BEHAVIOUR OF MgO-C BRICKS DURING BOF OPERATION: MICROSTRUCTURE EVALUATION ON THERMAL CYCLING

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ABSTRACT

Basic oxygen furnace (BOF) is the most popular process selection for oxygen steelmaking and is a relatively cheap conversion process for refining iron into steel. MgO-C is the widely accepted refractory used as working lining. BOF is the most important steel making application in terms of refractory tonnage and the new demands on low carbon steel have been increasing the oxygen volume flow and new process operation. Combination of top and bottom blowing are often used to lower operating costs through better stirring action in the steel bath. MgO-C bricks are been exposed to severe oxidation and corrosion by gases and slags, erosion due to higher emulsion agitation and thermal shock. Also normal thermal cycling due to tap to tap operation can affect the behavior of MgO-C bricks even if any other exceptional interference occurs.

Considering the complex heterogeneous microstructure of MgO-C bricks and the fact that their mechanical properties are strongly affected by in situ transformations during curing and heating process, measurements of the elastic modulus evolution with temperature may provide important information for the understanding the role of different additives and microstructure modification as well as for the development of novel products.

This work presents the evaluation of physical properties, cold and hot mechanical resistance, as well as in situ hot elastic modulus (E) measurements in the temperature range of 30 to 1400°C for antioxidants (Al, Si or Al-Mg alloy) containing MgO-C bricks in a reducing atmosphere. Cured and fired samples were evaluated throughout 1 or 2 heating-cooling cycles compared to the additive-free composition. A comparative evaluation of microstructures during thermal cycling is presented and discussed and linked to BOF operational conditions.

INTRODUCTION

Lining life is a technical and economic concern of converter steelmaking. An increase in lining life can not only decrease refractory consumption and reduce smelting costs, but can also promote efficient production and increase steel yield. Over the past decade, considerable progress has been made in extending the service life of the lining for BOF, in which the most are owing to the use of advanced refractory products, as well as the introduction of efficient techniques for maintenance and protection of the lining [1].

In top and combined blowing processes oxygen is injected through multihole lance to the molten bath. The metal droplets are generated as a result of jet impact and the shearing action of the gas flow from the impact region when the jet strikes the metal surface and the gases are deflected upwards. The jet-liquid interaction can be described in terms of three modes: dimpling, splashing and penetrating. The amount of iron droplets splashed into the gas and the slag influences metallic yield, refractory wear and the progress of decarburization [2]

Since 80´s, MgO-C refractories have been used widely in the steel making industries for BOF because of their high refractoriness and excellent thermal shock and corrosion resistances, resulting from high thermal conductivity, low thermal expansion and low wetability of graphite and high refractoriness of MgO. Despite the mentioned advantages, graphite's oxidation is the main drawback of MgO-C refractories, which results in increase of porosity and decrease of strength and corrosion resistance of brick. Two types of oxidation occurs: direct oxidation (reaction of graphite with O_2 is the main mechanism at temperatures from 600 to 1400 °C, and the indirect oxidation (reaction of graphite with MgO and formation of dense layer) becomes the main mechanism at higher temperatures. An efficient alternative to minimize the oxidation consists of adding antioxidant compounds to the refractory compositions [3].

Metals and alloys such as Al, Si, Al-Mg and Al-Si are the main antioxidants used in carbon-containing compositions in combination with B_4C due to their effectiveness to prevent the direct C oxidation. These additives act in different ways during the refractories´ working conditions, as temperature and partial pressure of O_2 or CO and N_2 strongly influence their stability. Based on experiments and thermodynamic calculations, it was reported that Al and Si should act as CO reducing agents and favor the generation of an oxide dense layer at the hot surface of the refractory, inhibiting carbon oxidation [4].

Considering the large size of MgO-C bricks, a broad temperature gradient is developed in these materials. At same time, the refractory lining in BOF is subjected to thermal changes by repeated heating and cooling cycles that can result in cracks and flaws, and eventually reducing the expected campaign. Consequently, partial hot repair may be required to prevent unsafe operation.

Despite the many efforts to understand the antioxidant mechanisms, the effect of metal powders on the mechanical properties of MgO-C refractories as a function of the temperature and the CO or O_2 partial pressure are still relevant for investigation. Elastic modulus evaluation has been used as a simple and very accurate technique to investigate microstructural transformations with temperature evolution [3].

Dynamic and nondestructive methods such as the resonant bar and ultrasonic echography techniques are been using to evaluate the elastic modulus of refractory materials. Compared with static tests, the dynamic ones have the additional advantage of maintaining the material′s integrity after measuring. As a result, the same sample can be used to evaluate the Young′s modulus with the temperature providing insights of the in situ chemical and structural evolutions. Furthermore, the simplicity and accuracy of this sort of method has made it suitable to investigate resin-pitch MgO bricks, whose mechanical strength is affected by microstructural changes during the curing and firing steps.

From a theoretical point of view, the elastic modulus can be obtained by the second-order derivative of the inter-atomic potential, indicating that it is closely related to the atomic bond strength. Consequently, in multiphase materials with complex heterogeneous microstructures, the elastic constants are also strongly dependent on the crystalline structure and flaws, such as porosity and cracks [5].

This work addresses the evaluation of physical and mechanical properties compared to in situ elastic modulus (E) measurements in the temperature range between 30 and 1400°C for the same MgO-C brick composition but with different antioxidant additions: Al, Si or Al-Mg alloy. E tests were carried out using the bar resonance technique under reducing conditions: samples were painted and wrapped in nickel foil before the experiments. Cured and fired samples were evaluated throughout 1 or 2 heating-cooling cycles up to 1400°C. All results were linked to real observations in the real operational conditions of the BOF.

EXPERIMENTAL PROCEDURE

MgO-C compositions are presented in Tab. 1 They comprised magnesia aggregates (98%wt MgO, CaO/SiO2=3.24, Magnesita Refratários S.A., Brazil), flake graphite (d < 200 µm, 99%wt C, Nacional de Grafite, Brazil), a phenolic resin as binder and three different antioxidants: aluminum, silicon or Al-Mg alloy.

Tab. 1: MgO-C compositions for comparison of the microstructural evolution by in situ elastic modulus (E) measurements in the temperature range between 30 and 1400°C.

(%wt)	Ref	Ref+Si	Ref+Al	Ref+Al-Mg
Fused MgO/ Total MgO (%)	100	100	100	100
Total MgO	88	85	85	85
Graphite	10	10	10	10
Antioxidant	**-**	**3**	**3**	**3**
Resin	++	++	++	++

The compositions were prepared in a roller mixer, pressed (FKL hydraulic press, 450t, Brazil, bricks = 160 mm x 85 mm x 63 mm) at Magnesita R&D center and cured at 200°C/6h under a 10ºC/min heating rate. For the physical and thermo-mechanical characterization steps, the prepared samples were cut into different sizes (according to the selected test) using a diamond saw. Samples were evaluated after cure and after coking at 1400ºC/5h (electric oven, 10ºC/min heating rate).

The apparent porosity (AP) and bulk density (BD) of cubic samples (40 mm x 40 mm x 40 mm) after curing or firing were measured according to ASTM C380-00, using kerosene as the immersion liquid. Cold crushing strength (CCS) was evaluated according to ASTM C133-97 in MTS equipment. Hot modulus of rupture (HMOR) measurements were carried out in three-point bending apparatus (HBTS 422 equipment, Netzsch, Germany) at 1400ºC, using pre-fired (1400°C/5h) prismatic samples (160mm x 40mm x 40mm – ASTM C583-80) wrapped in nickel foil (thickness < 0.1 mm, Votorantim Metais, Brazil) to prevent carbon oxidation during the tests. For each selected refractory composition, five samples were evaluated.

Cross-section areas were analyzed via optical microscopy (Axio Vert.A1, Zeiss, USA). Moreover, aiming to identify the main microstructural changes and their impact on the refractories' stiffness during heating and cooling cycles, in situ elastic modulus measurements were carried out according to ASTM C 1198-91 for cured (200°C/6h) or fired (1400°C/5h) bar samples (150mm x 25mm x 25mm) using the resonance bar technique (Scanelastic equipment, ATCP, Brazil). This method is based on the sample excitation and detection of the correspondent vibration spectrum, using piezoelectric transducers. The elastic modulus is calculated based on the resulting vibration spectrum applying Pickett equations, which correlates the E values, the natural vibration frequencies and the sample dimensions. For the fundamental flexural frequency of a rectangular bar, the Young's modulus is given by equation 1.

$$E = 0.9465 \frac{m f_f^2}{b} \times \frac{L^3}{t^3} \times T_1 \quad (1)$$

where E is the Young's modulus (Pa), m the mass (g), b the width (mm), L the length (mm), t the thickness (mm), ff the fundamental resonance frequency of the bar in flexure (Hz), and T1 the correction factor for fundamental flexural mode to account for the finite thickness of the bar, Poisson's ratio and others. Tests were conducted in the temperature range of 30 to 1400°C in air (pO_2 = 0.21 atm) with heating and cooling rates of 2°C/min. In order to prevent carbon oxidation, the refractory samples were coated with antioxidant paint (Fabuglas 1017, Budenheim, Germany) and wrapped in nickel foil. This double protective layer is more efficient against carbon oxidation and the main drawback of this procedure is most likely the attenuation of the resonant amplitudes obtained for the in situ E tests (due to using of the nickel foil).

RESULTS AND DISCUSSIONS

Tab. 2 shows the results for MgO-C compositions with no additives (reference) and with 3 wt% antioxidants (Al, Si and Al-Mg) after 200°C/6h and after 1400°C/5h. Based on the standard deviation values, all compositions presented similar cold crushing strength values after curing. The positive effect of the antioxidants was observed in porosity and HMOR after firing but a decrease in the cold mechanical strength. These results are related to the microstructural changes due to reaction of additives with carbon and magnesia during the thermal treatment at 1400°C, leading to new components, such as Al_4C_3, SiC and others [5].

Considering the complex heterogeneous microstructure of refractories and the fact that their mechanical properties are strongly affected by in situ transformations during curing and firing, measurements of the elastic modulus evolution with temperature may provide important information for understanding the role of different additives and also some behaviors observed during BOF operations. Fig. 1 shows the E profiles for the MgO-C refractories during their 1st and 2nd heating/cooling cycles under a reducing environment. The initial elastic modulus of the cured samples was around 60-75 GPa, but a major drop of these values was observed for all compositions when the temperature was increased (from 50 to 400-500°C) during their first heating. This softening of the refractory structure is associated with the pyrolysis of the phenolic resin and the presence of graphite in the formulations. As reported by some authors [6], although the elastic moduli of polycrystalline graphite usually rise with temperature, the E variation is not always positive. In fact, a well-defined minimum value should be observed around 100-300°C, depending on the nature of the carbon source. This behavior (occurrence of a minimum and the subsequent increase in the elastic modulus) might be associated with structural changes of this component [6]. Moreover, the E increase of the designed compositions between 500-700°C may also be attributed to the transformations of graphite [6].

Tab. 2: Results for MgO-C compositions with no additives (reference) and with 3 wt% antioxidants (Al, Si and Al-Mg) after 200°C/6h and after 1400°C/5h.

	Ref	Ref+Si	Ref+Al	Ref+Al-Mg
After 200°C				
BD (g/cm3)	3.07 ± 0.01	3.05 ± 0.01	3.04 ± 0.01	3.03 ± 0.01
AP (%)	3.97 ± 0.15	3.21 ± 0.12	3.17 ± 0.10	2.89 ± 0.16
CCS (MPa)	41.54 ±5.72	42.38 ± 4.44	42.57 ± 1.05	39.87 ± 5.37
HMOR (MPa)	9.24 ± 0.25	19.42 ± 0.48	11.41 ± 0.13	14.27 ± 0.84
After 1400°C				
BD (g/cm3)	2.99 ± 0.01	2.98 ± 0.01	3.02 ± 0.01	3.00 ± 0.01
AP (%)	9.29 ± 0.15	8.39 ± 0.17	6.93 ± 0.22	7.56 ± 0.27
CCS (MPa)	20.24 ± 2.2	29.52 ± 1.01	35.87 ± 0.99	33.04 ± 2.98
HMOR (MPa)	5.62 ± 0.13	12.25 ± 1.09	10.03 ± 0.44	14.35 ± 1.83

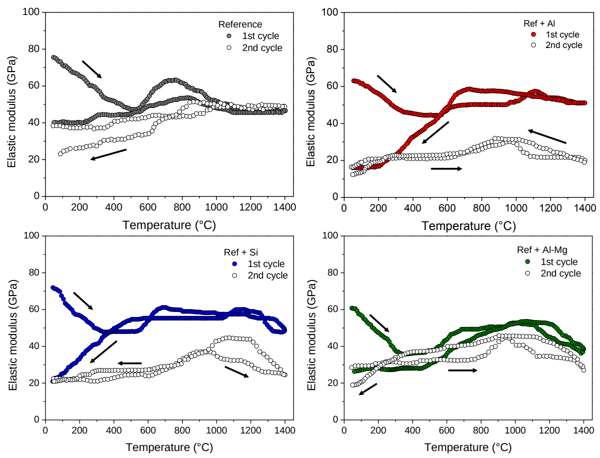

Fig.1: Elastic modulus evolution of MgO-C samples with 3 wt% antioxidants (Al, Si and Al-Mg) after 200°C/6h during two heating/cooling cycles up to 1400°C in a reducing environment.

After reaching 63 GPa at 760°C, a further drop in the elastic modulus was observed for the reference composition with the temperature increase and remained close to 45 GPa from 1000 to 1400°C. Regarding the antioxidants' performance at high temperatures and in a reducing environment, such additives should react with the composition components giving rise to novel phases, which can improve the overall thermo-mechanical properties of the refractories by sealing the open porosity and also minimizing further oxygen diffusion into the developed microstructure. It is reported that Al and Si might suppress carbon oxidation (considering their reactions with CO by decreasing the system porosity via volume expansions associated with the generation of novel compounds (i.e., $MgAl_2O_4$) and carbon precipitation. Al powder is expected to melt above 660°C and its interaction with C and the surrounding gases should mainly lead to Al_4C_3 and Al_2O_3 formation.

Despite these transformations, E values for the Ref+Al sample (1st cycle) in the 700-1400°C range did not present significant changes and 52 GPa was attained at the maximum evaluated temperature. The Al_4C_3 and $MgAl_2O_4$ phases were identified by XRD measurements of the fired materials and, consequently, these compounds improved the stiffness and thermo-mechanical performance of the Ref+Al composition compared to the Ref one (Tab.2).

On the other hand, the addition of Si to the Ref+Si formulation did not result in major E changes in the temperature range of 700-1300°C, but a further drop of this property could be detected between 1300-1400°C, indicating the softening of the refractory structure. As reported in the literature, Si should initially react with C above 1100°C, generating SiC. Then, this carbide may be oxidized depending on the CO partial pressure.

Additionally, forsterite (Mg_2SiO_4) generation can take place in MgO-C refractories containing Si above 1350°C. This transformation and/or liquid phase formation (due to raw materials impurities, such as CaO and SiO_2) might explain the softening of the Ref+Si refractory observed between 1300-1400°C, resulting in E = 48 GPa at 1400°C.

For the Ref+Al-Mg, the alloy reaction mechanism may be considered as combined effects of each one of their constituents. Mg oxidation and further $MgAl_2O_4$ generation above 1200°C are expected to take place. Based on the elastic modulus values attained at 1400°C, the following sequence of results was observed (1st cycle): Ref+Al-Mg (38.5 GPa) < Ref (45 GPa) < Ref+Si (48 GPa) < Ref+Al (52 GPa). Two samples of each refractory composition were analyzed via hot elastic modulus measurements in order to confirm the reliability of the attained data.

Although the antioxidant addition to the formulations and their further reactions with the refractory components led to samples with higher stiffness than the Ref one in the temperature range of 900-1300°C, a subsequent E drop during the refractories' cooling step indicated the thermal expansion mismatch among the novel phases and the original ones contained in the microstructure. Tab. 3 points out the thermal expansion coefficient of various components found in the evaluated refractories [5]. The E decrease was more significant in the antioxidant-containing compositions, but this effect was also observed for the Ref material resulting in lower elastic modulus values at the end of the 1st heating/cooling cycle. Different elastic modulus behavior was detected during cooling depending on the selected additive, as its drop mainly took place below 600°C, 500°C or 1000°C for the refractories containing Al, Si or Al-Mg, respectively.

Aiming to analyze the effects of the phase transformations on the refractories´ properties after keeping them at a high temperature for 5h, pre-fired MgO-C samples (1400°C/5h under a reducing atmosphere) were also tested in order to determine whether their E final values would reach even lower levels (due to crack and flaw formation). As indicated in Fig. 2, the Ref composition (additive-free formulation) presented initial elastic modulus of 13 GPa after the selected pre-firing step and this value raised to 20 GPa with a temperature increase up to 1400°C, which is associated to the release of tensile residual-stress and crack closure effect [5]. Nevertheless, an additional reduction in the stiffness was observed during the cooling step of the pre-fired Ref (E_{final} = 7 GPa), which is most likely also related to cracks opening and/or the generation of flaws in different locations or longer than the previous ones. The resulting E value was lower than the one attained in the 2nd thermal treatment of this refractory. Based on the hot elastic modulus measurements, it was observed that the MgO-C refractories represent a dynamic system prone to thermal-fatigue during their service condition.

Tab. 3: Thermal expansion coefficient of various components found in the evaluated MgO-C bricks.

Phases	**k* (°C^{-1} x 10^{-6})**
MgO	13.5
Carbonized resin	2.8 - 6.9
Graphite	a/b directions = -1.0 to 1.0 c direction = 25.0 to 40.0
Al_4C_3	5.0
Al_2O_3	8.0
SiC	4.0
$MgAl_2O_4$	7.6
Mg_2SiO_4 --	2.8 - 4.5

***Thermal expansion coefficient [5]**

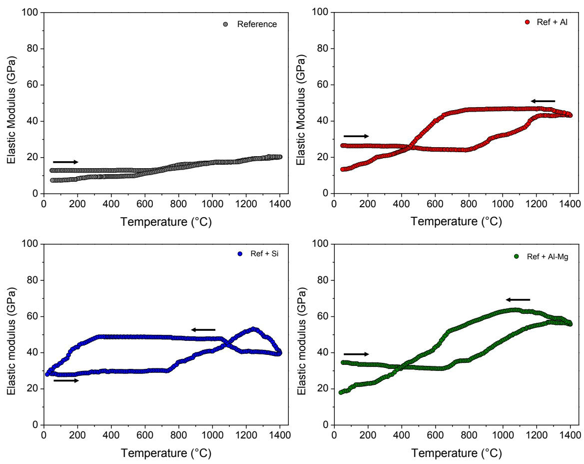

Fig.2: Elastic modulus evolution of MgO-C samples with 3 wt% antioxidants (Al, Si and Al-Mg) after 1400°C/6h during two heating/cooling cycles up to 1400°C in a reducing environment.

Continuous stiffness drop after heating/cooling cycles was also identified for the pre-fired antioxidant-containing formulations, except for Ref+Si, as despite the many E changes observed throughout the experiment, this sample showed the same initial and final elastic modulus values. As suggested by Takahashi et al [7], SiC oxidation may lead to crack healing of structural ceramics depending on the features of the generated SiO_2. If the formed silica is crystalline and bonded to the matrix components of the structure, then the crack-healed sample might present improved mechanical resistance even at high temperatures. On the other hand, glassy SiO_2 formation on crack-healed refractories may lead to a reduction in their mechanical strength at high temperatures. This latter effect was observed in Fig. 2 above 1200°C (during heating), as the Ref+Si sample presented an E drop due to the formation of a permanent liquid, which despite the Si reactions with the composition components during the pre-firing treatment at 1400°C/5h, the softening of the MgO-C structure was still observed resulting in a similar profile as the ones attained for the cured samples.

A positive aspect of the pre-fired Ref+Si composition observed during the samples' cooling step is that the E decrease (due to crack openings or generation of new flaws) took place only below 300°C, whereas Ref+Al and Ref+Al-Mg presented lower stability and their structure became weaker (< E) from 600°C and 1000°C during cooling, respectively.

SUMMARY AND CONCLUSIONS

Al, Si and Al-Mg antioxidants had an important role and directly affected the thermo-mechanical performance of MgO-C refractories. Despite the improved mechanical behavior, the interaction of the selected additives with other raw materials from the original composition and CO(g) from the reducing environment induced the generation of phases that could not be well accommodated in the microstructure due to the thermal expansion mismatch.

Elastic modulus measurements as a function of temperature for cured or pre-fired Ref+Al, Ref+Si and Ref+Al-Mg samples presented a significant E drop during the cooling step (mainly below 600°C), indicating that cracks and flaws were generated in the MgO-C refractories' structure

Considering that antioxidant-containing MgO-C bricks are usually applied in BOF vessels a good practice for preventing additional irreversible damage (cracking and spalling) of the lining consists of maintaining its temperature above 600°C.

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