UNFIRED ZERO CARBON MgO BRICKS FOR SAFETY LINING OF STAINELESS STEEL LADLE: PERFORMANCE ANALYSIS

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ABSTRACT

The search for new environment friendly processes and the reduction of pollutant emissions are the new driving force of the steelmaking industry. Steel ladles are most used in the secondary refining process and for alloy addition in the molten steel. The vessel is lined with refractories for working and safety lining according to different wear mechanisms. For stainless steel ladle, magnesia chrome direct bonded bricks, fired at temperatures above 1700°C are used in the safety lining. This material is specified due to its higher physical and mechanical properties and dimensional stability. A novel concept of tempered bricks at 200°C was developed using a special binder system that eliminates the firing process and lowers CO_2 emissions. The new brick is based on MgO-ZnO, and no chrome and carbon are added. Costumer's trials performed similar for both designs. The aim of this work is to present performance results of fired and tempered brick used in the safety lining of the stainless-steel ladle.

INTRODUCTION

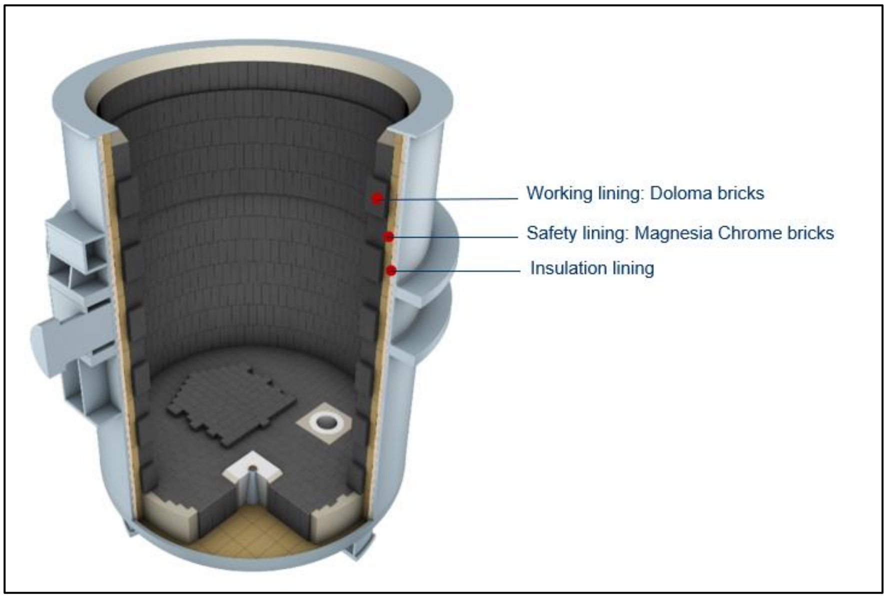
Stainless steels are an important class of alloys. They are used in different applications, from cooking utensils and furniture to very sophisticated ones, such as construction and space vehicles.

The word 'steel' means that iron constitutes the bulk of the material, while the use of the adjective 'stainless' implies absence of staining, rusting or corroding in environments where ''normal'' steels are susceptible (for instance, in relatively pure, dry air). In order to add these properties to steels, chromium must be added, so self-healing chromium oxide can be formed on the steel surface in relatively benign environments[1].

While the Fe–Cr system forms the basis, modern stainless steels, also contain a host of other alloying elements whose presence enhances specific properties, as Molybdenum (Mo) and Nickel (Ni). Stainless steel producers are continually developing their manufacturing processes with the aim of reducing costs, lowering emissions, shortening lead times, and improving quality[2].

During the secondary refining of stainless steel, the molten steel goes through a steel ladle, which is used to transportation and alloy addition. A steel ladle is assembled with different refractory grades depending on ware mechanisms that are present during operation. Figure 1. shows a schematic drawing of a stainless steel ladle.

Figure1. Stainless steel ladle assembled with different refractory brick grades



Doloma refractory bricks are commonly used in Si-killed steel production, due to their high compatibility with basic slags. These bricks may form a dense layer of Ca_2SiO_4 (C_2S) which has high refractiveness (2154°C) and protect the refractories against slag infiltration and corrosion[3].

Magnesia chrome refractory bricks are frequently used in safety lining of stainless steel ladle and they are known for their ability to develop ceramic bonds during sintering process. Main characteristics for MgO-Cr_2O_3 bricks applications are high mechanical properties, corrosion resistance, erosion, and thermal stability[4].

Under normal industrial temperatures and oxidizing conditions (in air), Cr^{3+}, which is present in $MgO-Cr_2O_3$ refractory, can oxidize to Cr^{6+}. Hexavalent chrome is soluble in water and known to be carcinogenic. Steel industries are increasingly conscious of this problem due to more stringent environmental regulations, so bigger efforts have been made to recycle and reduce solid wastes[5].

In addition, large amounts of refractories materials are consumed in steelmaking industries, and most of the refractories commonly used in stainless steel ladles are fired at high temperature and huge amounts of CO_2 is released. To decrease pollutant emissions, a new binder system for refractory bricks with zero carbon content and environmentally friendly was developed as an alternative to the currently used material.

In this context, zero carbon tempered MgO-ZnO bricks can enhance the desirable properties using the energy that already exists during operation, transforming bricks, that are delivered to customers just tempered at 200°C, to a fast-sintering capability product. The new development is free of chrome and showed good results in costumer trial. A comparative performance in field trial with post-mortem analysis is present in this paper.

RESULTS AND DISCUSSION

A commercial brand of $MgO-Cr_2O_3$ is used as standard safety lining in the stainless steel ladle of costumer A, and a panel with MgO-ZnO bricks was assembled in the same equipament to guarantee equal operational conditions. The $MgO-Cr_2O_3$ brick is fired above 1700°C and the MgO-ZnO is tempered at 200°C. Composition of both materials is presented in the Table 1.

The campaign ended with 40 heats due to a wear in the Doloma bricks used in the slag working lining. After demolition and inspection, it was observed a brittle aspect of the magnesia chrome bricks compered to MgO-ZnO bricks used in the safety lining as presented in the Figure 2.

Post mortem analysis was done in both materials. Chemical analysis was done by X-ray fluorescence in the MagiX Pro (Philips) equipament using SuperQ database, bulk density (BD) and apparent porosity (AP) were measured according to ASTM C20, XRD was done in the X'Pert PRO (Cu, 40 mA, 40 kV) equipament using the data base from International Centre for Diffraction Data (ICDD) optical microscopy was done in the Carl Zeizz (AXIO-Imager) equipament. Samples were divided into hot (HF) and cold face (CF), and the test above were performed in both of them.

Table 1. Composition of $MgO-Cr_2O_3$ fired above 1700°C and MgO-ZnO tempered at 200°C

	$MgO-Cr_2O_3$ (Fired – 1730°C)	**MgO-ZnO (Tempered – 200°C)**
Chromite	YES	NO
MgO	YES	YES
ZnO	NO	YES
Special Binder	NO	YES

Figure 2. $MgO-Cr_2O_3$ and MgO-ZnO after trial (40 heats).

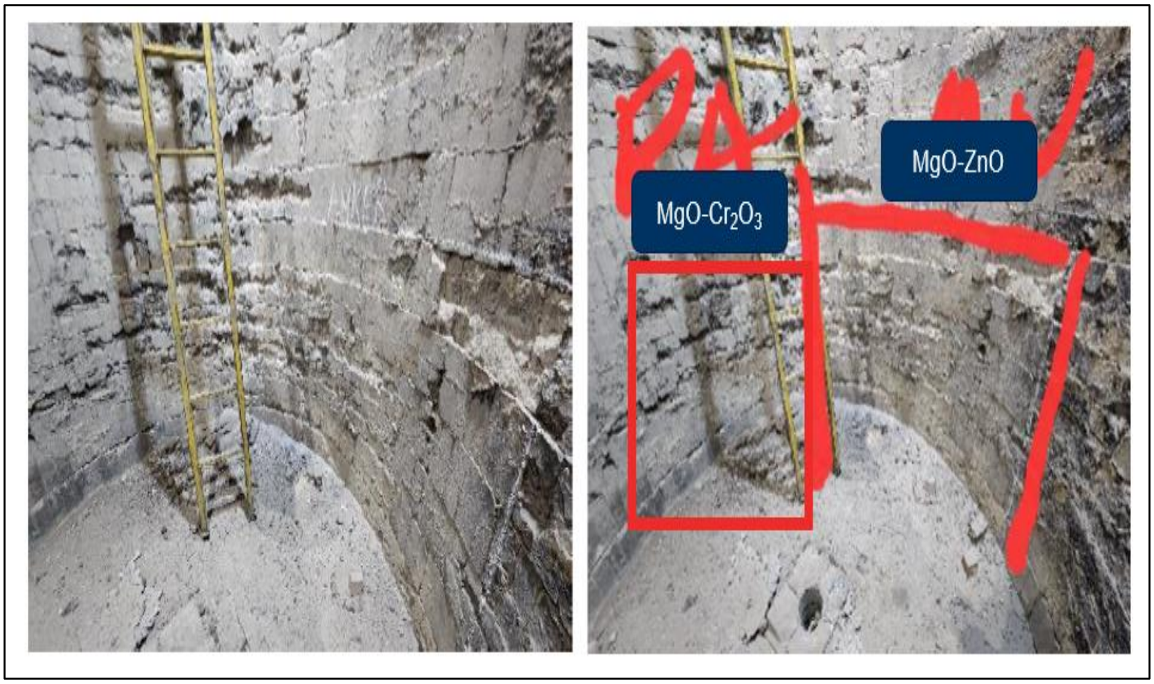
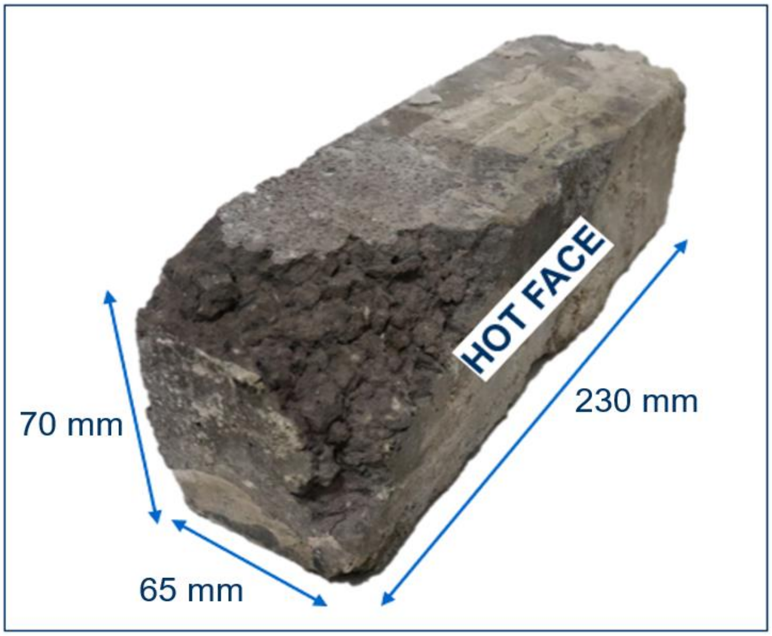


Figure 3. shows the residual thickness of the fired magnesia chrome brick (65 x 70 x 230 mm).

Figure 3. Sample of fired magnesia chrome brick after trial



Chemical analysis and physical properties of the magnesia chrome brick are present in the Table 2. There is a higher content of SiO_2 and CaO in the hot face of the material, also the presence of fluorine was detected in it due to the interaction with the process.

Physical properties show higher density and lower porosity in the hot face of the sample due to oxide migration into the matrix (CaO and SiO_2). XRD analysis presented in the Figure 4. shows the common crystallographic phases of the material.

It is possible to observe the presence of Chromite, MgO and secondary phases in all the sample as present in Figure 5. Even though the brick was already fired at high temperature, chromite seems to be porous due to SiO_2 migration to the matrix. So, it can justify the brittleness of bricks during demolition.

Table 2. Chemical analysis and physical properties of the fired magnesia chrome brick

Chemical Analysis (%)		
	HF	**CF**
SiO_2	3,74	1,93
TiO_2	0,25	0,07
Al_2O_3	4,52	4,43
Cr_2O_3	11,48	11,10
Fe_2O_3	5,16	5,16
CaO	3,79	0,76
MnO	0,10	0,10
MgO	70,26	76,33
F	0,28	0,00
C/S	1,01	0,39
Physical properties		
BD (g/cm³)	3,06 ± 0,06	2,94 ± 0,01
AP (%)	16,63 ± 1,84	20,06 ± 0,13

Figure 4. XRD analysis of the fired magnesia chrome brick

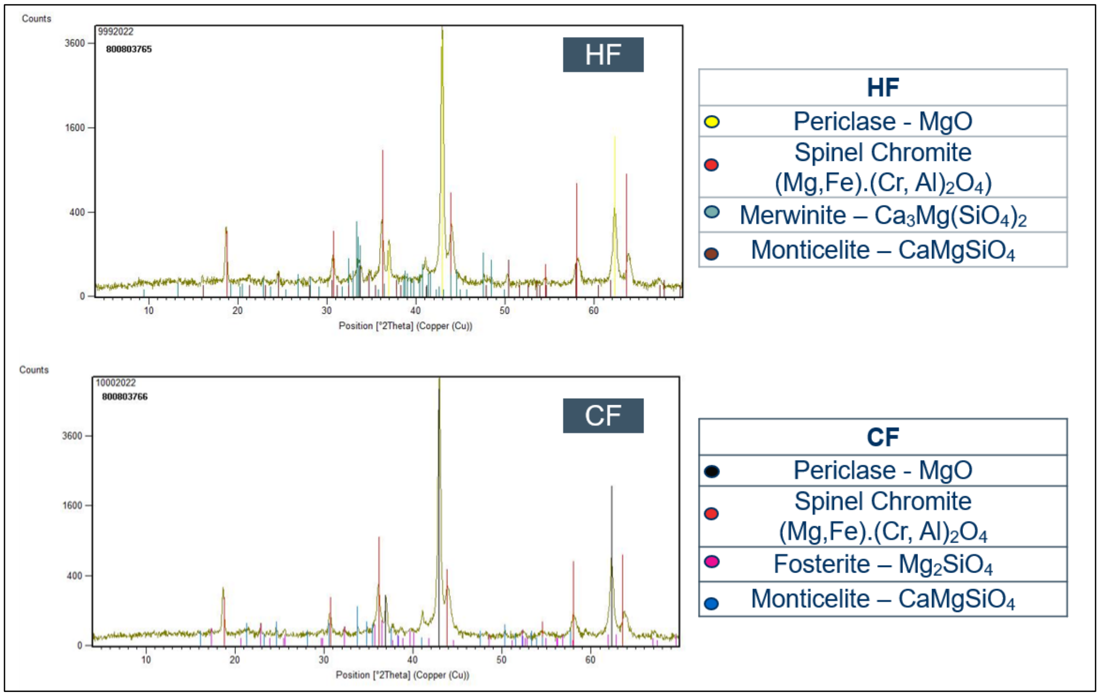


Figure 5. Optical microscopy of the fired magnesia chrome brick

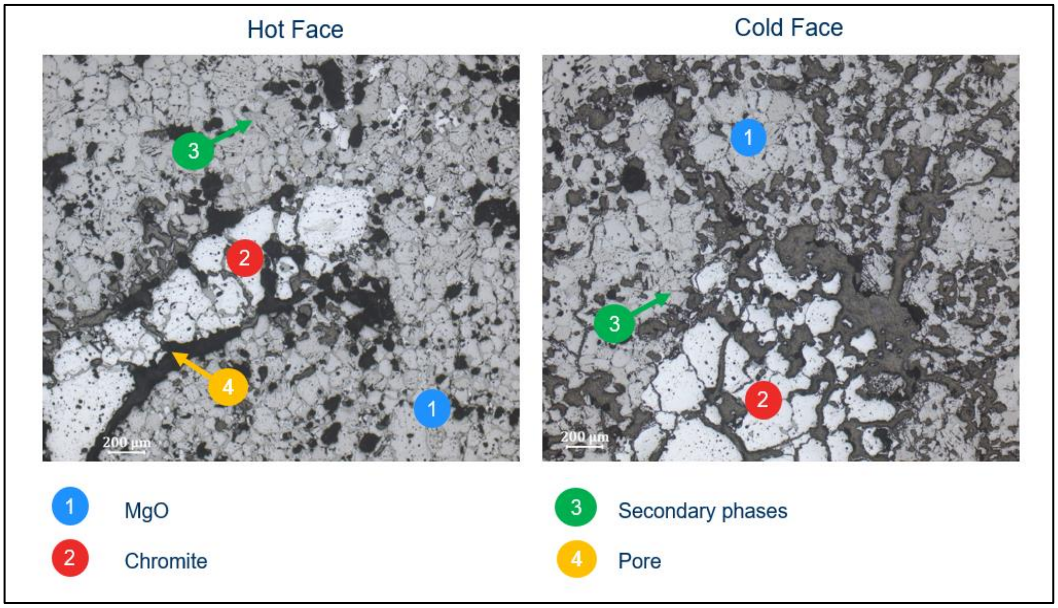


Figure 6. shows the residual thickness of the MgO-ZnO brick (65 x 70 x 230 mm). Chemical analysis and physical properties are present in the Table 3.

Figure 6. Sample of tempered MgO-ZnO brick

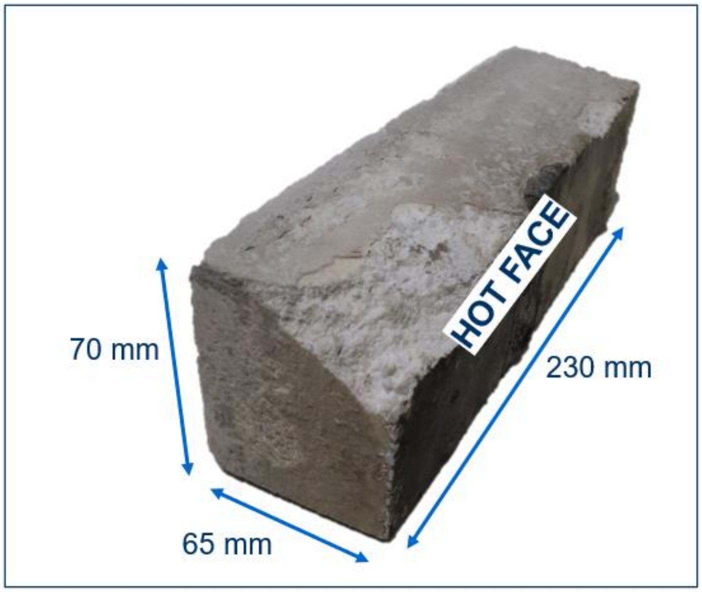
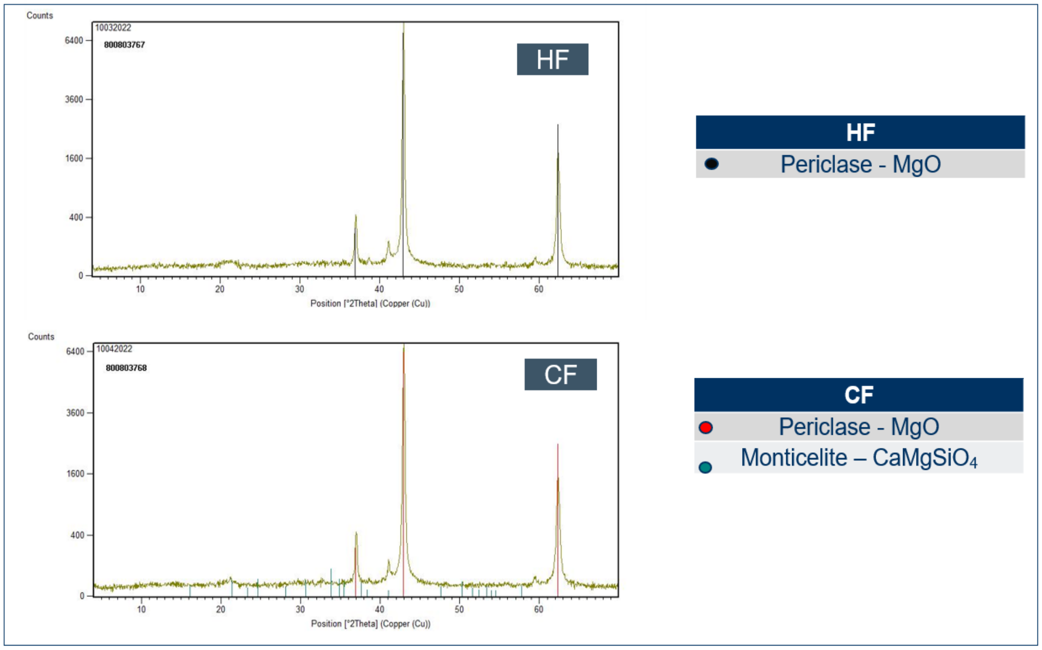


Table 3. Chemical analysis and physical properties of the MgO-ZnO brick

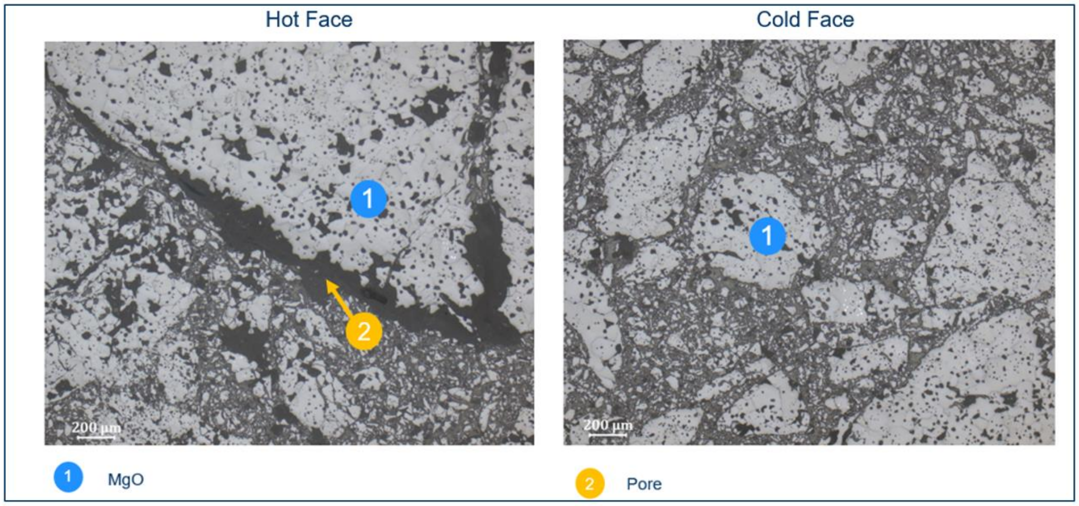
Chemical Analysis (%)		
	HF	**CF**
SiO_2	0,24	0,23
TiO_2	0,00	0,00
Al_2O_3	0,01	0,01
Cr_2O_3	0,55	0,42
Fe_2O_3	0,81	0,99
CaO	0,10	0,11
MnO	97,79	97,25
MgO	0,12	0,18
F	0,02	0,00
ZnO	0,25	0,61
C/S	3,38	4,30
Physical properties		
BD (g/cm^3)	2,91 ± 0,00	2,90 ± 0,01
AP (%)	16,09 ± 0,23	15,95 ± 0,21

Figure 7. XRD analysis of the MgO-ZnO brick



XRD analysis present in the Figure 7. shows the common crystallographic phases of the material.

Figure 8. Optical microscopy of the MgO-ZnO brick



According to physical properties, it is possible to observe that MgO-ZnO brick has similar chemical and physical properties in the hot and cold face after use. Although the brick is just tempered, it develops its microstructure during application.

Zinc may form a solid solution with magnesium, that is why no crystallography phases with it were identified in the XRD analysis. ZnO is reported in magnesia aluminate spinel systems as an additive to densification. It is supposed to enter into the spinel structure and create anion vacancy in it, thus favouring the densification process[6]. Although, ZnO is not repported in basic systems, it contributes to the effectiveness of sinterization as observed in post mortem analysis.

The tempered brick showed lower interaction with the process than the fired one, as there was no oxide migration into it. That is because it has a fast sintering capability due to the combination of the special binder system with the ZnO addition. Further trials are being conducted to confirm the field results.

CONCLUSIONS

Tempered MgO-ZnO bricks were developed for the safety lining of stainless steel with a unique binder system with zero carbon and chrome content. The new development is environmentally friendly, and an alternative solution to safety lining of the stainless steel ladle.

Tempered bricks have a fast-sintering capability due to special binder system and ZnO presence. The customer trial presented in this paper showed great results and new trials are being conducted.

REFERENCE

[1] K.H. Lo; C.H. Shek and J.K.L. Lai. Recent developments in stainless steels. Materials Science and Engineering R 65, 39–104 (2009).

[2] N.R. Baddoo. Stainless steel in construction: A review of research, applications, challenges, and opportunities. Journal of Constructional Steel Research 64, 1199–1206 (2008).

[3] C. T. Ricardo. Avaliação da camada protetora de silicato dicálcico em refratários Doloma-C empregados na produção de aço. Tese para obtenção do título de Doutor em Engenharia, Escola de Engenharia Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais, Porto alegre, 2016.

[4] B. Borges; C. Pagliosa; M. Borges; A. Campos; V. Madalena; V. C. Pandolfelli. Zero carbon tempered MgO-Cr_2O_3 bricks for RH Degassers: advances from customers' trials. UNITECR, 2022.

[5] Y. Lee and C.L. Nassaralla. Minimization of Hexavalent Chromium in Magnesite Chrome Refractory. Metallurgical and materials transactions B. V. 28B, Oct. 1997.

[6] A. Ghosh, S.K. Das, J.R. Biswas, H.S. Tripathi and G. Banerjee. The effect of ZnO addition on the densification and properties of magnesium aluminate spinel. Ceramics International V. 26, 605-608, 2000.