ROLES OF BORON CARBIDE IN Al₂O₃-C REFRACTORIES USING MWCNTS AS CARBON SOURCE

Yawei Li, Ning Liao, Gengfu Liu, Shaobai Sang

State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, Wuhan 430081, China

liyawei@wust.edu.cn

ABSTRACT

Al₂O₃-C refractories were prepared in coke bed at 1000-1400 °C when tabular alumina, reactive alumina and nano carbon black were used as main raw materials and boron carbide and/or silicon as additives. The results showed that the B₄C could catalyze resin binder into multi-walled carbon nanotubes (MWCNTs) at 1000°C. Over 1200°C, a B₂O₃ containing dense layer appeared on the surface and blocked the escape of SiO (g) from specimens, therefore much SiC whiskers with large length/diameter (L/D) grew in the matrix of the specimens. Owing to the *in-situ* growth of MWCNTs or SiC whiskers, the CMOR increase from 3.4 MPa to 11.6 MPa after coking at 1000 °C, from 17.5 to 28.2 MPa after coking at 1200 and 1400°C respectively. Additionally, the high temperature modulus of rupture and thermal shock resistance of B₄C containing Al₂O₃-C refractories are significantly improved simultaneously.

INTRODUCTION

Al₂O₃-C refractories are widely used as slide gates, submerged entry nozzles and monobloc stoppers in continuous casting system of steel-making industry owing to their slag corrosion resistance and thermal shock resistance ^[1]. However, the traditional Al₂O₃-C refractories containing a high content of carbon can hardly meet the increasing requirements of producing clean steel because of the carbon pick-up into molten steel ^[2]. With respect to the development of low-carbon Al₂O₃-C refractories, nano carbon black ^[3], MWCNTs ^[4] and graphite oxide nanosheets ^[5] are showing their potential applications.

In fact, these nano carbons produced impacts on the *in-situ* formation of ceramic phases in specimens as silicon was added (e.g. SiC), attributing to the fact that nano carbon sources have higher reactive activity than traditional graphite ^[6]. Therefore, the formation of ceramic phases in Al₂O₃-C refractories should be deliberately designed for achieving a trade-off performance between strength and toughness. Luo ^[7] et al. believed that the content of Si (g) and SiO (g) played a key role in controlling the growth of SiC ceramic phase when carbon nanotubes were used as carbon source. In our previous work, B₄C was adopted

to adjust the SiO (g) content in silicon and MWCNTs containing Al_2O_3 -C matrix. It confirmed that the addition of B_4C could suppress the MWCNTs transformation and trigger the growth of new MWCNTs from commercial MWCNTs ^[8].

In present work, B₄C was adopted in the silicon containing Al₂O₃-C refractories to further verify the effects of B₄C on the catalysis of resin binder and the formation of SiC ceramic phase without the addition of MWCNTs. Following that, the mechanical properties and thermal shock resistance of Al₂O₃-C refractories were investigated.

EXPERIMENTAL

Raw materials used for Al₂O₃-C refractories were 85 wt% tabular alumina (3.0~1.0, 1.0~0.5, 0.6~0.2, 0.3~0 mm, ~45 µm, ~20 µm, 98 wt% Al₂O₃, Qingdao Almatis Premium Alumina Co. Ltd., China), 10 wt% reactive alumina powder (~2µm, 98 wt% Al2O3, Qingdao Almatis Premium Alumina Co. Ltd., China), 1 wt% nano carbon black (CB, N220, 99.5 wt% fixed carbon, Wuhan Cobo New Materials Co. Ltd., China), 4 wt% silicon powder (45 µm, 98.47 wt% Si, Anyang, China) and B₄C powder (45 μ m, 99 wt% B₄C, China). There were two batches named as B0 and B1, corresponding to 0 and 1 wt% B4C addition. Additionally, 4 wt% thermosetting phenolic resin (liquid, ≥40 wt% fixed carbon, Wuhan Lifa Chemistry & Industry Co., Ltd., China) was added as binder. The fine powders were pre-mixed for 10 min firstly in a Hobart mixer, and then the aggregates were mixed for 3~5 min before the binder was introduced. After 5 min mixing of aggregates with binder, the pre-mixed fine powders were added and the mixing process held for another 30 min. The mixtures were then cold pressed into specimens of 25 mm × 25 mm × 140 mm at 165 MPa and cured at 180 °C for 24 h. Finally, the as-prepared Al₂O₃-C specimens were coked at 1000, 1200 and 1400 °C in a sagger filled with coke grit for 3 h. A heating rate of 5 $\,$ $^{\circ}C$ /min was applied before 1000 ${\rm C}$ and 2 ${\rm \ C}$ /min above 1000 ${\rm \ C}.$

Meanwhile, 20 g B_4C mixed with 100 g phenolic resin was coked at 800 and 1000 °C for soaking 3 hours in order to investigate the specific catalytic effects of boron carbide (<45 µm, 99 wt% B_4C , China) on resin binder.

CHARACTERIZATION

Apparent porosity and bulk density of Al₂O₃-C specimens were measured by Archimedes method. The phase compositions of the coked specimens were analyzed by X-ray diffraction (XRD, x'Pert Pro, Philips, Netherlands). Microstructures of specimens were observed by field emission scanning electron microscope (FESEM, Nova 400 NanoSEM, FEI Company, USA) and transmission electron microscopy (TEM-2100 UHR STEM/EDS JEOL), both of them were equipped with energy dispersive X-ray spectroscope (EDS, INCA IE 350 PentaFET X-3, Oxford, UK). The Raman spectra of resin with and without B_4C coked at 800 $^\circ$ C and 1000 $^\circ$ C were detected with a high-resolution dispersive Raman spectrometer system (Horiba-Jobin Yvon LabRam HR) equipped with a confocal microscope (Olympus BX-30) and a notch filter (532 nm). Cold modulus of rupture (CMOR) of coked specimens were measured by the three-point bending test at ambient temperature with a span of 80 mm and a loading rate of 0.5 mm/min using an electronic digital control system (EDC 120, DOLI Company, Germany). The thermal shock tests of specimens after coking at 1400 °C were carried out. Firstly, the specimens were heated in a coke bed at a rate of 5 $\,$ C /min to





850 °C soaked for 30 min. And then the specimens were quickly quenched into flowing water and cooled to room temperature. The residual strengths of the specimens after thermal shock were evaluated by three-point bending test.

RESULTS

Roles of B₄C in the catalysis of resin

Fig.1 shows the SEM and TEM micrographs of B_4C incorporated phenolic resin coked at 800 and 1000 °C. Apparently, Fig.1a shows that B_2O_3 particles are surrounded by clusters of nano fibers with 1-2 µm in length, where the fibers are identified as MWCNTs with B_xC imbedded at the tips through TEM observation (Fig.1c). An electron energy loss spectroscopy (EELS) spectrum from the tip of an individual nanotube is shown in the inset of Fig.1c, which displays two absorption features, one at 188 eV and another at 284 eV, corresponding to the B-K and C-K edges, respectively. This EELS result demonstrates that the imbedded tips should be B_xC . Similarly, MWCNTs are observed in specimen coked at 1000 °C, as shown in Fig.1b and Fig.1d. In contrast, only isotropic glassy carbon was observed in pure resin after coking at 800 and 1000 °C ^[9].





Fig.1. SEM micrographs of resin-B₄C coked at 800 °C (a) and 1000 °C (b) and TEM graphs of specimens coked at 800 °C (c) and 1000 °C (d).

Besides, XRD and Raman analysis of the resin specimens with and without B_4C were also conducted. As shown in Fig.2a, only broad peaks around 25 degrees are detected in pristine resin, which corresponds to low graphitization carbon. In contrast, sharp and strong peaks of graphite (around 26 degrees) together with B_2O_3 and B_4C phases are detected in resin- B_4C specimens. For Raman characterization (Fig.2b), the Raman band appearing in the 1300-1385 cm⁻¹ spectral region is known as D band (disorder induced band) and the one appearing in the 1550-1650 cm⁻¹ region of the wavenumber is attributed to G

band (graphite band). In the present case, no obvious peaks are detected in pristine resin coked at 800 °C. With further increasing the temperature to 1000 °C, relatively higher G band and D band are presented because of the partial graphitization of phenolic resin. In comparison, a clear G band is detected in resin-B₄C specimens when coking at 800 and 1000 °C, which indicates the formation of graphitized carbon such as MWCNTs. The peak intensity ratio $I_{(G)}/I_{(D)}$ indicates that the



pyrolysized carbon should be crystalline graphite structure. These results strongly demonstrate the fact that B_4C can stimulate the formation of MWCNTs from resin binder and the growth mechanism can be expressed as follows. The micron-scaled B_4C is firstly oxidized into B_2O_3 vapor and then it reacts with hydrocarbon gases generated from resin to form nano-sized B_xC droplets, which function as catalyst for the growth of MWCNTs through classical V-L-S mechanism.



Fig.2. XRD (a) and Raman spectrum (b) of resin and resin-B₄C specimens coked at 800 and 1000 °C.

Microstructures of Al₂O₃-C refractories

The microstructures of specimens are shown in Fig.3 -Fig.4. As for specimen B0 coked at 1000 °C, no new phase is observed. After coking at 1200 and 1400 °C, a few whiskers are observed, which are determined as SiC whiskers by XRD and EDS analysis. In contrast, fibrous material is observed in B_4C containing specimen at 1000 °C and these fibres are identified as MWCNTs according to EDS and above analysis. When the specimens were coked at 1200 and 1400 °C, much SiC whiskers are observed in comparison with specimens B0. This phenomenon could be explained by the fact that a B_2O_3 containing dense layer formed on the surface suspending the escape of SiO (g) and thus SiC whiskers with large length/diameter grew in the matrix of specimens B1.



Fig.3 SEM micrographs of specimen B0 coked at 1000 (a), 1200 (b) and 1400 °C (c).



Fig.4 SEM micrographs of inside area of specimen B1 coked at 1000 (a), 1200 (b) and 1400 °C (c).

Physical and mechanical properties of Al₂O₃-C refractories

Table 1 shows the apparent porosity (A.P.) and bulk

density (B.D.) of the treated specimens. It is clear to see that the B_4C containing specimens show much lower A.P. than specimen B0 under almost every coking temperature. Besides, the A.P. of all the specimens decrease due to the growth of SiC whiskers when the specimens were coked above 1000 °C.

The strengths of specimens at room temperature, high temperature and after thermal shock test were evaluated and the results are shown in Tab.1. Apparently, the CMOR of specimens B1 are much higher than those of specimens B0 when they were coked at 1000 °C. There are two factors contributing to higher strengths of B_4C containing specimens, one is the higher density and the other important factor is the *in-situ* growth of MWCNTs. No distinct difference is detected for the specimens with and without B_4C addition when they were coked at 1200 °C. However, the CMOR of specimens B1 are dramatically increased at 1400 °C, which is because of the synergetic strengthening effects of MWCNTs and SiC whiskers. Besides, the high temperature strength (HMOR) and residual strength after thermal shock (CMOR_{TS}) of B_4C containing Al₂O₃-C refractories are remarkably improved.

Table 1 Physical and mechanical properties of Al₂O₃-C refractories.

Specimen No.		B0			B1	
Temperature/°C	1000	1200	1400	1000	1200	1400
Apparent porosity/%	17.3±0.8	14.6±0.3	15.9±0.7	15.4±0.1	14.7±0.1	14.4±0.6
Bulk density/(g cm ⁻³)	3.01 ±0.02	3.07±0.01	3.08±0.02	3.01±0.01	3.02±0.01	3.03 ±0.01
CMOR/MPa	3.35±0.17	16.16±0.27	11.97±1.64	11.56±1.14	17.50±2.11	28.22±1.58
HMOR/MPa		15.98±0.16			22.99±0.36	
CMOR _{TS} /MPa		6.68±0.43			11.65±2.41	

CONCLUSIONS

1. B_4C could catalyze resin binder into multi-walled carbon nanotubes (MWCNTs) at 1000 °C. Besides, it prevented the escape of SiO (g) due to the formation of a B_2O_3 containing dense oxide layer on the surface of specimens above 1000 °C. Therefore, much SiC whiskers with large L/D formed in the matrix of B_4C containing Al₂O₃-C refractories.

2. The *in-situ* formed MWCNTs and SiC whiskers develop synergetic strengthening and toughening effects to improve mechanical properties and thermal shock resistance of B_4C containing Al_2O_3 -C refractories.

ACKNOWLEDGMENTS

The project was financially supported by Natural Science Foundation of China (51574186, 51372176) and Department of Science and Technology (2014CB660802).

REFERENCES

- Ewais EMM. Carbon based refractories[J]. Journal of the Ceramic Society of Japan. 2004; 112(1310): 517–32.
- [2] Li N. NAIHUOCAILIAOXUE (in Chinese), Beijing: Metallurgical Industry Press, 2010: 214.
- [3] Tamura S, Ochiai T, Takanaga S, Kanai T, Nakamura H. Nano-tech refractories-2: the development of the nano structural matrix to MgO-C bricks. In: Proceedings of UNITECR'3, Japan, 2003.
- [4] Luo M, Li YW, Jin SL, Sang SB, Zhao L, Li YB.

Microstructures and mechanical properties of Al₂O₃-C refractories with addition of multi-walled carbon nanotubes. Mater. Sci. Eng., A. 2012; 548: 134-141.

- [5] Zhu TB, Li YW, Jin SL, Sang SB, Wang QH, Zhao L, et al. Microstructure and mechanical properties of MgO-C refractories containing expanded graphite. Ceram. Int. 2013; 39: 4529-4537.
- [6] Wang QH, Li YW, Luo M, Sang SB, Zhu TB, Zhao L. Strengthening mechanism of graphene oxide nanosheets for Al₂O₃-C refractories. Ceram. Int. 2014; 40: 163-172.
- [7] Luo M, Li Y, Sang S, et al. Reaction mechanism between silicon-containing gaseous species and multi–walled carbon nanotubes at high temperature[J]. Journal of the Chinese Ceramic Society. 2011; 39(8): 1295–300.
- [8] Liao N, Li Y, Jin S, et al. Combined effects of boron carbide, silicon, and MWCNTs in alumina–carbon refractories on their microstructural evolution[J]. Journal of the American Ceramic Society. 2017; 100: 443–50.
- [9] Luo M, Li YW, Sang SB, Zhao L, Jin SL, Li YB. In situ formation of carbon nanotubes and ceramic whiskers in Al₂O₃-Crefractories with addition of Ni-catalyzed phenolic resin. Mater. Sci. Eng., A. 2012; 558: 533-542.