

Corrosion Study and Thermodynamic Calculations for MgO-C Refractories Containing CMA Additive

M. Ludwig^{*1}, M. Sułkowski¹, M. Klewski¹, E. Wojtaszek-Jajków¹, D. Madej²

¹ArcelorMittal Refractories, Ujastek 1, 31–752 Kraków, Poland

²AGH University of Science and Technology Faculty of Materials Science and Ceramics, al. Mickiewicza 30, 30–059 Kraków, Poland

received August 15, 2024; received in revised form July 19, 2025; accepted August 18, 2025

Abstract

MgO-C refractories are extensively utilized in the steel industry, particularly in steel ladles, basic oxygen furnaces, and electric arc furnaces. These materials are subjected to intense mechanical and thermal stresses, as well as aggressive interactions with corrosive agents. The most severe wear typically occurs upon contact with slag or molten metal; therefore, the use of high-purity raw materials is essential to ensure durability under such conditions. To enhance the thermomechanical performance of MgO-C refractories, antioxidants are commonly incorporated, leading to the formation of high-temperature ceramic phases (e.g. MgAl_2O_4 , AlN , SiC) that reinforce the material's structure. However, alternative additives may also be considered to further improve their performance in demanding environments. Raw materials containing CaO and MgO-bearing aluminates not only enhance slag resistance but are also considered among the most promising solutions for stabilizing steel ladle linings. Laboratory tests involving the addition of various grain sizes of CMA additives to MgO-C refractories demonstrated improved slag resistance through the formation of a protective contact layer. Furthermore, these modifications enabled better control over dimensional changes after heating, as well as thermal expansion behavior. The study also investigated the feasibility of incorporating recycled raw materials in combination with aluminates. The obtained results enabled the design of a complete ladle lining system optimized for use in silicon-killed steel processes and environments subjected to high thermomechanical stress in secondary metallurgy. Microstructural analysis of post-mortem samples using SEM/EDS methods provided insight into the influence of aluminates on slag attack resistance and thermal stress behavior, particularly through reinforcement of joint areas. The corrosion study was further supported by thermodynamic calculations.

Keywords: MgO-C refractories, CMA, SEM/EDS, corrosion, post-mortem.

1. Introduction

MgO-C refractories play a critical role in the daily operation of high-temperature units in steelmaking facilities. They are widely used in steel ladles (SL), basic oxygen furnaces (BOF), and electric arc furnaces (EAF) ¹. In many cases, these units are lined entirely with MgO-C materials. Depending on process conditions, either resin-bonded or carbon-bonded refractories may be selected. The key distinction lies in the behavior of the bonding agent at high temperatures: resin tends to be brittle, while carbon offers greater elasticity and is less sensitive to abrupt changes in operating conditions. The primary raw material used in MgO-C refractories is magnesia, which imparts high corrosion resistance and excellent refractoriness to the final product. Fused magnesia with MgO content above 96 % is typically employed, although combinations of sintered and fused magnesia are also commonly utilized. Graphite used in MgO-C refractories must exhibit a high carbon yield, as it significantly enhances thermal shock resistance due to its high thermal conductivity (λ) and low

thermal expansion coefficient (α) ². However, the overall carbon content – including graphite – must be carefully optimized, as excessive carbon can negatively impact the mechanical properties of the material ^{3, 4}. In MgO-C refractories, bonding is typically obtained using phenolic or carbon-based resins, which are available in both powder and liquid forms ⁵. To improve oxidation resistance, various antioxidants such as Al, Si, SiC, B_4C , $\text{Al+B}_4\text{C}$, and Al-Mg are commonly introduced ^{5–7}. Additional performance enhancements can be achieved with the incorporation of special additives, which contribute to prolonged refractory lifetime. These include Fe ⁸, $\text{ZrO}_2\text{-Al}_2\text{O}_3$ powder ⁹, nano- ZrSiO_4 ¹⁰, micro and nano- Al_2O_3 ¹¹ and calcium-aluminate-containing raw materials, such as CMA additive. The latter has emerged as one of the most promising solutions for improving the overall performance of MgO-C refractories ^{12, 14}.

CMA is a raw material derived from the $\text{CaO-MgO-Al}_2\text{O}_3$ system, composed primarily of magnesia aluminate spinel (MgAl_2O_4), calcium aluminate (CaAl_2O_4), and calcium dialuminate (CaAl_4O_7), with a typical phase ratio of approximately 7:2:1 by mass ¹⁵. The beneficial

^{*} Corresponding author: maciej.ludwig@arcelormittal.com

effects of CMA have been previously demonstrated in castables^{16,17}, ramming mixes¹⁸ and Al_2O_3 -MgO-C refractories¹⁹. In recent years, numerous studies have focused on the influence of CMA on the physical and mechanical properties, as well as the slag and metal corrosion resistance, of MgO-C refractories – particularly in relation to their performance after service in steel ladles.

Wöhrmeyer *et al.*²⁰ compared the performance of MgO-C refractories containing 14 % carbon and Si+Al antioxidants with analogous materials incorporating CMA aggregate in the slag zone of steel ladles. The decarburized layer in the CMA-containing samples was notably thinner (500–600 μm vs. 600–800 μm). Furthermore, the iron oxide content from the slag was lower in the hot face, the decarburized zone, and the matrix of the unaffected refractory region. The primary protective mechanism was attributed to the formation of a densified layer at the brick's hot face. In another study Wöhrmeyer *et al.*¹² evaluated similar materials in a steel-refining ladle. A comparable service life was achieved: 138 heats for the CMA-based refractory versus 132 heats for the reference material, with wear rates of 0.8 mm and 1.2 mm, respectively. The CMA aggregate enriched the slag layer at the refractory interface with CaO and Al_2O_3 , which contributed to the formation of the brownmillerite phase (C_4AF) in the presence of iron oxide. However, it was noted that the CMA content must be carefully controlled, as excessive amounts can negatively impact slag viscosity. Dudczig *et al.*²¹ conducted a laboratory corrosion study using acidic slag to compare MgO-C refractories containing 3 % additions of CMA powder, alumina-rich spinel AR78 (1–3 mm), and a standard reference material. Slag infiltration was highest in the standard MgO-C material (1200 μm), lower in the sample containing alumina-rich spinel AR78 (800 μm), and lowest in the material with CMA powder addition (100–200 μm). The superior performance of the CMA-modified refractory was attributed to multiple mechanisms: the reaction between MgO from the CMA and Al_2O_3 from the slag forming spinel; the generation of a higher-viscosity slag with reduced penetration capacity; and the formation of forsterite (Mg_2SiO_4 , MS) and monticellite (CaO-MgO-SiO_2 , CMS) as products of subsequent reactions. A similar study was presented by Gehre *et al.*¹³. Gao *et al.*¹⁵ compared a standard MgO-C refractory with one containing CMA aggregate in both the metal and slag zones of steel ladles. In the metal zone, a 10 % increase in service life was observed. Corrosion at the brick joints was effectively mitigated by the formation of a protective coating layer rich in brownmillerite (C_4AF). In the slag zone, the decarburized layer in the CMA-containing material was significantly thinner (0.5–0.6 mm) compared to that in the standard refractory (1.8–2.0 mm). The authors concluded that CMA aggregate provides superior protection against graphite oxidation compared to conventional metal-based antioxidants such as e.g. Al or Si. The mechanism behind the formation of the protective slag layer was further explored by Guo *et al.*²² combining thermodynamic calculations with microstructural analysis. Their findings

suggested that slag infiltrates the MgO-C refractory through the decarburized matrix, where CaAl_2O_4 from CMA dissolves in the liquid slag phase. Simultaneously, Al_2O_3 from the CMA aggregate diffuses into the slag via neck regions, promoting the *in-situ* formation of MgAl_2O_4 spinel crystals. This process results in the development of a protective layer that limits further slag penetration into the matrix.

Most previous studies on CMA-containing MgO-C refractories have focused on materials with either low carbon content (3–5 wt.%) or high carbon content (>13 wt.%), typically in combination with additional antioxidants (e.g. metallic Al). However, there remains a lack of comparative data for laboratory-scale MgO-C refractories incorporating CMA without other additives, especially at intermediate carbon levels. Moreover, most corrosion studies have been conducted using slags with alumina content exceeding 10 %, so there has been limited insight into material behavior in contact with low-alumina slags.

Therefore, the aim of this study was to develop MgO-C refractories containing CMA raw material in two grain size fractions (with d_{50} described in *Experimental* part), with a carbon content of 10 wt.% and no additional antioxidants. This approach was intended to isolate and clearly demonstrate the intrinsic effects of CMA on the properties and corrosion resistance of MgO-C refractories. The corrosion performance was evaluated in contact with a model slag with reduced alumina content.

Industrial-scale trials were also conducted, enabling post-mortem analysis of the refractory lining in the metal zone of steel ladles used in vacuum degassing and silicon-killed steelmaking processes for long product manufacturing. The goal was to assess the corrosion mechanisms under conditions involving low-alumina slags. The findings provided guidance for optimizing ladle lining design using CMA-modified MgO-C refractories. Additionally, the study was supplemented with thermodynamic calculations to support and explain the observed corrosion phenomena.

II. Experimental

The experimental part of the present study was divided into four main sections:

- Preparation of model MgO-C refractories containing CMA additive
- Characterization of industrial MgO-C containing CMA additive
- Post-mortem analysis of CMA-modified MgO-C refractory after industrial use
- Thermodynamic calculation of MgO-C containing CMA additive

(1) Preparation of model MgO-C refractories containing CMA additive

Fused magnesia was used as the primary source of MgO in all samples. Flake graphite was included in each formulation to provide carbon, and phenol-formaldehyde resin served as the binding agent. CMA was introduced in two granulometric forms characterized by: $d_{50} = 120 \mu\text{m}$ (marked as **CMA coarse**) and $d_{50} = 39 \mu\text{m}$ (marked as

CMA fine). These granulates were selected for comparative analysis of their behavior during the corrosion test. Additionally, a mix containing both CMA fractions was prepared at a mass ratio of CMA coarse to CMA fine equal to 2 (ascribed as **CMA mix**). For comparison purposes, reference samples without any CMA addition were also produced (marked as **Reference**). All compositions were designed to contain a total carbon content of 10 wt.%. To isolate the effect of CMA on the properties of MgO-C refractories, no antioxidants were intentionally added. Summarized compositions of the prepared MgO-C products are shown in Table 1.

Table 1: Composition of model MgO-C containing CMA additive with designation of samples.

Raw material	Reference	CMA coarse	CMA fine	CMA mix
Fused magnesia, graphite, resin	+	+	+	+
CMA (d ₅₀ = 120 μm)	-	3 wt. %	-	2 wt. %
CMA (d ₅₀ = 39 μm)	-	-	3 wt. %	1 wt. %
Antioxidant	-	-	-	-

The raw materials were homogenized in a laboratory-scale mixer for several minutes at ambient temperature. The resulting mixtures were then shaped using an industrial pressing machine. After forming, the samples were tempered at 200 °C to cure the phenol-formaldehyde resin. Following heat treatment, the samples were subjected to further testing, as described in the final subsection of the experimental part.

(2) Characterization of industrial MgO-C containing CMA additive

An industrial MgO-C refractory provided by Arcelor-Mittal Refractories sp. z o.o. incorporating CMA additive was selected based on a thorough analysis of corrosive factors and operating parameters within the steel shop. The material was based on fused magnesia and utilized the same type of flake graphite as the laboratory-prepared samples. The total carbon content was comparable as well (approx. 9 wt.%). As part of an environmentally friendly approach, recycled aggregates processed by means of enriched separate grinding were also introduced into the composition^{23–25}. Previous studies have confirmed that the inclusion of this recycled material – up to 30 wt.% – does not compromise the physical or mechanical properties of the final product. In the industrial formulation, CMA was combined with metallic aluminum, serving as an antioxidant. This type of refractory material is designed for use in the metal zone of steel ladles with VOD process under the following operating conditions:

- Service temperatures exceeding 1 700 °C,
- Exposure to slags with low Al₂O₃ content,
- Extended residence time of steel in the ladle.

(3) Post-mortem analysis of CMA-modified MgO-C refractories after industrial use,

A post-mortem sample was obtained from the metal zone of a steel ladle used in the ArcelorMittal long products steel plant. The sample was collected directly from the working lining after service. The properties of the MgO-C refractory delivered to the steel shop are presented in Section III (2) and its characteristics in terms of raw material were described in subsection above. The methodology for microstructural characterization of the post-mortem material is outlined in the following subsection.

(4) Methods for characterization of slags and MgO-C products containing CMA

The chemical composition of slags was determined on powdered samples (< 0.063 mm) using X-ray fluorescence (XRF) in accordance with the PN-EN ISO 12677:2011 standard.

Static slag corrosion resistance test was conducted using model laboratory-prepared samples in an induction furnace. The composition of the slag used in these tests is presented in Table 2.

Table 2: Chemical analysis of slag used for the corrosion resistance test in an induction furnace.

SLAG 1	
Slag component	Content [wt. %]
CaO	55.9
SiO ₂	16.1
MgO	12.9
FeO _x	0
Al ₂ O ₃	15.1

The arrangement of samples used for the corrosion test, along with their positioning and assembly in the mold, is shown in Fig. 1:

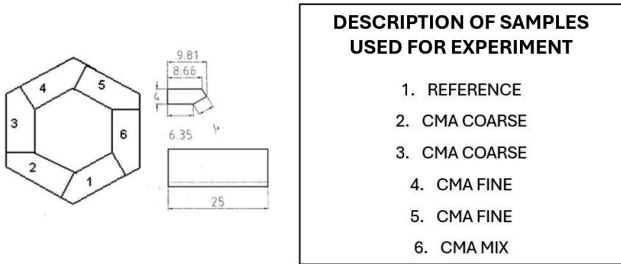


Fig. 1: Scheme showing the assembly of the MgO-C products for the corrosion resistance test in an induction furnace with dimensions of samples.

Steel and model slag (a few hundred grammes) were melted in an induction furnace, and the temperature during testing was maintained at 1 670 °C. Throughout the 70-minute experiment, the slag was replaced three times to simulate realistic steelmaking conditions. After completion of the test, the samples were cooled, cut longitudinally, and visually inspected. The wear depth was measured individually for each sample, as described in²⁶.

Table 3: Chemical analysis of slag from the post-mortem sample of MgO-C containing CMA additive.

Sample	SLAG 2						
	SiO ₂ [wt. %]	Al ₂ O ₃ [wt. %]	MgO [wt. %]	CaO [wt. %]	FeO _x [wt. %]	MnO [wt. %]	Other [wt. %]
Slag from post-mortem sample	21.2	5.8	8.6	38.4	21.2	3.4	1.4

Microstructural analysis of the post-mortem sample obtained from the metal zone of a steel ladle (Arcelor-Mittal long products plant) containing CMA additive was conducted using a scanning electron microscope (SEM, NOVA NANO SEM 2000, FEI Europe Company), coupled with an energy-dispersive X-ray spectroscopy (EDS) system (EDAX). Samples were sectioned from the spent refractory brick and prepared using standard cross-sectional metallographic procedures, including embedding in epoxy resin, grinding, polishing, and coating with a carbon layer for SEM observation. The chemical composition of the industrial slag from the post-mortem MgO-C brick containing CMA additive was presented in Table 3.

III. Results and Discussion

(1) Slag corrosion test of model MgO-C refractories containing CMA additive in the induction furnace

Fig. 2 presents the macroscopic appearance of samples after the corrosion test conducted in an induction furnace. Corroded areas were visible in both the slag and metal zones. Oxidation of the samples occurred primarily at the upper part of the specimens. In the slag zone, no significant visual differences were observed between the CMA-containing and reference samples. However, in the metal zone, the reference sample exhibited pronounced corrosion depth, whereas the MgO-C sample containing CMA additive demonstrated significantly improved resistance to molten metal attack. This phenomenon is particularly important in the context of the present study, as the post-mortem sample discussed in Section III (3) originates directly from the metal zone of a steel ladle. All slag-related corrosion parameters (Fig. 3) were markedly improved in the CMA-containing samples, with the exception of the wear cross-section area, which was comparable in three cases (410, 415, and 430 mm², respectively). The beneficial influence of CMA has been consistently reported in various studies^{12, 13, 15, 21, 22}. Notably, some works^{13, 21, 26} indicated that, for MgO-C materials without antioxidants (as in the current study), the wear depth can be up to ten times higher compared to CMA-containing refractories. The improvement in performance is attributed to the formation of a protective layer at the brick surface, promoted by the diffusion of CaO and Al₂O₃ from CMA into the slag^{12, 27}. This interaction alters slag viscosity, effectively reducing its infiltration into the refractory material²². Despite limited literature on the corrosion resistance of MgO-C refractories containing different CMA fractions²⁸ the present results – supported by thermodynamic calculations for low-alumina slag (Section III (3)) – confirm that both CMA coarse and CMA fine provide compa-

table protection. It is likely that, at high operating temperatures, overlapping effects of the different CMA grain sizes contribute to this behavior. However, further investigation is required to fully explain the surprisingly low wear cross-section observed in the sample containing a mixture of both CMA fractions.

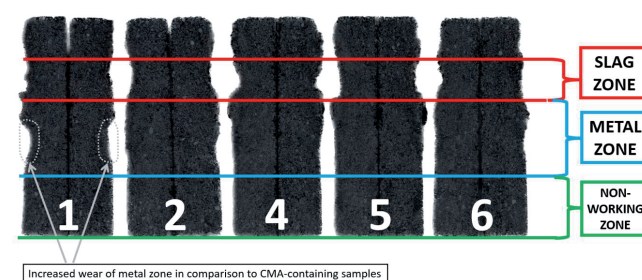


Fig. 2: Macroscopic appearance of samples after the corrosion test in the induction furnace. Sample No. 3 was damaged during the experiment and was excluded from the calculation of slag corrosion parameters.

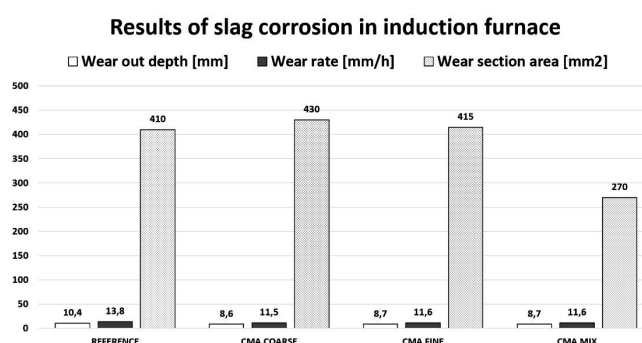


Fig. 3: Average results of corrosion resistance parameters of MgO-C refractories containing CMA additive and reference sample.

(2) Post-mortem analysis of CMA-modified MgO-C refractory after industrial use

(a) Analysis of hot face area

A detailed post-mortem analysis of the MgO-C refractory brick modified with CMA additive was carried out using microstructural investigation by means of SEM-EDS. The SEM overview of the hot face of the refractory after service in the metal zone of a steel ladle (Fig. 4 b) was presented in Fig. 5. Within the hot face region, three distinct zones were identified: the slag-affected area (Fig. 5 a, b), the decarburized zone infiltrated by slag (Fig. 5 c, d), and the interface between the slag and refractory brick (Fig. 5 e, f). The corroded brick exhibited a clearly defined hierarchical structure consisting of a porous reaction layer, a dense infiltration layer, and the unreacted original material. Figs. 5 and 6 illustrate the progressive microstructural evolution from the slag layer

into the intact brick. The observations indicated that the MgO-C refractory modified with CMA exhibited relatively good resistance to slag penetration. Slag infiltration was halted at the slag-refractory interface, with no evidence of molten metal or slag phases detected beyond this boundary (i.e. no metallic inclusions or slag residues were observed within the bulk of the refractory). Slag primarily infiltrated the structure through open pores and progressed via the matrix, facilitated by complete carbon oxidation in the affected area. Rounded edges observed on MgO grains confirmed progressive dissolution into the slag, a typical degradation mechanism in MgO-C refractories used in steelmaking applications^{29–31}. A more detailed analysis of the hot face region was provided in Fig. 5 b, d, f. The primary phases identified in the slag build-up on the refractory surface (Fig. 5 a, b) were low-melting merwinite, C_3MS_2 (where C = CaO, M = MgO, S = SiO₂; $T_m = 1575^\circ\text{C}$ ³⁰) dicalcium silicate C_2S ($T_m = 2130^\circ\text{C}$ ³⁰) and MgO. Table 4 summarizes the EDS results of the slag build-up, along with phase identification. The detection of MgO within the slag layer indicates that it was a solid-liquid mixture rather than a purely molten phase. This aligns with service temperatures in steel ladles, which may exceed 1600°C .

As shown in Fig. 5 c and Fig. 5 d, the decarburized zone infiltrated by slag exhibited a distinct microstructure characterized by increased porosity and a higher concentration of MgO grains. According to the EDS analysis (Table 4), this region also contained silicate phases such as C_3MS_2 and C_2S , along with MgO and metallic inclusions. The presence of rounded MgO grains in this zone suggests that the temperature remained sufficiently high for the slag to remain aggressive toward the refractory,

promoting further dissolution of magnesia. However, it is important to note that not all pores were infiltrated by slag. The detection of metallic Fe particles indicates that iron oxide from the steelmaking process contributed to carbon oxidation within the refractory matrix, as previously reported¹². Additionally, direct oxidation of carbon could have occurred due to exposure to atmospheric oxygen during periods of service when the ladle was empty.

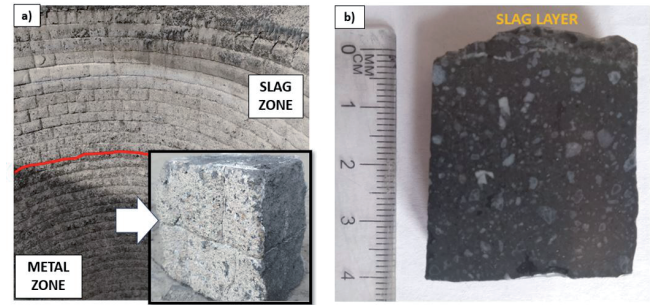


Fig. 4 a) Macroscopic appearance of the post-mortem sample taken from the metal zone of the steel ladle (a), and (b) the sample section from the hot face of the brick prepared for microstructural analysis.

Further microstructural analysis revealed the formation of a distinct protective slag layer at the interface between the decarburized, slag-infiltrated zone and the non-corroded region of the MgO-C refractory brick (Fig. 5 e and Fig. 5 f). This layer served as an effective barrier, impeding further slag penetration and preventing direct contact between the molten slag and the underlying refractory structure. According to EDS results (Table 4), the primary constituents of this protective layer were dicalcium silicate (C_2S), calcium magnesium silicate (C_3MS_2), MgO, and secondary spinel

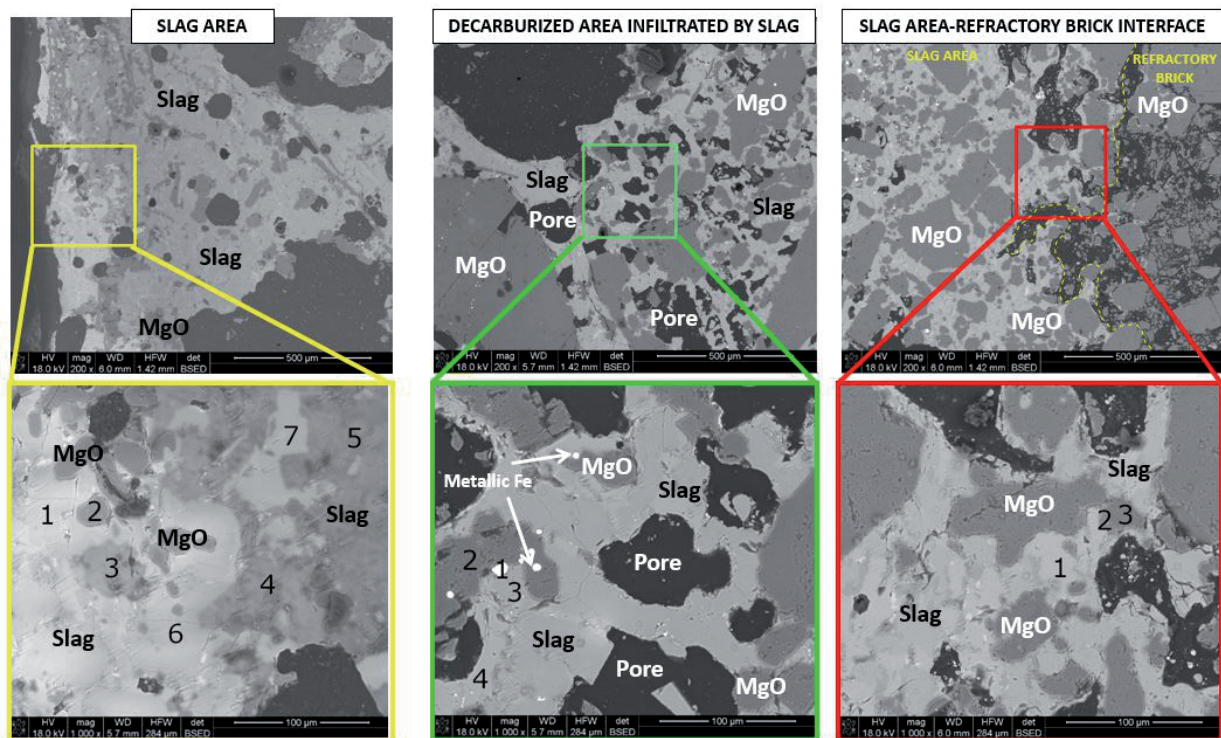


Fig. 5: SEM overview of the hot face of the MgO-C refractory containing CMA additive after service in the metal zone of the steel ladle: (a, b) slag-affected region, (c, d) decarburized zone infiltrated by slag, (e, f) interface between slag and refractory brick.

Table 4: EDS point elemental analysis corresponding to the specific areas marked in Fig. 5.

	Origin	Element [wt. %]							
		O	Mg	Si	Ca	Fe	Cr	Al	F
Slag area (Fig 5b)	Point 1, C ₃ MS ₂	35.8	9.6	21.3	33.3	-	-	-	-
	Point 2, MgO	36.7	63.3	-	-	-	-	-	-
	Point 3, C ₂ S	20.4	-	20.8	53.5	5.4	-	-	-
	Point 4, C ₃ MS ₂	17.7	8.7	23.8	49.8	-	-	-	-
	Point 5, C ₃ MS ₂	19.2	7.9	23.5	49.4	-	-	-	-
	Point 6, C ₃ MS ₂	31.5	8.8	22.0	37.7	-	-	-	-
	Point 7, C ₃ MS ₂	26.9	8.3	21.5	43.3	-	-	-	-
Decarburized area infiltrated by slag (Fig 5d)	Point 1, Fe-Cr-O	4.4	-	-	-	92.5	3.1	-	-
	Point 2, Fe-doped MgO	18.1	74.6	-	-	7.3	-	-	-
	Point 3, C ₃ MS ₂	18.3	8.0	23.5	50.2	-	-	-	-
	Point 4, C ₂ S	15.4	-	20.3	59.3	-	-	-	5.0
Slag area-refractory brick interface (Fig. 5e)	Point 1, C ₂ S	14.4	1.3	20.6	58.9	-	-	-	4.8
	Point 2, secondary spinel MA	22.3	21.4	-	-	-	-	56.3	-
	Point 3, MgO	38.3	61.7	-	-	-	-	-	-

of the MgAl₂O₄-type. Notably, the spinel phase was observed to precipitate preferentially at the MgO grain boundaries (Fig. 5 f, point 2), thereby inhibiting further dissolution of magnesia and contributing to the overall corrosion resistance of the refractory.

Similar to findings reported in the literature, infiltration of slag, oxidation of carbon, and progressive dissolution of MgO grains were confirmed in many cases^{12, 13, 21, 27}. In the current study, CMA additive was not detected in the hot face area of the refractory, which suggests that it fully reacted with the slag during service. This observation aligns with previous studies, where even coarse CMA particles were also found to be absent from the hot face due to similar reactivity¹². However, it is important to highlight differences in slag composition when comparing results. The slags investigated in earlier studies typically had significantly higher basicity and alumina content – for example, C/S (CaO/SiO₂) ratios of 6.7 with 42.4 wt.% Al₂O₃²¹, C/S = 3.7, Al₂O₃ = 17.5 %¹², C/S = 8.5, Al₂O₃ = 32.5 %¹³). In contrast, the slag used in the present study exhibited a much lower basicity (C/S = 1.8) and a significantly reduced Al₂O₃ content (5.8 wt.%, Table 3), indicating a more acidic character and alumina deficiency. These compositional differences are crucial, as they can strongly influence slag-refractory interactions and the resulting corrosion mechanisms.

Therefore, it is not surprising that the penetration depth of slag was lower in the previously cited studies^{12, 13, 21} compared to the results of the present research. The higher alumina content in those studies facilitated the formation of protective phases such as calcium aluminoferrite (C₄AF)^{12, 15} and secondary magnesia-aluminate spinel

(MgAl₂O₄)^{21, 27} which are known to enhance slag resistance. The presence of CMA additive further accelerated these processes by contributing both CaO and Al₂O₃ to the melt²⁷. In the current study, secondary spinel was also identified at the edge of MgO grains (Fig. 5 d), likely formed through the reaction of the CMA additive with the slag. However, due to the relatively low Al₂O₃ content in the slag (5.8 wt.%, Table 3), the formation of secondary spinel was less pronounced. The slag in this study was primarily composed of dicalcium silicate (C₂S) and calcium magnesium silicate (C₃MS₂) across all observed zones: the slag area (Fig. 5 a, b), the decarburized zone (Fig. 5 c, d), and the slag-refractory interface (Fig. 5 e, f). This contrasts with other studies where the corrosive medium included phases such as melilite²¹, gehlenite (C₂AS)^{12, 15} and CMAS phases²⁷. Some authors further suggested the potential formation of monticellite (CMS) and forsterite (M₂S) during continued interaction between the refractory and slag^{13, 21}. These variations highlighted the critical influence of slag chemistry – particularly its alumina and silica content – on the corrosion behaviour and phase development in MgO-C refractories modified with CMA additives.

(b) Analysis of cold face area

Analysis of the cold face of the post-mortem sample revealed two key phenomena. First, no residual CMA additive was detected throughout the volume of the brick. This likely indicates that the CMA reacted with MgO grains during service, as operating temperatures exceeded 1600 °C. Second, no evidence of slag infiltration was observed within the graphite-containing matrix. Only at the edges of MgO grains were C_xM_yS_z phases detected

(with variable x:y:z ratios), which are typical of natural impurities found in magnesia-based raw materials^{23, 25} (Table 5). Additionally, magnesia-aluminate spinel was identified within one grain, as shown in Fig. 6 b. This phase was likely formed through a reaction between the antioxidant and magnesia, as reported by Aneziris *et al.*²⁸.

(3) Thermodynamic calculation of MgO-C containing CMA additive

Thermodynamic modeling of saturation limits and slag viscosity in the presence of CMA (CaO-MgO-Al₂O₃) modifiers of MgO-C refractories was performed using the internal software CEQCSI CRYSTAL, developed by ArcelorMittal as in-house built thermodynamic equilibrium calculation software³². This tool is specifically designed for complex multi-component systems and is particularly well-suited for simulating slag-refractory

interactions under high-temperature steelmaking conditions.

The CEQCSI software supports equilibrium calculations related to solid-state phase transformations and includes capabilities for predicting slag viscosity using the Generalized Central Atom (GCA) thermodynamic model³². These features make it especially valuable for assessing slag infiltration mechanisms and refractory corrosion resistance.

The viscosity model, based on the GCA framework, allows accurate estimation of slag fluidity as a function of temperature and composition. By varying slag constituents – such as increasing MgO or Al₂O₃ content – the model can identify conditions that reduce slag fluidity and enhance refractory performance. This predictive ability is crucial for optimizing refractory design and extending service life in demanding metallurgical environments.

Table 5: EDS point elemental analysis corresponding to the specific areas marked in Fig. 6.

Origin		Element [wt. %]							
		O	Mg	Si	Ca	Fe	Cr	Al	F
Fig. 6 b	Point 1, CMAS	22.4	15.6	24.9	33.8	-	-	2.9	0.4
	Point 2, MA	25.5	20.7	-	-	-	-	53.8	-
	Point 3, MgO	36.8	63.2	-	-	-	-	-	-

Table 6: Summary of phases identified during SEM/EDS investigation of post-mortem MgO-C containing CMA additive.

Origin	Identified phases
Slag area	MgO, C ₃ MS ₂ , C ₂ S
Decarburized area infiltrated by slag	MgO, C ₃ MS ₂ , C ₂ S, Fe inclusions
Slag area-refractory brick interface	MgO, MgAl ₂ O ₄ , C ₂ S, C ₃ MS ₂
Cold face	MgO, MgAl ₂ O ₄ , CMAS, Carbon (graphite)

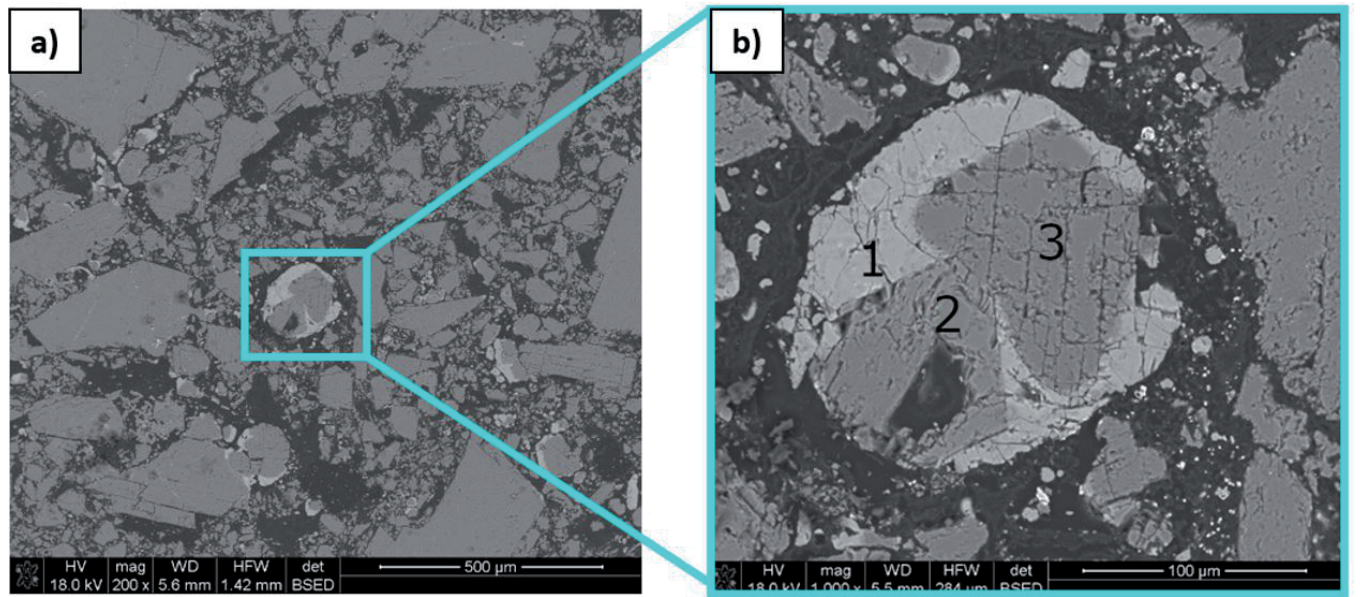


Fig. 6: SEM image overview of the cold face area of the MgO-C containing CMA additive after service in the metal zone of a steel ladle.

In laboratory-scale corrosion tests – such as those performed in induction furnaces – CEQCSI has been employed to simulate the thermodynamic behavior of model slags in contact with MgO-C refractories. These simulations support the interpretation of experimental results by identifying stable and metastable phases, saturation limits, and potential high-temperature reaction products (e.g. at 1700 °C)³³.

Recent studies utilized CEQCSI to model the equilibrium between CaO-MgO-Al₂O₃-SiO₂-FeO slags and MgO-C refractory systems. The results demonstrated that the formation of spinel (MgAl₂O₄) at the slag-refractory interface can act as an effective protective barrier. However, depending on slag composition, this spinel layer may become destabilized, allowing further slag infiltration and corrosion of the refractory. The presence of calcium aluminates in the slag was found to enhance spinel stability, thus improving corrosion resistance³³.

CEQCSI CRYSTAL was utilized to investigate the slag corrosion mechanism, with particular focus on the influence of the CMA additive within the material's microstructure in the decarburized zone.

Slag 1 was characterized by a high FeO content and low viscosity, remaining fully liquid from approximately

1583 °C, with viscosity values not exceeding 120 mPa·s (Fig. 7 a). Upon heating to the 1600–1700 °C range, CMA (CaO-MgO-Al₂O₃) aggregates – regardless of grain size – release between 22 % and 36 % of liquid phase. This process is accompanied by the transient formation of the calcium hexaaluminate (CA₆) phase, which subsequently decomposes at 1700 °C. Simultaneously, crystallization of MgAl₂O₄ (MA) spinel occurs, which facilitates the incorporation of iron oxides into the solid phase and contributes to a further reduction in slag fluidity.

In the decarburized region of the MgO-C refractory lining, periclase (MgO) progressively dissolves into the slag. The introduction of CMA promotes the precipitation of MA spinels enriched with FeO and MnO from the melt, observed at MgO contents of approximately 9 % at 1600 °C, 12 % at 1650 °C, and 12.8 % at 1700 °C. These events are associated with a moderate increase in slag viscosity.

Locally, in the vicinity of CMA particles, saturation of the melt is achieved. At 1600 °C, with 40 % CMA content, approximately 9 % of complex secondary spinel phases precipitate, raising the viscosity to around 2000 mPa·s (Fig. 7 b). At 1700 °C, saturation corresponding to 50 % CMA content results in a fourfold increase in viscosity to 500 mPa·s.

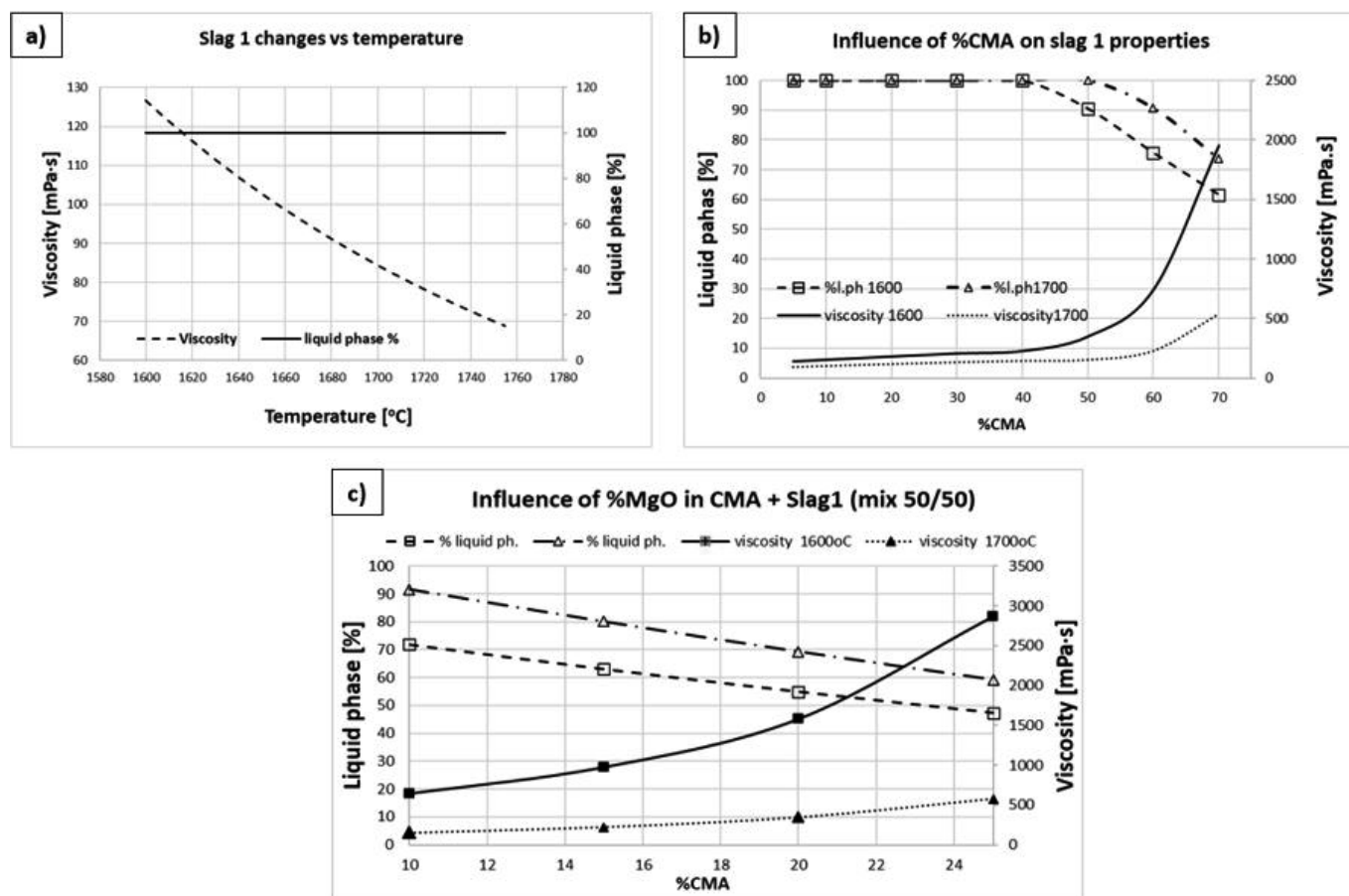


Fig. 7: a) Slag changes as a function of temperature, b) influence of CMA content on slag properties and c) influence of CMA content on slag properties (50 % of CMA) in Slag 2 (Table 2) derived from post-mortem samples of steel ladle linings containing CMA additive.

The addition of MgO further amplifies this effect. For instance, in a system with 50 % CMA and 25 % MgO in the decarburized layer, viscosity at 1600 °C increases to 3000 mPa·s with a crystallinity level of 50 %. At 1700 °C, viscosity reaches 500 mPa·s with 40 % crystallinity (Fig. 7 c). In both cases, the dominant crystalline phase was secondary MA spinel.

These spinel precipitated preferentially on fused periclase grains in a low- Al_2O_3 slag environment, enhancing the structural integrity of the refractory material and effectively impeding both slag penetration and graphite oxidation (Fig. 5 f). This mechanism significantly contributes to the improved corrosion resistance and mechanical cohesion of the MgO-C refractory under steelmaking conditions (Fig. 5 a).

(4) Design implications for steel ladle construction considering the use of magnesia-carbon bricks with CMA additive

Industrial trials (Fig. 4) conducted in the metal zone of a steel ladle used in long-product metallurgy revealed that no additional allowance for backfill mix is required when using MgO-C bricks containing CMA additives, compared to conventional MgO-C materials. The refractory composition, with 9 % carbon content, demonstrated strong adhesion to the ladle wall during operation, resulting in the formation of a monolithic block within the working lining. This monolithic behavior contributes to the protection of joints from erosion, which is especially beneficial under conditions of intensive stirring during secondary metallurgy.

However, the tendency of CMA-modified MgO-C bricks to form a monolithic lining also introduces the necessity for careful structural design of the entire ladle assembly. Due to the thermal expansion characteristics of MgO-C materials containing CMA additive and antioxidants, it is recommended to incorporate a 10–15 mm layer of a basic-type backfill mix. This layer should include a temporary binder and be formulated with an appropriate granulometry to accommodate the thermal expansion and contraction of the working lining throughout operation. Such a design prevents adhesion to the safety lining, thereby reducing the risk of vertical cracks and horizontal open joints.

Laboratory tests (Fig. 2–3) and industrial trials (Figs. 4–7) confirmed that the use of CMA additives in MgO-C bricks provides a viable solution for the high-stress conditions encountered in the metal zone of steel ladles. The enhanced corrosion resistance and structural integrity offered by CMA-modified refractories support their application in demanding metallurgical environments.

IV. Conclusions

- Laboratory corrosion tests conducted in an induction furnace demonstrated that MgO-C refractories with CMA additives exhibit superior corrosion resistance compared to reference samples, particularly in areas exposed to molten metal.
- Industrial trials of MgO-C bricks containing CMA and antioxidant additives showed improved

performance relative to similar products evaluated in previous studies,

- Post-mortem analysis revealed that even under exposure to acidic slags ($\text{C/S} = 1.8$) with low Al_2O_3 content (5.8 %), CMA additives promoted the formation of secondary MgAl_2O_4 spinel. This spinel phase effectively inhibits slag infiltration into the refractory microstructure.
- The post-mortem observations were corroborated by thermodynamic modeling, which confirmed the stability and protective role of MgAl_2O_4 spinel under the tested conditions.

Acknowledgements

This work was partially financially supported by the statutory funds of the Faculty of Materials Science and Ceramics, AGH University of Krakow, No. 16.16.160.557.

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