

# Designing Stronger and Tougher MgO–C Bricks for Basic Oxygen Furnace (BOF)

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Basic oxygen furnace (BOF) or LD converter is a relatively cheap process for refining iron into steel. However, the novel demands on low carbon metal production have been leading to: (I) the increase of the applied oxygen volume flow, and (II) the use of top and bottom blowing, in order to decrease operational costs via more efficient stirring of the molten steel in such equipment. Based on these aspects, MgO–C bricks (commonly used as refractory lining in BOF) have been continuously exposed to severe oxidation and corrosion by gases and slags, erosion due to molten metal turbulence and thermal shock stresses. Consequently, a new approach (based on mimic some biological and natural materials, i.e. nacre, sea-shells, human cortical bones, etc.) was used to design MgO–C refractories with improved strength and toughness. In this sense, a special phenolic resin binder was combined with nanographite particles or a special alumina in various proportions. Thermomechanical characterization of classic MgO–C bricks and bio-inspired compositions indicated that nanographite addition to the HTM (High Thermal Mechanical, which comprises phenolic resin and pitch in a particular ratio) binder was effective in increasing CCS and HMOR values of the refractories after curing (200 °C for 6 h) and firing (1400 °C for 5 h). Moreover, adding special alumina to such composition also increased its HMOR and thermal shock resistance, indicating that this might be a likely route to design damage tolerance materials.

## Introduction

As MgO–C bricks are subjected to different wearing mechanisms when applied in BOF equipment, some of them can be highlighted as follows [1, 2]:

- Trunion side: oxidation and mechanical stress at high temperature;
- Tapping side: erosion and corrosion due to contact with molten metal and slag, respectively;
- Charging side: mechanical stress induced by the contact/impact with scrap and molten steel;
- Slag side: corrosion due to interaction with slag;
- Bottom parts: erosion derived from heavy turbulence of metal due to gas injection;
- Cone: oxidation and thermal shock.

MgO–C bricks designed for BOF trunnions and charging zones can be classified as engineering structural products due to the mechanical and thermal stresses that they are subjected to. Such application requires refractories with both, improved strength and toughness (damage tolerant), although

these properties are mutually exclusive in most materials. Whereas strength represents the material's resistance to non-recoverable deformation (at least in ductile components), toughness is related to its fracture resistance and, as such, is measured via the energy needed to fracture it. Toughness can also be evaluated using fracture-mechanics methods, which determines the critical value of a crack-driving force [3, 4].

The ability of a material to undergo deformation is a critical aspect to provide toughness, as this feature enables the local dissipation of high stresses that would otherwise cause its fracture. This is the reason why hard materials tend to be brittle, whereas the ones presenting lower strength can be deformed more readily and are commonly tougher (higher fracture energy).

Mollusc shells are good example of nature's design of damage-tolerant materials. Dating back to some 545 million years ago, these materials (such as nacre = red abalone shell) developed a "brick-and-mortar" structure (Fig. 1), where the "bricks" are ~0,5 µm thick, 5–10 µm wide platelets

of the mineral aragonite (95 vol.-% of the overall structure), and the "mortar" comprises an organic biopolymer. The ceramic

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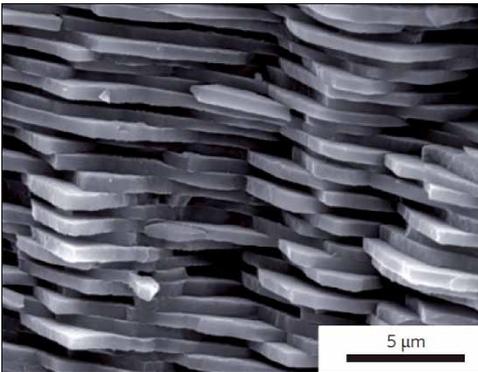
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Keywords: refractory, MgO–C,  
bio-inspired, wear

Received: 26.08.2016

Accepted: 12.09.2016



**Fig. 1** Nacre has a natural structure of ~0,5  $\mu\text{m}$  thick aragonite mineral “bricks” separated by a biopolymeric “mortar” [3]

mineral accounts for the high strength. However, as this component is inherently brittle, if the aragonite platelets were rigidly locked together, the resulting toughness would be low as there would be limitations for relieving any local high stresses. Therefore, the role of the organic “mortar” is to act as a lubricant, allowing some displacement between the platelets and inducing intrinsic toughening plasticity mechanism. This sliding between the mineral platelets must be limited to  $\sim 1 \mu\text{m}$  or the material will lose its strength. In order to attain this target, nature overcame this drawback by roughening the surface of the mineral component to provide frictional bumps and by generating small “bridges” linking these layers. The tortuous crack paths and pull-out of the mineral platelets further provides a major contribution as an extrinsic toughening. The overall result is an hybrid material with toughness of at least an order of magnitude higher than any of its constituent phases [3].

Based on these aspects, this work focused on mimicking nature in order to design stronger and tougher MgO–C bricks by adding nanographite or special alumina to the selected binder component. Phenolic resins (commonly used as binder additives in such refractories) become rigid after cross-linked bonds are generated during their curing process, resulting in materials with good mechanical resistance. Even when combined with solid pitch (giving rise to a resin-pitch binder named HTM) [5], the phenolic resin is still a brittle component that links all aggregates. Nanographite, on the other hand, is a soft material and, when well dispersed into the resin, it could act as crack deflector or a plastic compound.

**Tab. 1** General information of the evaluated MgO–C bricks compositions.

Raw Materials	Compositions				
	A1	A2	A3	B1	B2
MgO [mass-%]	84,0	84,0	84,0	84,0	84,0
Carbon [mass-%]	13,0	13,0	13,0	13,0	13,0
Mg–Al powder	++	++	++	++	++
Nano graphite [mass-%]	–	0,5	1,0	–	–
Special alumina [mass-%]	–	–	–	–	0,5
Binder	HTM	HTM	HTM	HTM	HTM

An additional, but inherent, challenge for designing refractory damage tolerance materials is the high temperature exposure. Phase transformations, expansive reactions and mismatching of different aggregates make refractory into a mutable microstructure. Mechanisms for relieving local high stresses through limited inelastic deformation (providing intrinsic toughness and further extrinsic transformations) can be much more complex than the examples found in nature. Thus, this work presents an initial exploration of this novel concept for the development of enhanced refractory bricks.

### Experimental

Three MgO–C compositions (A1, A2 and A3, Tab. 1) containing different amounts of nanographite (99,1 mass-% of C,  $d_{50} = 70 \mu\text{m}$ , Magnesita Refratários/BR) were firstly analysed, as this compound might improve the refractory toughness. The designed mixtures presented the same amount and grain size distribution of fused magnesia (98,5 mass-% of MgO, Magnesita Refratários) and fixed graphite content (99,0 mass-% of C, Nacional de Grafite/BR). Moreover, the same binder system (blend of phenolic resin + solid pitch, named here as HTM – High Thermal Mechanical binder) and Mg–Al alloy powder content ( $d < 200 \mu\text{m}$ , 49 mass-% of Al, Magnesita Refratários) were added to all evaluated refractories. Composition A1 is the original one (reference).

Nevertheless, the authors were not sure whether the nanographite would be seen by the crack as a barrier due to its compatibility with the resin. Therefore, an alternative design was planned, where an inert phase (i.e., special alumina supplied by Elkem/NO,  $d_{\text{max}} < 8 \mu\text{m}$ ) would be added to the formulation, although it is harder than the resin matrix. This could be an “mortar-

and-brick” structure. Based on that, two new compositions (B1 and B2, Tab. 1) were prepared. In order to attain suitable dispersion of nanographite and special alumina particles in the selected resin, the following procedure was conducted during the raw materials mixing:

- Novolac resin was heated up to  $60 \text{ }^\circ\text{C}$  for 30 min (in a recipient with a lid to prevent solvent loss) to decrease its viscosity;
- Heated resin was transferred to a hot plate at  $60 \text{ }^\circ\text{C}$ , where an organic dispersant was incorporated to the mixture. These materials were mixed and homogenized for 1 min;
- Nanographite was further added to the heated resin and mixed for more 5 min;
- The final mixture was cooled to room temperature before adding to MgO–C dry-composition. No segregation was observed.

Prismatic samples ( $160 \text{ mm} \times 40 \text{ mm} \times 40 \text{ mm}$ ) were prepared using a friction press (FKL 450 t/BR), cured at  $200 \text{ }^\circ\text{C}$  for 6 h and fired at  $1400 \text{ }^\circ\text{C}$  and  $1600 \text{ }^\circ\text{C}$  for 5 h (heating rate =  $10 \text{ }^\circ\text{C}/\text{min}$ ) in a coke sealed box, in order to attain a reducing atmosphere.

Physical and mechanical properties of the cured and fired refractory samples were evaluated. Bulk density and apparent porosity were measured according to ASTM C20, whereas cold crushing strength (CCS) was carried out in universal mechanical testing equipment (EMIC, Model PC200C/BR), as indicated in ASTM C133.

Cured samples were used for the hot modulus of rupture (HMOR) measurements at  $1400 \text{ }^\circ\text{C}$  and the analyses were carried out in homemade testing equipment (Magnesita Refratários), but following ASTM C583. In order to prevent the refractory oxidation, all samples were wrapped in nickel foil before testing. Besides that, elastic modulus of

cured and fired refractories was evaluated by sonic resonance method (James Instrument, Model V Meter/US) according to ASTM C885. Permanent volumetric expansion (PVE) of the fired materials was measured (ASTM C134). Thermal shock tests was also carried out by placing prismatic samples (pre-fired at 1000 °C for 5 h in order to withdraw the volatile species before testing) wrapped in nickel foil in an electric oven at 1200 °C and cooling down such materials in a copper refrigerated plate. After cooling, the residual refractory elastic modulus (ASTM C885) was measured to evaluate the damage induce by the thermal changes (total of 10 cycles).

### Results and discussion

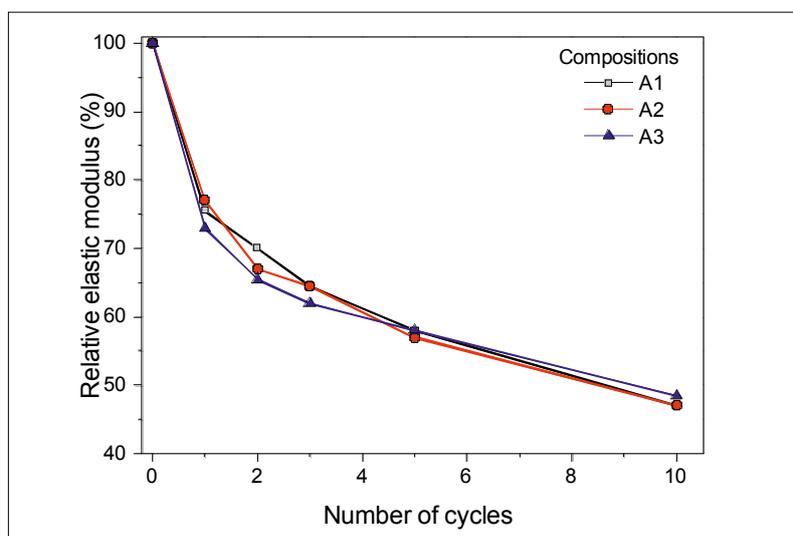
Aiming to provide a fair comparison among the results of the MgO–C nanographite (nG)-containing compositions, in addition to the measured physico-mechanical properties, specific CCS (sCCS = CCS/bulk density) and specific HMOR (sHMOR = HMOR/bulk density) are also presented in Tab. 2–3. 1 mass-% nG addition mainly slightly increased the HMOR values and reduced the resulting elastic modulus of A3 samples, when compared to A1 (Tab. 2). This higher hot mechanical strength might be associated with the greater and finer carbon content in this composition, which could result in a more effective aluminium carbide formation at high temperatures. Nevertheless, the same effect (HMOR increase) was not observed for the 0,5 mass-% nG-containing material. Additionally, a bulk density decrease, followed by apparent porosity increase (with is in tune with the elastic modulus drop) were detected for the A3 refractory. Conversely, sHMOR highlighted that the composition with 1 mass-% nG presented some improvements in the measurements carried out at high temperature (>sHMOR, Tab. 2).

Similar results for the cured samples of the three analyzed compositions (A1, A2 and A3) were attained for the elastic modulus profile after 10 cycles of thermal shock tests (Fig. 2). However, further microstructural changes are still expected to take place in the refractory samples, when subjecting these materials to higher firing temperatures (>1000 °C).

Regarding the pre-fired MgO–C refractories (Tab. 3), sCCS and sHMOR values were still

**Tab. 2** MgO–C bricks properties after curing at 200 °C for 6 h

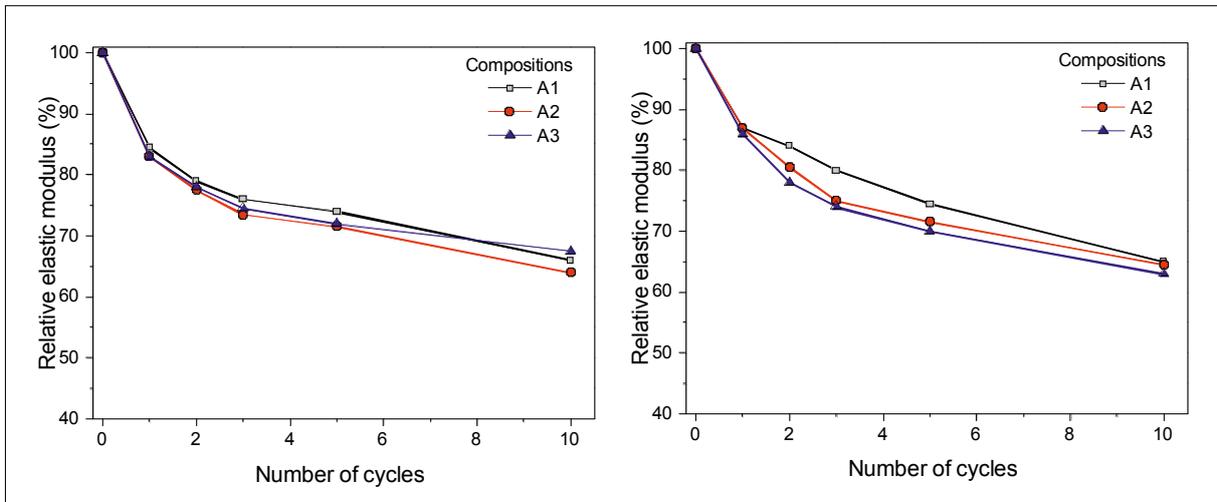
Properties	Compositions		
	A1 [Ref.]	A2 [0,5 mass-% nG]	A3 [1,0 mass-% nG]
Bulk density [g · cm <sup>-3</sup> ]	2,97 ± 0,01	2,94 ± 0,01	2,91 ± 0,05
Apparent porosity [%]	3,79 ± 0,07	4,53 ± 0,14	5,00 ± 0,17
Cold crushing strength [MPa]	38,57 ± 1,19	39,33 ± 1,57	37,87 ± 0,63
Specific cold crushing strength [MPa/(g · cm <sup>-3</sup> )]	12,97	13,40	13,03
Hot modulus of rupture [MPa]	13,71 ± 0,38	12,79 ± 0,18	15,12 ± 0,68
Specific hot modulus of rupture [MPa/(g · cm <sup>-3</sup> )]	4,61	4,36	5,20
Elastic modulus [GPa]	48,24 ± 1,74	42,43 ± 0,53	40,09 ± 0,60



**Fig. 2** Relative E drop attained during the thermal shock tests ( $\Delta T \sim 1175$  °C) for the MgO–C bricks cured at 200 °C for 6 h. All samples were also pre-fired at 1000 °C for 5 h in order to allow the volatiles release before testing

**Tab. 3** MgO–C bricks properties after firing at 1400 °C or 1600 for 5 h

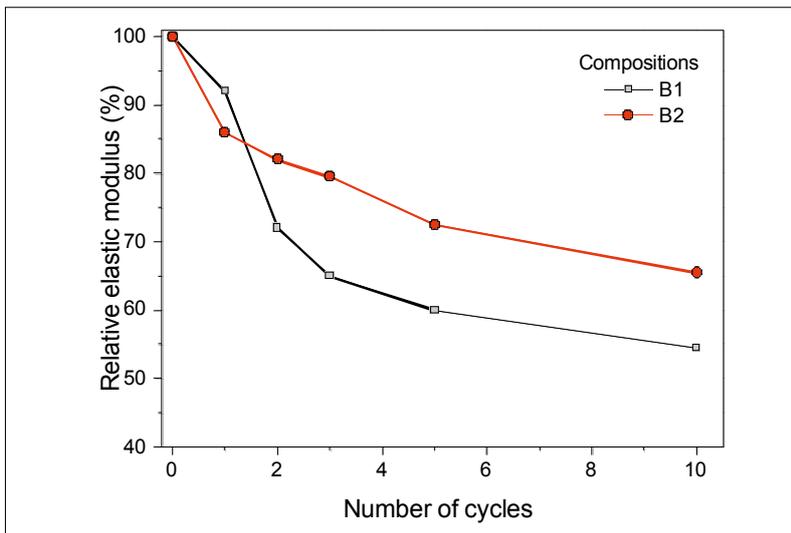
Properties	Firing Temperature [°C]	Compositions		
		A1 [Ref.]	A2 [0,5 mass-% nG]	A3 [1,0 mass-% nG]
Bulk density [g · cm <sup>-3</sup> ]	1400	2,96 ± 0,01	2,91 ± 0,01	2,87 ± 0,02
	1600	2,96 ± 0,01	2,92 ± 0,01	2,90 ± 0,01
Apparent porosity [%]	1400	9,58 ± 0,18	10,11 ± 0,11	9,40 ± 0,26
	1600	9,40 ± 0,06	10,18 ± 0,13	10,05 ± 0,29
Cold crushing strength [MPa]	1400	28,69 ± 2,46	25,06 ± 1,57	28,48 ± 2,70
	1600	28,38 ± 2,01	24,88 ± 1,57	25,86 ± 1,08
Specific cold crushing strength [MPa/(g · cm <sup>-3</sup> )]	1400	9,68	8,60	9,94
	1600	9,58	8,53	8,92
Hot modulus of rupture [MPa]	1400	13,37 ± 0,44	12,65 ± 1,05	13,00 ± 0,72
	1600	15,53 ± 1,73	14,08 ± 1,07	13,85 ± 0,47
Specific hot modulus of rupture [MPa/(g · cm <sup>-3</sup> )]	1400	4,51	4,34	4,54
	1600	5,25	4,82	4,78
Elastic modulus [GPa]	1400	33,05 ± 0,5	30,63 ± 0,42	31,87 ± 0,77
	1600	40,61 ± 1,38	33,04 ± 0,42	32,10 ± 2,09



**Fig. 3** Relative E drop attained during the thermal shock tests ( $\Delta T \sim 1175 \text{ }^\circ\text{C}$ ) of MgO–C bricks pre-fired at (a) 1400 °C or (b) 1600 °C for 5 h

**Tab. 4** MgO–C bricks properties after curing at 200 °C for 6 h

Properties	Compositions	
	B1	B2 [0,5 mass-% $\text{Al}_2\text{O}_3$ ]
Bulk density [ $\text{g} \cdot \text{cm}^{-3}$ ]	$2,97 \pm 0,01$	$2,98 \pm 0,02$
Apparent porosity [%]	$3,07 \pm 0,10$	$3,49 \pm 0,44$
Cold crushing strength [MPa]	$35,27 \pm 2,80$	$36,10 \pm 2,18$
Specific cold crushing strength [ $\text{MPa/g} \cdot \text{cm}^{-3}$ ]	11,87	12,11
Hot modulus of rupture [MPa]	$13,40 \pm 2,10$	$15,51 \pm 1,60$
Specific hot modulus of rupture [ $\text{MPa/g} \cdot \text{cm}^{-3}$ ]	4,51	5,20
Elastic modulus [GPa]	$49,37 \pm 2,82$	$51,61 \pm 2,28$



**Fig. 4** Thermal shock resistance after curing at 200 °C/6h

higher for the composition with 1 mass-% nG and treated at 1400 °C for 5 h, but a further decrease of these parameters became more significant after firing at 1600 °C for 5 h. Such change on the samples behaviour is related to the interaction between

the HTM binder with the nanographite at high temperatures, as these carbon sources should undergo various significant transformations and the designed structure tends not to be kept under these conditions or seen as different phase by the crack, af-

fecting the attained improvements in intrinsic toughness. Minor changes in the apparent porosity and bulk density values for the refractories fired at 1400 °C and 1600 °C for 5 h could be detected and, considering the attained standard deviation, the three compositions showed similar results for these properties.

Based on the physical and mechanical properties (Tab. 3) and the thermal shock resistance of the prepared MgO–C refractories after firing at high temperature (Fig. 3), no major benefits was obtained in the intrinsic toughness of such materials with the nanographite addition.

An additional attempt to investigate the generation of a “brick-and-mortar” structure in the designed refractories, but with an inert raw material, consisted in the preparation of two new compositions (Tab. 2). B1 was the reference one, whereas B2 comprised 0,5 mass-% of a special alumina that was incorporated to the resin before mixing with the other raw materials. In this case, all tests were carried out initially for samples only cured at 200 °C for 6 h. Tab. 4 and Fig. 4 present the physico-mechanical properties and thermal shock resistance of these materials, respectively.

Bulk density and apparent porosity of the samples were not affected by the addition of the special alumina, and sCCS and sHMOR values presented the same trend that the original properties (CCS and HMOR). Nevertheless, a remarkable improvement in the thermal shock resistance was observed (Fig. 4). These results pointed out that when less reactive particle is mixed

with HTM binder system, a better effect in intrinsic toughness is attained. Further studies will be conducted with this special alumina, as well as other sorts of inert raw materials and nanographite should be incorporated to the resin.

Additionally, it is planned to evaluate the refractories performance at higher temperatures and via wedge splitting measurements.

### Final remarks

A new design of MgO–C bricks was conducted in order to mimic some materials in the nature to attain both improved strength and toughness.

A big challenge for designing refractory damage tolerance refractories is the high temperature exposure that results in major

microstructural changes. Nanographite addition into the HTM binder was effective in increasing sCCS and sHMOR values of the refractories after curing (200 °C for 6 h) and firing (1400 °C for 5 h).

However, no clear evidence for improvement in the extrinsic toughness was observed for the thermal shock resistance of such materials.

After firing the samples at 1600 °C, no benefits were also observed. Using an inert material and changing the design concept, composition B2 had their sHMOR and thermal shock resistance increased significantly. Further investigations will be carried out in order to better understand, whether the incorporation of inert particles to the refractory binder system is a suitable real solution for the development

of stronger and tougher for BOF refractories.

### References

- [1] Yamaguchi, A.: Consideration of the development of refractories. *J. Tech. Assoc. Refractories, Japan* **27** (2007) [3] 162–168
- [2] Anan, K.: Wear of refractories in basic oxygen furnaces (BOF). *J. Tech. Assoc. Refractories, Japan* **21** (2001) [4] 241–246
- [3] Ritchie, R.O.: The conflicts between strength and toughness. *Nature Mater.* **10** (2011) 817–822
- [4] Ritchie, R.O.; Launey, M.E.; On the fracture toughness of advanced materials. *Adv. Mater.* **21** (2009) 2103–2110
- [5] Pagliosa, C.; et al.: High performance MgO–C bricks for BOF: From now to nanotechnology. *Proc. of the Iron & Steel Technology Conference and Exposition, Pittsburgh, PA, 2013*