CORROSION MECHANISM OF AMC LADLE BRICKS BY POST MORTEM STUDY AND LAB CONDITIONS

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ABSTRACT

Alumina – Magnesia - Graphite (AMC) bricks are used in the metal zone of steel ladles in Ternium Siderar steelmaking. These bricks are based on different types of alumina aggregate, carbon in graphite form and have magnesia as an additive. When heated, in situ spinel is formed which ensures sufficient expansion. This behavior closes the joints between the bricks and the slag / steel penetration is reduced.

The wear mechanism of the lining refractory bricks for steel ladle metal line corresponds to a combination of different chemical (carbon oxidation, steel and slag attack), thermal (heating and cooling cycles) and mechanical stresses. In the current work, a post mortem study of different AMC bricks suppliers was performed through optical and electronic microscopy (SEM) and EDS analysis. By using these techniques the refractory microstructural changes were evaluated.

Also, three different grades of AMC bricks are comparatively characterized and their degree of spinel formation in–situ is determined as a temperature function. Inmersion tests or "dipping test" were carried out in air atmosphere at 1600° C for 1 hour using steel and ladle slag. Corrosion mechanisms were analyzed.

As a result, the correlation between the laboratory test and the post mortem study defined the most important parameters to select AMC bricks for steel ladles.

Keywords: AMC bricks, steel ladles, wear mechanism, spinel formation.

INTRODUCTION

The aggressive operational environment of the steel ladles brings into discussion the need to better understand the main lining wear mechanisms in order to increase the ladles availability and reduce costs associated with refractory installation and maintenance [1]. The wear mechanism of the Alumina-Magnesia-Graphite (AMC) bricks used at the metal zone of ladle corresponds to a combination of different chemical, thermal and mechanical stresses.

AMC refractory is characterised by its high thermal and structural spalling resistance besides the good slag resistance at high temperature due to in-situ spinel formation [2]. This expansive reaction can close joints and densify the brick structure.

In the current work, three AMC bricks (AMC1, AMC2 and AMC3) examined from different suppliers are examined. All materials have been manufactured by the refractory industry and they are used in the metal zone of Siderar steel ladles.

The different grades of AMC bricks are comparatively characterized and their degree of spinel formation in-situ is determined. Also, a post mortem study of different AMC bricks was performed and inmersion tests or "dipping test" were carried out at 1600°C using steel and ladle slag. In both cases, the refractory microstructural changes were evaluated and the corrosion mechanisms were analyzed.

EXPERIMENTAL

The bricks characterization tests performed were: chemical composition by X ray fluorescence and weight loss at 950ºC, crystalline phases by XRD, bulk density and apparent porosity takes place according to ASTM C 830 and cold crushing strength according to ASTM C 133.

The oxidation test had been carried out at 1150ºC for 4 hours in air atmosphere.

In order to study the spinel formation, X-ray diffraction, linear changes, open porosity and mechanical properties were determined on samples coked at 1000ºC during 5 hours and subsequently fired at 1250ºC and 1450ºC during 2 hours, both under reducing conditions.

The dipping tests were carried out at 1600ºC for 1 hour, with a rotating speed of 20 rpm. A mix with 83% of low carbon steel and 17% of slag was used. Slag chemical composition is shown in Table 1 and this slag is not saturated with periclase at 1600°C. After the corrosion test, the samples wear was measured.

Tab. 1. Chemical composition of slag ladle before the treatment in the ladle furnace.

	MgO (%)	Al_2O_3 (%)	SiO_2 (%)	CaO (%)	Fe_2O_3 (%)	MnO (%)
Slag	8	36	3	49	3	1

A post mortem study of the different bricks after service was performed through chemical analysis, X – ray diffraction phase identification, cold crushing strenght, optical and electronic microscopy and EDS analysis. By using these techniques the refractory corrosion mechanisms were evaluated.

RESULTS AND DISCUSSION

Bricks characterization

Alumina-magnesia-carbon bricks under study are resin bonded and made from brown fused alumina, calcined bauxite, graphite and sintered magnesite of different grain size according to AMC quality (Table 2). The content of magnesia is 14-25% and the total carbon content is between 5,5% and 9 %. AMC 3 does not have anti-oxidant elements. On the other hand in AMC1 was identified presence of Al and Si (Table 3).

Tab. 2. Raw materials

	AMC1	AMC2	AMC3
Main material:			
- Brown fused alumina	✓	✓	✓
- Sintered magnesite	-	-	✓
Secondary material:			
- Calcined bauxite	✓	-	-
- Sintered alumina	-	✓	-
MgO grain size (mm)	0-1	0-1,5	0-5

Tab. 3. Chemical composition by FRX and crystalline phases by XRD

	AMC1	AMC2	AMC3
MgO (%)	14,0	15,0	25,0
Al_2O_3 (%)	76,0	80,0	70,0
SiO_2 (%)	6,0	2,0	3,0
Weight loss – 950ºC (%)	7,5	5,5	8,8
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	✓	✓	✓
Graphite (C)	✓	✓	✓
Aluminium (Al)	✓	✓	-
Silicon (Si)	✓	Traces	-

Table 4 shows physical and mechanical properties of AMC bricks where AMC1 presented the best results of density and apparent porosity. Those are related to the better microstructure packing. Also, after heating to 1450ºC under reducing conditions AMC1 had the same order of cold crushing strength as AMC2. This behavior could be associated with the antioxidant elements reactions.

The decarburization of AMC refractories in air is controlled by the oxygen diffusion in the open pores [3]. AMC 1 presented the lowest decarburized thickness (Table 5).

Tab. 4. Physical and mechanical properties

	AMC1	AMC2	AMC3
Bulk density (g/cm^3)	3,23	3,21	3,21
Bulk density after heating at 1150°C in reduction atmosphere (g/cm^3)	3,19	3,17	3,14
Apparent porosity (%)	2,0	2,0	2,8
Apparent porosity after heating at 1150°C in reduction atmosphere (%)	6,6	9,4	9,1
Cold crushing strength (Mpa)	59,0	97,0	41,0
Cold crushing strength after heating at 1150°C in reduction atmosphere (Mpa).	59,0	90,0	35,0
Cold crushing strength after heating at 1450°C in reduction atmosphere (Mpa).	43,0	43,0	22,0

Tab. 5. Oxidation resistance test

	AMC1	AMC2	AMC3
Decarburized thickness (mm)	8,2 	8,9 	9,7 

Spinel formation

The amount of spinel formation depends on a number of variables such as: temperature, duration of firing, amount of MgO, type of MgO and Al_2O_3 (fused or sintered), surface area of MgO and Al_2O_3/MgO ratio in the matrix [4]. The x-ray diffraction analysis of the fired bricks samples is shown in Tables 6 to 8. All bricks qualities at 1450ºC presented partial spinel formation as MgO presence was identified. Only in AMC 3 the spinel formation starts at 1000ºC.

Tab.6. Main crystalline phases by XRD

AMC 1	1000ºC	1250ºC	1450ºC
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	✓	✓	✓
Graphite (C)	✓	✓	✓
Silicon (Si)	✓	Traces	-
Spinel ($MgO.Al_2O_3$)	-	Traces	✓
Silicon carbide (SiC)	-	Traces	✓

Tab.7. Main crystalline phases by XRD

AMC 2	1000ºC	1250ºC	1450ºC
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	✓	✓	✓
Graphite (C)	✓	✓	✓
Aluminium (Al)	Traces	Traces	-
Spinel ($MgO.Al_2O_3$)	-	-	✓

Tab.8. Main crystalline phases by XRD

AMC 3	1000ºC	1250ºC	1450ºC
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	✓	✓	✓
Graphite (C)	✓	✓	✓
Spinel ($MgO.Al_2O_3$)	Traces	✓	✓

The post firing expansion due to spinel formation begins at about 1250ºC as shown in Figure 1. AMC 3 presented the minor thermal expansion in spite of the highest MgO content. Basically, the thermal expansion of AMC refractory is governed by the Al_2O_3/MgO ratio in the matrix but AMC 3 has MgO as its main aggregate.

The correlation between open porosity of the bricks as delivered and after coking and firing up to 1250ºC and 1450ºC under reducing condition is presented in Figure 2. Coking of the as delivered bricks results in an increase of the porosity as well as after firing at 1250ºC and 1450ºC. AMC 1 and AMC 2 presented lower porosity at 1450ºC as regards 1250ºC. At higher firing temperature, the sintering reaction and new phases formation are promoted in the matrix structure.

The changes in strength during heating-up give information about brick structure evolution, sintering phenomena and abrasion behavior in service. In Figure 3, cold crushing strength of the bricks after firing under reducing conditions is presented. The strength of AMC2 and AMC 3 decreases as the firing temperature increases. However, AMC2 presented strength recuperation at 1450ºC.

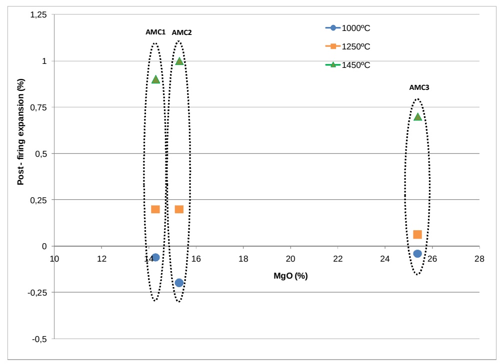

Fig. 1 Relationships between post – firing expansion and MgO content of the AMC bricks under different firing conditions.

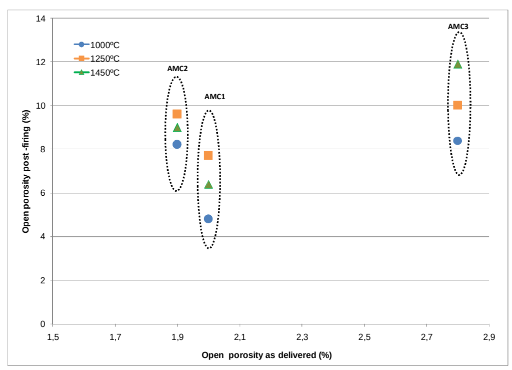

Fig. 2. Relationships between open porosity as delivered and after firing under reducing conditions.

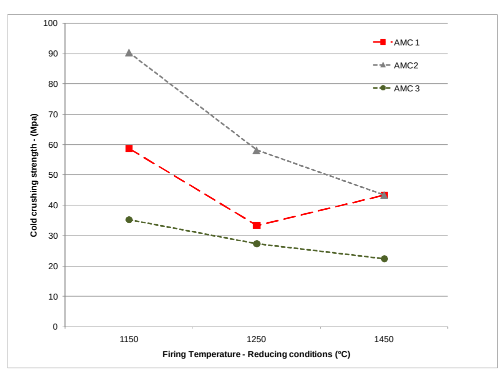

Fig. 3. Cold crushing strength evolution with increasing firing temperature under reducing conditions.

Corrosion test.

In many cases, both in practice and in laboratory tests brick erosion is observed along three phases line slag/steel/refractory. This can be explained by Marangoni convetion. The refractory reacts with both the slag and the steel. The carbon dissolution into the liquid steel may be hindered by the oxide and, viceversa, the oxide dissolution into the slag may be hindered by the graphite [5].

Each sample's aspect after the dipping test and the cross section profile is shown in Figure 4. The brick wear was determined through the sample dimension variations (Table 9). The three bricks under the same test conditions presented different behaviour against the action of slag and steel and own interactions:

AMC 1 presented SiC formation and about 80% spinel development (Table 10). Brown fused alumina corrosion by calcium oxide was identified with calcium aluminate formation. Also, the slag interacts with the brick matrix and gehlenite is formed. The wear rate was 2,2 mm/h.

A completed spinel formation was observed in AMC 2 and passive corrosion of alumina grains by calcium oxide and gehlenite formation were identified. The wear rate was 1,9 mm/h.

AMC 3 presented partial spinel formation and alumina corrosion by calcium oxide. The wear rate was 2,6 mm/h.

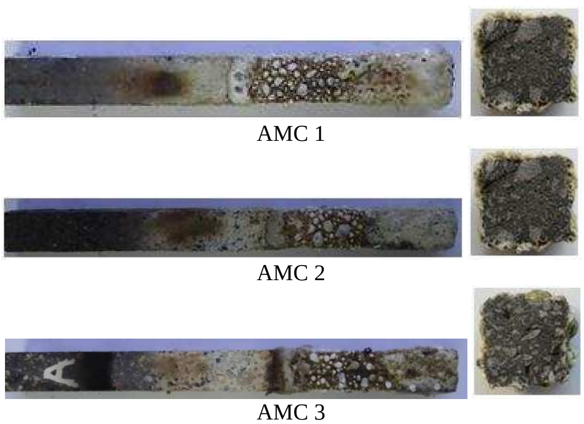

Fig.4. Sample aspect after the dipping test

Tab. 9. Samples average wear

Corrosion test	AMC1	AMC2	AMC3
General wear (%/h)	11	10	13
Cross section wear (%/h)	15	20	22

Tab.10. Main crystalline phases by XRD

Corrosion test	AMC1	AMC2	AMC3
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	✓	Traces	✓
Graphite (C)	✓	✓	✓
Silicon carbide (SiC)	✓	-	-
Spinel ($MgO.Al_2O_3$)	✓	✓	✓
Calcium aluminate ($CaAl_2O_4$)	✓	✓	✓
Calcium aluminate ($CaAl_{12}O_{19}$)	-	✓	-
Gehlenite ($Ca_2Al_2SiO_7$)	Traces	Traces	-

Post mortem study.

The internal post mortem macroestructural aspects of the three bricks used in the metal zone of steel ladles are shown in Figure 5. The slag thickness varies between 0,5 and 2 mm. Slag penetration and steel infiltration at different distance from de hot face are observed. Parallel cracks to the hot face and some cracks pass through the entire width of the brick that have caused the different loss off thickness according to AMC types. Also perpendicular cracks that cross all the brick thickness are observed in AMC1 and AMC 2.

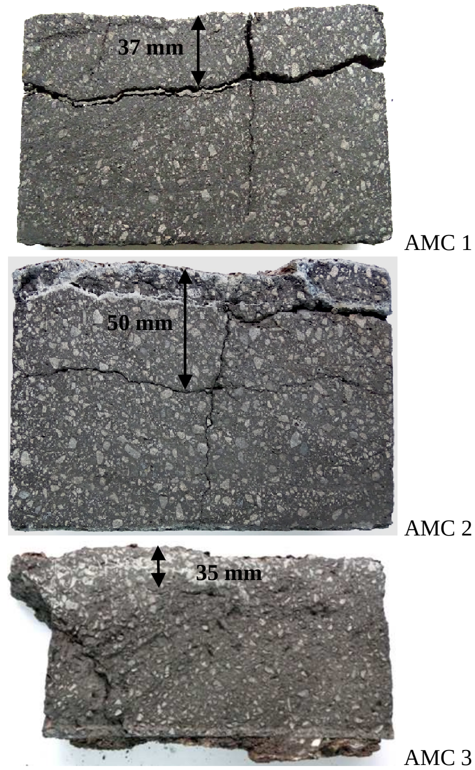

Fig. 5. Post mortem AMC bricks used in the metal zone of steel ladles.

Density, apparent porosity, chemical analysis and crystalline phases in hot and cold face of the post mortem bricks are shown in Tables 11 and 12. Complete spinel formation were identified in AMC1 and AMC2 hot face bricks. The lowest density of AMC3 is caused by the lack of structural integrity between the matrix and the different main aggregate.

Tab. 11. Different properties in post mortem bricks

Hot face	AMC1	AMC2	AMC3
Bulk density (g/cm^3)	3,16	3,05	2,91
Apparent porosity (%)	5,1	6,2	10,6
MgO (%)	10,0	14,0	21,0
Al_2O_3 (%)	82,0	80,0	67,0
SiO_2 (%)	5,0	3,0	2,0
Weight loss – 950ºC (%)	5,6	5,2	4,0
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	-	-	✓
Graphite (C)	✓	✓	✓
Spinel ($MgO.Al_2O_3$)	✓	✓	✓
Silicon carbide (SiC)	✓	-	-
Calcium aluminate ($CaAl_{12}O_{19}$)	-	✓	✓

Tab. 12. Different properties in post mortem bricks

Cold face	AMC1	AMC2	AMC3
Bulk density (g/cm^3)	3,15	3,06	2,95
Apparent porosity (%)	3,6	4,2	12,5
Cold crushing strength (Mpa)	70,0	66,0	18,0
MgO (%)	10,0	15,0	25,0
Al_2O_3 (%)	82,0	78,0	68,0
SiO_2 (%)	5,0	3,0	4,0
Weight loss – 950ºC (%)	5,9	5,9	6,2
Corundum (Al_2O_3)	✓	✓	✓
Periclase (MgO)	Traces	✓	✓
Graphite (C)	✓	✓	✓
Spinel ($MgO.Al_2O_3$)	✓	✓	✓
Silicon carbide (SiC)	✓	-	-

Usually the three post mortem bricks under study presented the same chemical wear: graphite oxidation, slag penetration through the decarburized matrix which produced alumina grains being detached from the brick structure (erosion) and alumina grains corrosion (Figure 6). In the presence of slag containing calcium oxide, this element diffuses through the alumina grain making it easier to form phases such as calcium aluminates (CA_2 y CA_6). These new phases decrease alumina grain refractoriness and also delay the wear speed of the refractory material. This mechanism is known as alumina grain indirect dissolution and is shown in Figure 7.

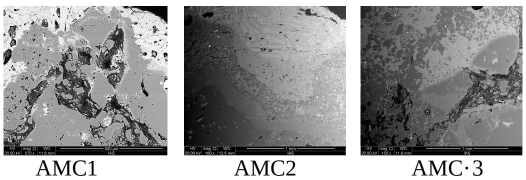

Fig. 6. Phases distribution in bricks hot face.

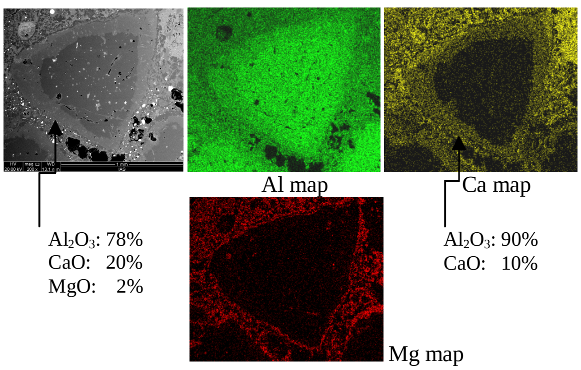

Fig.7. EDS analysis and elements distribution in alumina grain - AMC2 brick

The spinel formation has been different in each post mortem brick. In the interface between the slag and the brick AMC 1 matrix a spinel barrier was observed. This barrier is composed of spinel cristals with different Al_2O_3/MgO ratio based on the thermal profile inside the brick and the particles size. This is a refractory lining mechanism protection as is shown in Figure 8.

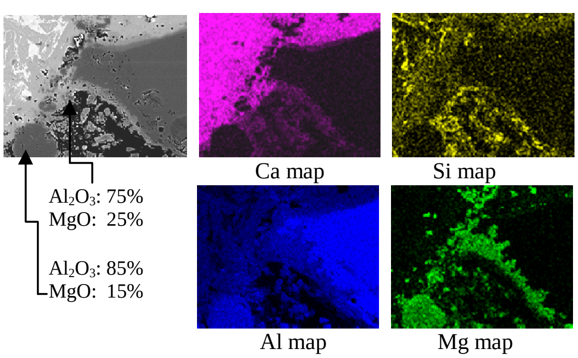

Fig. 8. EDS analysis and elements distribution in AMC1 brick hot face.

The magnesium aluminate spinel formation mechanism was identified inside brick AMC 2, where a spinel layer is formed on the surface of the alumina grains (Figure 9).

The interface between the slag and AMC3 brick is shown in Figure 10. Spinel layer is formed on the surface of the MgO grain. Also the slag penetrates into the intragranular silicate bond of the sintered MgO grains. This interaction promotes low temperature phases formation (softening temperature of 1335°C) and facilitates the crystal loosening.

All the mechanisms described promote the structural spalling of the bricks.

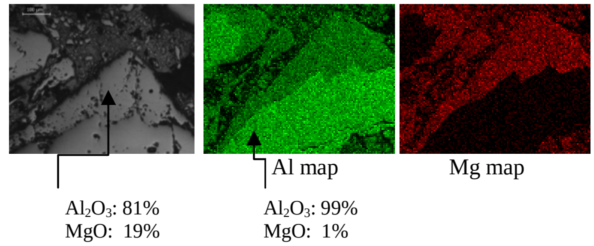

Fig. 9. EDS analysis and elements distribution in AMC2 brick

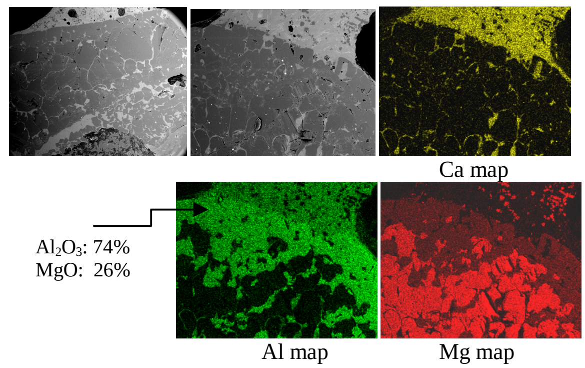

Fig. 10. Phases and elements distribution in AMC3 brick hot face.

CONCLUSIONS

The wear mechanisms of Al_2O_3-MgO-C bricks used in the metal zone of steel ladles corresponds to a combination of different chemical (carbon oxidation, steel and slag attack), thermal and mechanical stresses. These stresses promoted cracks generation and slag/steel penetration.

A pattern of parallel and perpendicular cracks from the hot face are presented in the post mortem bricks. These cracks are associated to thermal spalling due to different heating and cooling cycles that generated internal thermal gradients in the lining refractory. The thickness loss varies between 35 mm and 50 mm according to AMC brick quality.

Also the main aggregates types and the Al_3O_2/MgO ratio, the bricks behavior in service will depend on the apparent porosity, the thermal expansion and the spinel formation, properties that have direct influence on corrosion and oxidation mechanisms.

The laboratory test and the post mortem study are important tools to select AMC bricks for steel ladles

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