

MgO–C Bricks Containing Nano-boron Carbide

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MgO–C refractories are widely used as working lining for BOF vessels. Nowadays, the association of top and bottom gas blowing is a usual procedure exposing bricks to severe oxidation, corrosion, erosion and thermal shock. In order to attain such requirements, the MgO–C bricks are produced using high quality raw materials, novel binding systems and specific additives. Adding a blend of metals prevents oxidation, increases hot mechanical properties and also induces better physical and corrosion properties.

Boron carbide (B_4C) is a key additive which provides high oxidation resistance, speeds up the phenolic resin crystallization and helps to mineralize the magnesia dense layer in MgO–C bricks at high temperatures. Besides that, B_4C and Al metal induces the formation and growth of $MgO \cdot Al_2O_3$ spinel crystals in the matrix. In this work, nano- B_4C was synthesized to replace commercial coarser grain boron carbide. Comparative tests between these two antioxidant sources were carried out to evaluate the effects of nanotechnology in MgO–C bricks. The powder characterization and the product properties are highlighted in this paper.

1 Introduction

The role of carbon in advanced refractories is already well established due to its excellent slag resistance, high thermal conductivity and low thermal expansion coefficient [1]. However, it is highly vulnerability to oxidation results in lower mechanical strength products due to its weakly-bonded nature. In order to improve the oxidation resistance of carbon containing refractories and to keep their positive effects during the working life, antioxidants, such as metals (Mg, Al, Si), alloys (Mg–Al), and carbides (B_4C , SiC) are often added to the products [1–4].

These additives play different roles during the refractory's campaign. Metal/alloy and carbide mainly act as CO-reducing agents, inhibiting carbon oxidation and/or improving the hot mechanical strength by forming high-temperature ceramic bonds.

Aluminum is the most used antioxidant in MgO–C refractory and not only helps to preserve the carbon, but also to decrease the

porosity, increase the hot mechanical modulus of rupture (HMOR) and build up a surface protective layer that reduces slag corrosion. Nevertheless, the formation of Al_4C_3 is a major drawback as this phase is easily hydrated, resulting in a large volume expansion and deterioration of the material during reheating [1, 3, 5, 6].

Carbides have been used as antioxidants because the carbon yield is higher than those for metals and alloys. Besides that, B_4C can speed up the crystallization of carbon from the resin binder. The mechanism by which B_4C acts as an effective antioxidant in carbon-containing refractories has been already studied and a resulting boron-containing liquid phase has been found as a key issue to induce the formation of the MgO dense layer close to the working surface, thus protecting the carbon from oxygen ingress [2, 4, 1].

Nevertheless, adding B_4C has a negative impact on MgO dissolution due to high partial pressures ($>10^{-4}$ atm) of $BO_{(g)}$, $B_2O_{2(g)}$ and $B_2O_{3(g)}$ at 1650 °C, resulting in significant

amounts of these gas phases that not only react with $CO_{(g)}$ and MgO generating in $3MgO \cdot B_2O_3$ (M_3B) liquid in the refractory, but also diffusing towards the slag layer. When these gases reach the decarburized dense MgO and/or slag layers they react with the magnesium oxide forming low melting phases which would quickly be dissolved in the local slag. Furthermore, the increase of B_2O_3 content in the slag would enhance MgO solubility and thus further speed up the MgO dissolution [2].

Differently from the other blends, the addition of Al + B_4C markedly improved the oxidation resistance as follow:

- $CO_{(g)}$ is reduced back to C by Al and/or B_4C
- Fe_xO and MnO from the slag were reduced by Al to form $Fe_{(g, l)}$ and $Mn_{(g, l)}$ preventing C oxidation
- M_3B liquid formed fills in the pores and coats the C surfaces.

Another important microstructural feature is that many larger MA ($MgO \cdot Al_2O_3$) crystals can be found among the graphite flakes in the matrix, often coexisting with the borate phases, suggesting that at high temperatures, liquid M_3B might play a role in their formation and growth. Boron-containing li-

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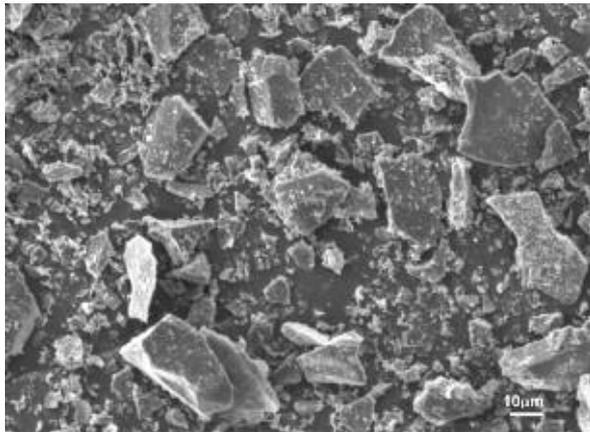


Fig. 1 Commercial boron carbide (ESK Ceramics GMBH/DE)

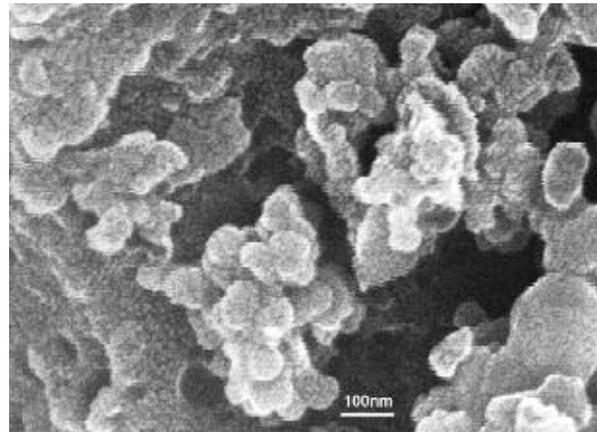


Fig. 2 Nano-boron carbide produced by Magnesita/BR

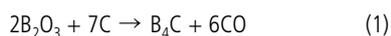
quid has a strong mineralising effect on MA crystallisation. This fact further indicates that graphite in the refractory matrix was also bonded together by MA crystals at the testing temperature [2, 4].

The drawbacks of adding Al + B₄C to the MgO dissolution are similar when each component is added separately. The former would also speed up the MgO dissolution by increasing the local slag Al₂O₃ and/or B₂O₃ contents [4, 6].

B₄C powder is synthesized using several methods such as:

- solid state reaction from boron and carbon elements
- co-reduction in an autoclave using BBr₃ and CCl₄ as the reactants and metallic Na as the co-reductant
- the magnesiothermic reduction of boron oxide (B₂O₃) in the presence of carbon
- laser irradiation of boron nanoparticles dispersed in an organic solvent
- the carbothermal reduction of B₂O₃ by graphite or petroleum coke [7].

Among these methods, the carbothermal reduction is the most usual method for producing B₄C owing to the lower cost of the raw materials. The process is carried out at approximately 2000 °C, according to Eq. 1.



Tab. 1 Properties of commercial (cB₄C) (ESK Ceramics GMBH) and nano-boron carbide (nB₄C)

	cB ₄ C	nB ₄ C
Density [g/cm ³]	2,61	2,53
SSA [g/cm ²]	1,31	15,83
Particle size (D ₅₀)	11 μm	70 nm

Boron carbide presents a very high hardness and, therefore, the milling time process to obtain fine particles from commercial products can consume over 100 h and it is very expensive. In order to avoid this cost, *Magnesita Refratários/BR* developed a carbothermal process to obtain B₄C already starting with raw materials on a nano scale. This approach resulted in a cost effective nano-B₄C compatible to the commercial micro one. The initial results after adding this nano powder to MgO–C refractory compositions are presented in this paper.

2 Experimental procedure

2.1 Boron carbide sources

Nano-boron carbide (nB₄C) was synthesized at Magnesita and compared according to the commercial compound (*ESK Ceramics GMBH/DE*). Powder density was measured by helium pycnometry according to the ASTM C604 – 02 (*Quantachrome* Ultrapyc 1200e), the specific surface area was determined by the B.E.T method (*Quantachrome* Autosorb IQ) and the particle size (D₅₀) was evaluated using the laser diffraction tech-

nique (*Malvern Mastersizer 2000* and *Zetasizer Nano ZS*). The characterization between these two sources is presented in Tab. 1.

Fig. 1 and Fig. 2 show typical morphology and particle sizes of both boron carbide sources.

The main difference between commercial and nano-boron carbide is associated to the primary particle size.

2.2 MgO–C bricks evaluation

2.2.1 Materials and techniques

Three identical MgO–C compositions were selected to study the effect of nano-boron carbide as an additive as presented in Tab. 2. They were designed in order to have the same amount and grain size distribution of fused MgO (98,5 mass-% of MgO, *Magnesita Refratários*) and graphite content (99,0 mass-% of C, *Nacional de Grafite/BR*), the same binder system (referred to as HTM – high thermal mechanical binder [8]) and amount of aluminum powder (99,5 mass-% of Al, *Alcoa/BR*). 0,3 mass-%t of commercial boron carbide (*ESK Ceramics GMBH*) was added to composition A1 and the same

Tab. 2 MgO-C bricks compositions for boron carbide sources evaluation

	A1	A2	A3
Fused MgO/Total MgO [%]	100	100	100
Total MgO [%]	84	84	84
Al powder	++	++	++
Commercial B ₄ C [mass-%]	0,3	–	–
Nano-B ₄ C [mass-%]	–	0,3	–
Binder	HTM	HTM	HTM
Total C [%]	13	13	13

amount of nano-boron carbide to composition A2. Composition A3 had no boron carbide source.

All prismatic samples (160 mm × 40 mm × 40 mm) were prepared and pressed (*Gardelin*/BR friction press, 100 t) at Magnesita R&D Center and cured at 200 °C/6 h under a 10 °C/min heating rate.

Physical, mechanical and chemical properties were evaluated for all compositions. Bulk density and apparent porosity were measured according to ASTM C20. Cold crushing strength was carried out in universal mechanical testing equipment (*EMIC*/BR, Model PC200C) according to ASTM C133. For HMOR evaluation, no previous thermal treatment was carried out and tests were performed using homemade equipment (Magnesita). Samples were wrapped in nickel foil to prevent oxidation. The elastic modulus was measured by the sonic resonance method (*James Instrument*/US, Model V Meter) according to ASTM C885.

For the corrosion tests, samples were thermally treated at 1000 °C/5 h to eliminate any volatile to prevent explosion and were performed immersing samples into molten steel and synthetic slag 40 mass-% FeO in an induction furnace at 1700 °C/3 h. Oxidation was carried out by air blowing at 1000 °C/1 h in an electrical furnace. The permanent volumetric expansion (PVE) was measured according to ASTM C134 after firing the samples at the described temperature and time.

2.2.2 Results and discussions

Results after curing at 200 °C/6 h are presented in Tab. 3.

Physical properties were very similar for all compositions as expected due to very small changes in grain size distribution. CCS and EM results were close because they are directly associated to the phenolic resin crosslink. HMOR at 1000 °C increased for composition A2 with a significant benefit (10 % increase) when compared to compositions A1 (with Al powder + cB₄C) and A3 (only Al powder). HMOR results at 1400 °C were slightly better for compositions with boron carbide addition, but no significance difference was observed between the compositions with commercial and nano-particles. Moreover, metal and slag corrosion results were similar but with a measurable advantage for the nano-containing compos-

Tab. 3 MgO–C bricks properties after curing at 200 °C/6 h

	A1	A2	A3
	cB ₄ C	cB ₄ C	No B ₄ C
BD* [g/cm ³]	2,99 ± 0,01	2,99 ± 0,01	3,01 ± 0,01
AP* [%]	2,31 ± 0,37	2,27 ± 0,27	1,93 ± 0,21
CCS* [MPa]	41,06 ± 1,86	43,93 ± 1,10	40,91 ± 1,50
HMOR* at 1000 °C [MPa]	15,62 ± 1,34	17,17 ± 1,21	14,69 ± 1,09
HMOR* at 1400 °C [MPa]	16,84 ± 0,60	16,49 ± 0,52	16,02 ± 0,56
EM* [GPa]	61,91 ± 0,50	63,26 ± 0,62	58,13 ± 1,11
Metal corrosion [%]	2,12 ± 0,30	1,37 ± 0,23	2,18 ± 0,10
Slag corrosion [%]	21,82 ± 0,77	19,74 ± 0,96	21,68 ± 1,92
Oxidation [%]	31,85 ± 2,04	27,52 ± 2,39	32,84 ± 2,00

*BD: bulk density, AP: apparent porosity, CCS: cold crushing strength, HMOR: hot modulus of rupture, EM: elastic modulus

Tab. 4 MgO–C bricks properties after thermal treatment at 1400 °C/5 h and 1600 °C/5 h

After firing at 1400 °C/5 h			
	A1	A2	A3
	cB ₄ C	nB ₄ C	No B ₄ C
BD [g/cm ³]	2,96 ± 0,01	2,93 ± 0,01	2,95 ± 0,01
AP [%]	3,23 ± 0,25	2,83 ± 0,15	5,01 ± 0,26
PVE* [%]	0,86 ± 0,04	0,36 ± 0,06	1,41 ± 0,08
CCS [MPa]	40,87 ± 0,48	43,72 ± 0,67	33,77 ± 0,84
HMOR at 1400 °C [MPa]	17,46 ± 0,78	17,49 ± 0,88	16,79 ± 0,49
EM [GPa]	34,01 ± 0,36	37,84 ± 0,60	25,42 ± 0,56
After firing at 1600 °C/5 h			
	A1	A2	A3
	cB ₄ C	nB ₄ C	No B ₄ C
BD [g/cm ³]	2,96 ± 0,01	2,93 ± 0,01	2,95 ± 0,01
AP [%]	7,70 ± 0,23	7,63 ± 0,17	8,53 ± 0,21
PVE* [%]	1,42 ± 0,10	0,60 ± 0,17	1,57 ± 0,16
CCS [MPa]	47,22 ± 1,86	43,14 ± 1,77	36,06 ± 0,82
HMOR at 1400 °C [MPa]	19,05 ± 1,14	18,64 ± 1,07	18,05 ± 0,85
EM [GPa]	47,22 ± 1,18	43,14 ± 1,16	36,06 ± 0,68

*PVE: permanent volume expansion

ition. Oxidation in air at 1000 °C showed less decarburization damage for the composition with nano B₄C, which is compatible with previous HMOR results at 1000 °C that showed an earlier reaction of the nano-additive.

Results after firing at 1400 °C/5 h and 1600 °C/5 h for all compositions are presented in Tab. 4.

Physical and mechanical properties after firing at 1400 °C better highlight the benefits of the boron carbide in MgO–C bricks. Nano-sized additive was slightly more

effective to reduce the open porosity and increase CCS and ME, but results are very close to the commercial additive. Furthermore, HMOR results after firing at both temperatures were similar for the compositions showing less effect of boron carbide for this property.

PVE indicates the overall dimensional change of the products and it is an indirect measurement of the interaction between aggregates and matrix. Composition A2 with nano-B₄C showed a lower value compared to composition A1 (with Al powder + cB₄C)

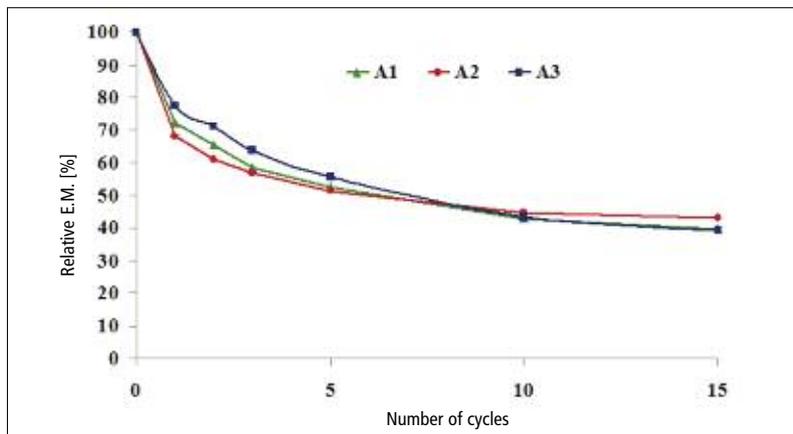


Fig. 3 Thermal shock evaluation: relative elastic modulus [%] by the number of thermal shock cycles for MgO-C bricks (ΔT close to 1175 °C)

and A3 one (only Al powder). Lower PVE can result in less expansion stress and a more predictable performance during the BOF operation. Fig. 3 presents the decay in elastic modulus by the number of the thermal cycles for samples pre-fired at 1000 °C. Each cycle was carried out at 1200 °C and water quenched with the help of copper cooled plates. Samples were coated with nickel foil to prevent oxidation. All compositions presented very close behavior.

3 Conclusions

Nanotechnology can be a powerful tool to improve MgO-C compositions for BOF. Nano-graphite can be used replacing natural graphite and substantially decrease the final carbon content of the bricks. Nano-boron carbide can also be an option as an additive

for better properties, even when a very small content is added.

Nano-boron carbide showed to be more effective than microsized commercial boron carbide only after evaluating the cured bricks, showing a faster increase in HMOR results and better oxidation resistance. At higher firing temperatures, both boron carbide grain sizes showed similar benefits.

Due to very small particles, nano-boron carbide needs less temperature to start acting so that benefits can be found in the final properties. This can be an interesting aspect for MgO-C bricks performance in the early stage of BOF operation where initial heating always results in oxidation damage. In continuous operation, nano-particles will behave as commercial boron carbide. The cost of both powders (nano-synthesized and

commercial one) are similar at the present, but the nano-B₄C can be even more competitive after large production scale.

References

- [1] Wang, T.; Yamaguchi, A.: Oxidation protection of MgO-C refractories by means of Al₆B₄C₇. *J. of Amer. Ceram. Soc.* **84** (2001) [3] 577–582
- [2] Zhang, S.; Lee, W.E.: Influence of additives on corrosion resistance and corroded microstructure of MgO-C refractories. *J. Europ. Ceram. Soc.* **21** (2001) 2393–2405
- [3] Yamaguchi, A.: Role and behavior of additive in the carbon-containing refractory (on new additive: Al₄O₄C, Al₂OC, Al₆B₄C₇ and Al₄SiC₄). *Proc. of 10th Int. Ceramics Congress Int. Symposium, Florence/IT* (2002) 43–51
- [4] Zhang, S.; Marriot, N.J.; Lee, W.E.: Thermochemistry and microstructures of MgO-C refractories containing various antioxidants. *J. Europ. Ceram. Soc.* **21** (2001) 1037–1048
- [5] Gokce, A.S.; et al.: The effect of antioxidants on the oxidation behaviour of magnesia-carbon refractory bricks. *Ceram. Int.* **34** (2008) 323–330
- [6] Sadrnezhad, S.K.; et al.: Effect of Al antioxidant on the rate of oxidation of carbon in MgO-C refractory. *J. Amer. Ceram. Soc.* **90** (2007) [2] 509–515
- [7] Kakiage, M.; et al.: Low-temperature synthesis of boron carbide powder from condensed boric acid-glycerin product. *Mater. Letters* **65** (2011) 1839–1841
- [8] Pagliosa, C.; et al.: High performance MgO-C bricks for BOF: From now to nanotechnology. *Proc. of The Iron & Steel Technol. Conf. and Exposition, Pittsburgh, PA, USA, 2013*