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Key features of alumina/magnesia/graphite refractories for steel ladle lining

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Abstract

The corrosion resistance of resin bonded alumina/magnesia/graphite refractories containing different kinds of aggregates were investigated when submitted to the action of slags of several CaO/SiO_2 ratios. The laboratory testing was performed by means of the rotary slag attack test. Specifically evaluated was the influence of alumina/carbon ratio and magnesia and silica contents on the refractories corrosion resistance. It was found that this property could be improved by increasing the refractory Al_2O_3/SiO_2 ratio as well as by choosing the appropriate Al_2O_3/C ratio. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: $Al_2O_3/MgO/C$; Refractories; Slag resistance; Steel ladle lining

1. Introduction

The development of magnesia/alumina/graphite resin bonded materials for steelmaking applications is a very important recent refractory development which can be considered as being evolved from the high performance magnesia-carbon and alumina-carbon refractories.[1–3] This new class of refractories not only displays superior chemical and thermodynamic stability characteristics when compared to high alumina and doloma steel ladle refractories, but also excellent thermal and mechanical properties.[4] As a consequence, in the last decade a new class of refractory products based on the $Al_2O_3/MgO/C$ system has been successfully applied to several steelmaking processing vessels,[5,6] mainly in steel ladles.

Considering that this product is a combination of basic and amphoteric aggregates, a superior performance has been achieved when compared to refractories based only in high alumina or dolomitic products. A very important property of the $Al_2O_3/MgO/C$ refractories is its residual expansion during the usage. Such expansion is responsible for the formation of a monolithic refractory lining[5] resulting in a decreased steel penetration through the refractory joints.

Considering it is a somewhat recent refractory material development, there are still some obscure points concerning the relevant parameters which may influence the material performance.[7–9] Based on this last aspect, in the present work the effects of several key components on the slag corrosion resistance of an alumina–magnesia–graphite base composition were investigated, using a steel ladle refractory lining.

2. Experimental procedure

Two series of compositions were prepared. The first one containing as aggregates a combination of bauxite and electrofused alumina with different amounts of carbon (graphite), intended to render several Al_2O_3/C ratios namely: 12.9; 13.6 and 19.2.

The second composition contained similar aggregates. However, the carbon content was kept constant and equal to 4.0 wt%. In this case, the objective was to obtain different Al_2O_3/C and Al_2O_3/SiO_2 ratios in the refractory. In all the compositions, the MgO content

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was mantained close to 7 wt%. A phenolic resin was employed as the binding agent.

The refractories were uniaxially dry pressed in the form of bricks whose dimensions were: 229×114×63 mm. After thermal treatment at 180°C for 24 h, the bricks were characterized according to ASTM standards. The following tests were carried out: Bulk density (BD), Apparent porosity (AP), Cold Crushing Strength (CCS), and Linear Dimensional Change (LDC) after reheating at 1500°C during 4 h under a reducing atmosphere. It was also determined the Refractoriness Under Load (RUL) and Hot Modulus of Rupture (HMR) at 1400°C.

Slags with different binary basicities within the calcia/alumina/silica system were used to evaluate the resistance of the refractories under rotary slag attack testing. The tests were completed in 2 h at 1750°C. After attack, the corroded areas were examined using scanning electron microscopy (SEM) and EDS analyses were performed in several points of the samples, aiming the qualitative determination of the local chemical composition of the products.

Table 1
Physical and chemical properties for the first and second experimental series

	First experimental series		Second experimental series		
	A/C = 12.9	A/C = 13.6	A/C = 19.3	A/C = 19.7	A/C = 20.0
Physical properties					
B.D. (g/cm3)	3.17	2.91	2.97	3.06	3.14
A.P. (%)	4.0	5.0	6.5	4.5	4.0
C.C.S. (MPa)	60	64	75	82	80
L.D.C. (1650°C)	+4.2	+2.80	+5.5		
RU.L. (ti) °C	>1800	>1750	1640		
H.M.R. (1400°C)	20	11	8.4		
Chemical properties					
Al_2O_3 %	82.8	76.2	77.4	79.9	81.5
MgO %	7.0	6.8	7.0	7.2	7.0
C %	6.4	5.6	4.0	4.1	4.1
SiO_2 %	2.3	8.2	8.2	5.0	6.2
TiO_2 %	0.9	1.4	1.6	1.4	1.6
Fe_2O_3 %	0.3	1.5	1.7	1.0	1.2
Total	99.6	99.7	99.9	98.59	101.6
A/C[a]	12.9	13.6	19.3	19.7	20.0
A/S[a]	36	9.3	9.4	16.0	18.5

[a] A = Al_2O_3; C = Carbon; S = SiO_2.

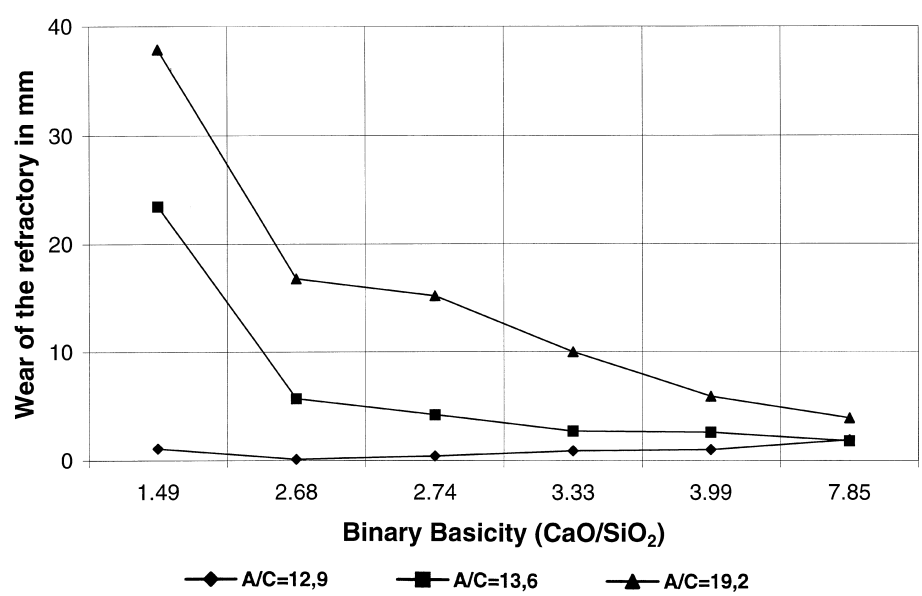

Fig. 1. Wear results of the selected formulations of refractories, submitted to the dynamic slag attack test.

3. Results and discussion

Once the two main base refractory compositions and their respective derivatives were established and processed, the main physical properties and chemical composition of each formulation were determined, as shown in Table 1.

The dynamic slag attack tests, were conducted using slags whose basicity indexes ranged from 1.49 to 7.85. The results of the wear rates in Fig. 1, show the same trend for all the tested formulations. However, the composition A/C = 12.9 displayed the highest corrosion resistance under the action of the several slags. The excellent performance of this formulation is explained on the basis of its physical and chemical properties listed in Table 1.

According to the results of chemical analyses, the formulation having A/C ratio equal to 12.9 presented the highest concentrations of Al_2O_3 and C, as well the smallest SiO_2 content, when compared to the whole group of formulations, as shown in Fig. 2.

In order to make it easier to understand the different wear behavior of the compositions, three chemical ratio parameters were established as paradigms, namely: Al_2O_3/SiO_2 (A/S), Al_2O_3/Carbon (A/C) and Carbon/MgO (C/M), which were plotted for each formulation, as shown in Fig. 3.

X-ray diffraction analyses indicate that all the crystalline SiO_2 present in the formulations is bonded to Al_2O_3 in the form of mullite ($3Al_2O_3.2SiO_2$), whereas the remaining Al_2O_3 is found in the form of corundum (α-Al_2O_3). On the other hand, MgO is in the form of

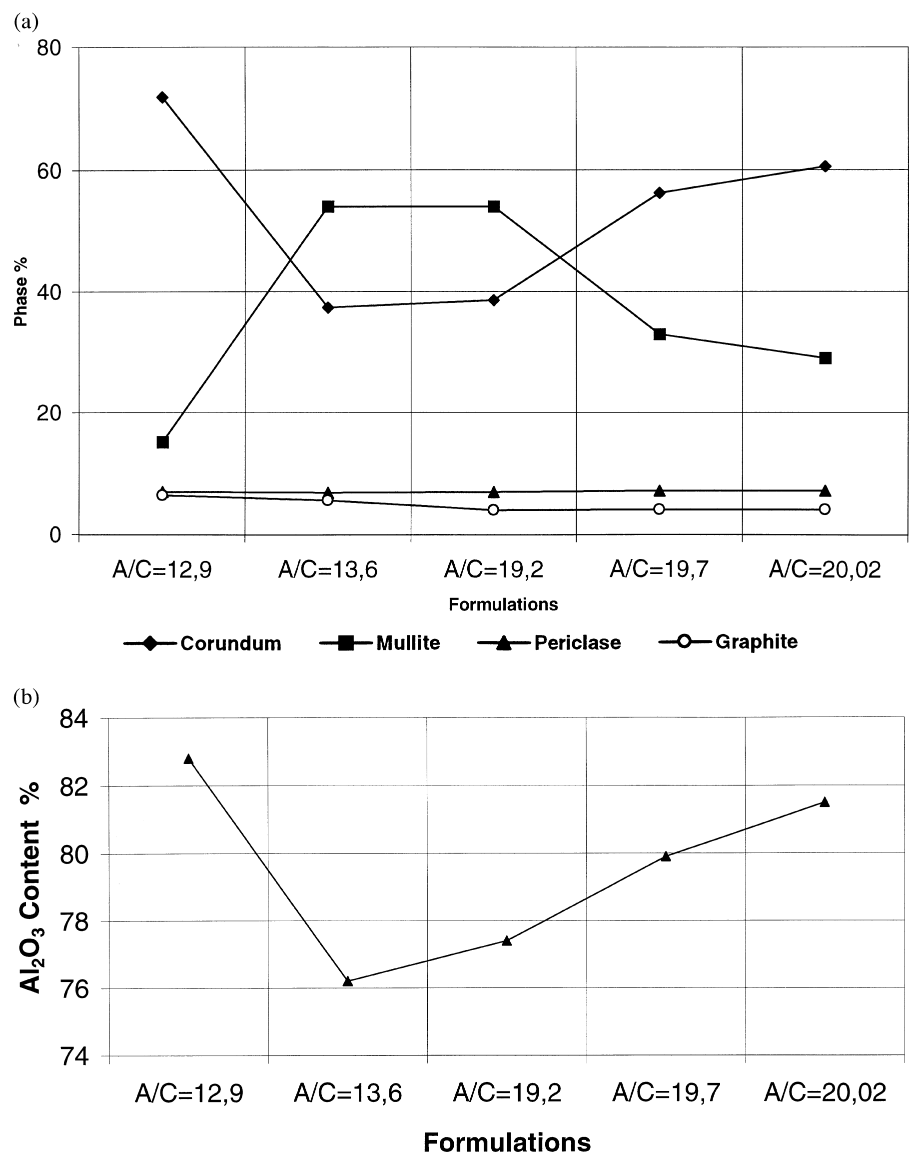

Fig. 2. Mineralogical and chemical composition of the prepared refractory formulations.

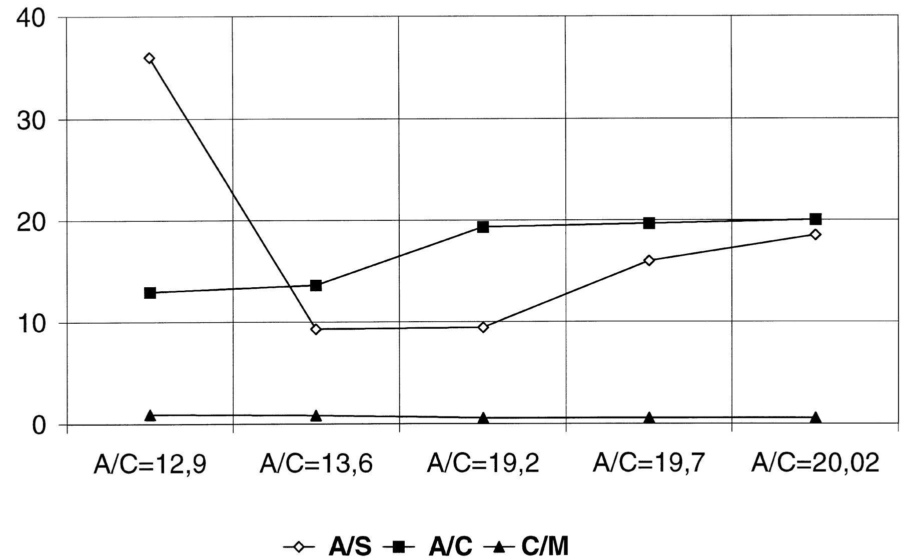

Fig. 3. Chemical ratios for the prepared refractory formulations.

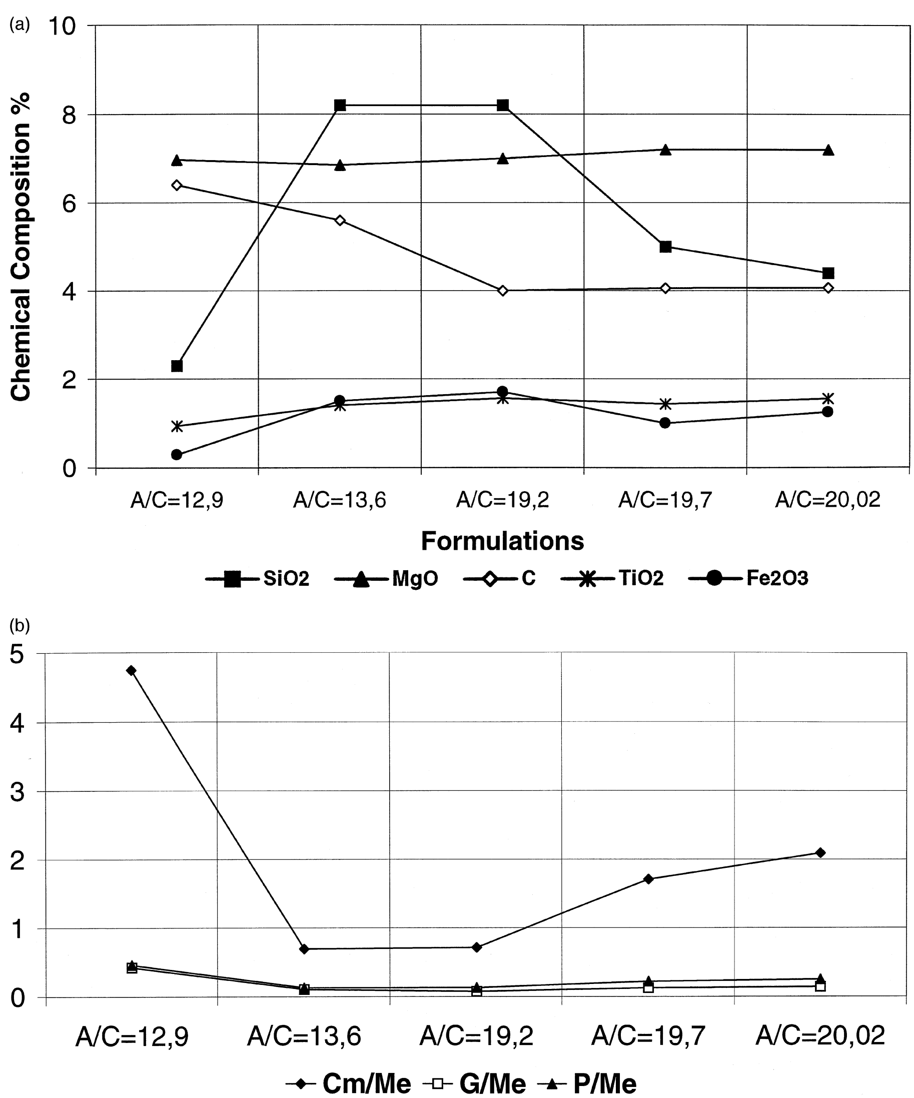

Fig. 4. Mineralogical compositions and mineralogical ratios for the different refractory formulations.

periclase and carbon in the form of graphite. Therefore, three additional mineralogical ratio parameters were also established, that is: corundum/mullite (Cm/Me), graphite/mullite (G/Me) and periclase/mullite (P/Me). Fig. 4 shows the mineralogical compositions as well the mineralogical ratios for the developed formulations.

The results shown in Figs. 2–4 indicate that there is a strong relation between high wear resistance with the higher A/S, Cm/Me, G/Me and P/Me ratios. This is indeed the case, considering that the corrosion sites of the developed formulations are concentrated in the refractory matrix. In this way, the presence of high mullite contents in the matrix will promote in combination with the CaO contained in the slag (even in the presence of corundum in the matrix), the production of large amounts of the calcium alumino silicates anorthite and gehlenite. These phases are responsible for the formation of an eutectic composition at the temperature of 1265°C.[10] Therefore, smaller concentrations of SiO_2, and consequently, smaller mullite phase concentration in the matrix will promote a smaller production of the eutectic composition. The representative reactions of calcium alumino silicates formation are the following:

Anorthite (MP = 1553°)

$$3Al_2O_3.2SiO_{2(s)} + 3CaO + 4SiO_{2(s)} \rightarrow 3(CaO.Al_2O_3.2SiO_2)_{(s)} \quad (1)$$

Gehlenite (MP = 1593°C)

$$3Al_2O_3.2SiO_{2(s)} + 6CaO + SiO_{2(s)} \rightarrow 3(2CaO.Al_2O_3 \cdot SiO_2)_{(s)} \quad (2)$$

On the other hand, higher concentrations of graphite and periclase in the matrix will promote improved protection due to the following reasons:

1. Graphite is characterized as a phase displaying high refractoriness, high thermal conductivity, low thermal expansion and low wettability by the slag,

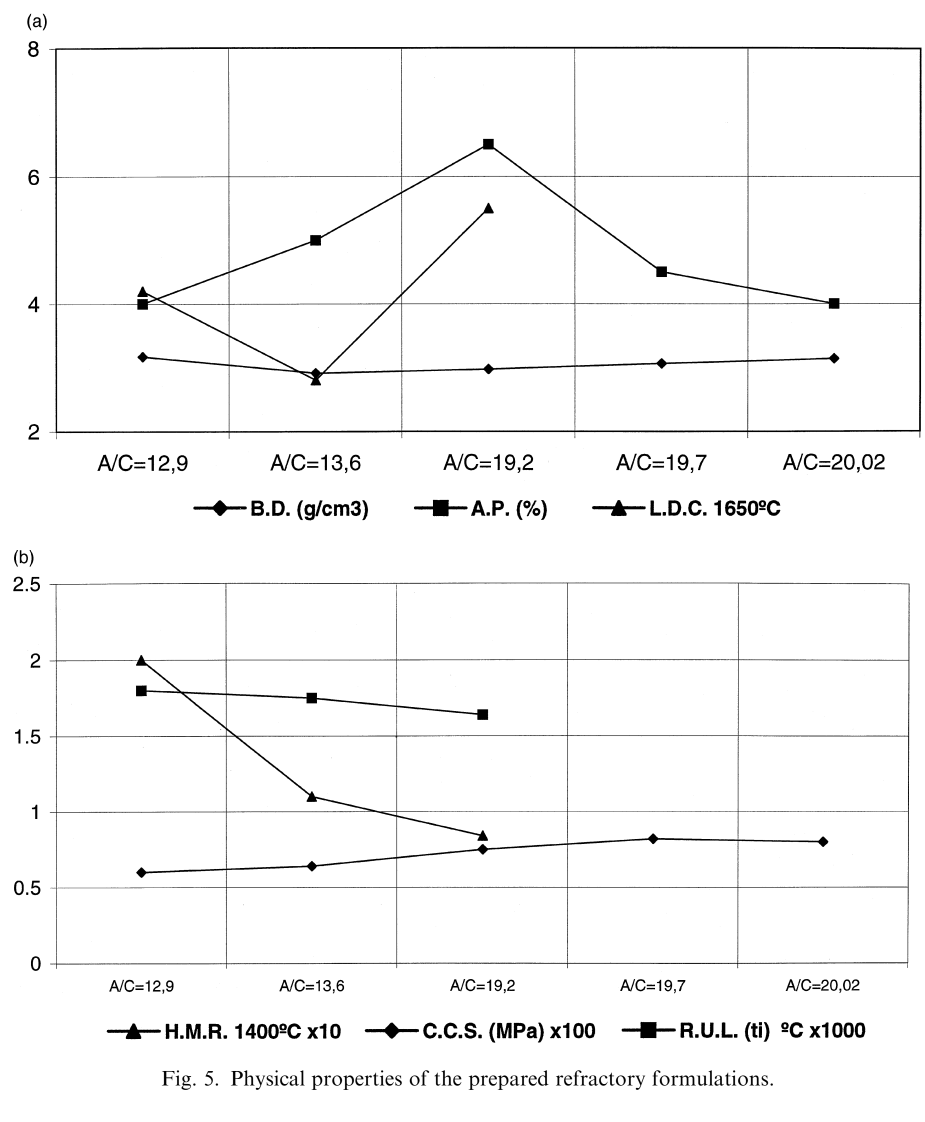

Fig. 5. Physical properties of the prepared refractory formulations.

conferring to the refractory matrix better thermomechanical properties and higher resistance to slag penetration. Higher G/Me ratios indicate a somewhat large comparative amount of graphite with respect to mullite in the matrix, providing a better protection.

2. Periclase is also characterized by high refractoriness and basic character, which presents a favorable behavior related to corrosion resistance, when submitted to high basicity slags. Higher P/Me ratios indicate a higher mullite consumption through the reaction with periclase. This reaction creates inside the open porosity of the refractory microstructure a barrier composed of forsterite ($2MgO.SiO_2$). As a result of the mullite phase consumption, the production of calcium alumino silicates is reduced, being accompanied by the precipitation of a highly reactive alumina in the matrix.

Heat treatments applied to the formulations having ratios A/C equal to 12.9, 13.6 and 19.2, during 4 h in a reducing atmosphere (coke breeze) at a temperature of 1600°C, led to the the confirmation that the

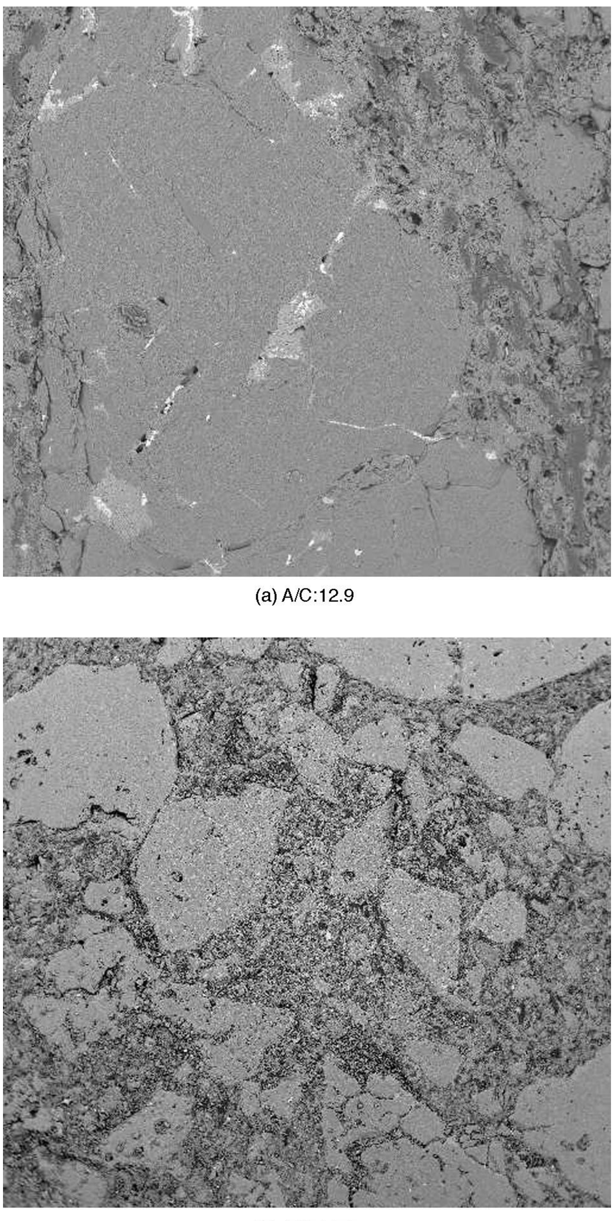

Fig. 6. SEM micrograph showing the compositions A/C: 12.9 and A/C: 19.2 before being submitted to the dynamic slagging corrosion test. (20×). Working distance 18 mm, 25 kV BSE. (a) A/C:12.9; (b) A/C:19.2.

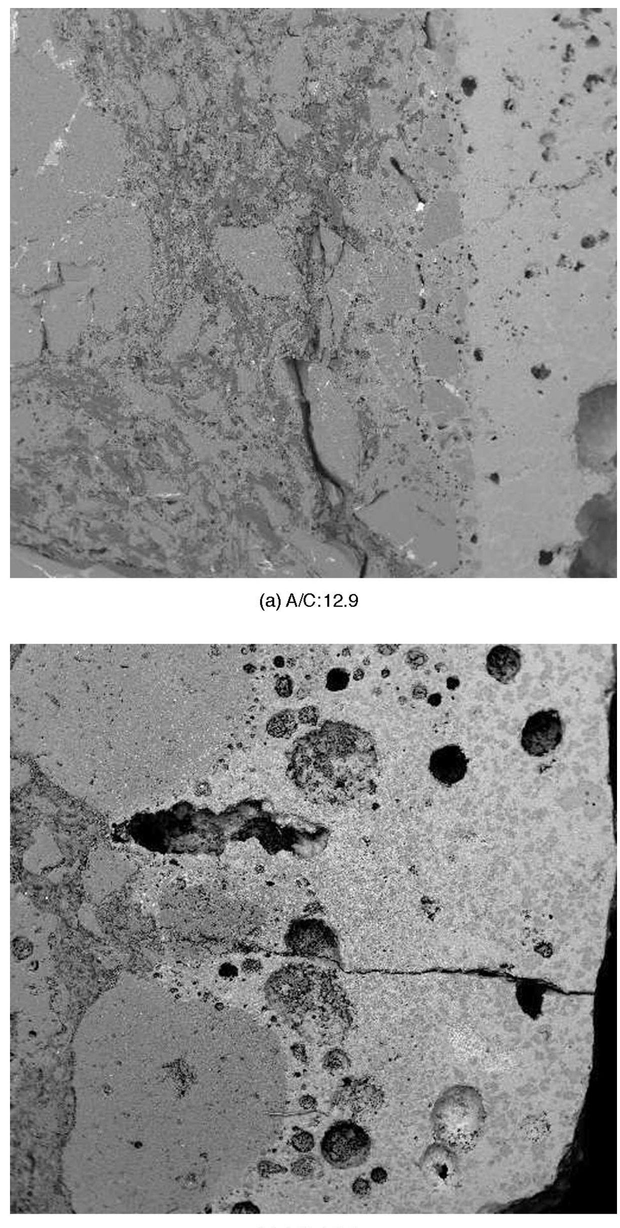

Fig. 7. SEM micrograph showing the interface between slag and refractory for the compositions A/C = 12.9 and A/C = 19.2. (20×). Working distance 18 mm, 25 kV BSE. (a) A/C:12.9; (b) A/C:19.2.

consumption of the mullite and periclase phases is associated with the development of forsterite and magnesium aluminate (Spinel) as demonstrated by their X-ray peaks (Mg–Al–O) and schematically shown in Reaction 3.

$$6MgO_{(s)} + 3Al_2O_3.2SiO_{2(s)} \rightarrow 2(2MgO.SiO_2)_{(s)} + 2(MgO.Al_2O_3)_{(s)} + Al_2O_{3(s)} \quad (3)$$

The results of the physical properties of the prepared formulations are shown in Table 1. Their analyses clearly indicate that the highest value of apparent density and lowest value of apparent porosity are again related to the formulation A/C = 12.9. This indicates a better packing of this microstructure, as shown in Fig. 5.

It was also noticed that the composition A/C = 12.9 presents intermediary values of linear dimensional change, that confers a higher resistance to the attack through the joints of the brickwork when under industrial usage.[5]

The results of refractoriness under load and hot modulus of rupture indicate that the best results are obtained for the formulations that present the highest carbon (graphite) content in the matrix, associated with highly packed microstructures.

Scanning electron microscopy results ratify what was insofar obtained. Preliminary SEM exams of the samples, before slag attack tests, allow to visualize the better packing of the formulation A/C = 12.9 compared with the formulation A/C = 19.2 (Fig. 6).

Fig. 7 presents the image of compositions of the refractory–slag interface for the formulations A/C = 12.9 and 19.2 (formulations which displayed the best and the worst performances respectively for slag test realized under a binary basicity equal to 2.74).

It can be concluded that the formulation A/C = 12.9 presents a smaller dissolution under slag attack when compared with the formulation A/C = 19.2. This performance is attributed to a set of superior physical and chemical properties of the first formulation, compared to the remaining formulations. This results in a better packing of the microstructure (smaller pore sizes), higher concentration of graphite in the matrix (lower wettability of the matrix by the slag), reasonable content of aggregates of electrofused alumina (higher resistance to dissolution by the slag), higher concentration of periclase (consumption of the mullite phase for the production of forsterite and magnesium aluminate).

X-ray mapping of the identified elements, via EDS — Fig. 8 — shows the higher wear undergone by the

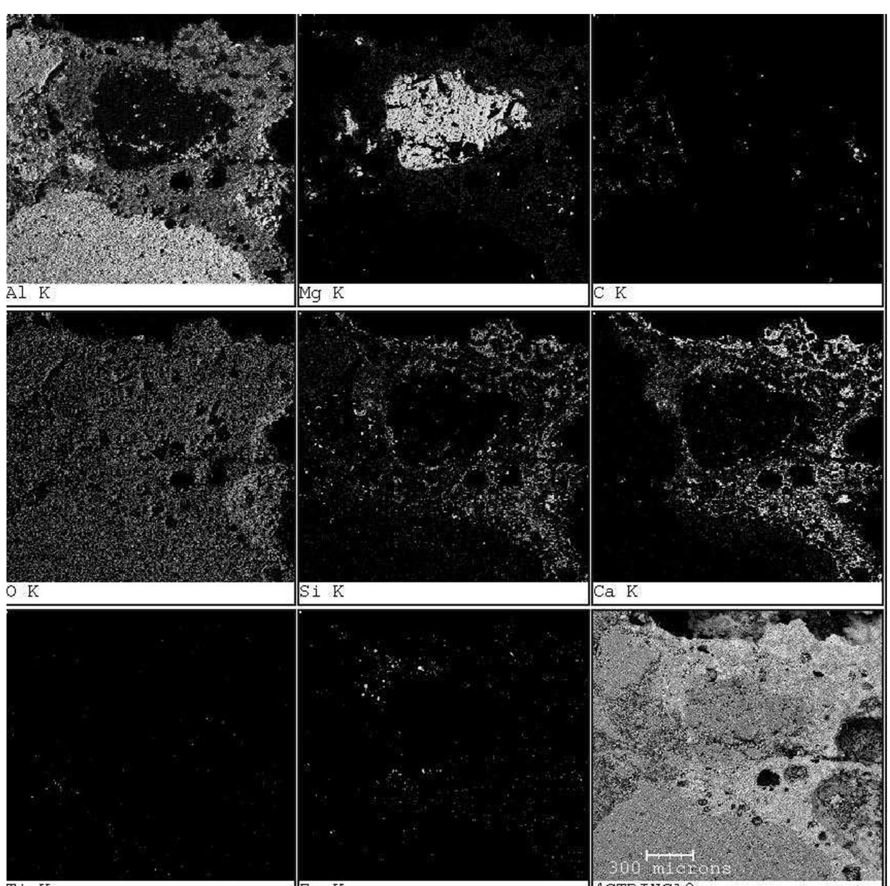

Fig. 8. Image composition associated with X-ray mapping for the formulation A/C = 19.2, after the slag test, detail of the crack. amplification 20×.

formulation A/C = 19.2. The co-existence of the elements Al, Si and Ca in the same region is evidence that the consumption of the corundum and mullite rich matrix by the slag attack occurs due to the production of calcium alumino silicates. The lower density and thermal expansion of these phases are responsible for the thermal expansion mismatch and the creation of stresses in the microstructure, leading to crack propagation and, as a consequence the wear of the brickwork by structural spalling as shown in Fig. 7b.

It can observed that the periclase (MgO) grains are not consumed due to its excellent compatibility with the slag.[11]

Image compositions, coupled to X-ray mapping, via EDS of the Formulation A/C = 12.9 — Fig. 9 — before being submitted to the slagging tests were evaluated. This evaluation allows the conclusion that the use of large aggregates, composed mainly of corundum together with controlled amounts of periclase (≅7 wt%) and graphite (≅6 wt%) both uniformly distributed into a refractory matrix of low mullite concentration, results in an elevated degree of packing of the microstructure which will provide a material of superior performance before the attack of steel ladle slag.

4. Conclusions

The physical and chemical properties of the studied formulations, as well as the evaluation of the rotary slag attack test led to the following conclusions.

A graphite content of the order of 6 wt% in the refractory matrix, apparently helps to build an appropriate set of thermo-mechanical properties and higher corrosion resistance, due to the low thermal expansion coefficient, high thermal conductivity, high refractoriness and a low wettability by the slag. At the same time this graphite content is high enough to give good sinergism and small enough not to hinder the diffusion of ions responsible for the the Spinel formation, as was pointed out by Sasajima et al.[7]

Lower concentrations of the mullite phase result in a smaller production of calcium alumino silicates (eutectic composition anorthite–gehlenite MP.: 1265°C). Higher periclase/mullite ratios result in higher mullite consumption due to its reaction with periclase, producing the forsterite ($2MgO.SiO_2$) phase and alumina. This precipitated, highly reactive alumina is able to combine with the excess of periclase, forming initially magnesium aluminate and later magnesium–aluminum Spinel

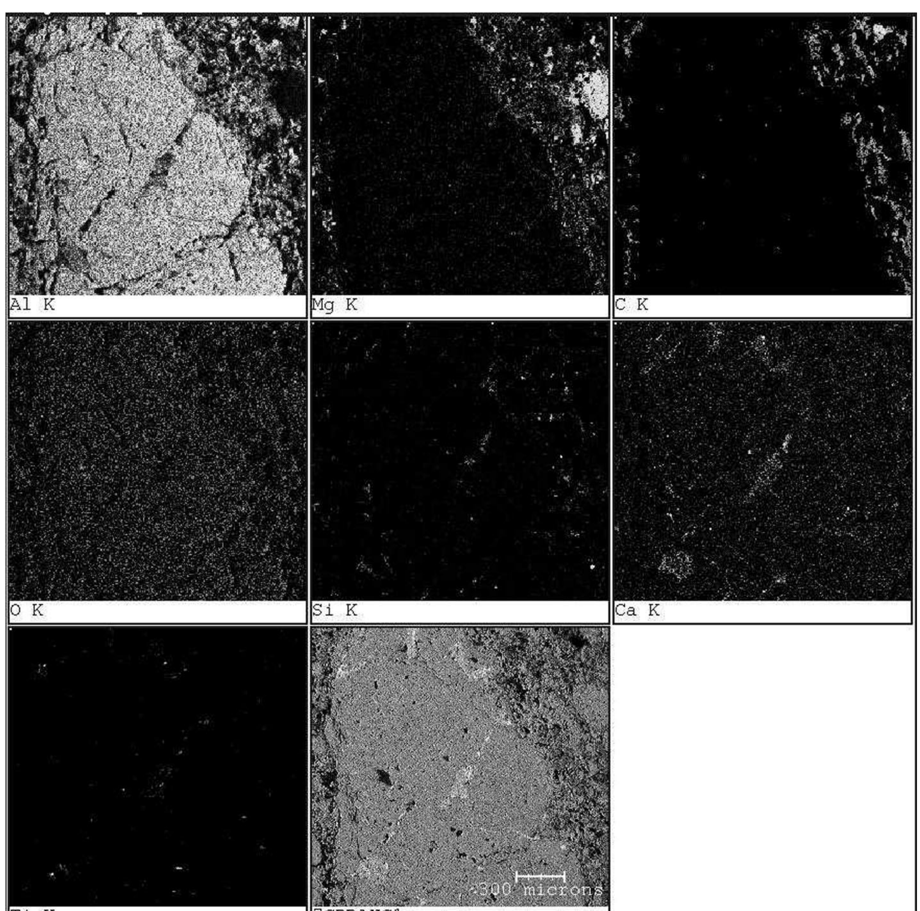

Fig. 9. Image composition associated with X-ray mapping for the formulation A/C = 12.9 Before the slagging test. amplification 20×.

($MgAl_2O_4$). The combined effect of these reactions in the refractory microstructure creates barriers in the open porosity originating a concurrent mechanism of protection.

The use of electrofused alumina in substitution to sintered alumina and bauxite in the formulations promoted an increase in the corrosion resistance as a consequence of the smaller rate of dissolution by the slag.

Considering the rotary Slag attack test, it can be concluded that the formulation A/C = 12.9 presented the best performance, ratifying the aforementioned conclusion statements.

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