



Deliverable D 2.2 Report about fundamental corrosion mechanisms and influencing factors

Document type	Deliverable D 2.2
Document Version / Status	2.2
Primary Authors	Jacek Szczerba, jszczerb@agh.edu.pl, AGH, Ryszard Prorok rprorok@agh.edu.pl, AGH
Distribution Level	PU (Public)
Project Acronym	ATHOR
Project Title	Advanced THermomechanical multiscale mOdelling of Refractory linings
Grant Agreement Number	764987
Project Website	www.etn-athor.eu
Project Coordinator	Marc Huger, <u>marc.huger@unilim.fr,</u> UNILIM
	Jacek Szczerba, <u>iszczerb@agh.edu.pl</u> , AGH
	Ryszard Prorok <u>rprorok@agh.edu.pl</u> , AGH
Document Contributors	Camille Reynaert, <u>reynaert@agh.edu.pl</u> , AGH
	Sina Darban, <u>darban@agh.edu.pl</u> , AGH
	Glyn Derrick, <u>glyn.derrick@unilim.fr</u> , UNILIM

History of Changes

Version	Date	Author (Organization)	Change	Page
1.0	03/12/2020	Camille Reynaert(AGH), Sina Darban(AGH) and Glyn Derrick(UNILIM)	Sections of text added, general formatting	All
1.1		Camille Reynaert(AGH),	Corrections	
1.2		Sina Darban(AGH)	Corrections	
1.3	06/04/2021	Camille Reynaert(AGH), Sina Darban(AGH), Glyn Derrick (UNILIM)	Corrections combined, further check	All
1.4	05/05/2021	Sina Darban(AGH), Glyn Derrick (UNILIM)	Corrections, further check	2-12
1.5	06/05/2021	Camille Reynaert(AGH)	Minor corrections	22
2.0	09/05/2021	Camille Reynaert(AGH), Sina Darban(AGH)	Reorganization and modification of the content	All
2.1	10/05/2021	Camille Reynaert(AGH), Sina Darban(AGH)	Reorganization and modification of the content	All
~	12/05/2021	Marc Huger (UNILIM)	Final corrections	A11
۲.۲		and Glyn Derrick(UNILIM)		



European





1 INTRODUCTION	2
2 TYPES OF SLAGS EMPLOYED	3
3 CORROSION OF ALUMINA-SPINEL BRICK	3
3.1 Alumina Spinel brick	3
3.2 Experimental procedures	3
3.3 Results	4
3.3.1 Corrosion using the standard slag	4
3.3.2 Corrosion using 10SiO ₂ addition slag	6
3.4 Discussion	8
3.5 Alumina-spinel brick conclusion	9
4 CORROSION OF MGO-C	9
4.1 Magnesia-carbon brick	10
4.2 Experimental procedures	10
4.2.1 Contact test	10
4.2.2 Dipping test	10
4.2.3 Factsage	10
4.3 Results	10
4.3.1 Sample corroded using the contact test	10
4.3.2 Sample from the dipping test	13
4.4 Discussion	14
4.4.1 Oxidation of carbon and formation of a MgO layer in the sample	14
4.4.2 Dissolution of MgC	13 17
	17
5 CONCLUSIONS	17
6 REFERENCES	18

1 Introduction

Refractory materials are used in high-temperature applications such as the production of steel, glass, and cement. Today, the challenge is to optimize the economic and environmental aspects of refractory materials [1,2]. The degradation process of refractory materials, and the related parameters, play an important role. The chemical and mechanical wear consist of complex reactions and processes called "corrosion". The corrosive mediums, gas, molten metals, molten glasses, or molten salts (slag) result in the loss of thickness and mass; therefore, refractory materials are replaced repeatedly [3]. The objective of this deliverable is to identify fundamental corrosion mechanisms of refractory linings used in the steel ladle. Therefore, selected refractories (Al₂O₃-Sp and MgO-C) will be corroded by specified slags. The samples will be investigated by (a) chemical analysis (XRF) (b) phase composition (XRD) and (c) SEM/EDS for chemical analysis in micro areas. The basic corrosion mechanisms of the two refractory materials, alumina-spinel (Al₂O₃-Sp) and magnesia-carbon (MgO-C), will be detailed. These materials have been selected due to their use in the steel ladle: the alumina spinel bricks are used for the side wall and the MgO-C are used for the slag line.

This deliverable will discuss the corrosion of alumina-spinel and magnesia-carbon bricks. The composition of the slags employed will be given in the first section. This will be followed by sections dedicated to the corrosion of alumina-spinel and magnesia carbon bricks. These two sections will be divided in several subsections: the material employed, the experiments performed, the results, their analysis and a conclusion.







2 Types of slags employed

Experiments performed in this work used three different types of slag. The first one is a synthetic slag, used without modification, which served as a reference and is called standard slag. The second on is based on the previous one with the addition of SiO_2 to increase the SiO_2 to 10 wt.% in the slag and is called $10SiO_2$. The third one is also based on the standard slag with the addition of MnO to reach 10 wt.% of MnO and is called 10MnO slag.

The composition of the synthetic slag was modified for two main reasons. Firstly, future steel grade slag will potentially evolve in these directions, in particular for the addition of MnO. The second reason is the lack of literature on the impact on the addition of MnO in calcium aluminate slag on the corrosion of MgO-C brick and on the impact on SiO₂ on the corrosion of alumina-spinel. The compositions of the three types of slag are shown in Table 1.

Compounds	Concentration (wt. %)		
	Standard	10SiO ₂	10MnO
Al ₂ O ₃	41.4	38.9	37.3
CaO	51.8	48.6	46.6
SiO ₂	4.1	10.0	3.7
MgO	0.6	0.6	0.6
Fe ₂ O ₃	2.1	1.9	1.9
MnO	0.0	0.0	10.0
Basicity (C/S)	12.6	4.9	12.6

Table 1: Slag composition used in the corrosion test.

3 Corrosion of alumina-spinel brick

3.1 Alumina Spinel brick

Alumina-spinel bricks degrade due to two main mechanisms, firstly, when they come into contact with slag during the steel pouring phase of steel production, and secondly, during the healing (repair) of the steel ladle. At this point, the steel ladle is upside down and the slag comes back into contact with the ladle walls. To perform the experiments, alumina-spinel brick, described in Deliverable 2.1, has been used. Its composition is given in Table 2.

Table 2: Chemical composition of the alumina-spinel brick used for corrosion test.

Compounds	Concentration (wt.%)
AI_2O_3	87.68
MgO	5.82
SiO ₂	4.82
Na ₂ O	0.45
Fe ₂ O ₃	0.25
CaO	0.17
P_2O_5	0.03
Others	0.78

3.2 Experimental procedures

To prepare the alumina-spinel samples for the corrosion test, first the alumina-spinel brick was cut and drilled into a circular shape (d=25 mm, h=25 mm), then dried for 24h at 150 °C. Next, the sample was incased in slag using a hydraulic press as shown in Figure 1 then positioned in a graphite crucible. The corrosion test was conducted with the standard slag and the modified $10SiO_2$ slag, at 1350 °C for 10 and 30 hours.











Figure 1: Schema of refractory sample pressed with slag pellet.

Table 3 shows the history of the corrosion tests. After corrosion, two different zones of the sample were selected, for phase composition analysis and microstructure investigations.

The two zones selected were:

1) the edge part, in contact with the slag (interface zone)

2) the core part, the internal part of the refractory sample.

Sample name	Slag type	Temperature (°C)	Dwell time (h)	Atmosphere
Al-1-1	Standard	1350	10	Reducing
Al-1-2	Standard	1350	30	Reducing
Al-2-1	10SiO ₂	1350	10	Reducing
Al-2-2	10SiO ₂	1350	30	Reducing

Table 3: Heat-treatment history of corrosion test.

3.3 **Results**

3.3.1 Corrosion using the standard slag

3.3.1.1 Phase composition

European

Figure 2(a) shows the phase composition analysis of the edge of Al-1-1 (1350 °C - 10h) and Al-1-2 (1350 °C - 30h) samples, respectively. Mayenite (C₁₂A₇) peaks are present in both XRD patterns (AI-1-1 and AI-1-2) which is due to remnants of slag on the edge parts after cooling, due to partial slag's infiltration. By prolonging the dwell time to 30h, the intensity of the mayenite (C₁₂A₇) peaks decreased, as a result of higher infiltration and less remained slag.

Furthermore, Figure 2(a) shows the presence of calcium aluminates like calcium monoaluminate (CA), calcium dialuminate (CA₂) and calcium hexaluminate (CA₆). This indicates that, not only did the slag infiltrate into the alumina-spinel sample, but that it also reacted chemically, leading to the formation of some minor new phases in the edge parts. Peaks, belonging to the calcium monoaluminate (CA) and calcium dialuminate (CA₂) phases, can be observed forming after 10h and those associated with a calcium hexaluminate phase (CA₆), are present after 30h. It can therefore be inferred, due to the observed differences between 10 and 30h, that the slag could not reach the equilibrium condition even after 10h.

Figure 2(b) shows the XRD pattern from the core region of Al-1-1 (1350 °C - 10h) and Al-1-2 (1350 °C - 30h), respectively. Corundum (Al₂O₃), spinel (MgAl₂O₄), beta-alumina (Na₂Al₂₂O₃₄), and silica (SiO₂) phases are present in both samples and there







is no peak of mayenite, calcium aluminates or other new phases. Therefore, it can be concluded that there was no reaction between the slag and the alumina-spinel refractory sample in the core part of the corroded samples after 10 and 30h.



Figure 2: XRD patterns of corroded Al-1-1 and Al-1-2 alumina-spinel samples with standard slag (a) edge part of the samples, and (b) core part of the sample.

3.3.1.2 Microstructure

The overview SEM image of the edge and core part of the Al-1-1 (1350 °C - 10h) is shown in Figure 3(a) and (b), respectively. Figure 3(a) shows that mayenite ($C_{12}A_7$), calcium monoaluminate (CA) and calcium dialuminate (CA₂) are observed on the edge part of the Al-1-1 sample. Although the slag has reacted with alumina grains, there are still fine spinel grains which remain unreacted in the matrix phase. Figure 3(b) shows the SEM overview of the core part of Al-1-1 sample, some calcium monoaluminate (CA) is observed in the matrix and calcium dialuminate (CA₂) around alumina grains. Some unreacted spinel phase was also observed as fine grains in the matrix.









a)

b)

Figure 3: SEM micrographs of Al-1-1 sample corroded at 1350 °C, for 10h, showing phases present in a) the edge of the sample, and b) the core of the sample.

Figure 4(a) and (b) show the SEM micrographs of the edge and core part of Al-1-2 sample, respectively. Mayneite ($C_{12}A_7$), calcium dialuminate (CA_2), spinel, and gehlenite (C_2AS) are present in the edge and core parts of the sample. This result confirms the phase composition analysis and shows that the remaining slag (mayneite) on the right side of the Figure 4(a) and gehlenite (C_2AS) among fine spinel grains in the matrix. Moreover, there are some accumulated calcium dialuminate (CA_2) from the reaction of alumina (from refractory side) and calcium dioxide (from slag side).



a)



b)

Figure 4: SEM micrographs of Al-1-2 sample, 1350 °C, 30h showing phases present in a) the edge of the sample, and b) the core of the sample.

3.3.2 Corrosion using 10SiO₂ addition slag

3.3.2.1 Phase composition

Figure 5(a) shows the edge part's XRD pattern of Al-2-1 (1350 °C - 10h) and Al-2-2 (1350 °C - 30h) corroded by slag modified with silica (10SiO₂). After 10h, the mayenite ($C_{12}A_7$), CA, and CA₂ are present. Additionally, a small amount of calcium alumina silicate (gehlenite (C_2AS)) is present. By extending the time to 30h, the amount of the gehlenite phase is increased, and the CA₆ phase peaks appear in the XRD pattern. Fig.5(b) shows the core part's XRD pattern of Al-2-1 (1350 °C - 10h) and Al-2-2 (1350 °C - 30h) corroded by 10SiO₂. Gehlenite (C_2AS), which was not observed after 10 hours of corrosion with the standard slag, is







present in the XRD pattern after 10h of corrosion with $10SiO_2$. Though, after 30h, the gehlenite phase and calcium aluminate phases were also observed in the core. This may show that silicon dioxide might facilitate slag penetration. Also, the peak intensity in 7.85° has increased due to the overlapping of calcium hexaluminate (CA₆) and beta-alumina (Na₂Al₂₂O₃₄) peaks at this point.



(b)



3.3.2.2 Microstructure

Figure 6(a) and (b) illustrate the overview SEM pictures of the edge part of Al-2-1 sample corroded with $10SiO_2$ after 10h. The present calcium aluminate phases are calcium monoaluminate (CA), calcium dialuminate (CA₂), and calcium hexaluminate (CA₆), as well as calcium alumina silicate (C₂AS). The difference between the formed phases in the microstructure of corroded samples with standard slag (Al-1-1 and Al-1-2) and $10SiO_2$ slag (Al-2-1 and Al-2-2) is the presence of calcium hexa-aluminate (CA₆) alongside coarse alumina grains at 1350 °C, after 10h corrosion, as well as presence of calcium aluminium silicate. This could point out that silicon dioxide addition to the slag composition may accelerate the reactions between Ca⁺² and Al⁺³ within the microstructure.

Figure 7(a) and (b) shows an SEM overview image of the edge and core parts respectively, of the Al-2-2 sample, corroded by $10SiO_2$ slag after 30h. It seems that the matrix is fully corroded, and there is no distinguishable barrier between corroded and un-7 / 18

European Commission





corroded areas which was present in Figure 6. The sample microstructure is full of calcium aluminate phases like CA, CA₂, and CA₆. The noticeable difference that should be mentioned about this sample is that the edge parts were completely corroded, and the centre of the sample was corroded and changed considerably. According to Jia et al. [3], calcium aluminum silicate called gehlenite (C₂AS) has a pore self-forming behaviour which happens between 900-1450 °C. This characteristic may encourage abnormal expansion during the sintering process of gehlenite. Hence, the higher slag impregnation may relate to this pore self-forming behaviour of the gehlenite (CA₂S) phase inducing further micro-cracking in the local infiltrated microstructure.



(a)

(b)

Figure 6: SEM micrographs of corroded alumina-spinel - 10SiO₂ slag (1350 °C - 10h) (a) edge part and (b) core part of the sample.



(a)

(b)

Figure 7: SEM micrographs of corroded alumina-spinel - 10SiO₂ slag (1350 °C - 30h) (a) edge part of the sample, and, (b) core part of the sample.

3.4 Discussion

The corrosion test of the alumina-spinel sample was conducted in a reducing atmosphere. The sample was corroded with standard and $10SiO_2$ slags at 1350 °C for 10 and 30 hours. The sample was then divided into two distinct parts to check the phase degradation: the edge part and core part of the sample. Referring to the deliverable 2.1, the XRD and SEM investigations of un-corroded alumina-spinel brick showed that the alumina-spinel main components are alumina (Al₂O₃) and alumina-rich spinel (Mg_{7.5}Al₁₆O₃₄). At 1350 °C, after 10h of corrosion test, both slags (standard and $10SiO_2$) had minor infiltration into the microstructure. By increasing the corrosion time to 30h, the level of diffusion of the standard slag stayed constant, however, $10SiO_2$ showed higher infiltration in the microstructure, and the alumina-spinel brick had been impregnated by the $10SiO_2$ slag. However, it should be considered that by extending the time from 10h to 30h, the reactions between calcium oxide (CaO) from the slag side and alumina (Al₂O₃) from refractory side, can continue leading to the formation of hexaluminate (CA₆). According to









the Braulio et al [4] the corrosion process begins with the infiltration of CaO and subsequent reactions with Al₂O₃ according to the Equ. 1:

$$CaO + Al_2O_3 \rightarrow CaO.Al_2O_3 + Al_2O_3 \rightarrow CaO.2Al_2O_3 + 4Al_2O_3 \rightarrow CaO.6Al_2O_3$$
Equ. 1

Furthermore, SiO₂ can react with CA₆ to form the calcium aluminium silicate (CA₂S) according to Equ. 2.

$$SiO_2 + CaO.6AI_2O_3 \rightarrow 2CaO.AI_2O_3.SiO_2 \text{ or } CaO.AI_2O_3.SiO_2$$
 Equ. 2

Calcium aluminates are formed on the alumina grains enhancing the corrosion resistance of alumina-spinel brick and preventing alumina grains from dissolution and further corrosion. Figure 8 shows the binary phase diagram of alumina (Al_2O_3) and calcium oxide (CaO). According to this binary diagram, calcium aluminate layer formation is ($C_{12}A_7+CA$), ($CA+CA_2$), and (CA_2+CA_6) and after that again ($CA_6+Al_2O_3$). In other words, by increasing temperature, and reaching CA₆ formation, the reaction between CaO and Al_2O_3 is completed and no new calcium aluminate will be produced. CaO, and SiO₂ components in the slag accelerate this reaction. The CA₆ phase is the final phase of reacted CA and CA₂ with Al_2O_3 , which induces local densification. This local densification protects the coarse alumina grains from further infiltration by the slag [5–10].



Figure 8: Binary phase diagram of Al₂O₃-CaO.

3.5 Alumina-spinel brick conclusion

This section delivers an investigation of alumina-spinel refractory corroded by standard slag and $10SiO_2$ slag. For this purpose, laboratory corrosion tests at 1350 °C in a reducing atmosphere were performed. Samples were principally studied by microstructural techniques (SEM with energy-dispersive X-ray analysis). The results showed that after 10h of corrosion test, standard and $10SiO_2$ slags both resulted in minor infiltration. The infiltration of reactants, specifically Ca^{2+} , into the refractory material leads to the formation of calcium aluminate phases CA, CA₂ and CA₆. Regarding the corrosion with $10SiO_2$ slag, gehlenite ($Ca_2Al_2SiO_7$) was observed both in the XRD pattern and SEM micrographs. This indicates that an additional amount of silicon dioxide in the system leads to the formation of a low melting phase (called gehlenite). An increase in the reactions between the Al⁺³ and Ca⁺² ions is thus possible, in the interaction area, resulting in calcium hexa-aluminate (CA₆) formation after only 10h of corrosion. Moreover, according to the SEM overview images, by extending time to 30h, the $10SiO_2$ slag showed a higher level of infiltration in the microstructure. Overall, standard and $10SiO_2$ slags both infiltrated into the microstructure, but the results showed that by extending the corrosion test dwell time a higher presence of SiO₂ in the slag composition could decrease alumina-spinel's corrosion resistance and increasing slag's infiltration.

4 Corrosion of MgO-C

Magnesia carbon bricks are typical refractory bricks used in the slag line of steel ladle. They exhibit a good resistance to corrosion thanks to the non-wetting properties of the carbon matrix, however, they are still degraded by the slag in the ladle.

The corrosion mechanisms of MgO-C will be described here based on a study of the influence of slag composition on the corrosion of the brick. This study will be use as a support to describe the fundamental corrosion mechanisms of MgO-C and how the slag composition influences them.

9/18



European Eu Commission for





4.1 Magnesia-carbon brick

To perform the experiments, a commercial resin bonded magnesia-carbon brick (MgO-C brick), described in more details in Deliverable 2.1, has been used. The composition of this brick is given in Table 4.

Compounds		Concentration (wt. %)
Mineral phases 90 wt. %	MgO	96.9
	Al ₂ O ₃	0.2
	SiO ₂	0.5
	CaO	1.9
	Fe ₂ O ₃	0.3
Matrix 10 wt. %	С	100

Table 4: Composition of the MgO-C brick used for the corrosion test.

4.2 Experimental procedures

4.2.1 Contact test

The first corrosion test, called contact test, consists of putting a pellet of pressed slag onto a piece of brick and heat treating the ensemble. Its purpose is to determine what happens when the amount of slag is low compared to the amount of brick. Pellets of slags were prepared and small pieces of brick were cut out of the commercial brick. A pellet of slag was put onto a piece of brick and each ensemble was put on a carbon bed in a close carbon crucible to generate a reducing atmosphere. The sample were heat treated for 1h at 1450 °C and 1550 °C with a heating rate of 5 °C/min and with a natural cooling. After the heat treatment, the samples were cut in two, the sections were polished with diamond paste, and then the brick/slag interface was observed with an SEM coupled with EDS (SEM FEI NovaNanoSem 200 and LEO Zeiss Type 440i- Oxford Link Isis, germanium detector).

4.2.2 Dipping test

The second test, called dipping test, consists of dipping MgO-C bar in a large quantity of molten slag. The goal is to determine what happen when the amount of slag is large compared to the amount of brick. To perform the test, the 2kg of slag was first melted under air in an open vacuum chamber. When the slag was molten, the chamber was closed, evacuated and filled with argon. Then 25 x 25 x 125 mm prismatic bars were lower down and kept just above the slag for 10 minutes to avoid thermal shock during the dipping. The bars were dipped into and kept in the melted slag for 1h at 1550 °C and 1600 °C. After 1 h, the bars were removed from the slag and allowed to cool down naturally in air. After cooling, they were cut in two, the sections were polished with diamond paste, and observed with an SEM coupled with EDS (SEM FEI NovaNanoSem 200 and LEO Zeiss Type 440i-Oxford Link Isis, germanium detector).

4.2.3 Factsage

In order to facilitate the interpretation of the results, some thermochemical calculations were managed to estimate slag viscosity from its composition and predict potential phases that could be obtained from the reaction between the slag and the brick. These calculations were performed using the commercial software *Factsage 7.3*. Two modules were used: Viscosity and Equilib. The module viscosity was used for the properties of the melts. The module Equilib was used, with the databased FactPS, FToxid and FSsteel, to obtain the potential phases.

4.3 Results

In fact, the microstructures of the corroded samples have been already described in Deliverable 2.1. Nevertheless, to facilitate the reading of the current deliverable 2.2, the microstructure of the corroded samples will be briefly revisited.

4.3.1 Sample corroded using the contact test

In Figure 9, pitting, in the shape in the MgO grains (indicated by orange lines), can be observed. Looking more locally at the interface between the MgO grains and the slag, the surface of the MgO grains is irregular, as can be seen in Figure 10a) and Figure 11a), b) and c). Looking at the slag side, the formation of many MgO dendrites can be seen, which suggests that the amount of MgO in the slag has increased. All of these observations suggest that the MgO has been dissolved by the different types of slag.











Figure 9: Pitting (indicated in orange) in the shape of MgO grains at the interface between MgO-C brick and slag.

Moreover, metallic droplets are present on the surface of the bricks. They are composed mainly of Fe for the samples corroded by the standard or the $10SiO_2$ slag, and Fe and Mn for the samples corroded using the 10MnO slag. An MgO layer is observed on the surface of the sample corroded using the 10MnO slag at 1450 °C and 1550 °C, as shown in Figure 10c) and d) and Figure 11c) and d). The carbon matrix has also been slightly oxidized as indicated by the decarburized area shown in Figure 11. These observations, combined together, indicate a carbothermic reaction between the carbon matrix and MgO.









Figure 10: Micrographs of the MgO-C bricks after corrosion with the contact test in a reducing atmosphere at 1450 °C using a) standard slag, b) 10SiO₂ slag, c) 10 MnO slag and d) a zoom of the magnesia layer (10MnO slag).

The samples corroded at 1450 °C and 1550 °C appear mostly similar but the sample prepared at 1550 °C appears to have been corroded to a greater extent as more slag can be observed behind the slag/MgO interface, as shown in Figure 11.













b)

d)

Figure 11: Micrographs of the MgO-C brick after corrosion with the contact test in a reducing atmosphere at 1550 °C using a) standard slag, b) 10SiO₂ slag, c) 10 MnO slag and d) a zoom of the magnesia layer (10MnO slag).

4.3.2 Sample from the dipping test

The second test performed was the dipping test. First, the corrosion of the samples using the standard and the 10MnO slag was low at both temperatures, no difference in the width could be measured. For the samples corroded using the $10SiO_2$ slag, the corrosion was low at 1550 °C and higher at 1600 °C: the sample lost about a third of its width, as is observed in Figure 12.





European European European For







Figure 12: Pictures of the corroded MgO-C samples obtained with the dipping test under an argon atmosphere at 1550 °C and 1600 °C using the 3 slags.

The microstructure of the samples from the dipping test observed by SEM are mostly similar to those observed in the previous test. MgO is partially dissolved into the slag as show in Figure 13 Metallic particles of Fe for the sample corroded using the standard and 10SiO₂ slags and Fe and Mn for the samples corroded by the 10MnO slag are present at the surface of all the bricks. A small amount of carbon is oxidized and replace by the slag. The only difference is the absence of the MgO layer in all the samples.



Figure 13: Micrographs of MgO-C samples obtained after the dipping test under argon atmosphere at 1600 °C for 1h using a) standard slag, b) 10SiO₂ slag and c) 10MnO slag.

4.4 Discussion

Two mechanisms are mainly responsible for the corrosion of MgO-C bricks: the oxidation of the carbon matrix and the dissolution of magnesia. How they take place and how the composition of slag impact them will be described below.

4.4.1 Oxidation of carbon and formation of a MgO layer in the sample

The first phenomenon responsible for the corrosion of the MgO-C brick is the oxidation of the carbon from the matrix. The oxidation occurs at the interface of the sample, as indicated by the decarburized area, the presence of metallic droplets of Fe or Fe-Mn at the brick/slag interface observed in Figure 10, Figure 11 and Figure 13 and the formation of an MgO layer in the sample corroded



European





$$C_{(s)} + MgO_{(s)} \leftrightarrow CO_{(g)} + Mg_{(g)}$$
 Equ. 3

It leads to the removal of the C in the matrix and the formation of a Mg gas. The Mg gas subsequently reacts with easily reducible elements (according to Ellingham diagram) from the slag: FeO and MnO, according to Equ. 4 and Equ. 5. This results in the formation of solid MgO and metallic Fe and Mn droplets at the interfaces [14-17].

$$3 Mg_{(g)} + Fe_2 O_{3(slag)} \leftrightarrow 3 MgO_{(s)} + 2 Fe_{(l)}$$
 Equ. 4

$$Mg_{(g)} + MnO_{(slag)} \leftrightarrow MgO_{(s)} + Mn_{(l)}$$
 Equ. 5

While the metallic droplets are present in all the samples, the layer of MgO was only observed in the samples from the pellet test corroded using the 10MnO slag. The presence of the MgO layer in these samples has two possible explanations: more Mg gas can form, and thus be oxidized, in these samples and/or the dissolution of MgO is lower in the 10MnO slag. This latter mechanism will be examined in the following subsection.

The amount of Mg gas that can be oxidized when the amount of MnO increases in the slag was examined qualitatively by performing thermochemical calculations with Factsage. The Factsage calculations were performed with the Equilib module by inputting 20 g of Mg gas and 100 g of slag with increasing MnO content. The results are presented in Figure 14.





The quantity of Mg gas that can be re-oxidized by the slag and form the MgO layer, increases when the quantity of MnO in the slag increases. This is suggested by the parallel increase of MgO, Mn and Fe in **Error! Reference source not found.**a). Indeed, Equ. 4 and Equ. 5 indicate that metallic Fe and Mn form as the result of the oxidation of Mg gas by the slag. Moreover, Figure 14b) indicates that the quantity of MgO increases as the quantity of Mg gas decreases, which again suggests that increasing the amount of MnO in the slag leads to greater MgO layer formation. However, if the formation of the MgO layer is the only phenomena taking place, the MgO layer should also be observed in the sample from the dipping test. Hence another degradation phenomenon is taking place in the sample, the dissolution of MgO in the slag.

4.4.2 Dissolution of MgO.

In all samples, MgO is dissolved, as indicated by the pitting observed in Figure 9, as well as the irregular surface of the MgO grains and the presence of MgO dendrites in the slag in Figure 10, Figure 11 and Figure 13. The dissolution of MgO is diffusion controlled [11,18,19], hence the dissolution of MgO in the slag can be described by the Noyes-Nernst's equation Equ. 6 and Equ. 7 for static diffusion (the experiments performed were static tests) [11].

$$V \frac{dC}{dt} = jA = AD(C_{sat} - C_{slag})/\delta^*$$
 Equ. 6
$$D = (kT)/(6\pi r\eta),$$
 Equ. 7

with

15/18

European Commission f





Where *A* is the surface of the interface, *D* is the coefficient of diffusion, C_{sat} is the saturation concentration of the component considered, C_{slag} its concentration of the same component in the melt, δ^* the effective boundary layer for diffusion, *k* is the Boltzmann constant, *D* is the diffusivity coefficient, η is the slag viscosity and *r* the diameter of the diffusing component.

This equation indicates that the dissolution of MgO depends on C_{sat} of the slag. It can explain why the MgO layer is only visible in the samples from the pellet test and why the sample corroded using the $10SiO_2$ slag is corroded to a greater extent, as seen in Figure 12.

As mentioned above, the MgO layer is only observed in the samples corroded with the contact test using the 10MnO slag and not the dipping test. This originates from the different amounts of slag used to perform the dipping and contact tests. For the contact test, the quantity of slag used is low. At the end of the experiment, the slag is close to saturation or saturated in MgO: $C_{slag} = C_{sat}$ hence the dissolution stops. The presence of MgO dendrites (an indication that MgO precipitates in the slag) in the sample from the contact test in Figure 10c) and d) and Figure 11c) and d), and their absence in the sample from the dipping test in Figure 13c) corroborate this observation. For the dipping test, the quantity of slag is large compared to the size of the samples and the slags used for the experiments are far from MgO saturation. The slag is not saturated at the end of the experiment: $C_{slag} < C_{sat}$. Thus, the entire MgO layer formed is dissolved by the slags and cannot be observed.

On the other hand, the sample from the dipping test corroded using the SiO₂ slag had a higher dissolution compared to the other sample. This can be explained by the C_{sat} of MgO in the different slags. C_{sat} of the three slag was thus compared by performing calculations with the Equilib module of Factsage. The results were obtained by inputting 100 g of MgO with 100 g of slag (composition given in Table 1). The obtained results are presented in Figure 15. The graph indicated that the C_{sat} of the 10SiO₂ slag is the highest and the C_{sat} of the 10MnO slag is the lowest which is in accordance with the literature [21].





According to the Noyes-Nernst's equation Equ. 6 and Equ. 7, the corrosion of MgO will increase with a higher C_{sat} . The C_{sat} of the 10SiO₂ is the highest according to Figure 15. This explained why the samples corroded using the 10SiO₂ exhibits the highest corrosion. Moreover, according to literature, increasing SiO₂ content in the slag (i.e decreasing the basicity of the slag) increases the dissolution of MgO and consequently the corrosion of the MgO bricks [19-22].

The graph also indicates that the C_{sat} of the 10MnO slag is the lowest. In addition to the higher formation and reoxidation of MgO gas, this can explain the presence of the MgO layer in the sample corroded by the 10MnO slag and its absence in the samples corroded using the standard slag or the 10SiO₂ slag. Moreover, the viscosity of the slag can also affect the dissolution of MgO according to Equ. 6 and Equ. 7. The calculation of the viscosity was performed using the viscosity module of Factsage. The results are presented in Figure 16.





European







Figure 16: Calculation of the viscosity of calcium-aluminate slag with increasing content of a) SiO₂ and b) MnO using Factsage at 1550 °C.

This indicates that adding SiO₂ to the slag will increase the viscosity of the slag; it should lead to a decrease of the dissolution of MgO. However, the results of the dipping test suggest that the corrosion of the samples using the $10SiO_2$ slag was the highest as the highest width loss was observed for the sample corroded by the $10SiO_2$ slag at 1600 °C in Figure 12. On the other hand, adding MnO to the slag will decrease the viscosity of the slag and thus should increase the corrosion of MgO. However, the sample corroded using this slag exhibits the same corrosion as the sample corroded using the standard slag. This indicates that the MgO layer protects, in part, the sample from corrosion and/or that C_{sat} has a higher impact on the corrosion than the viscosity η .

4.5 MgO-C brick conclusion

The identified basic mechanisms of MgO-C brick corrosion are:

- the oxidation of carbon due to the carbothermic reaction of C from the matrix with the MgO aggregates,
- the formation of an MgO layer at the surface of the bricks due to the formation and subsequent oxidation of Mg gas,
- the dissolution of the MgO aggregates in the slag.

The modification of the slag composition could influence one, or several, of these mechanisms. The addition of silica in the slag increases the corrosion of the MgO-C brick due to an increase of the concentration to saturation of MgO in the slag.

On the other hand, the corrosion of the samples using the standard slag and the slag with additional manganese oxide is similar, hence the addition of manganese will not increase the corrosion of the MgO-C brick compared to a more regular slag. Furthermore, the addition of manganese oxide favours the formation of a MgO layer at the interface between the brick and the slag. In a slag saturated in MgO, which is often the case in industrial slag found in the steel ladle, it might protect the MgO-C brick and reduce its corrosion.

5 Conclusions

Corrosion tests, on two different types of refractory brick used in a steel ladle, have been performed and briefly reported in this deliverable. These tests have provided insights into the corrosion mechanisms of alumina spinel and magnesia carbon bricks in contact with calcium aluminate slags.

In the case of alumina spinel bricks, the samples were infiltrated and the Ca^{2+} ions reacted with the alumina grains to form CA, CA_2 and CA_6 . In addition, in the samples corroded using the $10SiO_2$ slag, more gehlenite formed compared to the sample corroded using the standard slag. Gehlenite is a low melting point phase, when present in the sample, it promotes the further infiltration of the slag. Hence, the samples corroded using the $10SiO_2$ were corroded to a greater extent than the samples corroded using the standard slag.

In the case of magnesia carbon brick, the carbon matrix was oxidized due to the carbothermic reaction between MgO and C. This leads in turn to the formation of Mg gas. The Mg gas further reacted with easily reducible elements, FeO and MnO, from the slag to form a MgO layer at the surface of the brick. With the 10MnO slag, the amount of reducible elements was higher, hence the formation of the magnesia layer increased. Additionally to the oxidation of carbon, the magnesia grains are dissolved by the slag. Due to the higher concentration to saturation of MgO in the $10SiO_2$ slag, the extent of corrosion of the sample treated using the $10SiO_2$ slag was higher than with the two other slags.

17 / 18

European







6 References

[1] de Bilbao, E., Dombrowski, M., Traon, N., Tonnesen, T., Poirier, J., & Blond, E. (2014). Study of Reactive Impregnation and Phase Transformations During the Corrosion of High Alumina Refractories by Al2O3-CaO Slag. In Advances in Science and Technology (Vol. 92, pp. 264-271). Trans Tech Publications Ltd.

[2] Darban, S., Kakroudi, M. G., Vandchali, M. B., Vafa, N. P., Rezaei, F., & Charkhesht, V. (2020). Characterization of Ni-doped pyrolyzed phenolic resin and its addition to the Al2O3–C refractories. Ceramics International, 46(13), 20954-20962.

[3] Jia, D., Kim, D., & Kriven, W. M. (2007). Sintering Behavior of Gehlenite. Part I: Self-Forming, Macro-/Mesoporous Gehlenite— Pore-Forming Mechanism, Microstructure, Mechanical, and Physical Properties. Journal of the American Ceramic Society, 90(6), 1760-1773.

[4] Braulio, M. A. L., Rigaud, M., Buhr, A., Parr, C., & Pandolfelli, V. C. (2011). Spinel-containing alumina-based refractory castables. Ceramics International, 37(6), 1705-1724.

[5] Řeháčková, L., Rosypalová, S., Dudek, R., Kukutschová, J., & Dobrovská, J. (2015). Effect of CaO/SiO₂ ratio on viscosity and structure of slag. Metalurgija, 54(3), 455-458.

[6] Yilmaz, S. (2006). Corrosion of high alumina spinel castables by steel ladle slag. Ironmaking & steelmaking, 33(2), 151-156.

[7] Gehre, P., Aneziris, C. G., Berek, H., Parr, C., & Reinmöller, M. (2015). Corrosion of magnesium aluminate spinel-rich refractories by sulphur-containing slag. Journal of the European Ceramic Society, 35(5), 1613-1620.

[8] Park, H. S., Kim, Y., Kim, S., Yoon, T., Kim, Y., & Chung, Y. (2018). A study on the wetting behavior of liquid iron on forsterite, mullite, spinel and quasi-corundum substrates. Ceramics International, 44(15), 17585-17591.7

[9] Poirier, J., Qafssaoui, F., Ildefonse, J. P., & Bouchetou, M. L. (2008). Analysis and interpretation of refractory microstructures in studies of corrosion mechanisms by liquid oxides. Journal of the European Ceramic Society, 28(8), 1557-1568.

[10] Luz, A. P., Martinez, A. T., Braulio, M. A. L., & Pandolfelli, V. C. (2011). Thermodynamic evaluation of spinel containing refractory castables corrosion by secondary metallurgy slag. Ceramics International, 37(4), 1191-1201.

[11] McCauley, R. A. (2004). Corrosion of Ceramic and Composite Materials (2nd edition ed.). Dekker.

[12] Leonard, R. J., & Herron, R. H. (1972). Significance of Oxidation-Reduction Reactions Within BOF Refractories. Journal of The American Ceramic Society, 55(1), 1-6.

[13] Sadrnezhaad, S.K., Mahshid, S., Hashemi, B., & Nemati, Z. (2006). Oxidation Mechanism of C in MgO–C Refractory Bricks. 89(4), 1308-13016. doi:10.1111/j.1551-2916.2005.00863.x

[14] Guo, M., Parada, S., Jones, P. T., Boydens, E., Van Dyck, J., Blanpain, B., & Wollants, P. (2009). Interaction of Al₂O₃-rich slag with MgO–C refractories during VOD refining - MgO and spinel layer formation at the slag/refractory interface. Journal of the European Ceramic Society, 29, 1053-1060. doi:10.1016/j.jeurceramsoc.2008.07.063

[15] Guo, M., Parada, S., Jones, P. T., Van Dyck, J., Boydens, E., Durinck, D., Wollants, P. (2007). Degradation mechanisms of magnesia-carbon refractories by high-alumina stainless steel slags under vacuum. Ceramics International, 33, 1007-1018.

[16] da Rocha, V. C., Pereira, J., Yoshioka, A., Bielefelt, W. V., & Vilela, A. C. (2017). Evaluation of Secondary Steelmaking Slags and Their Relation with Steel Cleanliness. Metallurgical and Materials Transactions B, 48(3), 1423-132.

[17] Baudin, C., Alvarez, C., & Moore, R. E. (1999). Influence of Chemical Reactions in Magnesia–Graphite Refractories: I, Effects on Texture and High-Temperature Mechanical Properties. journal of the american ceramics society, 82(12), 3529-3538.

[18] Um, H., Lee, K., Kim, K. Y., Shin, G., & Chung, Y. (2014). Effect of carbon content of ferromanganese alloy on corrosion behaviour of MgO-C refractory. Ironmaking and Steelmaking, 41(1), 31-37.

[19] Lee, W., & Zhang, S. (1999). Melt corrosion of oxide and oxide-carbon. International Materials Reviews, 44(3), 77-104.

[20] Cooper, A., & Kingery, W. (1959). Kinetics of High-Temperature Process. Wiley.

[21] Jung, S.-M., Min, D.-J., & Rhee, C.-H. (2007). Solubility of MgO in New Ironmaking Process-typed Slags. ISIJ International, 47(12), 1718-1722.

[22] Wang, D., Li, X., Wang, H., Mi, Y., Jiang, M., & Zhang, Y. (2012). Dissolution rate and mechanism of solid MgO particles in synthetic ladle slags. Journal of Non-Crystalline Solids, 358, 1196-1201.

