

Effect of microstructural modifications at high temperature on the work of fracture of magnesia-graphite refractories

Sebastián E. Gass^{1,2}, Analía G. Tomba Martínez¹, Pablo Galliano³, Norberto Bellandi⁴, Carmen Baudin^{1*}
¹Instituto de Cerámica y Vidrio, CSIC, 28049 Madrid, Spain, ²INTEMA, Mar del Plata, Argentina,
³Tenaris REDE AR, Campana, Argentina, ⁴Magnesita Refractorios Argentinos, San Nicolás, Argentina.

*cbaudin@icv.csic.es

ABSTRACT

Graphite containing refractories are highly resistant to mechanical and thermal cycles. The mechanical parameter that determines the resistance of the materials to crack development under subcritical conditions is the work of fracture. This parameter depends on the microstructure of the materials and, particularly, on the nature of the matrix. As-fabricated, unfired MgO-C and MgO-C-antioxidant bricks have very low porosity (< 5 %), determined by the characteristics of the raw materials and the type of binder. The loss of volatile components of the binders, the inherent instability of the bricks caused by the carbothermal reduction of MgO that yields CO and Mg(g), and the oxidation of residual carbon from binders and of graphite flakes lead to increases in porosity during thermal treatments. Moreover, new phases that depend on the atmosphere could be formed at high temperature due to reactions between the components of the brick. Therefore, the nature of the matrix of the graphite containing refractories experiences significant changes during use. These changes will determine the mechanical performance of the materials. In this work, non-commercial MgO-C and MgO-C-antioxidant model materials have been used to determine the relationships between the microstructure and the work of fracture. Main composition was 83-85 wt.% of magnesia (fused/sinter: 70/30) and 12 wt.% of graphite flakes. The effect of two different organic binders, phenolic resin and a new eco-binder (chemically modified pitch) has been evaluated. Fully microstructural evaluation of the "as received" and thermally treated (up to 1400°C) materials has been done. The work of fracture has been determined using controlled fracture tests. Relationships between the microstructure and the obtained work of fracture values are presented and the effect of the different binders and the antioxidant is established.

INTRODUCTION

Graphite containing refractories are an essential part of steelmaking practice in the last 40 years. MgO-graphite bricks present characteristics that clearly differentiate them from other refractories: as fabricated bricks lack ceramic bonding and the main constituent phases are not thermodynamically compatible at the use temperatures and present extremely different sizes, shapes and mechanical properties. MgO-C bricks are highly resistant to mechanical and thermal cycles^[1,2]. The mechanical parameter that determines the resistance of the materials to crack development under subcritical conditions is the work of fracture.

This parameter depends on the microstructure of the materials and, particularly, on the properties of the constituents and the interfaces between them^[3]. In particular, the grain-matrix interface has been found to play the critical role in the initiation and propagation of the fatigue cracks in MgO-C materials^[4].

For the production of magnesia-carbon materials either coal tar pitch or phenolic resin is used as a binder. Resin is used as environmental friendly alternative against coal tar pitch. Resin-containing coked products show isotropic glassy phases resulting in a high brittleness.

As compared to resins, pitches present higher carbon yield after coking, increased adhesion to the oxide constituents and anisotropic graphitizable coke structure after carbonization. As a result, pitch-bonded materials have been reported to present superior oxidation resistance and mechanical performance in terms of modulus of rupture than resin bonded bricks^[5,6].

A major drawback of pitch is the high amount of carcinogenic aromatics like benzo[a]pyrene (B[a]P) which content ranges from 10,000 to 15,000 mg/kg. Moreover, the production of pitch-bonded bricks requires a hot mixing process. The combination of liquid phenolic resin and solid pitch powders has been proposed as means of avoid hot mixing and decrease the amount of environmentally unfriendly constituents^[6,7].

As-fabricated, unfired MgO-C bricks present very low porosity (2-5 vol.%), determined by the characteristics of the raw materials, the type of binder and the way it is added to the mix, and the pressing efficiency. The loss of volatile components of the binders, as well as the inherent instability of the bricks caused by the carbothermal reduction of MgO that yields CO and Mg(g), lead to increases in porosity during thermal treatments. Moreover, oxidation of residual carbon from binders and of graphite flakes is another major source of porosity in these bricks after exposure to temperature. The reduction of impurities is added source porosity.

Aluminum is included in the composition of the bricks as an antioxidant, on the basic premise that a metal with greater tendency to oxidize via the corresponding oxide formation will protect the carbon phase. However, most investigations report the formation of new phases, such as aluminum carbide (Al₄C₃) and magnesium aluminate (MgAl₂O₄), in the temperature range 700-1600°C^[1-2, 8-10].

The objective of this work is to investigate the effect of the matrix characteristics on the mechanical behavior of MgO-C refractories in terms of toughness. Three non-commercial MgO-C bricks

with similar basic microstructural parameters – characteristics, proportion and size distribution of MgO aggregates and graphite flakes- have been studied. Two of them -with and without Al as antioxidant- contained phenolic resin as organic binder and the third one was fabricated using a chemically modified pitch powder mixed with phenolic resin. The effect of heat treatments at 1400°C has been analysed. Toughness has been evaluated using the critical energy release rate in mode I, G_{IC} , and the work of fracture

MATERIALS AND METHODS

Three model brick formulations were prepared from the same sintered and electrofused MgO and graphite flakes and 3 wt.% of organic binder using the standard commercial practices. In two of them, R12-1 and R12-2, the organic binder was phenolic resin and in the other one, SB12-2, the binder was a mixture of pitch powder and liquid resin. In addition, 2 wt.% of Al was present in material R12-1. All materials contained 12 wt.% of graphite flakes and 83-85 wt.% of magnesia (fused/sinter: 70/30).

Two bricks of each material were machined using a diamond disc to obtain eight parallelepiped bars (150mm x 25mm x 25mm) for mechanical evaluation. For each material, four specimens were tested as machined and the other four were thermally treated in a graphite bed at 1400°C for 1h previously to mechanical testing, using an electrical furnace of SiC heating elements (5°C/min).

The bulk density, ρ_b , of the bars was determined geometrically prior to testing. In order to assure the validity of the measurements, the density of cylindrical specimens of the “as fabricated” materials was also determined by immersion in kerosene and compared to the geometrical one. Differences were inside the variability limits of the obtained data.

The Young’s modulus, E , was determined from the resonance period of the parallelepiped bars tested in flexure by impact (Grindosonic, Belgium). The bulk density and the characteristic value of Poisson’s ratio (0.17) for refractory materials were used for calculations.

Straight through notches were introduced in the parallelepiped specimens using a Buehler sawing machine (IsoMet 4000, USA), with diamond disc of 300 μm width. Relative notch lengths were $\alpha = a/W = 0.50$, (a = notch length, W = specimen width). The notched specimens were tested in three-point bending (SENB: Single Edge Notch Beam), in a universal testing machine (EM1/150/FR Microtest) using a span of 125 mm. Tests were performed using the displacement of the frame load as control parameters, at rate 0.1 mm/min.

The load-displacement curves were recorded and work of fracture (γ_{wor}), the critical stress intensity factor (K_{IC}) and the energy for crack initiation (γ_{nb}) were calculated as described elsewhere^[3].

All reported mechanical parameters are the average of the four determinations and errors are the standard deviation.

The fracture surfaces and the lateral fracture were analysed macro and microscopically, by reflected light optical microscopy (RLOM, Zeiss Axiophot, Germany), scanning electrical microscopy (SEM

Hitachi TM 1000, Japan) and field emission scanning microscopy with analysis by energy dispersive X-ray spectroscopy (FE-SEM-EDS Hitachi S-4700, Japan). Additional observations on diamond polished surfaces (1 μm) were done to assure the chemical composition of the phases observed in the fracture surfaces.

The size distributions of the aggregates were evaluated from scanned (HP Scanjet 5550C, USA) images of the lateral surfaces (150 mm x 25 mm x 25 mm) of untreated specimens using the Leica Qwin software (UK), at least 500 aggregates (diameter eq. > 1000 μm) were analysed for each material. Macroscopic observation of the crack paths as well as the measurement of the notch length, a , were done using this kind of images.

Once the fracture zones of the bar specimens were separated, two of the remaining pieces were milled (< 100 μm , ball mill Retsch, Germany) and mixed to be used for true density, ρ_t (He picnometry, Quantachrome, USA), pore size distribution (intrusion Hg, AutoPore II 9215 Micromeritics, USA) determinations and mineralogical analysis (XRD, Bruker D8 Focus, Germany. Cu $K_{\alpha 1}$ $\lambda = 0.15418$ nm, at 40 kV and 40 mA). The true porosity, π_t , was calculated from the apparent and true densities.

RESULTS AND DISCUSSION

As seen in Table 1, differences between the porosity values of the “as fabricated” resin-bonded materials were inside the variability limits while the “as received” material containing the pitch-based binder presented slightly higher porosity, probably due to the difficulty associate to mixing the two component binder. Porosity differences between the treated materials were inside the variability limits in spite of the large differences in weight loss between the material containing Al and the other two. This fact is due to the mass gain associated to the formation of oxide phases, in particular, Mg-Al spinel was detected by XRD.

Table 1: Physical properties of the studied materials and mass loss during the thermal treatments

Material	ρ_b (g/cm ³)	ρ_t (g/cm ³)	π_t (vol. %)	Δm TT (%)
R12-1	2.98 ± 0.01	3.126 ± 0.003	4.7 ± 0.4	0.63 ± 0.10
R12-1t4	2.88 ± 0.04	3.272 ± 0.004	12 ± 1	
R12-2	3.03 ± 0.03	3.158 ± 0.001	4 ± 1	1.87 ± 0.04
R12-2t4	2.88 ± 0.05	3.243 ± 0.004	11 ± 2	
SB12-2	2.94 ± 0.02	3.157 ± 0.004	6 ± 1	1.95 ± 0.07
SB12-2t4	2.78 ± 0.03	3.226 ± 0.004	14 ± 1	

Young’s modulus values of the untreated materials without antioxidant were similar while that of the material containing Al was higher due to differences in pore size distributions (R12-2 and R12-1: 90 and 40 % of pores of diameter > 15 μm , respectively). Stable fracture was attained in all test and results for different specimens of the same material were fairly coincident (e.g.: Fig 1). The toughness parameters calculated from the load-displacement curves are summarized in Table 2. Up to the knowledge of the

authors stable fracture testing of MgO-C refractories has not been reported in the literature. As terms of comparison, the untreated Al-containing material presents γ_{wof} in the range of those of well-designed castables while this parameter is similar to those of oxide refractories for the materials without Al^[3]. In all cases, the energy required for crack propagation, γ_{wof} , is much higher (≥ 10 x) that the energy required for crack initiation, γ_{nbt} , which reveals the occurrence of toughening mechanisms during fracture. These mechanisms can be identified by observation of the fractured specimens.

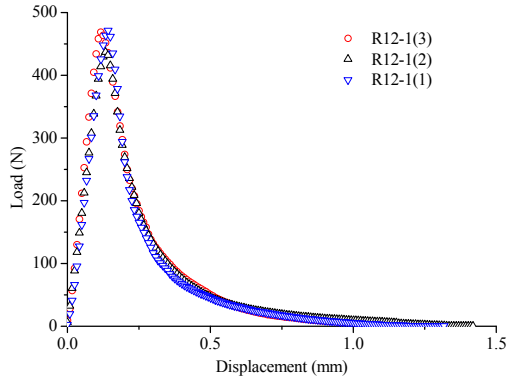


Figure 1. Load-displacement curves for three different specimens of the material containing Al, R12-1.

Table 2: Mechanical properties of the studied materials

Material	E (GPa)	γ_{wof} (J/m ²)	K_{IC} (MPam ^{1/2})	γ_{nbt} (J/m ²)	$\gamma_{wof} / \gamma_{nbt}$
R12-1	57 ± 3	141 ± 4	1.25 ± 0.07	13 ± 2	≈ 10
R12-1t4	14 ± 2	81 ± 6	0.33 ± 0.03	4.0 ± 0.4	≈ 20
R12-2	39 ± 2	67 ± 2	0.86 ± 0.08	9.5 ± 1.4	≈ 10
R12-2t4	3.6 ± 0.2	48 ± 2	0.102 ± 0.003	1.4 ± 0.2	≈ 35
SB12-2	37.7 ± 0.1	70 ± 5	0.7 ± 0.2	7 ± 4	≈ 10
SB12-2t4	3.4 ± 0.1 ≈	34 ± 4	0.13 ± 0.02	3 ± 1	≈ 10

Characteristic macroscopic features observed in the lateral surfaces of tested specimens are shown in Figure 2. The crack path is tortuous, being deflected by the MgO fines and aggregates (Fig. 2 a) and the aggregates act as bridges in the crack wake (Fig. 2 b).

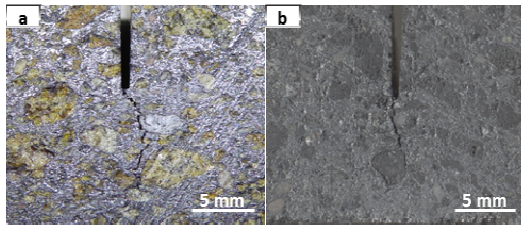


Figure 2. Characteristic macroscopic features observed in the lateral surfaces of tested specimens. (a): R12-1. (b): R12-2T.

Characteristic microscopical features observed by RLOM in the lateral surfaces of tested specimens are shown in Figure 3. Graphite flakes oriented perpendicular to the fracture acted as bridges and MgO fines acted as crack deflection and branching sites (Fig. 3a) while those graphite flakes oriented

parallel to the direction of crack propagation were delaminated by the crack (Fig. 3b).

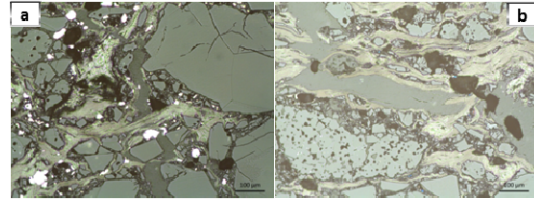


Figure 3: examples of characteristic microscopical features observed by RLOM in the lateral surfaces of tested specimens. Material R12-1T.

As observed in Figures 4-6 a, graphite flakes and MgO particles acting as bridges were observed in the three untreated materials which explains the similarity of the values of γ_{wof} for both materials without Al. The aspect of the small Al particles traversed by the crack allows inferring that they also acted as bridges that would be plastically deformed due to the nature of Al (Fig. 3 a). Thus, even for such small bridges, the expected toughening would be relatively high and, in fact, γ_{wof} of the material with Al is the highest. In addition, plastic deformation of Al at the crack tip would also lead to higher γ_{nbt} , as observed.

After the heat treatments, all toughness parameters decrease, what is partially due to the decrease of the Young's modulus for all materials. In addition, the microstructural characteristics observed in the fracture surfaces - gaps between the MgO aggregates and the matrix- as well as the formation of Mrozowsky cracks in the graphite flakes^[1], would contribute to the decrease of the efficiency of the toughening mechanisms. The substitution of the ductile Al particles (Fig. 5a) by the rigid spinel that partially covers the MgO particles in the treated material (Fig. 5b) is an added factor for the drop of the toughness values for the material containing Al. Nevertheless, both energy toughness parameters are still higher in the resin bonded thermally treated Al-containing material than in the one without Al. The bonding of the microstructural elements of the brick by spinel will contribute to the increase of γ_{nbt} . In addition, the increased rugosity of the surface of the MgO particles due to the presence of spinel will increase friction at the crack wake and, consequently, γ_{wof} .

The pitch-based binder was well distributed through the matrix of the heat treated material in the shape of a layer covering the microstructural elements, as observed in Figure 6b. This layer would be intimately bonded to the microstructural elements as revealed by the fact that graphite flakes oriented perpendicular to the direction of fracture were traversed by the crack (Fig. 6b). Fracture of the toughening elements decrease their efficiency in this material which presents the lowest γ_{wof} values. The relative decrease of γ_{nbt} in this case is lower because strong bonds are usually related to higher resistance to fracture initiation.

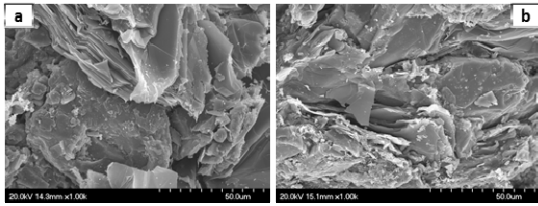


Figure 4: Fracture surface, a) R12-2 y b) R12-2t4

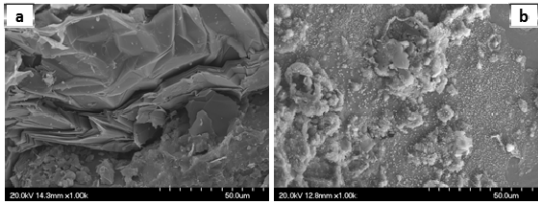


Figure 5: Fracture surface, a) R12-1 y b) R12-1t4

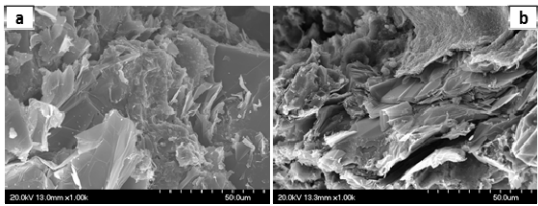


Figure 6: Fracture surface, a) SB12-2 y b) SB12-2t4

CONCLUSIONS

MgO-C materials present much higher resistance to crack propagation than to crack initiation. The main toughening mechanism is crack bridging by MgO particles and graphite flakes. The efficiency of the mechanism is the lowest when the bonding between graphite and the carbon structure originated from pyrolysis of the organic binder is strong. Efficiency is the highest when Al is present due to the formation of spinel on the surface of the MgO particles.

Acknowledgements

This work has been performed in the frame of the CYTED network 312RT0453 (HOREF) S.E. Gass acknowledges the financial support of the CONICET outside fellowship program to CPA.

References

[1] Baudin C. High Temperature Mechanical Behavior of magnesia-graphite based refractories. pp.

73-92 en *Fundamentals of Refractory Technology*, Ceramic Transactions vol 125. Ed. James P. Bennett and Jeffery D. Smith. The Am. Ceram. Soc., Westerville OH, 2001.

[2] Zhu TB, Li YW, Sang SB, Jin SL. The Influence of Al and Si on the Microstructure and Mechanical Properties of Low-Carbon MgO-C Refractories. *J. Ceram. Sci. Tech.*, 07 [01] 127-134 (2016).

[3] García-Prieto A, Dos Ramos-Lotito M, Gutiérrez-Campos D, Pena P, Baudín C. Influence of microstructural characteristics on fracture toughness of refractory materials. *J. Eur. Ceram. Soc.* 35 (2015) 1955-1970.

[4] Andreev K, Boursin M, Laurent A, Zinngrebe E, Put P, Sinnema S. Compressive fatigue behaviour of refractories with carbonaceous binders. *Journal of the European Ceramic Society* 34 (2014) 523-531.

[5] Aneziris CG, Borzov D, Ulbricht J. Magnesia Carbon Bricks - A high-Duty Refractory Material. *InterCeram: International Ceramic Review* 1:22-27 · January 2003

[6] Liu Jun, LiHongXia, FengHaixia. Influence of carbones binder on the strength of Magnesia-Carbon materials.

3rd International Conference on Material, Mechanical and Manufacturing Engineering (IC3ME 2015) Published by Atlantis Press, pp. 1815-1820.

[7] Weber A, Mertke A, Ludwig S, Aneziris CG. Carbon Bonded MgO-C Refractories With Low PAH Containing Binder System. *UNITECR 2015 Proceeding* 393.

[8] Baudin C, Alvarez C, Moore RE. Influence of Chemical Reactions in Magnesia-Graphite Refractories, Part I: Effects on Texture and High Temperature Mechanical Properties. *J. Am. Ceram. Soc.*, 82 (12) 3529-38 (1999).

[9] Baudin C, Alvarez C, Moore RE. Influence of Chemical Reactions in Magnesia-Graphite Refractories, Part II Effects of Graphite and Aluminum Contents in Generic Products. *J. Am. Ceram. Soc.*, 82 (12) 3539-48 (1999).

[10] Luz AP, Souza TM, Pagliosa C, Brito MAM, Pandolfelli VC. In situ hot elastic modulus evolution of MgO-C refractories containing Al, Si or Al-Mg antioxidants. *Ceramics International* 42(2016)9836-9843.