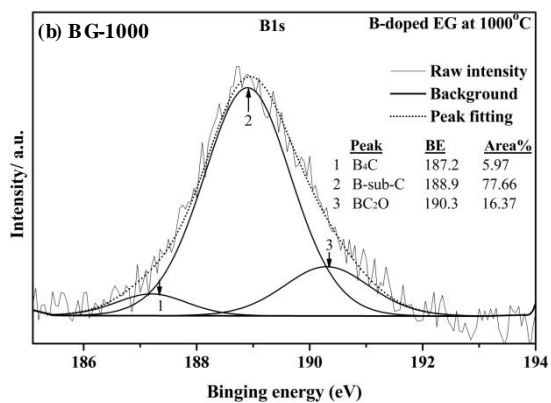


Fig. 1 B 1s XPS spectra of (a) BG-700 and (b) BG-1000

Table 3 presents the characteristic temperatures of exothermic peaks using TG/DSC measurement. It is obvious that the starting temperatures (T_s), peak temperatures (T_p) and terminating

temperatures (T_t) of the exothermic peaks for EG were much lower than graphite flake (Table 1). However, with the doping of boron on EG, the above characteristic temperatures of B-doped

EG increased significantly in comparison with original EG. Meanwhile, the characteristic temperatures increased continuously with the doping temperature. These results manifested the oxidation of B-doped EG was delayed and the oxidation resistance was greatly improved.

Table 3 Characteristic temperatures (°C) of exothermic peaks of carbon sources

Temperatures (°C)	Graphite flake	EG	BG-700	BG-1000
T _s	663.9	634.6	770.7	790.2
T _p	843.2	736.7	863.1	897.9
T _t	927.4	796.6	935.9	955.4

The reactivity of EG, BG-700 and BG-1000 may be revealed by their activation energies of oxidation according to DSC curves. Both Kissinger's and Ozawa's methods for analyzing non-isothermal kinetics were employed to estimate activation energies of oxidation for carbon in the present study [3]. The oxidation activation energy was listed in table 4. In comparison with EG, the B-doped EG had higher oxidation activation energies, indicating the lower reactivity and lower density of defects existing in B-doped EG. Besides, the oxidation activation energy increased with the doping temperature. It means the reactivity of B-doped EG can be controlled by

adjusting the doping temperature.

Table 4 The oxidation activation energies (kJ/mol) of expanded graphite and B-doped expanded graphite in air.

Methods	EG	BG-700	BG-1000
Kissinger	200.01	229.00	258.78
Ozawa	202.42	232.19	256.83

3.2 Microstructure and performances of Al₂O₃-C specimens

The SEM micrographs of ruptured surfaces of the specimen E5 and EB fired from 1200 °C to 1400 °C are shown in Fig. 2. In specimen E5 fired at 1200 °C, many β-SiC whiskers (identified by XRD and EDS analysis) were observed on the surface of partially disintegrated EG (Fig. 2a) due to the VS reaction between EG and Si-containing (Si or SiO gaseous phase) [3]. At 1400 °C, more β-SiC whiskers *in-situ* formed around residual graphitic layers at the cost of the collapse of EG (Fig. 2b). Meanwhile, many β-SiC whiskers formed in the matrix (Fig. 2c). For the specimen EB, the B-doped EG remained intact at high temperatures due to the lower reactivity. For instance, the original lamellar structure of BG-1000 could be observed, although some β-SiC whiskers formed on its surface (Fig. 2d and e). In fact, at 1400 °C, some intact BG-1000 particles still could be observed in specimen EB (Fig. 2f).

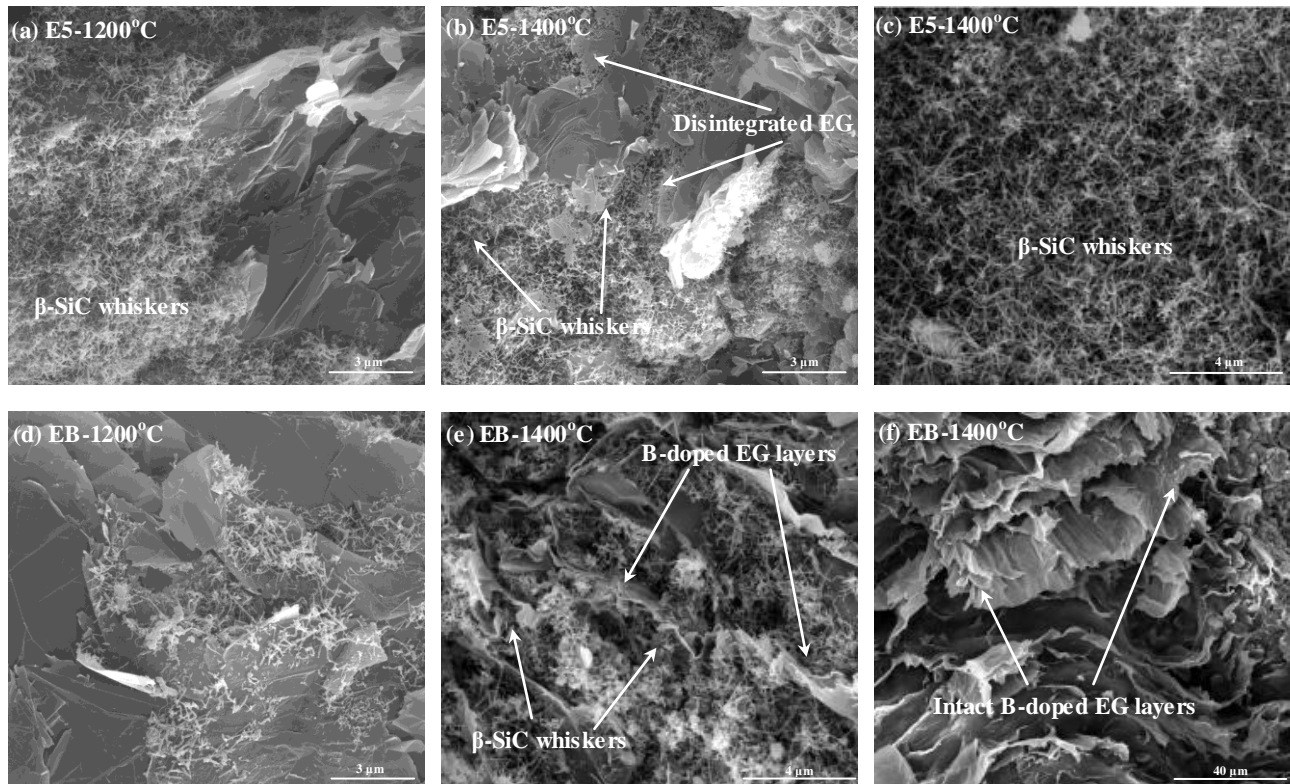


Fig. 2 SEM images of the specimen E5 fired (a) at 1200 °C, (b-c) 1400 °C and the specimen EB fired at (d) 1200 °C, (e-f) 1400 °C

Table 5 presents the CMOR and FM of Al₂O₃-C refractories specimens. It's obvious that the CMOR and FM values of the specimen E5 are larger than those of the specimen F1.

Meanwhile, the specimen EB possessed the largest CMOR and FM values, indicating the addition of B-doped EG produced the positive influence on the mechanical properties. For the

specimen F1 and E5, both CMOR and FM decreased substantially with the temperature from 1200 °C to 1400 °C. However, those values decreased slightly in specimen EB. This may attribute to the remained relative intact of B-doped EG which strengthened the Al₂O₃-C refractories at higher temperature.

Table 5 CMOR and FM of specimens.

Temperature	Index	F1	E5	EB
1200 °C	CMOR (MPa)	19.29	26.44	28.75
	FM (GPa)	3.65	3.96	5.19
1400 °C	CMOR (MPa)	14.50	19.72	26.74
	FM (GPa)	3.06	3.86	4.62

The mass change of cylindrical specimens fired from 200 °C to 1300 °C in air was shown in Fig. 3. For all the specimens, the oxidation would happen, resulting in weight loss. For example, the mass change rate decreased significantly from 200 °C to 730 °C due to the release of volatile species of the binder. Then, it decreased mildly from 730 °C to 1097 °C, which was attributed to the formation of ceramic phases (Al₄C₃, AlN and SiC) in the specimens [6]. However, when the firing temperature increased from 1097 °C to 1400 °C, the mass change rate increased substantially, which may result from oxidation of ceramic phases, residual Al and Si powder. It's worth noting that the specimen EB possessed largest mass change values no matter what firing temperatures was. In a word, the B-doped EG addition improved the oxidation resistance of Al₂O₃-C specimens.

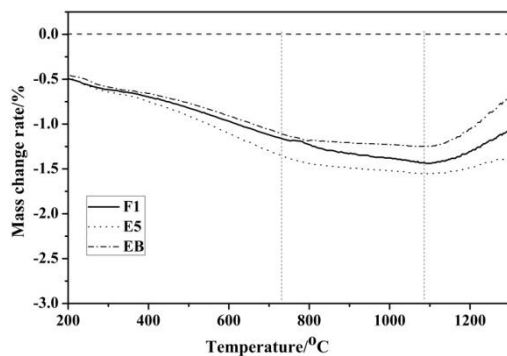


Fig. 3 Mass change rate of the specimens fired from 200 °C to 1300 °C in air.

The photographs of the cross section of specimens F1, E5 and EB after oxidation test are shown in Fig. 4. A considerable central black zone in the specimen F1 could be observed after oxidation test (Fig. 4a). In contrast, the specimen E5 exhibited a smaller black core, manifesting the EG was easier oxidized due to its higher reactivity (Fig. 4b). It's worth noting that the specimen EB possessed largest black zone (Fig. 4c), further demonstrating that B-doped EG addition could improve the

oxidation resistance of Al₂O₃-C refractories greatly.

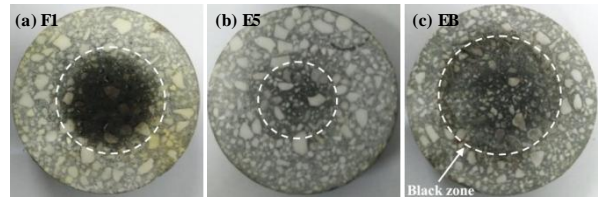


Fig 4 Cross-section photographs of specimens after oxidation test.

4 CONCLUSION

Boron-doped EG was synthesized by hydrothermal method and used as carbon source in Al₂O₃-C refractories. Boron atoms were doped in the graphitic layers of EG via the replacement of C atoms. The B-doped EG possessed lower reactivity and higher oxidation resistance in comparison with EG. With addition in Al₂O₃-C specimens, the B-doped EG remained relative intact structure at high temperature. Therefore, it provided positive influence on mechanical properties of Al₂O₃-C specimens. In addition, the oxidation resistance of Al₂O₃-C specimens was improved with addition of B-doped EG.

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