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PROTECTION MECHANISMS FOR BLAST FURNACE CRUCIBLE USING TITANIUM OXIDES

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Abstract

In modern steelmaking the duration of a working campaign for a blast furnace is related to the life of the crucible. Adding titanium oxide has been a frequent practice in the operation routines for modern blast furnaces, seeking the protection of the crucible walls, independently from its physical or chemical characteristics. These practices, as conventional operation of iron and steelmaking installations, present both advantages as well as undesirable consequences.

The work proposes the incorporation of rutile (TiO_2) or illmenite ($FeO{\cdot}TiO_2$) in the refractory matrix of the linings, as a practice that results in a protection of the crucible without altering, under any circumstance, the regular operation of the installation.
Key words: blast furnace, campaign extension, crucible, titanium dioxide additions.

Introduction

The existence of a blast furnace and its auxiliary installations (sinter, coke and pelletizer plants), are still indispensable in the 21st century steelmaking industry. Around 65% of the world's steel production is made with it; and in an economic consideration, 60% of the production costs for steelmaking as a whole are related to the functioning of its installations in a correct fashion [1,2].

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Therefore, during the last decades, all the problems related to the extension of the working campaign of a furnace along with assuring high production rates of pig-iron, have been widely discussed in the specialized bibliography. Even though while prolonging the working campaign of a blast furnace, a large number of variables must be taken into account, the work focuses only on those operation practices related to the addition of titanium dioxide, with the purpose of repairing crucible zones affected by considerable wear (specially on below the taphole or at the corners of the hearth): formation of "*elephant foot*" or "*mushroom type*" profiles as shown in Figure 1 [3,4,5].

One phenomenon that must be considered when studying the protection of furnaces and pyrometallurgic reactors is the formation of scabs/accretions at the interface of the lining with the corrosive fluid. Fredman [6] analyzed the benefits and disadvantages that scabs in the stack/bosh zones of the blast furnace may cause in a general (not specific) way, though some references are indicated to study the consequences of accretions forming in the crucible.

Since the 1950s, the addition of titanium oxides in the material fed to the blast furnace has been considered as an alternative to the protection of the crucible, as the precipitation of titanium carbide, TiC, is expected. However this operation practice was uncommon until the beginning of this century [7]. These practices include the addition of titanium minerals (illmenite or rutile) inside the ferric charge fed to the furnace inlet, in a continuous or discontinuous way (figure 1). Likewise, taking advantage of the generalized use of injection technologies of carbon through the tuyeres, the selective injection of titanium minerals is done, at zones surrounding the damaged lining, as shown in figure 1 [8,9].

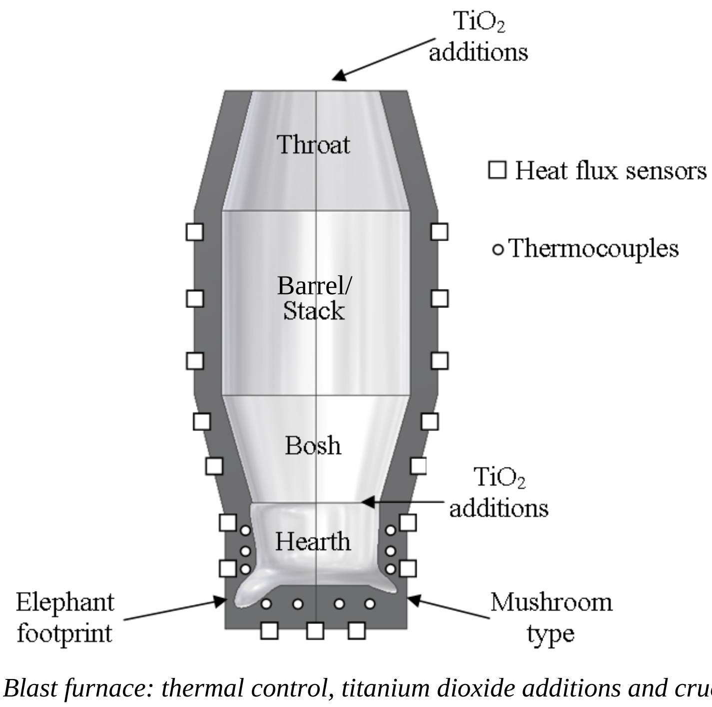

Figure 1. Blast furnace: thermal control, titanium dioxide additions and crucible wear profiles

Protection mechanism by adding titanium compounds

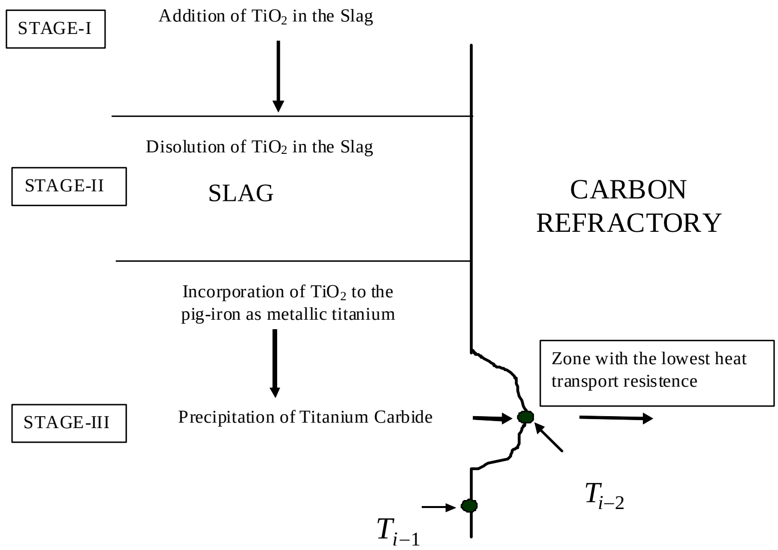

Figure 2. Protective mechanism for a carbon refractory on zones with wear through the precipitation of titanium carbide, TiC

Figure 2 presents the protection mechanism of a zone with wear in the crucible, through the precipitation of titanium carbide, TiC, or complex titanium carbonitrides, TiC_xN_y; it may be described by the following stages [10,11]:

Stage-I: Addition/dissolution of titanium oxides from the mineral charge towards the slag.

Stage-II: Reduction of titanium inside the slag and its incorporation to the pig-iron:

$$TiO_2(dis;\ slag)+2C(dis;\ pig\text{-}iron) \Leftrightarrow 2CO(g)+Ti(dis;\ pig\text{-}iron) \qquad (1)$$

Stage-III: Precipitation/protection of TiC at zones with high wear in the crucible:

$$Ti\ (dis;\ pig\text{-}iron)+C(dis;\ pig\text{-}iron) \Leftrightarrow TiC(s) \qquad (2)$$

From the thermodynamic point of view, reaction (2) is exothermal and consequently the equilibrium constant diminishes as temperature rises. If free energy, ΔG, associated to reaction (2) is analyzed, its variation as temperature rises becomes less negative (or more positive): precipitation of titanium is promoted when temperature lowers [12]. This circumstance will explain why, at equal conditions, titanium carbide will thermodynamically tend to precipitate at zones of the lining most affected by wear:

$$T_{i-1} > T_{i-2} \text{ in Figure 2} \qquad (3)$$

where T_{i-1} is the nodal temperature at the lining wall and T_{i-2} is the temperature at the maximum wear zone.

Experimental tests confirm that the reading of the thermocouples located at the cold zones of the lining and affected by wear are higher than the ones at zones which are not eroded. According Fourier's First Law, the resistance to heat flux, J_q ($W \cdot m^{-2}$), would be lower at zones with wear due to the reduction in the ratio:

$$\left(\frac{\Delta x}{\lambda}\right) \tag{4}$$

where Δx is the thickness (m) and λ is the thermal conductivity of the lining ($W \cdot m^{-1} \cdot °C^{-1}$). Nevertheless, taking the Le Chatelier Principle into account (principle of action and reaction from a chemical point of view), the system will have a tendency to react by opposing itself to the increase in heat flux caused by the diminishing in the thermal conductivity resistance at the damaged zones of the lining [12]. Therefore, a heat flux reduction will take place through a diminishing in the thermal gradient, ΔT :

$$\Delta T = (T_i - T_{cold}) \tag{5}$$

Consequently, a reduction in ΔT will be produced, either by a reduction of the nodal temperature at the interface between refractory and pig-iron, T_{i-2} of Figure 3, or by an increase in temperature at the thermocouples of the cold zone of the lining ($T_{cold} \leq 500°C$).

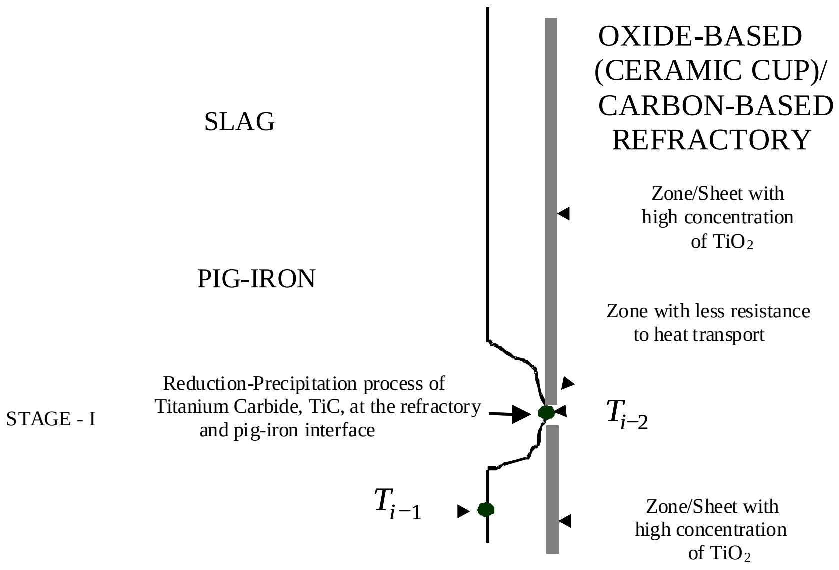

Figure 3. Protective mechanism for any kind of refractory quality at zones with wear through the precipitation of titanium carbide, TiC, in laminated ceramic compounds

New protection system proposal

Addition of titanium mineral to the blast furnace charge with the purpose of protecting the zones of the crucible affected by considerable wear (Figure 2) has the following disadvantages:

1. The performance of the precipitation of titanium is low, which is why a discontinuous treatment with 20~30 kg of TiO_2 per ton of pig-iron is preferred, compared to continuous addition campaigns of 3~5 kg of TiO_2 per ton. Both from the kinetic as well as the thermodynamical point of view, it is advisable for the amount of titanium in the pig-iron to be at least 0.10% [7,11].
2. Due to the low performance of the titanium additions, in recent years it has been preferred to make selective treatments to those zones most affected by wear, by injecting through the tuyeres most adequate for each case, the titanium compounds [7,11].
3. Any of the treatments previously mentioned, requires an specific coke consumption that represents the most important variable both in the operation as in the cost of the blast furnace [7,11].
4. The presence of amounts close to 0.10% of titanium in the pig-iron, results in a content of TiO_2 in the slag between 1.0 and 2.0%. The properties of the slag, such as density and viscosity, are substantially modified and increased (specially viscosity), changing the patterns of the furnace cast: number and duration of casts per day, decreasing the productivity of the furnace as viscosity becomes higher [4,5,7,11,12].
5. In all the revised bibliography, the only substrate (heterogeneous nucleation) for the precipitation of TiC or TiNC, is the carbon-based material. There isn't any information about the possible formation of these compounds on substrates different than carbon [13,14].

Just as previously mentioned and without considering the inconvenience of the presence of titanium in operations and processes subsequent to the blast furnace, this work proposes an alternative route to reach the objectives sought: prolong the operation life of the furnaces through the precipitation of TiC or TiNC at damaged zones of the crucible, avoiding the disadvantages produced by existing conventional practices.

Taking into account solutions currently applied by scientists and engineers in the aeronautical field, and applying them to the design and construction of blast furnaces [13,14], the most recent structural designs used for fuselage, wings or rudder: metal-ceramic-polymer laminated compounds, new ceramic laminated compounds for blast furnaces are being designed just as shown in figure 3. For these new crucible designs, it will be possible to find zones of the lining (thin sheets): materials with high percentage of TiO2 that react with the metallic melt or the slag when the erosion of the crucible facilitates the contact between them.

The use of linings with *laminated ceramic compounds* may avoid most of the disadvantages of current conventional treatments, as in this type of lining the formation mechanism of titanium carbide will only be activated when the zones with high TiO_2 content make contact with the pig-iron. In this case, the protective reactions will be:

$$TiO_2(lining)+3C(dis;\ pig\text{-}iron) \Leftrightarrow 2CO(g)+TiC(s) \qquad (6)$$

$$3(FeO \cdot TiO_2)(lining)+13C(dis;\ pig\text{-}iron) \Leftrightarrow 9CO(g)+Fe_3C+3TiC \qquad (7)$$

Supposing that the ratio:

$$\frac{P(CO)}{a(C)} \approx 1.0 \qquad (8)$$

as both the carbon activity in the pig-iron, $a(C)$, and the partial pressure of the carbon monoxide, $P(CO)$, in the crucible of the blast furnace, are very close to its standard activity/unit pressure states. The free energy associated to reaction (6) starts showing negative values when T > 1200 ºC, while for reaction (7) the same happens, but for T > 1100 ºC (1,10).

Finally, the presence in the design of the crucible of *laminated ceramic compounds* with enriched TiO_2 zones with thickness between 20~40 mm (Figure 3) may be compatible with the expansion zones needed (2D expansion in x and y) in the crucible at the start of operation [11,13].

Conclusions

Though it's an operational practice to use the protection mechanisms of carbide and carbonitride precipitation of titanium using titanium minerals as addition to the blast furnace charge, it results in low performance and affects operative variables and costs of the steelmaking process.

An alternative to these problems is to design the crucibles with *laminated ceramic materials* containing high titanium oxide sheets, in order to produce precipitation at zones where erosion facilitates the contact of pig-iron with high titanium content sheets.

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List of symbols, abbreviations and acronyms

ΔG	free energy
T_{i-1}	nodal temperature at the lining wall
T_{i-2}	nodal temperature at the maximum wear zone
J_q	heat flux
Δx	wall thickness
λ	thermal conductivity of the lining
ΔT	thermal gradient
T_i	nodal temperature
T_{cold}	temperature at the cold zone of the lining
$P(CO)$	partial pressure of carbon monoxide
$a(C)$	carbon activity in the pig-iron