Corrosion Behavior in Graphite Refractories Impregnated with ZrO₂ and CeO₂ Carrying Solutions

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1. Introduction

Blast Furnace locates on the beginning of the metallurgical process, tends as main function the production of the iron, through the reduction of the iron oxide ores. The coke combustion in front of the tuyeres, nozzles through which a hot air blast is delivered to Blast Furnace, results in the continuous creation of an empty space around of the hearth periphery that allows the flow of the raw materials.

Depending on the kinetic energy of the blast, the depth of the combustion area reaches 1–2 m. Therefore, the activated area that exists independently around each tuyeres like a ring 1–2 m of depth around the periphery of the hearth, termed the “raceway”. Close to the “raceway” exists a central column of coke strongly packed, known as the “deadman” zone. This coke column floats on the liquid iron in the hearth and can reach the hearth bottom. Some slag and iron stay in the pores of the coke column, being drained during the “tapping”.

No section of a Blast Furnace calls for such a wide variety of designs, conflicting practices, in-depth studies and performance history, which are as widely distinct as the hearth. Indeed, the hearth is viewed as the main reason for Blast Furnace campaign end.¹²)

It is of paramount importance, prior to deciding on the type of refractory, to assess the wear mechanisms involved as well as refractory/cooling configuration size and shape of refractories, and the design concepts used may strongly impact their performance.

Refractories which are used in the BF hearth are subjected to the following chemical etching mechanisms¹³): oxidation; alkali attack; CO disintegration; and erosion and dissolution owing to hot metal and slag flow. In addition to the aforesaid chemical etching mechanisms, hearth refractories are subjected to thermal stresses because of temperature fluctuations, which may reach as high as 500°C.

The wearing mechanisms found in literature suggest that they may vary for each zone, i.e., from hearth bottom to “tuyeres”.⁴,⁵)

Hearth findings, upon BF campaign completion, showed 4 different layers in the wearing profile, across lining thickness, from hot to cold side: a) Worn layer: the carbon blocks were both dissolved and eaten away by hot metal; b) layer with penetrating hot metal: hot metal passes through carbon block pores; c) brittle layer: carbon blocks disintegrated, and d) unchanged layer: carbon blocks kept their original physical/chemical properties.

The materials chosen to be used in the hearth consisted of at least 80% carbon. It is claimed that the degree to which carbon refractory is etched depends upon the kind of carbon which is present. Commercial carbon refractory samples were looked into by Schrot and Robinson,⁶ and the findings suggested that the pore structure and the graphitization degree may impact on oxidation reaction behavior.

In-depth, trial and theoretical studies have been conducted for hearth liquid flow.⁷,⁸) The mathematical model developed by Preuer et al.⁹ showed that the mushroom-like and elephant’s foot wearing process is ascribed to liquid flow. Increasing BF production rate may lead to a substantial increase in the erosion rate. Conversely, an increase in the dead man permeability as well as the coke zone may reduce this wearing process.

Kurita and Tanaka¹⁰ demonstrated the liquid flow effect on temperature distribution across the hearth, based upon a trial study, cold and hot 3-D models. The main information arising out of this study was as follows:

This paper investigates corrosion behavior in graphite refractory hot metal impregnated with ZrO₂ and CeO₂ carrying solutions used in Blast Furnace hearth, consisting of 50% graphite and 50% anthracite. Corrosions tests were carried out by means of finger test method in an induction furnace, using bar-shaped 30×30×280 mm test specimens and hot metal from CSN #2 Blast Furnace runner. The temperature chosen for this test was 1 520°C and 60-min isotherm. Upon test completion, test specimens were characterized by their dimensional variation, X-ray diffractometry and Scanning Electronic Microscopy (SEM).

KEY WORDS: corrosion; hot metal; graphite; zirconia; ceria.
a) The distance effect between tap hole and hearth bottom on flow line profile is only felt in the vicinity of tap hole; and

b) Liquid flow maximum speed on hearth bottom surface is found in the area between tap hole and center. This maximum speed increases as the distance between tap hole and hearth bottom reduces.

As expected, based upon flow results, the erosion speed at the beginning of tapping is quite low compared with erosion high speed when the “dead-man” is sitting on hearth bottom (free domain restricted to wall vicinity). Moreover, the “dead-man” hangs just for a while.

One of the ways to gauge the refractory lining used in the Blast Furnace from a laboratory standpoint is through “finger” test.11) This test is conducted by submerging a stick-like specimen into molten slag and hot metal, with rotation, over a certain period of time. After testing, wear shape and specimen area loss were looked into. Another way to test it is by “scorification” technique,12) in which the test specimen resembling a cylindric hearth is filled with hot metal and slag and heated in a Tammann Furnace, the burden in the liquid state is kept under stirring over a certain period of time.

In this paper graphite refractories (BC8SR) wear was examined. These refractories were used in CSN Blast Furnace hearth lining and in the “finger” test and “scorification” procedures. Also, BC8SR refractories were Impregnated with cerium and zirconium/cerium Carrying Solutions (ICS), which after thermal decomposition become CeO2 and Zr0,84Ce0,16O2 (t-ZrO2), filling up refractory pores.

2. Experimental Procedure

In order to carry out this work, BC8SR carbon refractories were used, which are the main lining utilized in the Blast Furnace hearths run by Companhia Siderurgica Nacional (CSN), Volta Redonda, RJ, Brazil. Manufactured by Nippon Electrode Company, the supermicropore carbon refractory (BC8SR) is made up of graphite particles (50 % in mass) with a high degree of crystallization and anthracite carbon (50 % in mass), with a low crystallization degree. It has low permeability (double densification) and a low ash content, silicon, silicon carbide and aluminum oxide, which are added to the matrix, with a view to enhancing hot metal erosion resistance.

Impregnations were conducted under ambient temperature and pressure, by fully submerging the test specimens in the cerium (CS/ Ce) and zirconium/cerium (CS/Zr) carrying solutions for 12 h. Upon impregnation the test specimens were heat treated in air at 350°C to cause decomposition of organic phases. This impregnation/decomposition cycle has been performed 3 times, an ideal value to prevent degradation of refractory mechanical properties through spalling.12)

In order to facilitate identification of the formed phases during “scorification” and “finger” test, X-ray diffractometry (XDR) analyses were conducted an impregnated and mixing refractory samples (1:1) between the oxides formed upon thermal decomposition of solutions and the slag and hot metal used in the corrosion testing. All mixtures were heat treated at 1 500°C for 60 min.

“Finger” tests were carried out in an induction furnace at a temperature of 1 470°C for 60 min, with 25 rpm and the “scorifications” tests were conducted in a Tammann Furnace at 1 650°C in nitrogen atmosphere and kept under stirring at 100 rpm for 32 h. After testing, the refractories were characterized by X-ray diffractometry and SEM.

3. Results and Discussions

Figure 1 shows XRD spectra related to BC-8SR conventional refractories, impregnated with CS/Ce and CS/Zr, thermally treated at 1 500°C, the graphite phases, Al2O3 and SiC can be noticed to make up the bulk of refractory BC8SR. In the CS/Ce and CS/Zr impregnations, phases CeO2 and Zr0,84Ce0,16O2, respectively were found, due to the low reactivity of the oxides concerned with refractory carbon. Figure 2 shows XRD spectra related to CSN #2 Blast Furnace slag and mixtures with products arising out of CS/Ce and CS/Zr (CeO2 and Zr0,84Ce0,16O2, respectively) thermal decomposition at 1 500°C. It was also found that #2 BF slag consisted mostly of the Gehlenite phase. The slag which was mixed with CeO2 and Zr0,84Ce0,16O2 did not show any new phase, suggesting that dissolution wear is unlikely to happen when such oxides are in contact with slag.

Figure 3 shows the photographic documentation of specimens which were subjected to “finger test” for 60 min with 25 rpm at 1 520°C, related to refractory BC8SR impregnated with CS/Zr and CS/Ce in comparison with non-impregnated test specimens. During the tests the upper areas of the specimens, Fig. 3, were submerged in the hot metal (hot metal line), and the neck-shaped areas, center of test speci-
men were in contact with the slag (slag line). One can notice in Fig. 3 that at 1520°C the refractories underwent a severe wear, including in the hot metal line area. The slag area was the hardest hit in all test specimens. On the other hand, the impregnated specimens presented a higher resistance to hot metal line wear. Based on test specimen area reduction values, upon the finger test shown on Table 1, it was found that the specimens impregnated with CS/Zr presented a fairly good resistance to wear (8.16%) whereas the specimen impregnated with CS/Ce presented an excellent resistance to wear (zero %), showing that at this temperature the use of impregnation technique both by CS/Ce and CS/Zr is of paramount importance to prevent refractory dissolutions in the blast furnace hearth area where hot metal moves in a turbulent way.

Figure 4 shows refractory surface image, BC8SR, im-

| Material | Hot Metal Area | Slag Area |
|----------|----------------|-----------|
| BC8SR    | 49.80          | 86.63     |
| CS/Zr    | 8.16           | 85.00     |
| CS/Ce    | Zero           | 81.90     |

Fig. 4. Refractory BS8SR surface image impregnated with CS/Zr, after “finger test”.

Fig. 5. EDS mapping images from test specimen surface impregnated with CS/Zr, after “finger test”, related to Fig. 4.
pregnated with CS/Zr, in which a pore was filled up with hot metal. With the help of Fig. 5, which shows Energy Dispersive Scanning (EDS) mapping images, it was found that the hot metal filled the pore, thus removing t-ZrO$_2$ that was in there, and t-ZrO$_2$ remained around the pore. It was also found that t-ZrO$_2$ is not dissolved by hot metal.

Figure 6 presents a surface overview of BC8SR refractory impregnated with CS/Zr. In this figure one can notice that there is a slag layer outlining a graphite grain. Figure 7 illustrates a magnification of slag layer in the area outlined by Fig. 6. On the other hand, with the help of EDS images shown in Fig. 8, it became evident that zirconia was removed from the pore around the graphite grain, but it was not dissolved by slag. This fact shows that t-ZrO$_2$ remained stable throughout the corrosion process.

Figure 9 shows a SEM image obtained from slag/refractory interface, BC8SR impregnated with CS/Ce, after “finger test”. With the help of EDS mapping images, shown in Fig. 10, it was found that the grains of a light shade are made of CeO$_2$, which were taken from refractories, but not dissolved by slag. Additionally, CeO$_2$ grains are hexagonal-shaped, as one can clearly see from Fig. 11.

Figure 12 shows an overview of hot metal/refractory interface impregnated with CS/Ce, after “finger test”. The image amplified in the area outlined in Fig. 12, presented in Fig. 13 demonstrates that CeO$_2$ in the presence of hot metal is not dissolved either. EDS image of this area shown in Fig. 14 corroborates this statement.

Figure 15 presents a photographic documentation of the cross section related to refractory BC8SR hearths, after “scorification test”. Upon conducting a visual analysis in the BC8SR refractory hearth with no impregnation, it is possible to spot a typical morphology for wear, which occurred in the Blast Furnace hearth lining, known as “elephant’s foot”.

Using the Corel Draw 6 software, it was possible to effectively spot the worn area during the “scorification test”,
as shown in Fig. 16. From the wear profiles, volumetric revolutions were produced of hearth inner section, upon wear, utilizing an Auto Cad software. The amount of material removed during “scorification test” was obtained, by subtracting the initial volume from the volume after wear (see Table 2). With the help of the Leica Qwin Standard V2.3 image analysis software, the worn areas of digital images obtained from Fig. 15 were determined and they are shown on Table 2. The “scorification test” wear results corroborate those results obtained from the finger test, suggesting that refractory BC8SR service life can be enhanced by means of impregnation techniques (ICS). Impregnation using CS/Ce produced without any doubt the best results, a drop by 41.30% of the worn amount, but CS/Zr also demonstrated that it can contribute toward lining service life enhancement with a 28.25% drop in the worn amount.

The results arising out of “finger and scorification tests” suggest that the hot metal corrosion mechanisms which influence the impregnated refractory do not depend upon the underlying impregnating solution, and are split into 4 main phases, namely:

In the 1st phase hot metal comes into contact with refractory and the material that fills up the pore, as a result of the
impregnation technique (Fig. 17.1). Right at this point ICS plays a major role, as on filling up the pore it will somehow be reducing the surface contact between hot metal and refractory per se, thereby precluding refractory premature corrosion.

In the 2nd phase hot metal attacks mostly graphite grain outlines, which possess the smallest and most corrosion prone grains, refractory sharp edges begin to become round and refractory surface becomes uneven. At this point the material that fills up the pore remains unchanged, as it has the required mechanical strength to remain united, Fig. 17.2, notwithstanding the pore being partially corroded by hot metal. As long as the pore walls are able to stand on their own, the material stemming from the ISP technique will play a preventive role.

When the pore walls cannot stand anymore for the ICS material, then the material will be dragged out of the pore, remaining on refractory surface (phase 3), Fig. 17.3, and finally ICS material is scattered by hot metal, but is not dissolved, remaining stable (phase 4), Fig. 17.4.

It should be noted that such mechanisms are of a cyclical nature, and while the refractories are being worn away, fresh pores filled up with material stemming from the ISP technique will play their role of reducing contact surface between refractories and hot metal, thereby precluding refractory premature corrosion.

### 4. Conclusions

The t-ZrO$_2$ and CeO$_2$ which are present in the refractory pores, as a result of the impregnation process (ICS), are not dissolved by either slag or hot metal during the corro-

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**Table 2.** Refractory BC8SR wear, after “scorification test”.

| Material | Removed Area (Traverse Section) [mm$^2$] | Removed Volume (Auto Cad) [mL] | Decrease in a Removed Volume [%] |
|----------|--------------------------------------|-------------------------------|---------------------------------|
| BC8SR    | 815.52                               | 80.15                         | -                               |
| CS/Zr    | 635.89                               | 57.03                         | 28.25                           |
| CS/Ce    | 510.24                               | 47.05                         | 41.30                           |

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**Fig. 17.** Schematic drawing of corrosion prevention mechanism by using ICS technique. 1st phase: Refractory pore is protected by the material from ICS technique, 2nd phase: Refractory is partially corroded and ICS material untouched, 3rd phase: Material is removed from pore, and 4th phase: Material is scattered by hot metal.
The “finger and scorification tests” showed that the impregnation technique is highly efficient when it comes to protecting refractories from premature degradation, filling up the pores, thus preventing erosion and dissolution.

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