CHEMICAL ATTACK EVALUATION OF ALUMINA-MAGNESIA-GRAPHITE BRICKS BY DYNAMIC TESTS AND THERMODYNAMIC SIMULATION

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ABSTRACT

Alumina-magnesia-carbon (AMC) refractories used in the steelmaking ladles support temperatures up to 1600-1700°C and are also exposed to the attack of melts (liquid metal and slag) and oxidant gases of the atmosphere. On the other hand, the high degradation of the bricks under real conditions in-service is difficult to reproduce at laboratory scale. For this reason, a combination of analytical methodologies is convenient to face the problem.

In this work, the corrosion of commercial AMC bricks by molten slag is studied by a combination of methodologies in order to achieve a deep understanding of the corrosion mechanisms and its relationship with refractory characteristics such as composition, microstructure and texture.

The dipping-test, which reproduces the relative movement between the slag and the refractory, is used together with the thermodynamic simulation of the system by commercial software. Prismatic specimens extracted from the brick are subjected to the corrosion test at 1600°C during 30 min, and a sample speed of 25 rpm. A typical industrial slag is evaluated with a CaO/SiO_2 ratio of 10.6. After the test, the sample wear is evaluated by dimensional variations, XRD, TGA, density and porosity measurements. Also, SEM/EDS microscopy is employed. A previous characterization of the commercial bricks is performed by the same analytical techniques in order to use this information as reference. The thermodynamic simulation of slag-refractory system is carried out using FactSage 7.0 commercial package and the chemical composition of the slag and the brick. An iterative procedure is employed until the amount of equilibrium liquid is null. The specimen wear as well as the identification of the new phases formed at the slag-refractory interface (mainly different calcium aluminates and $MgO.Al_2O_3$ spinel) are used as indications of sample corrosion. Moreover, the equilibrium calculations brings good prediction with regard to the phases present at the slag-refractory interface, and the degree of corrosion wear taking into account from number the iterative process steps..

From these results, the main steps of the corrosion process (mechanisms) are inferred, as well as the relationship between chemical attack and AMC bricks characteristics (raw materials, periclase content, etc.).

INTRODUCTION

The wear of the refractory materials in service is a gradual process that takes place under aggressive conditions. Corrosion is one of the most important factors limiting the material lifetime. In Al_2O_3-MgO-C (alumina-magnesia-carbon, AMC) materials [1], corrosion can be produced by molten steel, working atmosphere gases and liquid slags. The high difficulty to study the refractories corrosion is that is a multi-variable process. It depends on refractory as well as the reactive agent characteristics, and also on external conditions such as temperature, atmosphere, stirring, time and others. Thus, the utility of in-lab corrosion tests has been questioned because the extrapolation of the laboratory results to the plant practice is restricted by the difficult to reproduce the real conditions [2]. Nevertheless, the laboratories tests are used extensively in order to evaluate the corrosion resistance; there are available many tests with different configurations [3].

On the other hand, thermodynamic simulation is a powerful tool that complements laboratory testing. It gives the equilibrium phases in a system from its composition, temperature and pressure. This methodology has been successfully used for simulating the slag-AMC refractory system at high temperature [4]. In addition to the contribution for a better understanding of corrosion mechanism, thermodynamic simulation has the facility of changing the initial conditions easily in order to obtain the new thermodynamic equilibrium of the system.

In the present work, the analysis of the slag corrosion of AMC refractory bricks for steelmaking ladle bottom has been carried out. The laboratory test and thermodynamic simulation were performed aiming to understand the material behavior concerning its characteristics and composition. The dipping test was employed which produces a relative movement between slag and refractory, unlike cup static test. This condition simulates better the service conditions in some steps of the ladle campaign. Wear by erosion should be taken into account in addition to corrosion itself.

PROCEDURE

In this work, a commercial alumina-magnesia-carbon refractory brick (AMC4) used in the bottom of a steelmaking ladle was study. A specimen of 2x2x20 cm^3 (Figure 1) was extracted from the brick and subjected to a dynamic corrosion test in an induction furnace at 1600ºC during 30 minutes, with rotation rate of 25 rpm. The specimen was immersed in the slag about 3 cm in depth. A basic steelmaking slag (CaO/SiO_2 weight ratio: 10.9) was used, being their main components: CaO (54.9 wt.%), Al_2O_3 (30.8 wt.%), MgO (8.2 wt.%) and SiO_2 (5.0 wt.%).

The characterization of post-test material was carried out with the aim of find out corrosion indicators. Wear (i.e., material loss) was calculated by means of two methods as quantitative indicator of corrosion. The following equation was used:

$$\%wear = \frac{final\ size - initial\ size}{initial\ size} \cdot 100$$

Taking into account that the sample tends to loss material (by detachment or dissolution of particles) during dipping test, wear value would be negative. The first method is that currently used; it involves measuring the specimen's thickness before and after the test. The measurement was done at ~2.5 cm from the submerged end of the sample. The second method involves measuring the area of the cross section, as following: a) the initial area was calculated with the dimensions measured before the dipping test at ~2.5 cm from the submerged end of the sample; b) the final area was determined by image analyze (ImageJ software) of a cross-section photo at ~2.5 cm from the sample extreme, discounting the slag adhered to the external surface.

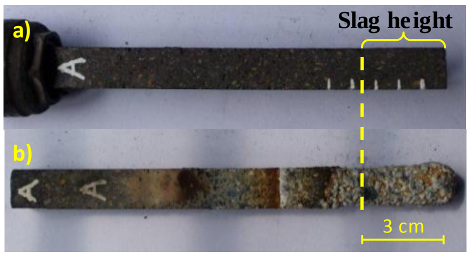

Fig. 1: Samples of AMC4 material: a) before test; b) after test.

Furthermore, the microstructure of the slag-refractory interface was observed by scanning electron microscopy coupled with X-ray dispersive energy spectroscopy (SEM/EDS).

The characterization of unused AMC4 refractory brick was published in a previous work [5]. The main information is reported in Table 1.

Tab. 1: Characteristics of AMC materials.

		AMC1	AMC2	AMC3	AMC4
Main phases (wt. %) (1)	Corundum	82.7	57.6	70.5	77.6
	Periclase	5.40	27.0	6.8	6.6
Secondary phases (wt. %) (1)	Graphite	1.7	3.5	3.0	1.9
	Resin	5.4	5.6	5.0	4.5
	Aluminum	1.4	1.4	1.60	2.9
	Silicon	-	-	-	0.3
Impurities (wt. %) (1)	Fe_2O_3, SiO_2, CaO, TiO_2 (2)	3.1	2.9	3.1	3.3
Apparent porosity (%) (3)		7.6	10.8	4.7	5.1

(1) Error < ± 0.3%

(2) Main impurities.

(3) Error = ± 0.5%

Some analyses of the sample where no contact with slag occurred during the dipping test were carried out to find out the material thermal evolution due to its exposure to the high temperature of the test. The mineralogical composition was carried out by X-ray diffraction (XRD; Panalytical X´PERT PRO) of powdered samples, using Cu Kα radiation at 40 kV, 40 mA, and 10ºC/min. Moreover, the thermogravimetric analysis (TGA) was performed on powder samples up to 1200ºC in air, using 10ºC/min of heating rate (Shimadzu TGA-50). The global density (ρ_g) and the apparent porosity (π_A) were determined for corroded sample without adhered slag in isopropyl alcohol.

The results of the corrosion tests for AMC4 were analyzed in comparison with those of other AMC bricks (AMC1, AMC2, AMC3), whose characteristics are also summarized in Table 1 [4].

Besides, the thermodynamic simulation of AMC4material in contact with slag was performed to compare the equilibrium composition with that experimentally obtained. For that, the simulation has been carried out using FactSage (version 7.0), a fully integrated database and software developed between Thermfact/CRCT (Montreal) and GTT-Technologies (Aachen). The calculations performed in this work were based on the minimization of the free energy of the system. The refractory and slag chemical compositions were taking into account; refractory's minority components were added to the slag composition. Resin of refractory was dismissed in the calculation because the used thermodynamic bases have no organic compounds data.

An iterative procedure was used in the thermodynamic calculations [4]. Firstly, 100 grams of AMC brick and 100 grams of a slag composition were considered in the first reaction stage. All calculations were performed for a constant temperature of 1600°C and a pressure of 1 atm. After the first reaction step, the resulting liquid (considered as the modified slag) was again put in contact with the same amount (100 g) of the original brick composition used before, and a further thermodynamic calculation step (CS) was carried out. This procedure was constantly repeated until no liquid was present at the equilibrium.

Moreover, equilibrium phases present in AMC4 at 1600°C in presence of gaseous oxygen (3 g of O_2 per 100 g of refractory) were calculated [6].

RESULTS AND DISCUSSION

Figure 1 shows the AMC4 specimen after the dipping test.

The formation of $MgAl_2O_4$ spinel was observed by XRD analysis of sample without slag (Figure 2), that also showed that aluminum was completely consumed. XRD peaks of graphite and periclase were already identified; hence, not all the magnesia turned into spinel and not all the graphite was oxidized. The SEM/EDS analysis of the original AMC4 material [4] showed that magnesia is distributed only as coarse particles. That characteristic is less favorable to spinel formation than if it would be distributed into the matrix. XRD peaks of Si were not found in tested material; however, it was not possible to detect any other Si-containing phase.

Thermograms of original and tested AMC4 materials are plotted in Figure 3 TGA curve of the original material shows two mass losses. The first one concerns the resin volatile compounds elimination and the second one corresponds to oxidation of graphite and residual carbon coming from resin; these processes produce CO_2 elimination as volatile. In the tested material, all the volatiles from the resin were removed during the corrosion test; however carbon was not completely oxidized. In fact, peaks of graphite were still s found by XRD, Figure 2.

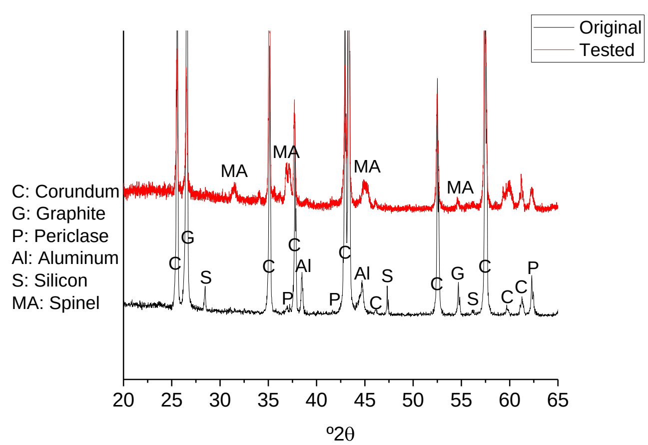

Fig. 2: XRD diagram of AMC4 before use and after test (without slag).

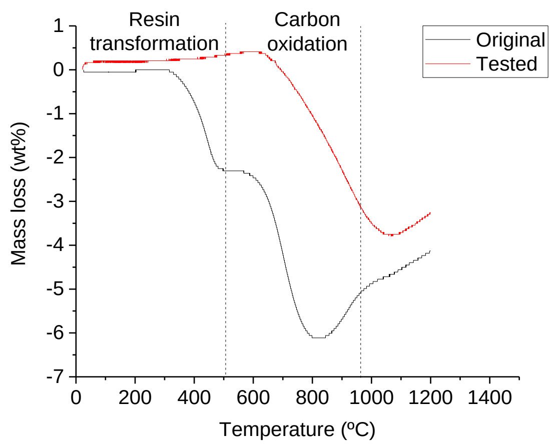

Fig. 3: TGA diagrams of AMC4 before (original) and after test (tested; without adhered slag).

The thermodynamic simulation gives the following phases when AMC4 refractory components reach the equilibrium at 1600ºC: 53.8 wt.% of Al_2O_3, 43.8 wt.% of $MgAl_2O_4$, 1.75 wt.% of graphite and 0.54 wt.% of Si. The results obtained in the tested portion of sample without slag are according with these obtained by simulation. Corundum (α-Al_2O_3), spinel $MgAl_2O_4$ and graphite were identified by XRD. Nevertheless, periclase was also found in this analysis, showing the effect of the large size of the particles of MgO in AMC4 which likely hindered its transformation of spinel during the test.

The density and porosity of AMC4 material tested at 1600ºC during the corrosion test were 3.2 g/cm^3 and 11 %, respectively. The density of tested material decreased with respect to the unused refractory and the porosity increased, but in much more proportion. A densification of the material should be expected due to spinel formation which is denser than precursor compounds (magnesia, aluminum or alumina) and the elimination of those low-density components such as resin or graphite. On the other hand, the resin pyrolysis and carbon oxidation increase the material's porosity throughout gas formation and elimination, reducing the global density. Therefore, this last factor seems to be determining in the decrease of global density.

Wear of corroded AMC4 and the other three AMC bricks calculated by the first method is shown in Table 2.

Tab. 2: Wear determined by the first method.

	Initial thickness (mm)	*Final thickness (mm)*	*Wear (%)*
AMC1	19.22	17.66	-8.2
AMC2	22.12	22.95	+3.8
AMC3	21.45	20.95	-2.3
AMC4	17.00	16.60	-2.3

The obtained results show that one of the materials (AMC2) underwent an increase of the thickness and thus, the wear is positive. This result was mainly attributed to the slag adhered to the sample surface which counterbalances the material loss. In order to avoid the incidence of this factor in the wear calculation, the second method was proposed, which discounts the remnant slag adhered on the specimen.

The wear estimated by the other method is reported for AMC bricks in Table 3.

Tab. 3: Wear determined by the second method.

	Initial Area (mm^2)	*Final Area (mm^2)*	*Wear (%)*	*CS* (1)[4]
AMC1	371	263	-29	3
AMC2	495	358	-28	100
AMC3	460	373	-19	4
AMC4	292	250	-17	3

(1) Number of calculation steps (CS) required for null content of liquid in the thermodynamic simulation.

Using this method, the wear resulted negative for all the cases, considering that this indicator estimates better the loss of material due to slag corrosion. However, these results show that AMC1, which is the refractory more resistant according with the cup static test [3, 7], was the material with the highest wear tested by dipping. This behavior is attributed to the erosion that takes place during the dynamic test. The smaller particle sizes, the greater wear by erosion because they are easy to drag during the slag movement. Thus, the corrosion effect was higher in AMC1 than in AMC3 which has similar corrosion resistance when evaluated by static tests [3] because the former has finer aggregates. The aggregates sizes of AMC2 are even smaller than those of AMC1 [3], which would make it more prone to loss particles and thus, less resistant. For this reason, it is considered that the corrosion index of AMC2 in Table 3 would be underestimated for due to the volumetric expansion produced by slag penetration, which should be greater than in the other materials according to cup test results [4] because the textural characteristics of AMC2. This effect could offset the volume (and area) reduction owing to material loss (wear).

On the other hand, it has been established that the number of calculation steps (CS) to reach zero-liquid condition in thermodynamic simulation of slag-refractory system is a good indicator of the material corrosion resistance (penetration and/or wear) [3]. Corrosion resistance of AMC1, AMC2 and AMC3 determined by cup test was correctly correlated with this simulation parameter. The number of CS for null amount of liquid is shown in Table 3. Taking in account these results, it is expected that AMC4 has similar wear to AMC3, which contains bauxite as alumina source and a similar quantity of MgO, as was actually found experimentally by dipping testing.

SEM image of a corroded fused alumina aggregate of AMC4 is shown in Figure 4, together with Ca, Al and Mg EDS maps. Rhomboidal particles of $MgAl_2O_4$ were found especially toward the slag. This morphology is typical when spinel had been formed from molten slag. The formation of various calcium aluminates can be inferred from the Ca and Al distribution, as has been reported extensively in other previous works [3, 8, 9]. CA and C_2A were identified in attacked aggregate and CA, CA_2 and C_3A in slag zone. In spite of CA_6 was not found in the selected EDS point, the formation of this phase as a boundary layer around of aggregate has been extensively reported [3, 6].

The equilibrium phases obtaining in the calculation steps of AMC4 material in contact with slag at same temperature of dipping test are shown in Table 4. In the first CS, liquid is the main phase, whereas a significant decrease of the liquid amount was calculated in the second step. Simulation predicted that alumina and magnesia are not present as solid phases in equilibrium, and they turned into MA spinel. Actually, spinel is a solid solution containing Fe dissolved. Other phases such as FeSi, SiC and C were obtained as minority phases in addition to those reported in Table 4.

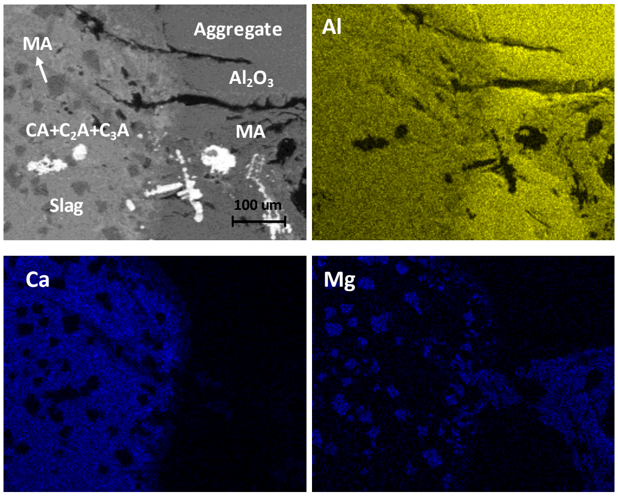

Fig. 4: SEM image of a corroded fused alumina aggregate, together with mapping (EDS) of Al, Ca, and Mg.

The presence of MA spinel has been confirmed in the refractory-slag interface. Taking into account the morphology of the crystals, they precipitated from the liquid. This agrees with the significant reduce of the liquid content in the second CS (Table 4), together with a remarkable increase of the amount of MA. Otherwise, CA_2 formation is predicted by simulation as stable thermodynamic phase firstly. According to the thermodynamic simulation, CA_2 would later react with alumina (coming from aggregates dissolution in the real system, for instance) leading to CA_6 formation. The distributions of Ca and Al are shown in Figure 4, and the previous reports in about this sort of refractories, support the hypothesis that those solids had been formed during interaction between slag and AMC4 in the dipping test. Furthermore, Al_4C_3 was not found experimentally due to this is an unstable phase which decomposes quickly under oxidant atmosphere.

Tab. 4: Composition of system (in wt.%) in each calculation step (CS).

	CS		
Phases	**1**	**2**	**3**
Liquid	88.1	34.2	0.0
$MgAl_2O_4$ (MA)	8.7	17.6	29.5
Al_4C_3	0.0	0.7	2.2
$CaAl_4O_7$ (CA_2)	0.0	46,4	56.4
$CaAl_{12}O_{19}$ (CA_6)	0.0	0.0	11.2

CONCLUSIONS

The wear of AMC bricks after dipping test has been determined by several techniques. A strong increasing of porosity due to resin pyrolysis, a partial decarburization and $MgAl_2O_4$ formation were determined as a consequence of the permanence of the refractory at high temperature (1600°C). The material wear by the slag has been calculated by two ways; the method that discounts the slag adhered to the material is a better indicator of the corrosion resistance. Nevertheless, there are some additional factors that could affect its value. Data obtained by thermodynamic simulation helped to interpret the experimental results, predicting some of the phases formed when the AMC refractory was in contact with slag. In addition, the steps calculation needed for liquid disappears as an equilibrium phase turned out a good indicator of the corrosion resistance in spite of the simulation model does not consider the material texture and microstructure effects.

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