Mechanical Behavior of MgO-C Refractory Bricks Thermally Treated In Low Temperature Range

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ABSTRACT

Steelmaking refractories performances have a strong impact on critical aspects of the industrial process, such as production costs and steel quality, between others. In this paper, the effects of thermal treatments on the mechanical behavior of MgO-C refractory materials are assessed using two non-oxidant atmospheres, argon flow and graphite bed, in addition to combination of both of them in different stages.
Non-commercial bricks with and without antioxidant are evaluated using cylindrical testing specimens (diameter: 30 mm, length: 45 mm). Microstructural and textural changes as consequence of heat treatments at temperatures < 1000ºC during 1h or 3h prior to mechanical test were analyzed by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM/EDS). As received materials, as well as those thermally treated, are mechanically tested in compression between room temperature and 1000ºC (in Ar) to obtain the stress-strain relationship in each case.
Stress-strain curves change according to alterations in the microstructure and texture of the brick, due to the events taking place during the different stage of thermal treatments prior and during mechanical tests (heating, permanence and cooling). Furthermore, the time of exposition is considered as a variable to evaluate the effect of different advance in the processes which occur during the thermal treatment. In the range of low temperatures (T < 1000ºC), the organic binder is the main component affected by thermal variations; however, the antioxidant additive actually affects the mechanical behavior even its reaction occurs at temperatures above 600ºC. The results obtained in the range of low temperatures can be interpreted taking into account factors such as mass losses (volatile elimination and carbon oxidation), thermal shrinking and expansion, and cracks healing.

INTRODUCTION

MgO-C refractory lining of steelmaking vessels pass through different stages during operation. One of the critical stages for the thermomechanical stability of bricks is the first heating at the beginning of furnaces and ladles campaigns, when the working lining is still at intermediate temperatures lower than 1000ºC. Among the transformation occurring in the refractory in this stage, stand out the pyrolysis of the organic binder characterized by mass losses (volatile elimination), besides shrinking and/or densification of structure during the formation of residual carbon. These phenomena prevail at temperatures ≤ 600ºC. Over this temperature, the intensification of oxidative processes could be expected, together with the carbide formation in case of the presence of Al as antioxidant additive. These transformations could also occur during successive cycles of cooling-heating that take place in the steelmaking vessel along its campaign, and will strongly depend on the temperature and atmosphere prevailing in each step.
With the aim of study those processes, a laboratory scale study of the mechanical behaviour of a set of MgO-C materials prepared with controlled variations in their compositions has been developed. These materials were tested after treatments at different pre-treatment, temperature, and atmosphere. In previous reports [1-3], some changes in the mechanical behavior of the materials after non-oxidant treatments at 600 and 1000°C for 1h, with and without cooling stage before the mechanical test were discussed. In general, it was observed that in spite of the antioxidant does not react after 1h at 600°C or transform in another phase either, it affected the mechanical properties of the system [3].
This paper is focused on the effect of extending the permanence time (from 1h to 3h) at 600ºC on the mechanical behavior of a set of resin bonded MgO-C refractories with and without antioxidant. The bricks have fix content of their main components (MgO and graphite). The effect of the non-oxidant atmospheres (two types of conditions were used: graphite bed and argon flow) and the presence or absent of a cooling step before the mechanical testing was also evaluated. Moreover, specimens treated at 1000°C for 1h under similar conditions were also evaluated.

MATERIALS AND METHODS

Two non-commercial MgO-C refractory bricks were used. They are constituted by 3 wt.% of phenolic resin organic binder, 12 wt.% of graphite, with 83-85 wt.% of magnesia (70/30 fused/sinter) as the majority phase. The addition of aluminum antioxidant (2 wt. %) was the distinctive compositional variable. This material was named as R12-1, whereas the brick without antioxidant was labeled as R12-2.
Cylindrical specimens (diameter: 30 mm, length: 45 mm) with flat and parallel surfaces were obtained from the bricks. One set of cylinders were selected for application of pre-treatment at 600ºC during 3h in a graphite bed. Similarly, other set was pre-treated at 1000°C during 1 h.
As received materials, as well as those thermally treated in graphite bed, were mechanically tested in compression at room temperature (RT) and 600ºC in argon flow (99.99 % purity), using a universal testing machine (Instron 8501). The deformation was measured with a capacitive extensometer (Instron, ±0.6 µm) in direct contact with specimen. For testing at high temperature, an electrical furnace of $MoSi_2$ heating elements and a chamber with argon gas supply (5 l/min) were coupled to the system. From stress-strain (s-s) curves, the following mechanical

parameters were determined: apparent Young's modulus $E_{0.001}$ (defined as a secant straight line to s-s curve at a strain of 0.001) and mechanical strength σ_F (as the maximum stress value).
In order to suppress the intermediate cooling stage between the thermal pre-treatment and the mechanical test, a set of specimens was maintained a longer time at 600ºC or 1000°C in the Ar atmosphere of the testing. Thus, permanence for 3h or 1h, respectively, was added to the current stabilization time of 30 min.
Tab. 1 indicates the nomenclature used for each type of specimen pre-treated or tested at 600°C.

Table 1. Specimens' nomenclature.

Material	Condition	Mechanical testing
R12-1	Original	RT
R12-2		
R12-1t3	600ºC, 3h graphite bed	RT
R12-2t3		
R12-1(Ar)	Original	600ºC (30min)
R12-2(Ar)		
R12-1t3(Ar)	600ºC, 3h graphite bed	600ºC (30min)
R12-2t3(Ar)		
R12-1p3	Original	600ºC (30min + 3h)
R12-1p3		

The mineralogical analysis of the original materials, as well as those subjected at different thermal conditions, was performed by X-ray diffraction (XRD, Phillips equipment), with Cu Kα radiation, at 40 kV and 30 mA. The mass losses were quantified by thermogravimetric analysis (TGA, Shimadzu TGA-50 equipment) up to 1000ºC in oxidant atmosphere with a heating rate of 10ºC/min. Both techniques were carried out on powder samples (< 210 µm, Fritsch Pulverisette mill).
The textural changes have been analysed by measurements of bulk density (ρ_B) and apparent porosity (π_A) using the Archimedes method employing kerosene as immersion liquid.

RESULTS

By increasing the duration of thermal pre-treatment from 1h to 3h, it is expected to analyse the progress of reactions caused during the pyrolysis of phenolic resin. The materials were preserved of carbon oxidation during treatment using graphite bed or argon flow. The X-ray diffraction analyses confirmed the presence of metallic aluminum (File N° 00-004-0787) in all thermal conditions at 600ºC (3h) for R12-1, as expected, verifying that this additive did not play a role as antioxidant at temperatures < 600ºC. The rest of components were properly identified: periclase (File Nº 00-045-0946) and graphite (File Nº 00-041-1487) in both refractories. The analysis carried out in specimens subjected to 1000°C (1h and 1.5h), confirmed the formation of aluminum carbide (Al_4C_3, File N° 00-035-0799)[1, 2] in R12-1, which starts around 700ºC [4], at the expense of attenuation of Al peaks intensities.
The mass losses during the thermal treatments in graphite bed at 600ºC resulted: 1.35 ± 0.03 wt.% for R12-1t3 and 1.37 ± 0.01 wt.% for R12-2t3, somewhat larger than those determined in treatments of 1h [3] (R12-1t1 ~ 1.30 wt.% and R12-2t1 ~ 1.34 wt.%).
The results obtained of TGA are shown in Tab. 2. The general behavior observed in materials treated 3h at 600ºC, is similar to previous ones for treatments at 600ºC for 1 h under each atmosphere [3], showing trends in accordance with permanence time increase. In argon atmosphere, the mass losses were less than those determined in graphite bed for 3h (600°C) of treatment, which also was observed in treatments of 1h. The most notable changes are present in the total losses registered by TGA at 600ºC: increasing the pre-treatment duration this loss is lesser, as expected. Furthermore, the mass losses determined after the thermal treatment at 600ºC for 3h are consistent with the differences displayed in the thermographs of R12-1t3 and R12-2t3, on one hand, and the respective original materials on the other hand.

Table 2. Bulk density (ρ_B), apparent porosity (π_A) and TGA mass losses (Δm).

Material	ρ_B [g/cm^3]	π_A [%]	$\Delta_{mvolatile}$ [1] [wt.%]	Δ_{mtotal} [2] [wt.%]
R12-1	3.01 ± 0.05	3.6 ± 0.6	1.6	3.7
R12-1(Ar)	2.98 ± 0.06	5 ± 1	0.9	2.8
R12-1t3	2.97 ± 0.06	8 ± 1	0.2	1.8
R12-1t3(Ar)	2.98 ± 0.06	8 ± 1	0.2	1.6
R12-1p3	2.98 ± 0.06	6 ± 1	0.8	2.4
R12-2	3.01 ± 0.05	2.8 ± 0.6	1.4	3.4
R12-2(Ar)	2.99 ± 0.06	5 ± 1	0.9	2.7
R12-2t3	2.98 ± 0.06	8 ± 1	0.2	1.8
R12-2t3(Ar)	2.98 ± 0.06	8 ± 1	0.2	1.6
R12-2p3	3.00 ± 0.06	6 ± 1	0.9	2.1

[1] Determined at 400ºC, [2] Determined at 600ºC

The extension of pre-treatment to 3h stabilizes the volatile losses matching the values of both, R12-1 and R12-2, whereas in the treatments of 1h, the former showed a lower loss by volatiles in general. This may be caused by the higher amount of pores of greater size (> 15µm) present in R12-2 (92 vol. % in respect to 38 % vol. in R12-1), making the migration of volatiles easy at the beginning.
The bulk density and apparent porosity do not show a significant change when the pre-treatment duration increases from 1h to 3h under the same condition [3].
In Fig. 1, typical s-s curves of materials evaluated at RT and 600°C are presented. Mechanical parameters ($E_{0.001}$ and σ_F) are reported in Tab. 3. Moreover, Fig. 2 displays the mechanical behavior of R12-1 testing to 1000ºC, as example. $E_{0.001}$ and σ_F in this condition are reported in Tab. 4 for both refractories (the nomenclature is analogous to that employed for 600°C). For comparative purposes, the mechanical parameters of specimens treated 1h and 3h at 600ºC are shown in Figs. 3 and 4. In these figures, the values of original materials and those pre-treated in graphite bed for 1h and 3h, mechanically tested at (RT), are linked with red lines. The continuous blue line joins the values of the same materials but tested at 600ºC (600°C). Finally, the parameter of specimens tested in Ar with 1h or 3h in addition to the standard time of 30 min are represented in dashed blue line.
Considering Figs. 3 and 4, the materials suffer the degradation inherent to binder transformations after of treatment at 600ºC-1h, which manifest in the reduction of mechanical properties of materials tested at RT. However, this effect does not progress with the

increase of time up to 3h, since the magnitude of parameters is maintained or even increased. When the mechanical testing was carried out at 600ºC, a similar mechanical response between the original refractory and that pre-treated 1h is observed. By extending the time to 3h, $E_{0.001}$ and σ_F show a general tendency to increasing, even more in the refractory without antioxidant. In the absence of cooling stage (dashed blue line) the properties were lower than those of materials that were cooled and heated again before mechanical testing (blue line), conversely to the response at 1000ºC (Tab. 4),

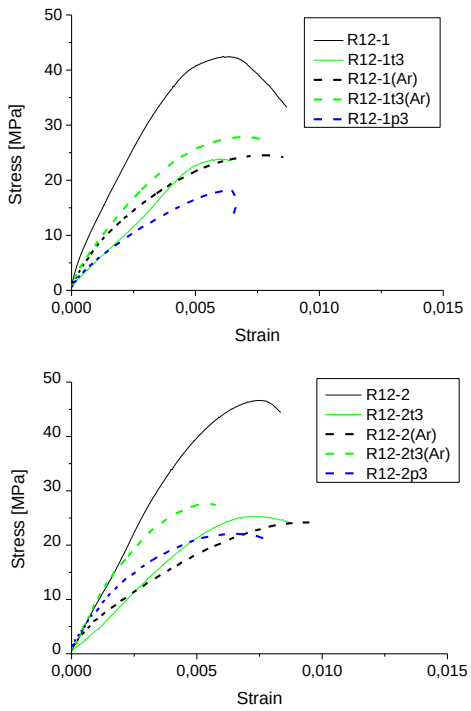

Figure 1. Stress-strain curves of original and pre-treated (600ºC, 3h) materials.

Table 3. Mechanical parameters (RT and 600ºC).

Material	σ_F [MPa]	$E_{(0.001)}$ [GPa]
R12-1	39 ± 5	11.0 ± 1.6
R12-2	45.4 ± 1.8	8.49 ± 0.16
R12-1t3	26 ± 3	4.6 ± 0.3
R12-2t3	25.30 ± 0.04	3.3 ± 0.7
R12-1(Ar)	27 ± 3	7.1 ± 0.4
R12-2(Ar)	24 ± 1	4.4 ± 1.8
R12-1p3	17.7 ± 0.8	4.87 ± 0.06
R12-2p3	21.5 ± 0.9	6.9 ± 1.2
R12-1t3(Ar)	27.0 ± 1.3	20.4 ± 1.3
R12-2t3(Ar)	27.0± 0.9	10.1 ± 1.5

DISCUSSION

The presence of Al_4C_3 into the matrix of the brick above 700ºC would tend to strengthening it, because contributes to retain carbon in the structure and provides cohesion of the structure generating new bonds. Nevertheless, its expensive character in addition with the holes generated by Al fusion prior to carbide formation are sources of damage or cracks located in the structure. This can be adverse under certain thermo-mechanical requirement but, at the same time, can be beneficial to respond better to thermal shock, for instance [1, 4, 6, 8].

In the mechanical evaluation of refractories treated to 1000ºC using the standard stabilization time (30 min) and 1.5h (30 min + 1h), loss of stiffness was observed in presence of antioxidant (Fig. 2). When the material was cooled between the pre-treatment and the testing, a greater degradation of the apparent Young's modulus was determined. During cooling, differences in the thermal expansion coefficients of the bricks' constituents lead to structural discontinuities. In analogous conditions but at 600ºC, the cooling stage was less harmful (Fig. 1), which was attributed to healing of pores and cracks during the heating with pre-load before the mechanical testing, when thermal expansion takes place [3].

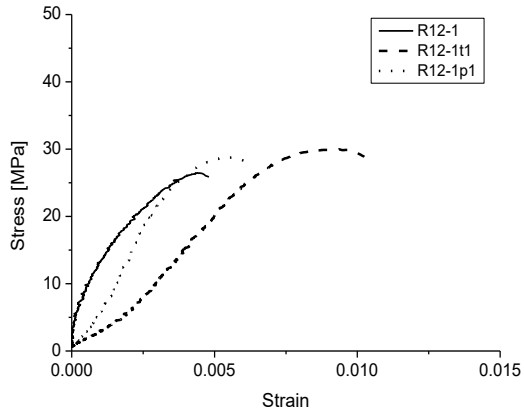

Figure 2. Stress-strain curves of R12-1 tested at 1000ºC, original (R12-1) and pre-treated (1h) in: graphite bed (R12-1t1) and argon (R12-1p1).

Table 4. Mechanical parameters (1000ºC).

Material	σ_F [MPa]	$E_{(0.001)}$ [GPa]
R12-1	27.4 ± 0.7	13 ± 0.9
R12-2	27.3 ± 0.7	9.1 ± 1.5
R12-1t1	27 ± 3	3.2 ± 1.5
R12-2t1	23 ± 2	3.0 ± 0.2
R12-1p1	27 ± 2	5.1 ± 0.3
R12-2p1	29.2 ± 1.6	8.1 ± 0.7

The chemical reactions and phase transformations involving Al do not occur below 600ºC. Therefore, the observed behavior is mainly related to: a) those effect of resin pyrolysis and oxidation of carbon (glassy-C and graphite), i. e., volumetric changes of the structure (shrinking and expansion) due to volatiles elimination and formation of carbonaceous condensed network, and b) differences of the expansion coefficients of several constituents of bricks. In this temperature range, the role of Al could be to act as discontinuity points which weaken the carbonaceous matrix. Moreover, its high thermal expansion coefficient could contribute to harm its adherence to surrounding matrix. The absence of this effect in R12-2 refractory may explain the increment of its stiffness when pre-treatment time increased up to 3h, in agreement with progress of the formation of more rigid C-C condensed structure.

The results obtained in materials which passed longer times at 600ºC (3h) showed the prevalence of the

advance in the formation of carbonaceous structure which increases the structure cohesion, against adverse effects such as: a) volatile elimination, which takes place mainly during the first hour of thermal treatment, in accordance with TGA results, and b) differential dilatation of matrix's particles (mainly Al, only in R12-1, and MgO fine aggregates).

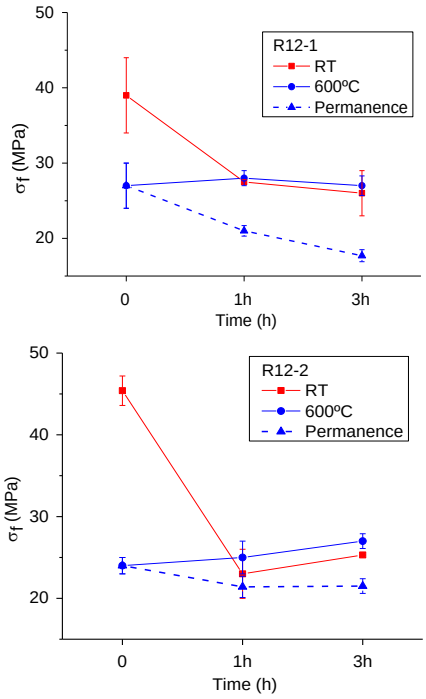

Figure 3. Mechanical strength of original and treated (600°C) refractories during 1h and 3h.

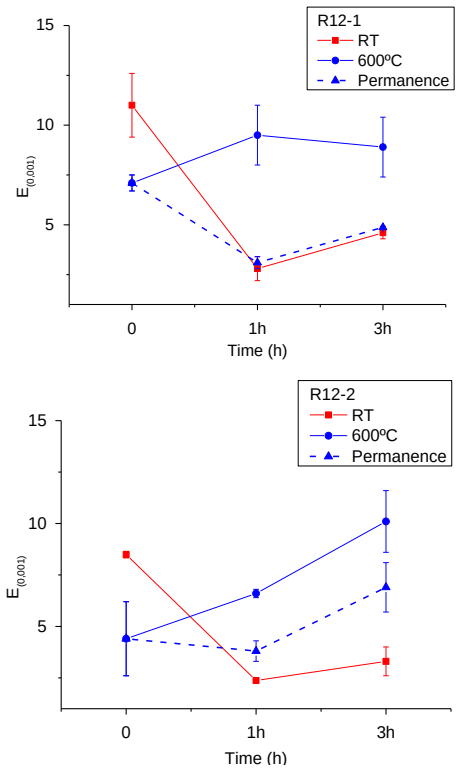

Figure 4. Apparent Young's modulus of original and treated (600°C) refractories during 1h and 3h.

CONCLUSIONS

Effects of thermal treatments at 600 and 1000ºC on mechanical behavior of MgO-C bricks were investigated in two non-oxidant conditions: graphite bed and argon flow. Furthermore, 1h and 3h of treatment were applied to analyze the progress of transformations which occurs during the pyrolysis of the organic binder (phenolic resin) and in presence of antioxidant (Al). The obtained results indicate that the formation of residual carbon under the evaluated conditions progresses with the treatment duration, making the brick structure more rigid. Besides, values of $E_{0.001}$ and σ_F exhibit variations associated to the presence of Al. At 600ºC it can act as structural discontinuity, and higher temperature (1000ºC), by carbide formation. The evolution of mechanical properties with longer duration of thermal treatments at 600°C are interpreted considering the porosity increase originated by volatiles elimination and carbon oxidation and changes in the microcracks generated by thermal expansion during the different steps of the thermal treatments.

Acknowledgements

This work has been performed in the frame of the CYTED network 312RT0453 (HOREF).

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