

REFRACTORY LINING WEAR MECHANISM IN BASIC OXYGEN FURNACE

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Abstract

The identification of the wear mechanism of the refractory lining of the basic oxygen furnace is a prerequisite for the optimization of the steelmaking process. Knowledge of the way in which a given factor acts on the amortization of the refractory lining is closely related to the development of technological procedures serving to limit their influence. The results of the analysis of the mechanism by which the thickness of basic oxygen furnace refractory lining is reduced during the campaign can be applied to the development of new refractories with more suitable chemical composition and physical properties. In this respect, the determination of a balanced consumption of gunning materials is also very important, since the expenditure on repair mixtures has a major portion of the total financial cost of the campaign. By determining the optimum consumption of gunning materials, it is possible to define the duration of the basic oxygen converter campaign during which the entire steelmaking process is financially viable for the producer. Based on the literature, the mechanism of wear of refractory lining has been developed. Temperatures from 1,300°C to 1,700°C, which can occur during the steelmaking process in the basic oxygen vessel, were considered. The wear process was divided into logical steps. In each step, the most probable course of the sub-processes and the products of the chemical reactions are described based on thermodynamic data.

Keywords: Refractory lining, basic oxygen furnace, wearing mechanism, gunning material

1. INTRODUCTION

At present, the main part of the production line of refractory materials for the steel industry has shifted to the field of unfired magnesia bricks, which are bound by organic binders with a carbon content of up to 7%, and magnesia-carbon materials with a carbon content of 7 to 30% [1]. In MgO-C refractories, the ceramic bond is replaced by a carbon bond. This bond is provided by organic binders such as coal tar and synthetic resins [2]. Pyrolysis leaves a carbon residue which is part of the carbon component of the products [3]. The peculiarity of the carbon bond is that the surface of the graphite is not wetted by liquids and the bond is formed by the periclase (MgO) component and the edges of the graphite crystals [4].

The wear mechanism of the basic oxygen furnace refractory lining is a complex process. The refractory lining of the basic oxygen furnace (BOF) is chemically degraded by corrosion, slag penetration and erosion - flaking of compacted layers [5]. Dissolution of refractory material by oxide melts is one of the most significant interactions [6]. The corrosion process and its mechanism substantially determine the wear rate of the BOF refractory lining material. The corrosion mechanism of refractory magnesium-carbon lining is characterized by the fact that the carbon is not wetted by the slag [7]. The slag only penetrates the refractory lining to the layer where the carbon or graphite in the bond is degraded. The carbon component also influences corrosion by reducing iron oxides [3,8].

The negative property of periclase-carbon (MgO-C) refractories is that the carbon contained in the material is not sufficiently resistant to the influence of oxygen [9]. The amortization process of the refractory starts with the diffusion of oxygen through the gaseous layer to the "gas-decarburized material" phase interface, where a carbon-free layer saturated with oxides from the slag is formed in the reaction zone. This is followed by diffusion through the decarburized layer of refractory material (MgO), which continues with the reaction at the "decarburized material (MgO)-intact material (MgO-C)" phase interface. Finally, CO diffuses to the outer surface of the lining block [10-12]. Repair procedures help to protect the refractory lining of the aggregate from wear caused by corrosive effects, while also helping to extend the life of the refractories and thus the oxygen converter campaign itself [13]. Gunning of refractory is one of the most effective ways of extending the life of the refractory lining of an oxygen converter and thus increasing the number of heats per campaign. It is a method of pneumatically applying non-shaped refractory mixtures to a precisely defined damaged area of the lining [14,15].

This paper focuses on the analysis of the wear mechanism of BOF refractory lining from the perspective of two opposing processes - the wear of the MgO-C lining during the steelmaking process and the subsequent repair of the refractory lining by gunning using non-shaped repairing mixtures. By interacting with the corrosive environment during the melting process and the subsequent formation of a protective layer by the gunning material, it is possible to significantly increase the number of heats within a single BOF campaign.

2. THERMODYNAMIC MODELING

Knowing the chemical composition of analyzed BOF slag (**Table 1**), MgO-C refractory (**Table 2**) and gunning material (**Table 3**) makes it possible to identify the chemical compounds that have attacked the refractory during the steelmaking process and which of them form a protective layer on the BOF refractory lining during repair operations, thus reducing the wear mechanism itself and extending the life of the BOF lining.

The mentioned mechanism of BOF refractory lining was analyzed using available literature and thermodynamic software HSC Chemistry 5.11 from Outokumpu (Metso Outotec).

Table 1 Average composition of analyzed BOF slag [16]

Component	CaO	Fe _{general}	SiO ₂	MgO	MnO	P ₂ O ₅	Al ₂ O ₃	S
Contents (%)	47	20	12	7	3.5	1	0.8	0.06

Table 2 Average composition of analyzed MgO-C refractory lining [16]

Component	MgO	SiO ₂	CaO	Fe ₂ O ₃
Contents (%)	98	0.4	1.2	0.5

Table 3 Average composition of analyzed gunning material [16]

Component	MgO	CaO	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
Contents (%)	87	7.7	2.7	1.3	0.4	0.1

Using thermodynamic modeling, the most likely products of chemical reactions in the BOF slag were found to be formed from the most represented chemical elements in the converter slag itself (Ca, Fe, Si, Mg, O). Chemical products of these elements are listed in **Table 4**.

Based on the chemical composition of the gunning material [16] listed in **Table 3** and particular temperatures, the most probable chemical compounds were modeled (**Table 5**).

Table 4 List of the most probable products within the input components in BOF slag

Name	Chemical formula	ΔG (kJ)		Melting point (°C)
		1,300 (°C)	1,700 (°C)	
Merwinite	Ca ₃ MgSi ₂ O ₈	- 274.424	- 285.121	-
Akermanite	Ca ₂ MgSi ₂ O ₇	- 146.355	- 126.345	1,454
Diopside	CaMgSi ₂ O ₆	-139.683	- 166.519	1,391
Monticellite	CaMgSiO ₄	- 101.513	- 101.158	1,503
Wolastonite	CaSiO ₃	- 90.774	- 91.510	1,190
-	Ca ₂ Fe ₂ O ₅	- 76.285	- 106.286	1,477
Cyclowollastonite	CaSiO ₃ (C)	- 66.134	- 50.025	1,540
Forsterite	Mg ₂ SiO ₄	- 58.338	- 58.020	-
-	CaFe ₂ O ₄	- 43.149	- 74.190	1,240
-	MgSiO ₃	- 40.568	- 46.535	1,577

Table 5 List of the most expected reaction products within gunning material

Name	Chemical formula	ΔG (kJ)		Melting point (°C)
		1,300 (°C)	1,700 (°C)	
Gehlenite	Ca ₂ Al ₂ SiO ₇	- 1,278.827	- 1,911.329	1,584
-	Ca ₂ P ₂ O ₇	- 520.103	- 529.981	1,353
-	Mg ₃ (PO ₄) ₂	- 419.220	- 430.862	1,353
Dicalciumferrite*	Ca ₂ Fe ₂ O ₅	- 342.090	- 290.176	1,477
Akermanite	Ca ₂ MgSi ₂ O ₇	- 146.355	- 126.345	1,454
Diopside	CaMgSi ₂ O ₆	- 139.683	- 166.519	1,391
Anorthite	CaAl ₂ Si ₂ O ₈	- 138.618	- 147.361	1,550
Monticellite	CaMgSiO ₄	- 101.513	- 101.158	1,503
Cordierite	Mg ₂ Al ₄ Si ₅ O ₁₈	- 98.826	- 155.127	1,467
Dicalciumferrite**	Ca ₂ Fe ₂ O ₅	- 76.285	- 106.286	1,477
Fayalit	Fe ₂ SiO ₄	- 21.446	- 31.835	1,217

* based on the reaction: $4 \text{CaO} + 4 \text{FeO} + \text{O}_{2(g)} = 2 \text{Ca}_2\text{Fe}_2\text{O}_5$

** based on the reaction: $2 \text{CaO} + \text{Fe}_2\text{O}_3 = \text{Ca}_2\text{Fe}_2\text{O}_5$

3. RESULTS AND DISCUSSION

3.1 Wear mechanism of MgO-C refractory in basic oxygen furnace

The wearing mechanism of periclase-carbon refractory in BOF consists of the following steps:

- Decarburisation of MgO-C refractory layer by oxygen: The decarburised refractory layer is created by saturation of free oxygen dissolved in metal, oxide form of oxygen in molten slag, or blown oxygen into the upper layer of refractory. This forms a decarburised layer saturated with slag oxides.

- Reaction of refractory and slag through glass phase
- Partial dissolution of iron oxides in periclase: Partial dissolution of iron oxides in MgO gives rise to solid solution of Fe₂MgO₄. This process reduces the amount of iron oxides in BOF slag and also inhibits the effects of refractory corrosion.
- Formation of magnesium silicate: BOF slag also contains a noticeable amount of SiO₂, which causes significant periclase corrosion. According to thermodynamic calculations, the most expected chemical products are given in **Table 6**.

Table 6 Thermodynamic parameters of incipient magnesium silicate

Name	Chemical formula	ΔG (kJ)		Melting point (°C)
		1,300 (°C)	1,700 (°C)	
Magnesium orthosilicate	Mg ₂ SiO ₄	- 60.411	- 60.211	1,898
Magnesium metasilicate	MgSiO ₃	- 40.568	- 46.535	1,577

- Formation of dicalcium silicate coating: Dicalcium silicate is formed by the interactive reaction of slag and periclase (**Table 7**). This dicalcium silicate forms a coating above the refractory. This shield slows down the corrosive action of the BOF slag into the refractory.
- Reaction of iron oxides with carbon: Carbon from refractory material reduces iron oxides from slag. The most expected results of carbon and iron oxides are given in **Table 8**.
- Solid solution formation: Iron oxides react not only with carbon but also with periclase (MgO). The reaction of iron oxides with periclase produces the solid solutions (melting point 1,750°C) according to the formula Fe₂O₃ + MgO = MgFe₂O₄.

Table 7 Thermodynamic parameters of incipient dicalcium silicate

Name	Chemical formula	ΔG (kJ)		Melting point (°C)
		1,300 (°C)	1,700 (°C)	
Larnite	Ca ₂ SiO ₄ (L)	- 141.138	- 148.840	-

Table 8 The most expected reactions of carbon from refractory and iron oxides

Iron oxide	Reaction	ΔG (kJ)	
		1,300 (°C)	1,700 (°C)
Fe ₂ O ₃	Fe ₂ O ₃ + 3C = 2Fe + 3CO	- 332.842	- 534.580
FeO	FeO + C = Fe + CO	- 88.797	- 144.791

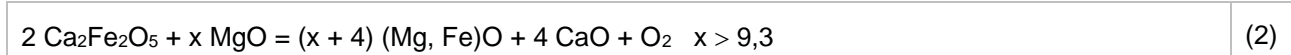
- Reduction of MgO by carbon at high temperatures: There is an interaction between the components of the refractory material - MgO (periclase) and C (carbon) at high temperatures. The reduction takes place through the following chemical reaction: MgO + C = Mg_(g) + CO_(g). The starting temperature of this reaction is 1,846°C.
- Formation and decomposition of spinel and magnetite: The formation of solid solutions such as spinel (by reaction MgO + Al₂O₃ = MgAl₂O₄) and magnetite (by reaction 3Fe + 4O_(g) = Fe₃O₄) can contribute to the destruction of the refractory lining by volume change. Decomposition is the main cause of volume change.

3.2 Protective layer formation mechanism of gunning material on MgO-C refractory lining in BOF

Gunning repair materials are characterized by easy sinterability, connectability and self-compacting ability due to the formation of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) (1). The system $\text{MgO} - 2\text{CaO} \cdot \text{SiO}_2$ melts at a temperature of $1,800^\circ\text{C}$. The melting point is rapidly reduced to $1,308^\circ\text{C}$ by the presence of $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$. The cumulative value of Fe_2O_3 causes an increase in melt quantity. If this state is not changed, the layer of gunning material would be destroyed and washed away. A significant change is caused by the decomposition of dicalcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$), which is unstable at low partial pressure of O_2 or by reduction in the gaseous environment of CO .



In the strong reduction environment, $\text{Ca}_2\text{Fe}_2\text{O}_5$ begins to reduce from 900°C to form finely diffused CaO , FeO and Fe . If there is sufficient MgO in the system and the temperature is higher than $1,200^\circ\text{C}$, FeO enters into solid solution in periclase and CaO is excluded as a solid phase beyond solubility. The process occurs by reaction (2) [14]:



The condition for the layer of gunning mixture to be formed and solidified is that it is covered with metal or the partial pressure of O_2 is sufficiently low and CO is present in significant concentrations.

An analysis of the mechanism by which the gunning repair mix detaches from the refractory lining indicates that the FeO content of the converter slag, as well as the FeO content of the gunning material itself, has the greatest effect on the process by which the gunning mixture detaches from the BOF refractory lining.

Since the gunning repair mixes are only chemically bonded to the converter shaped refractory lining, there is a synergy with BOF converter slag infiltration into the gunning material to detach the gunning mixture from the converter working refractory lining. This leads to an increased consumption of gunning repair mixture, as documented in **Figure 1**.

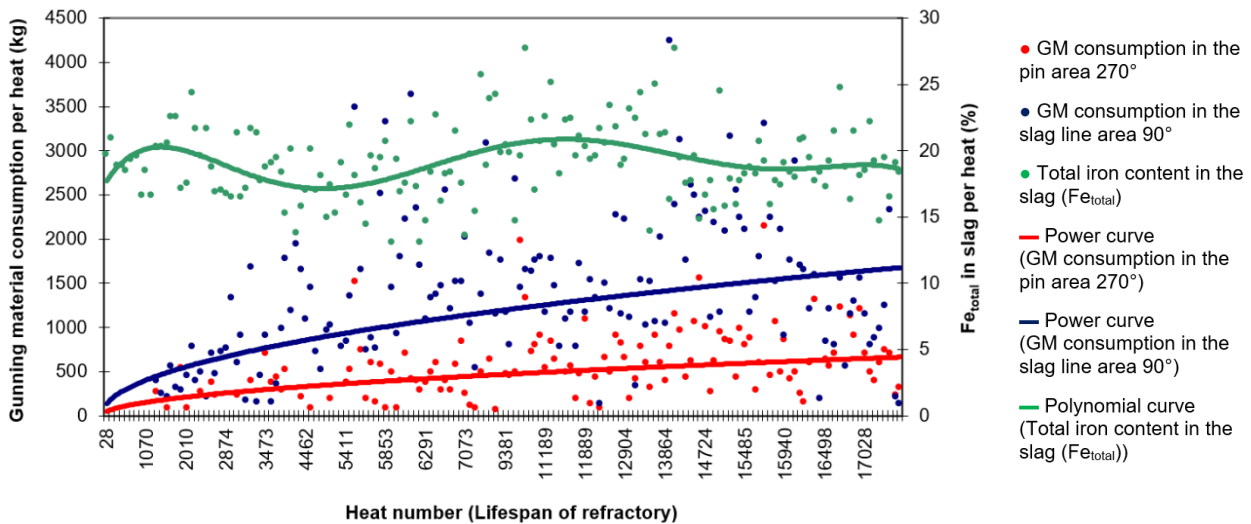


Figure 1 Comparison of gunning material (GM) consumption per heat in the most exposed areas of the BOF refractory lining and the total iron content of the BOF slag per heat during the analyzed campaign

4. CONCLUSION

Analysis of the mechanism affecting the wear of magnesium-carbon refractory linings of basic oxygen furnaces during the campaign, significantly helps to optimize the creation of technological and operational procedures, but also helps in the selection of a suitable refractory and the choice of an appropriate design of converter linings. Detailed knowledge of the wear mechanism of the periclase-carbon lining is also an indicator of the

adequacy of the converter process, since any deviation from the standard state of BOF process is reflected in the performance of the MgO-C basic oxygen converter refractory linings.

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