

DEGRADATION MECHANISMS OF Si_3N_4 -BONDED SiC BRICKS INSTALLED IN BLAST FURNACE'S SHAFT

María José Rimoldi, Pablo Marinelli², Juan Mirabelli², Silvia Camelli¹ and Adrián Vazquez¹

¹Instituto Argentino de Siderurgia, San Nicolás, Argentina

²Ternium Siderar, San Nicolás, Argentina

ABSTRACT

In November 2015 Ternium Siderar Blast Furnace #1 was blown down after 5 years in operation (2010-2015). In order to evaluate the main wear mechanism encountered in the working lining of the middle shaft, it was performed a post mortem study of SiC bricks. These are Si_3N_4 -bonded. The post mortem study included determination of the chemical and mineralogical composition, DT/ TG analysis and electronically microscopy (SEM and EDS analysis).

The SiC bricks under study presented thermal and structural spalling. Chemical attack by alkali penetration was identified, mainly potassium oxide with generation of new phases such as potassium hydrogen silicate. Cracks present in the material permit alkali condensation in the brick. Due to the thermal profile in its thickness during operation, alkali content in the cold face is greater than in the hot face.

Keywords: blast furnace, shaft, SiC , alkali.

INTRODUCTION

The refractory systems of the bosh, belly and stack of the blast furnace, probably, are the most critical in terms of their impact on the operating capability of the blast furnace. When selecting refractories for these zones, it is imperative to evaluate the wear mechanisms to be encountered, to identify the expected operation conditions which could affect the lining life and to evaluate all external factors which will impact refractory performance [1].

Silicon carbide linings are used in these zones of the blast furnace due to their higher resistance to chemical attack, abrasion and thermal shock than fireclay or high-alumina refractory. SiC refractories can have several different bond types which change the physical properties of the refractory. In general, silicon nitride (Si_3N_4) bonded SiC has proven to be preferred over various direct bonded, self-bonded or carbon silicon bonded materials [1, 2]. Although the SiC grains are stable when exposed to alkalis, this is not the case with bonding systems. Ceramic bonding and even oxi-nitride are affected by potassium [3]. SIALON ($\text{Si}_{6-x}\text{AlO}_x\text{N}_{8-x}$) bonded materials have also been used for their improved alkali resistance [1, 2].

In November 2015 Ternium Siderar Blast Furnace #1 was blown down after 5 years in operation (2010-2015). In order to evaluate the main wear mechanism encountered in the working lining of the middle shaft, it was performed a post mortem study of SiC bricks. These are Si_3N_4 -bonded. The post mortem study included determination of the chemical and mineralogical composition, DT/ TG analysis and electronic microscopy (SEM and EDS analysis).

POST MORTEM BRICKS

Figure 1 and 2 show the post mortem SiC bricks from the middle shaft of BF#1, where a wet external appearance, a remaining thickness between 20-60 mm, cracks parallel and normal to the hot face and a very fine dark deposit on crack surfaces can be observed.

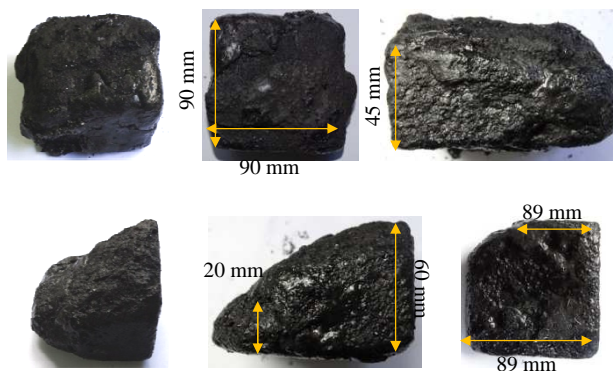


Fig. 1: External aspect of the post mortem SiC bricks.



Fig. 2: Internal aspect of the post mortem SiC bricks.

EXPERIMENTAL PROCEDURE

The post mortem study of the SiC bricks included determination of the chemical composition by X ray fluorescence and loss of ignition at 950°C , identification of the crystalline phases by XRD, differential thermal analysis and thermogravimetry at 1200°C , determination of the critical temperatures and microstructural observation (SEM and EDS analysis). For the study, one of the SiC bricks was divided in different zones, as shown in figure 3.

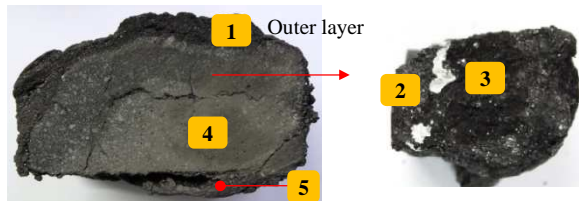


Fig. 3: SiC brick under study.

RESULTS

Table 1 shows the chemical composition and loss of ignition at 950°C of the outer layer and figure 4 shows the DTA/ TG curves of this layer. The total weight loss at 1200°C was 16,9%. At 1150°C the layer melted. In figure 5 are shown the cones before and after determining the critical temperatures.

Tab. 1: Chemical composition and weight loss of the outer layer.

	Oxides (wt. %)							LOI
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃	CaO	MgO	
Outer layer	65,8	1,2	29,3	0,6	1,1	1,1	0,3	6,4

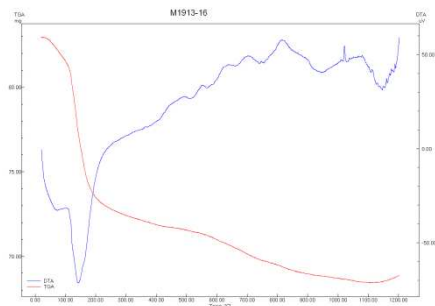


Fig. 4: DTA/ TG curves of the outer layer.



Fig. 5: Cones before and after the critical temperatures determination.

Table 2 shows the chemical composition of different zones inside the SiC brick. The hot face of the SiC brick is mainly composed of silicon carbide (Moissanite 4H and 6H); also metallic iron, potassium hydrogen silicate and an amorphous phase were identified.

Tab. 2: Chemical composition of the SiC brick.

Zone	Oxides (wt. %)						
	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Fe ₂ O ₃	CaO	MgO
1. Hot face	77,0	0,8	9,6	0,5	10,5	0,5	0,2
2. Grey	95,8	0,4	2,6	0,2	0,7	0,1	0,1
3. Black	95,5	0,4	2,9	0,2	0,7	<0,1	0,1
4. Global	94,0	0,4	4,5	0,4	0,6	0,1	0,1
5. Cold face	83,7	0,5	12,0	0,6	2,4	0,1	0,1

When cutting the post mortem sample, a thin piece separated from the brick. So, SEM observation and surface EDS analysis were performed onto both fracture surfaces: one side with a very fine dark deposit and the other grey coloured. The EDS analyses are shown in table 3 and figure 6 shows the corresponding spectrum and images of the analysed surfaces.

Tab. 3: EDS analysis of both sides of the SiC thin piece.

Side	Element (%)							
	C	O	Na	Al	Si	Cl	K	Fe
Deposit	22,9	23,4	0,7	0,7	30,8	2,9	17,9	0,7
Grey SiC	26,3	11,3	-	0,9	53,1	0,7	7,2	-

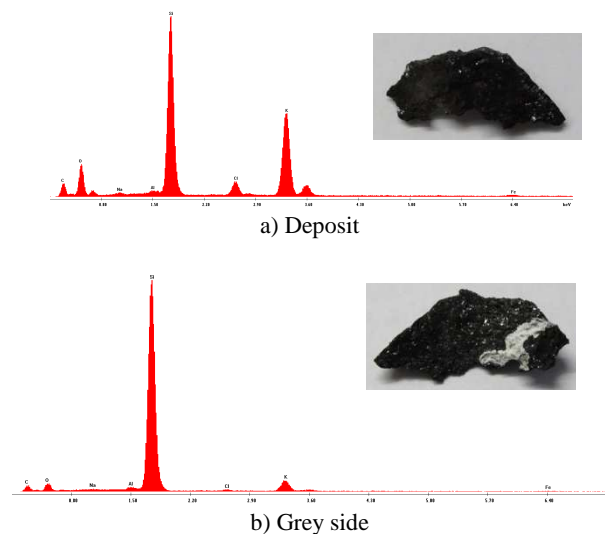


Fig. 6: EDS spectrum of SiC brick's piece.

DISCUSSION

The main wear mechanisms that suffered the refractory lining of the middle stack are chemical attack by alkalis and zinc, oxidation, abrasion by the descending burden and moderate thermal shock [4, 5]. Temperature plays an important role in many of these wear mechanisms, in particular the chemical ones. In table 4 the critical temperatures for each type of chemical attack are presented, the temperature at which each chemical reaction will take place [1, 4]. Therefore, to prevent wear by chemical action wall temperature should be below 400°C to ensure that none of these mechanisms will affect wall lining [4].

Tab. 4: Critical temperatures of the main chemical wear mechanisms.

Mechanism	Temperature range (°C)
CO-disintegration	450-850
Alkali and Zn attack	800-950
Oxidation by O ₂	>400
Oxidation by CO ₂ + H ₂ O	>700

Another operating factor that affects refractory life is furnace availability. Furnaces are continually cycled from on-wind to off-wind for maintenance shut-downs or suffer interruptions of full wind because of operation problems. These practices submit the refractories to thermal cycling, which results in thermal shock damage and fatigue to the refractories, shortening their life [1].

All ceramic refractories, including SiC materials, will spall and thermally crack if they experience severe temperature fluctuations. The thermal shock is more severe when refractories are cooled from one side, like with staves or externally cooled jackets. Thermal cracks occur parallel to the refractory hot face. These cracks permit the alkali vapors, which penetrate through the pores or joints, to condensate in the interior of the refractory, hastening the chemical attack. Furthermore, because these cracks occur parallel to the hot face, air gaps are formed, interrupting heat transfer to the cooling system, thus increasing hot face temperature and assuring refractory chemical attack [1].

Through the determination of the chemical and mineralogical composition, it was possible to verify that the

outer layer was composed of silicon carbide from the brick, metallic iron, potassium hydrogen silicate and an amorphous phase, with a variable content of potassium between 10-29%. In the interior of the SiC brick, potassium contamination was identified, being higher the content at the cold face (figure 7).

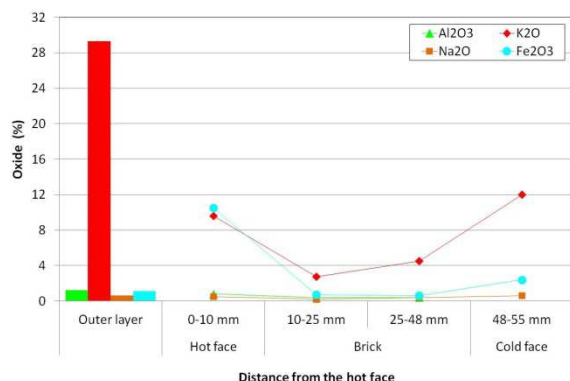


Fig. 7: Evolution of the chemical composition through SiC brick thickness.

Alkalis have three negative actions in the blast furnace: the attack to the refractory lining, formation of accretions or build-ups; and degradation of coke and burden quality. Alkali silicates enter the blast furnace with burden materials and remain stable until the appearance of liquid phase. At 1300°C they dissolve in the primary slag and are progressively reduced to metallic vapors. Metallic potassium vapor is transformed into different compounds as it is being dragged by ascending gases, according to blast furnace zones. In the bosh, this vapor is partially transformed to potassium cyanide (KCN), being able to condense in the form of fine drops on the refractory wall or on the coke and burden materials. At 1200°C, in the zone of the furnace with oxidizing conditions with respect to KCN, it is transformed into liquid carbonates (K₂CO₃), which can be also deposited on the charge or on the lining. The remaining metallic vapors exit through the top of the furnace in the form of potassium chloride [3].

Alkali vapors induce phase transformation with an associated volume increase and deposition of carbon, causing refractory swelling and cracking. Potassium penetrates into the refractory lining, oxidizes and reacts with silicon and alumina compounds or with carbon present in the refractory material. This results in the formation of compounds with low melting point and with specific volumen 6 to 20% higher than the original material (even up to 60% if combining K and C). Inner stresses arise and cause the destruction or cracking of the refractory material [3, 6].

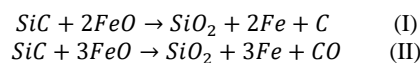
The formation of potassium silicates and aluminum silicates takes place below 1000°C, temperature at which refractories are brittle, rigid and unable to accommodate volumetric changes [6]. Carbon refractories materials and potassium vapors react between 200°C and 600°C, but potassium carbides are unstable and decompose between 600°C and 700°C. Above 700°C it is not possible their formation [3].

Scaffold or build-ups are formed by materials that adhere and grow onto the wall and can disturb the normal operation of the blast furnace. Accumulation of these impervious solids can occur from the bosh to the upper stack. In low-temperature zones, where the liquid phase is not present, such as middle and upper stack, scaffolds or adhesions can be formed. On the other hand, scabs are formed by viscous phases, semi-molten or liquid, in the bosh and belly, zones with higher temperatures [7].

According to the DTA/ TG, the outer layer present in the SiC brick under study has the main weight loss (12%) at low temperature, between room temperature to 234°C, due to water boiling. In the temperature range of 234-700°C, two exothermic

reactions take place associated with the melting of the potassium compound [8], with a weight loss of 3,4%.

At higher temperatures, in the outer layer, exothermic reactions due to iron oxidation above 570°C and subsequent SiC oxidation by FeO are observed [9, 10]:



These reactions, with the formation of CO gas, take place because the DTA was run under oxidizing atmosphere. In operation, these will not occur since the reducing atmosphere in the blast furnace, except in the tuyeres. Above 1000°C the weight increase is due to SiC oxidation by O₂ present in the atmosphere.

CONCLUSIONS

The SiC bricks under study presented thermal and structural spalling. Chemical attack by alkali penetration was identified, mainly potassium oxide with the generation of new phases such as potassium hydrogen silicate. Cracks present in the material permit alkali condensation in the brick. Due to the thermal profile through the thickness during operation, alkali content in the cold face is greater than in the hot face.

The outer layer that covers the post mortem bricks is a mix formed by the interaction of the SiC with alkali, iron and water.

REFERENCES

- [1] Dezemerjko, A. J., Baret, D. F., Hubble, D. H. Chapter 4. Ironmaking Refractory Systems. In: Wakelin, D. H, editor. The Making, Shaping and Treating of Steek, 11th Edition, Ironmaking Volumen; 1999; The AISE Steel Foundation; Pittsbrugh, USA. p. 229-248.
- [2] Shikano, H., Hatakeda, F., Honda, T., et al., editors. Refractory Handbook; 1998; Japan: TARJ. p. 150-155.
- [3] de Lorenzo Ferrera, G., Egea Molina, F. Causas de desgaste del refractario del horno alto y técnicas de reparación en caliente. p. 13-41.
- [4] van Laar, J., Tijhuis, G., Spreij, M., Stokman, R. Blast furnace lining life – A quantitative analysis of lining/ cooling systems. In: 53th Ironmaking Conference Proceedings; 1994; Warrandale, USA. ISS-AIME; 1994. p. 417.
- [5] Hebel, R., Steiger, R., Streuber, C. Advanced materials for the blast furnace lining in regard to long service life, reasonable cost and their theoretical qualification. In: 53th Ironmaking Conference Proceedings; 1994, Warrandale, USA. ISS-AIME; 1994. p. 397-406.
- [6] Godoy, E. F., Correa, G., Marconi Scudeller, L. A., Pereira Salgado, A. Ensaio para avaliação do ataque por vapor alcalino em refratários para injeção em alto-forno. Metalurgia-ABM. 1981 Mai; 37 (282): 275-9.
- [7] Geerdes, M., Lingardi, O., Toxopeus, H. Introducción al proceso de alto horno; 2005. Verlag Stahleisen. p. 100-101.
- [8] Handbook of chemistry and physics, Physical constants of inorganic compounds, 61st Edition, 1980-1981, CRC Press., p. B 136.
- [9] Domiciano, V. G., Ollmann, A. R., Clemente, E. I., et al. Desafios da ala de corrida de altos-fornos: Análise da falha de concreto refratário para canal de corrida. In: ABM 43º Seminário de Redução de Minério de Ferro e Matérias-primas; 2014 1-4 Sep; Belo Horizonte, MG, Brasil. p. 786-795.
- [10] Gupta, A. D., Mukhopadhyay, S. C. Characterization and performance of new generation SiC-based trough castable required for 2000 m³ blast furnaces at BSL. INTERCERAM Refractories Manual. 2013: 178-183.