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NEW ANTI-OXIDATION TECHNOLOGY FOR TROUGH AND RUNNERS CASTABLES: A SUCCESSFUL SOLUTION AT ARCELOR MITTAL TUBARÃO BLAST-FURNACE #02*

Eric Yoshimitsu Sako [1]
Wiliam Alves [2]
Bruno Gonçalves Rangel [3]
Nilton Fernando dos Santos Januário [4]
Douglas Fernando Galesi [5]
Cláudio Cesar da Costa [6]
Douglas Ruy [7]
Hiroshi Fujiwara [8]

Abstract
One of the main difficulties in the operation of trough and runners at Arcelor Mittal Tubarão (AMT) Blast-furnace no.02 is the reduced amount of time available for repair procedures. The consequence is that the castable installation must often be performed during hot conditions and the installed castable could easily detach from the base material during the early stage of operation, exposing the previously oxidized base material to molten iron and corrosive slag attack. When events like this happen, emergency repairs must be executed, resulting in increased refractory unit consumption and an unplanned shutdown of unit operation. Considering these targets, Nippon Crucible Co. and Saint-Gobain HPR Brazil have developed a high-performance Al_2O_3-SiC-C composition based on an entirely novel anti-oxidation technology. Oxidizing reactions could be attenuated by adding an oxidant inhibitor and a water reducing agent. As a result, the open porosity was significantly reduced, resulting in an improvement of campaign life in terms of pig iron throughput when compared with the regular castable. An analysis of this life improvement showed successful results for the material after 250 days of campaign. The main reason for such successful results was that the deterioration caused by the oxidation was significantly less and that this change made on the high cohesive structure of the base material was maintained for a long time. The attained results allowed Arcelor Mittal Tubarão to achieve longer trough campaigns, and avoid any unplanned stoppages with zero breakdown risks.
Keywords: Anti-oxidant; Trough and runners; Refractory castable.

[1] *Application and R&D Coordinator, Technical Department, Saint-Gobain Ceramics, Vinhedo-SP, Brazil.*
[2] *Application Technician, Technical Department, Saint-Gobain Ceramics, Vinhedo-SP, Brazil.*
[3] *Application Supervisor, Regional Comercial Department – Espiríto Santo, Saint-Gobain Ceramics, Serra-ES, Brazil.*
[4] *Development Technician, Technical Department, Saint-Gobain Ceramics, Vinhedo-SP, Brazil.*
[5] *Application and R&D Manager, Technical Department, Saint-Gobain Ceramics, Vinhedo-SP, Brazil.*
[6] *Blast-furnace #02/#03 Manager, Iron making Department, Arcelor Mittal Tubarão, Serra-ES, Brazil.*
[7] *Ironmaking Manager, Iron making Department, Arcelor Mittal Tubarão, Serra-ES, Brazil.*
[8] *Technical Manager, Toyota plant, Nippon Crucible Co. Toyota, Japan.*

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1 INTRODUCTION

The steel production in Arcelor Mittal Tubarão (AMT) plant in Serra, Brazil, is based on the operation of three blast-furnaces. Among the three of them, BF n.02 is the only one which is limited by two tap holes and, therefore, requires strict attention during repairs procedures in the casting house. When there is refractory maintenance in one of the main troughs, the blast-furnace production is carried out in a system of consecutive castings, using only one tap hole. In this case, the furnace drain out is not balanced and the pig iron constant flow leads to a concentrated wear in the hearth, very close to the side of the operating tap hole. For this reason, the troughs must be available for operation as quick as possible, and therefore the time spent for repairs is always limited.

As there is very little time for cooling down, the demolition step takes place at hot conditions, exposing the residual refractory lining to intense oxidation. When SiC and carbon are oxidized, the castable structure is compromised due to the higher porosity and its corrosion resistance is significantly reduced, as illustrated by Figure 1. Moreover, due to some issues in the back lining profile, oxidation was also intense in the cold face of the working lining, which makes this mechanism as the most aggressive for the Al_2O_3-SiC-C castables in AMT BF#02 main troughs.

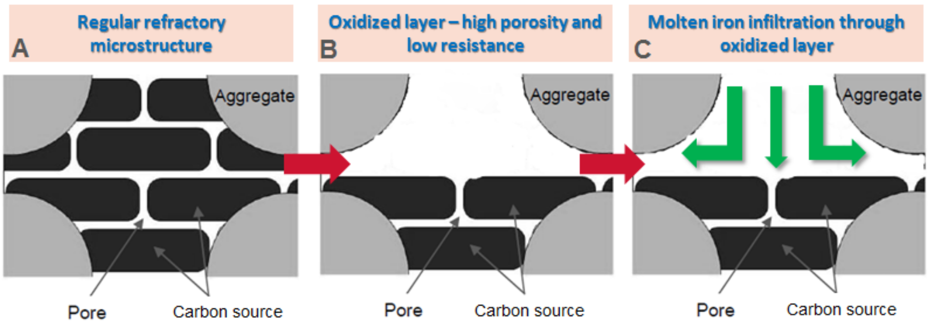

Figure 1. Oxidation mechanism of Al_2O_3-SiC-C castables. A: regular structure; B: oxidized structure; C: infiltration of molten iron.

In order to avoid an undesired increase in the wear rate during the trough campaign by the contact between molten pig iron and the oxidized castable, the working lining is mostly replaced during the trough repairs. Nevertheless, the high temperature faced in those occasions also leads to a poor adhesion between the new material and the residual one and, as a consequence, the just installed castable could easily detach from the base material during the early stage of operation. As described in Figure 2, when that happened, the oxidized residual material was exposed to molten iron and corrosive slag attack, increasing the wear rate and demanding an unplanned stoppage for refractory repair. That chaotic scenario was interfering in the blast-furnace operation at AMT facility, as the through availability was much different from the previous planned. Figure 3 shows the comparison between the planned trough campaign and the actual one.

The direct solution for that main hurdle to the furnace operation could be the development of a new technology of Al_2O_3-SiC-C castables focused on extremely high oxidation resistance materials. The oxidation mechanism takes place when oxidizing sources, such as O_2, CO or H_2O, for instance, interacts with C, SiC or other non-oxide compounds, mainly at high temperatures. The most effective way to prevent oxidation is, therefore, to create barriers in order to avoid the direct contact of

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the refractory with those gases. That is usually attained by using additives which generate glassy phase at high temperatures and create a chemical protection inside the refractory structure. The main drawback related to this practice is the reduced corrosion resistance due to the presence of such low-melting point phases. Aware that this practice would not work well at AMT BF#02, Saint-Gobain and Nippon Crucible came up with a different alternative: decreasing the refractory contact with gases by controlling the grains size distribution and by forming dense structure with another deflocculant, consequently reducing the castable porosity.

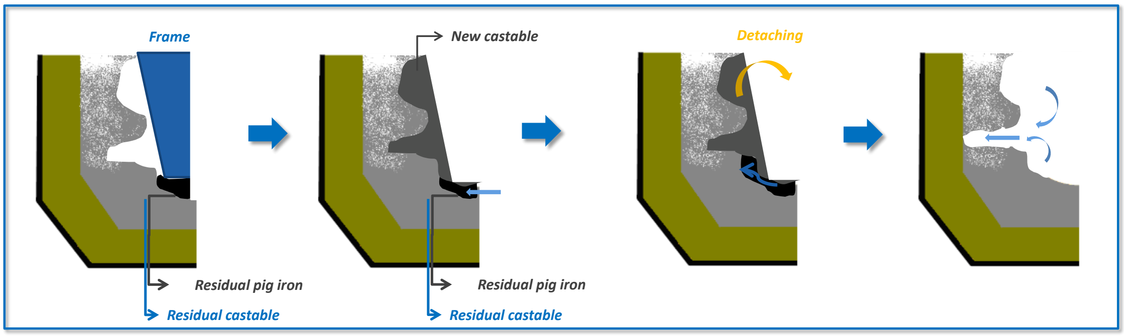

Figure 2. Wear mechanism during trough operation: new castable is detached during operation and the wear rate increases as the molten iron reaches the oxidized layer.

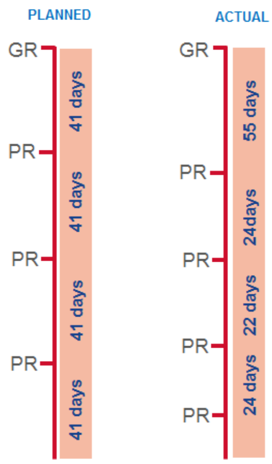

Figure 3. Comparison between planned trough campaign and actual one. GR: General repair; PR: Partial repair.

The present work addresses the results of such novel and innovative technology which not only showed very interesting lab results, but also led to a significant trough life improvement, helping to keep a stable and safe blast-furnace operation.

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2 EXPERIMENTAL PROCEDURES

Without any change on the overall chemical composition, as observed in Table I, the novel technology designed to improve the castable oxidation resistance was based on three main modifications on the original composition: an optimization on the grain size distribution, the use of a special deflloculant, and the combination with oxidant inhibitor. The new developed castable (hereafter denoted as "S25 NG" – NG stands for “new generation”), designed according to such innovative concepts, was comparatively evaluated with the previous castable used at ATM BF#02 main troughs (hereafter denoted as “S25 S – S stands for “standard”).

Table I. Main differences between S25-S and S25-NG.

	S25-S	**S25-NG**
Al_2O_3 (wt%)	68	68
SiC + C (wt%)	28	28
SiO_2 (wt%)	1.5	1.5
Additives	Regular deffloculant	Special deffloculant + oxidant inhibitor
Water (wt%)	5.2	4.4
Flow values (mm)	160	158

For samples preparation, the castables were mixed for 5 min following a two-step water-addition procedure. After mixing, the samples were cured at room temperature (~25°C) for 24 h and dried for additional 24h at 110 °C.
The following physical properties were evaluated after drying at 110°C and after firing at 1000°C/5h and 1450°C/5h in reducing atmosphere:
- Cold crushing strength (CCS): measured according to ASTM C133-94 standard, using cubic samples of 40mm x 40mm x 40 mm;
- Modulus of rupture: carried out under three-point bending tests (ASTMC 583) using prismatic samples (160 mm x 40 mm x 40 mm);
- Open porosity and apparent density: evaluated by using the Archimedes technique in kerosene, following the ASTM C380 standard;

Corrosion tests were conducted in a high frequency furnace, using samples calcined at 400°C for 5h. As the corrosive agent, a mix of blast-furnace slag and pig iron was used (80% slag + 20% pig iron for slag attack test). Table II presents the chemical composition of the blast-furnace slag used in the tests. The testing took place for four hours around 1550°C and the slag + pig iron mix was changed every each hour.

Table II. Chemical composition of the blast-furnace slag used in the corrosion tests (wt-%)

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	MnO	Basicity B2
34,0	45,5	10,4	0,4	5,5	0,7	1,3

At last, oxidation resistance tests were carried out according to the following procedure: cubic samples of 50mm x 50mm x 50mm were prepared and pre-fired for 5h at 1000°C, in reducing atmosphere. The samples were then placed inside a pre-fired furnace at 1000°C, under oxidizing atmosphere, so they could go through an aggressive oxidation process. They were withdrawn after 6h or 11h and, after cooling down, they were cut and the cross-sections were used for measuring the oxidized layer.

“S25-NG” castable was also installed at AMT BF#02 main trough in order to run a pilot trial and confirm the results attained at lab scale. After 250 days of operation, a post-mortem sample was brought back to laboratory and chemical analysis through X rays fluorescence was performed at different regions in order to analyze the carbon and SiC content in the castable structure after use. The results were compared to the ones attained with “S25-S” post-mortem sample after operating a similar campaign (roughly 250 days too).

3 RESULTS AND DISCUSSION

Table III presents the physical properties of S25 S and S25 NG after drying at 110°C/24h and thermal treatment at 1000°C/5h and 1450°C/5h

Table III. Physical properties of S25 S and S25 NG after heat treatment at different temperatures.

		S25-S	**S25-NG**
Apparent density (g/cm^3)	110°C	2.95	2.96
	1000°C	2.93	2.92
	1450°C	2.92	2.93
Open porosity (%)	110°C	14.3	12.2
	1000°C	20.3	17.9
	1450°C	18.6	17.6
CCS (MPa)	110°C	21.3	20.5
	1000°C	41.6	38.4
	1450°C	72.3	28.5
MoR (MPa)	110°C	7.6	7.0
	1000°C	9.0	7.6
	1450°C	14.3	6.0

With a more packed structure and an improved dispersion of the matrix components, the new developed castable demanded much less water during its process when compared to the standard material, as shown in Table II, contributing to reduce its open porosity value (Table III). The lower values of mechanical strength for S25 NG after firing at 1000°C and 1400°C are associated with the amount of carbon in the composition, which affects the sintering process and inhibits the excessive sintering at high temperature.

As predicted, such reduced porosity of the novel developed castable was essential to ensure an excellent oxidation resistance, even after long exposure to air. Figure 4 shows the castables cross-sections after the oxidizing test, whereas Table IV presents the oxidation index of both materials calculated by the cross-section areas measurements.

One can easily notice that, owing to the innovative concepts used for the formulation design, S25 NG presented an outstanding performance when exposed to air at 1000°C, which is the most critical temperature for Al2O3-SiC-C castables, even after 11h. Differently from S25 S, which presented no longer any residual carbon content, S25 NG kept most of its original structure. As a low oxidation rate leads to small variances on the castable porosity, those results indicate that the material’s corrosion resistance would clearly be increased during use.

In order to evaluate the effect of the different oxidation rate on the corrosion resistance, a pig iron attack test was performed with both castables (Figure 5). As expected, due to the combination of better particles packing, reduced porosity and,

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consequently, low oxidation rate, the new castable S25 NG presented an improved performance with a corrosion index 14% lower than the original one.

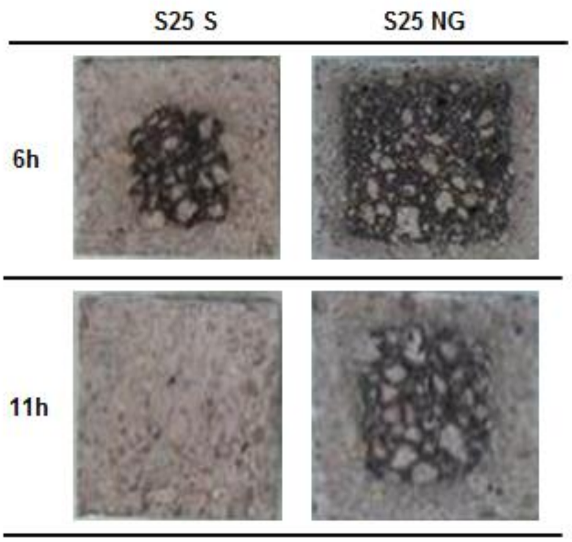

Figure 4. Cross-sections of S25 S and S25 NG samples after oxidizing test at 1000°C for 6h and 11h.

Table IV. Oxidation index of S25 S and S25 NG after oxidizing test at 1000°C for 6h and 11h.

		S25-S	**S25-NG**
Oxidized Layer (relative index)	6 h	100%	46%
	11 h	100%	39%

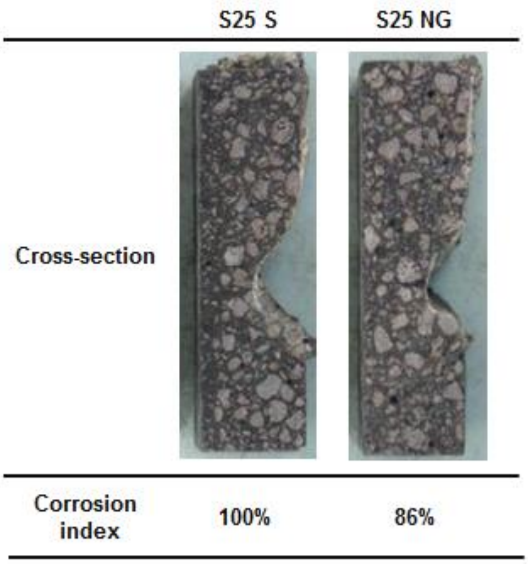

Figure 5. Corrosion index of S25 S and S25 NG after pig iron attack test at 1550°C for 2h

With promising results at lab scale, larger batches of S25 NG were produced and installed at AMT BF#02 for field trials. After 250 days of operation (with roughly 300.000 ton of pig iron throughput), a post-mortem sample was taken from the residual working lining, in a region close to the back lining (to ensure that the sample was representative to a portion of the base material that was not changed during any partial repair). The sample was then compared to another one from the standard material at the same conditions in terms of working life and location in the through.

Figure 6 shows pictures of the post-mortem samples of both materials, highlighting the regions where chemical analyses were performed. The results are expressed in Table V. It is clear that the reason for trough campaign instability at AMT BF#02 was directly related to the poor oxidation resistance of S25 S. The SiC + C content of the post-mortem sample was significantly reduced when compared to the reference values presented in Table I, mainly in the regions 1 and 2 (close to the cold face) where oxidation is constant during trough operation. The high oxidation rate is also evidenced by the high SiO_2 content in S25 S post-mortem sample, which resulted from SiC oxidation according to the following reaction:

$$SiC + O_2 \rightarrow SiO_2 + C$$

Conversely, S25 NG sample presented a much nicer structure after use, with very slight signs of oxidation. One can notice that in region 3, at the hot face, the SiC + C content barely changed, pointing out that the novel technology had positive outcomes at field trials as well. Additionally, S25 S sample presented some visible cracks at the hot face, which is most likely related to its inefficient adhesion to the base material during the repair step. At S25 NG sample picture, no signs of bad adhesion could be observed, which also helped to improve the material working life.

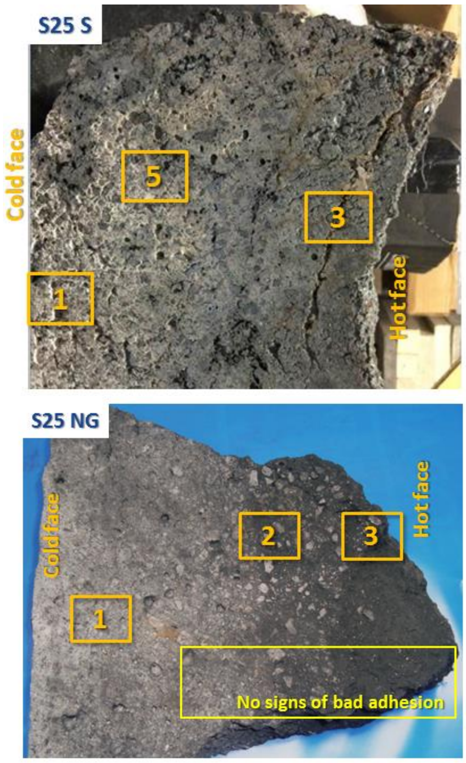

Figure 6. Post-mortem samples of S25 S and S25 NG after 250 days of operation.

Table V. Chemical analyses of different regions in the post-mortem samples of S25 and S25 NG (results are expressed in wt-%).

Material	Region	Al_2O_3	SiC + C	SiO_2
S25 S	1	62.2	11.7	22.4
	2	65.4	11.9	17.6
	3	59.6	13.7	16.2
S25 NG	1	68.3	19.4	9.6
	2	68.3	22.0	7.0
	3	64.7	27.0	4.9

Due to those positives results, S25 S castable was progressively replaced by S25 NG at AMT BF#02 and long trough campaigns could be attained. In Figure 7, a comparative evolution of the trough campaign is presented, where it is possible to observe that not only was the instability problem overcome, but also the intervals from repair to repair was extended. This result was of utmost importance to AMT production plan, as it resulted in a higher trough availability rate and consequently reduced the risks to the blast-furnace operation.

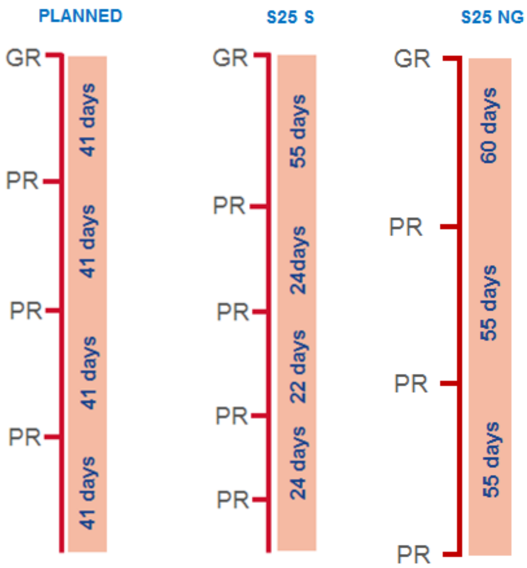

Figure 7. Comparison between planned trough campaign and actual ones with S25 S or S25 NG. GR: General repair; PR: Partial repair.

4 CONCLUSION

A high-performance Al_2O_3-SiC-C composition based on an entirely novel anti-oxidation technology was developed by Saint-Gobain and Nippon Crucible in order to solve the trough instability issue at AMT BF#02. Due to the combined use of a special deffloculant and the optimization of the particle distribution, the water required for mixing was reduced and the material's porosity was decreased. In addition the novel castable could achieve an outstanding oxidation resistance by adding the oxidant inhibitor to the dense structure, which led to an extended campaign life during field trials. With S25 NG entirely implemented, BF#02 was able to operate with reduced risks and a very stable production plan, which directly impacted on the productivity level and on the furnace lining preservation