IMPROVEMENT OF THERMOMECHANICAL PROPERTIES OF ALUMINA-CARBON-SILICON CARBIDE REFRACTORY MATERIALS USED IN TORPEDO CARS[1]

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Abstract

Alterations in the heat cycle of torpedo cars decrease the useful life span of refractory lining that is traditionally applied in the cars. This resulted in a request from users for a re-evaluation of the thermomechanical properties of alumina-carbon-silicon carbide refractory materials without incurring damage to the material´s resistance to corrosion, avoiding the premature retirement from service of the torpedo cars.

Key words: Torpedo cars; Alumina-carbon-silicon carbide Refractories; Desulphurization;

APRIMORAMENTO DAS PROPRIEDADES TERMOMECÂNICAS DOS MATERIAIS REFRATÁRIOS DE ALUMINA-CARBONO-CARBETO DE SILÍCIO USADOS EM CARROS-TORPEDO

Resumo

Alterações no ciclo térmico dos carros-torpedo diminuíram as campanhas dos revestimentos refratários tradicionalmente usados, obrigando seus usuários a solicitarem a reavaliação das propriedades termomecânicas dos materiais refratários de alumina-carbono-carbeto de silício, sem que houvesse prejuízo da resistência à corrosão, com o intuito de evitar afastamentos prematuros dos carros-torpedo, comprometendo a sua disponibilidade.

Palavras-chave: Carros torpedo; Refratários de Alumina-carbono-carbeto de silício; Dessulfuração

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1 INTRODUCTION

Owing to changes in pig iron treatment techniques in torpedo cars, the requests for refractory linings have changed recently and the performance of Al_2O_3-C-SiC has been affected considerably. Cracks parallel to the hot face of bricks, followed by chipping of the affected part, have been considered the main reason for wear mechanisms.

2 AIM

This technical paper aims at showing the behavior of Al_2O_3-C-SiC refractory materials used in the lining of torpedo cars at steel plants, under physical, chemical and mechanical variables as well as the search for maximizing their campaigns. The approach includes the methodology used for evaluating the thermo-mechanical properties of Al_2O_3-C-SiC refractory reformulated which showed, at the laboratory and later in field tests, more expressive results concerning chipping due to wear and consequent improved performance.

3 TORPEDO CARS: DEFINITION AND FUNCTIONS

The torpedo car is a vessel of metallurgical reactions which has two basic functions:

- Liquid pig iron transport;
- As a metallurgic reactor for desulphurization (transfer and removal of sulphur contained in the liquid metal for slag).

4 REFRACTORY MATERIALS FOR THE LINING OF TORPEDO CARS EVOLUTION OF REFRACTORY LININGS USED IN TORPEDO CARS

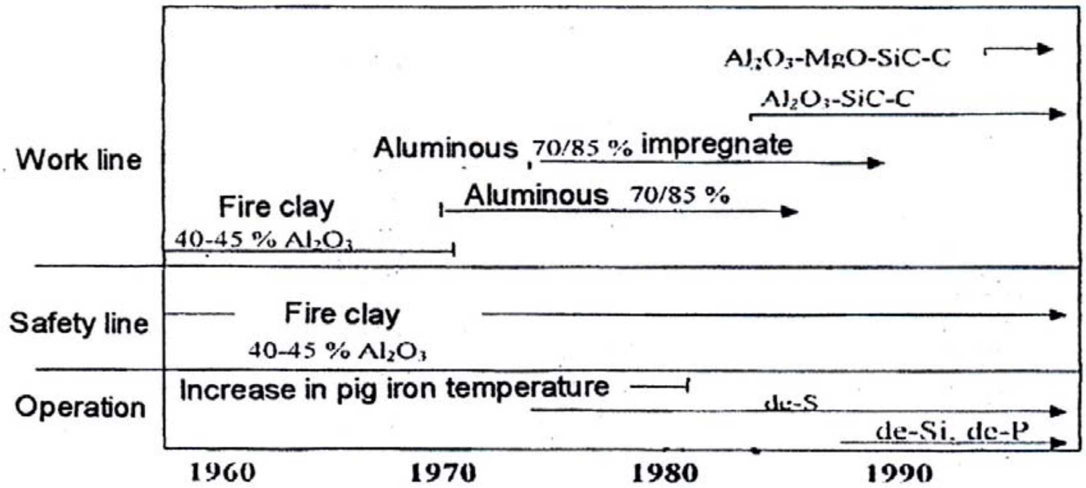
Technological advances in refractory linings for torpedo cars are mainly due to the synergy of both steel plants and refractory materials industries. The technological evolution in steel plants has prompted refractory material manufacturers to adjust the properties of refractory ceramics to the demands of linings for torpedo cars. Table 1 shows a summary of the main factors which brought about the development and improvement of linings for torpedo cars.

Table 1 - Main factors in the development of refractory linings for torpedo cars.

Steel plants	Refractory industry
Evolution and increase in the capacity to carry liquid pig iron.	Study of new ceramic systems and artificial raw materials (carbon, eletrofused raw materials)
Introduction and evolution of pig iron Pre-treatment process	New antioxidant systems (carbide, borid, metal alloys)
Increase in productivity and temperature of liquid pig iron;	New bonding systems (polymeric resins engineering;
Heat conservation (energy performance)	Automation of processes;
Modeling, maximization, simulation and automation of processes;	Evolution of manufactoring technology;
Evolution and need to produce cleaner steel, keeping deleterious elements (P/S) to a minimum.	Modelling, maximization and simulation of products and processes.

Source: Refractory Materials for iron reduction equipment- april/2002.

The direct consequence of these factors was the migration of linings from fire clay and aluminous impregnate systems to one whose base is Al_20_3-C-SiC and its variants, as the following figure shows:



Source: Refractory materials for iron reduction equipment - april/2002

Figure 1 – Improvement in refractory linings in torpedo cars.

LININGS COMPOSED OF Al_2O_3-C-SiC

In the alumina- silicon carbide-carbon system, each component has special characteristics and properties which act in synergy, improving the properties of the system.

In industrial use, Al_2O_3-C-SiC bricks undergo expressive structural changes in thickness, which give these materials a mutant or dynamic(1) character when their properties are taken into consideration. Although, initially, these changes may be beneficial, the greatest challenge in this field is to understand and control these transformations, which are influenced by several factors and/or variables:

- Raw materials for bricks; processing of these materials;
- Variables in the metallurgical process, such as time, temperature and atmosphere.

Table 2 shows a summary with the main characteristics and varieties of this system.

Table 2 – Al203-C- SiC System : Characteristics and Variables

Component	Sources	Function
Alumina	Eletrofused and calcined alumina	Resistance to corrosion. Resistance to wear. Structural Stability.
Silicon Carbide	Silicon carbide - SiC	Mechanical resistance to high temperatures. Resistance to thermal shock.
Carbon	Graphite - C	Resistance to spalling. Suppression of slag penetration.
	Resins (fenolic)	Resistance after thermal shock. Carbon source.
Antioxidants	Metallic silicon - Si	Antioxidant. Mechanical resistance at high temperatures.
	Metallic Aluminum - Al	Antioxidant. Mechanical resistance at high temperatures.
	Silicon Carbide - SiC	Antioxidant.
	Boron Carbide - B_4C	Antioxidant.
Variants (other Additives and Aggregates)	Magnesia - MgO	Spinel formation “in situ”. Joint closings. Resistance to corrosion.
	MgO Spinel – Al_2O_3	Resistance to corrosion. Resistance to wear.

5 CARBON EFFECTS IN REFRACTORY MATERIALS

In general, the refractory materials containing carbon have high resistance to slag corrosion and to damage by thermal shock, which are made possible, in part, by graphite. However, carbon is susceptible to oxidation,(2) which can cause increase in wetness and reduction in thermal conductivity of refractory materials, which results in more significant wear of the lining, due to corrosion as well as thermal shock, respectively. Thus, although carbon can provide the refractory material with excellent properties, its vulnerability to oxidation is still a reason for concern when these materials are exposed to an oxygen-rich atmosphere.

Broadly speaking, the resistance to oxidation of refractory materials containing carbon is the function of temperature, partial pressure of oxygen, oxygen availability in the raw material and carbon reactivity. Among the parameters controlling oxygen availability, porosity is the most important. Normally, the porosity of refractory materials in the oxide-C system connected to the fenolic resin, increases with temperature up to about 800ºC, owing to resin decomposition and vaporization .

6 SiC EFFECT IN REFRACTORY MATERIALS

SiC is an important component in the prevention against carbon oxidation up to about 1525ºC, by means of the reduction of $CO_{(g)}$ to $C_{(s)}$, according to reaction I. Owing to this reaction, the formed carbon fills the worn SiC area and, subsequently, according to reaction II, SiO $_{(g)}$ combines with the remaining $CO_{(g)}$ to form $C_{(s)}$ and $SiO_{2(s)}$. Finally, as a result of reactions 1 and 2, SiC reduces CO(g) to $C_{(s)}$ forming $SiO_{2(s)}$ (reaction 3):

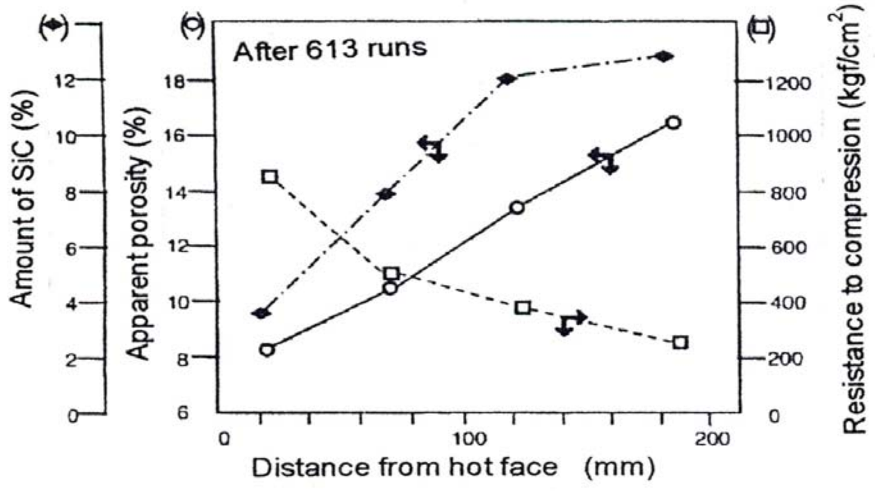
$$SiC_{(s)} + CO_{(g)} \leftrightarrow SiO_{(g)} + 2C_{(s)}; \tag{1}$$

$$SiO_{(g)} + CO_{(g)} \leftrightarrow SiO_{2(s)} + C_{(s)}; \tag{2}$$

$$SiC_{(s)} + 2CO_{(g)} \leftrightarrow SiO_{2(s)} + 3C_{(s)}. \tag{3}$$

In this case, carbon protection is believed to come basically from $SiO_{2(s)}$ formation and secondary precipitation of $C_{(s)}$ from SiC oxidation, which causes an expansion of the solid phase of approximately 3,4 times when the density of a-cristobalite (2,2 g/cm^3) is considered. Increase in size and pore redirection, in turn, may reduce refractory permeability, which helps in delaying carbon oxidation.

Additionally, SiC provides the refractory material with extra advantages such as high resistance to corrosion by the non-oxidized slag and high resistance to damage by thermal shock.



Source: Effect of Metallic Antioxidants and the fenolic resin in Al_2O_3-C-SiC refractory materials. Master Thesis , MAJELA, de Sá, Geraldo, abril 2007.

Figure 2 – Amount of SiC, apparent porosity and resistance to compression at room temperature along an Al_2O_3-C-SiC brick for torpedo cars after 613 runs.

7 BONDINGS

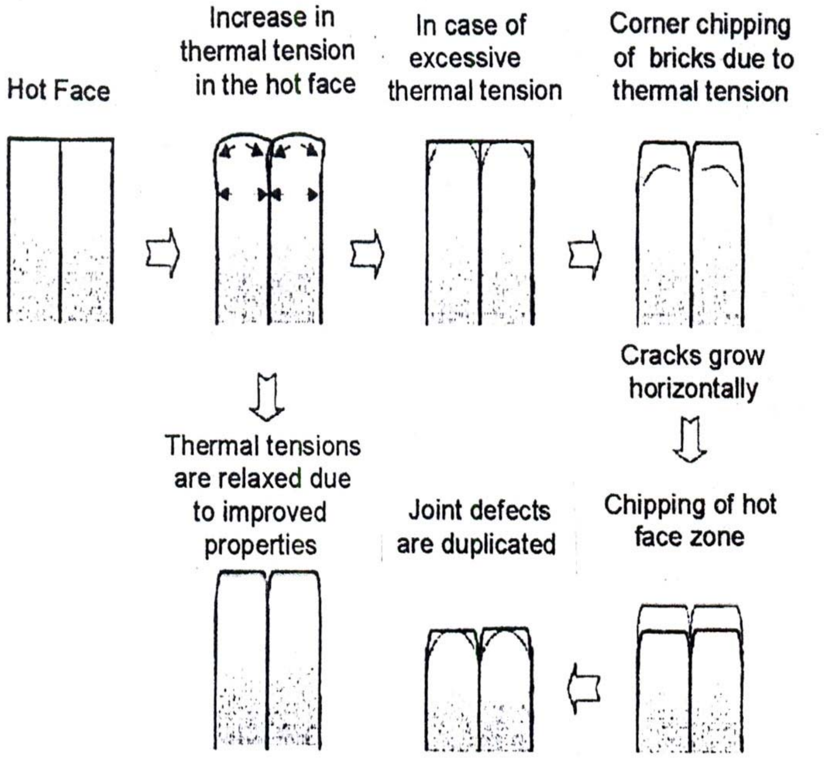
The bondings usually used in the refractory systems containing carbon are mineral tar pitches or synthetic resins. Instead, in Asia and the Americas, the refractory materials of the Oxide-C system linked to resins, containing antioxidants, are preferred. The main disadvantage of pitch derivates of tar is the presence of carcinogenic compounds, derivates of benzene.

In Brazil, for several years, the refractory materials made from the fenolic resin and metallic antioxidants have prevailed. It is believed that this trend stems from the inherent complexities of processing pitch-bonded bricks, for example: mixture homogeneity and hot pressing, and from adjustments in industrial facilities of refractory producers to meet demands by environmental departments.

8 WEAR BY CHIPPING

In general, refractory wear stems from chemical and/or physical phenomena, such as corrosion, including carbon oxidation erosion and fracture. As for the latter, the factors which contribute simultaneously or not to refractory material wear are tensions having mechanical and thermal natures. For instance, pre-heating practices, thermal cycling, the behavior of the metallic carcass of metallurgical vessels and structural changes along the refractory material´s length have great influence over the performance of these materials.

Although wear by corrosion is also of great importance for the industrial performance of refractory materials for torpedo cars, at present , the life span of such materials has been limited by cracks which appear on the brick`s hot face and spread, causing chipping of a portion of the brick. The main mechanism of wear, considering the type of degradation, stems from tensions developed in the system. Figure 3 shows the proposed wear mechanism schematically:



Source: Effects of Metallic Antioxidants and the Fenolic Resin in Al_2O_3-C-SiC refractory properties, Master Thesis, MAJELA,de Sá, Geraldo, abril/2007

Figure 3 – Schematic representation of one of the wear mechanisms of bricks for torpedo cars.

9 PROJECTS FOR REFRACTORY LININGS FOR TORPEDO CARS

As previously mentioned, torpedo cars are used for pig iron transport and desulphurization (De-S) . The refractory material used in the lining of this equipment must, consequently, stand chemical, mechanical and thermo-mechanical conditions involved in these processes. Thus, ceramic materials selection should be done from detailed operational conditions of this equipment. In addition, the refractory project must be carefully planned and performed to avoid premature flaws in order to obtain the desired campaigns. Table 3 shows the physical and chemical properties of several refractory materials, produced with different kinds of aggregates for use in different places in the torpedo car. This balance shown below applies to some cases of torpedo cars where the factors in the process cause uneven wear in the lining.

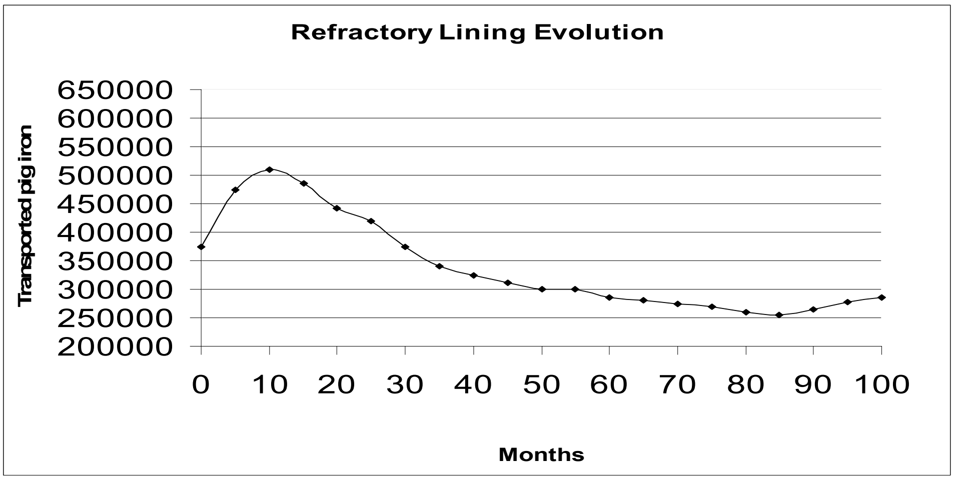
Table 3 – Characteristics of Al_2O_3-C-SiC refractory materials for use in torpedo cars

Characteristics	A	B	C
SiO_2	4,5	3,5	4,2
Al_2O_3	81,0	79,0	87,5
MgO	5,0	---	---
Fe_2O_3	0,5	0,8	0,3
SiC	7,5	15,5	6,8
Fixed carbon	7,0	6,0	14,0
MEA (g/cm³)	3,10	3,10	3,00
PA (%)	6,0	5,0	8,10
RCTA (MPa)	80	90	50
VLD (%)	0,0	0,0	0,0
Region applied	Roof Slag line	Impact Zone	Metal Line Slag line

10 CAMPAIGNS OF REFRACTORY LININGS

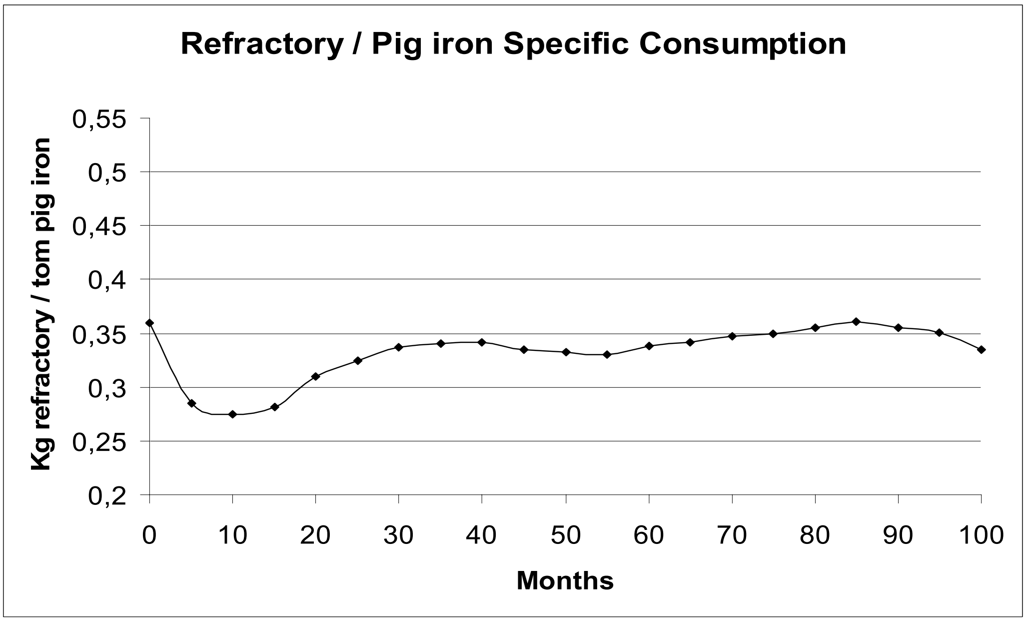
The following data show the evolution of campaigns of refractory linings for torpedo cars between January 1998 and April 2006, at national steel plants.

Recent years have seen a considerable decline in the performance of refractory linings for torpedo cars due to the biennial 1998/1999 (Figures 4 and 5). Refractory wear has been caused mainly by cracks$^{(3)}$ which form up to about 70mm of the lining´s hot face. For this reason, the traditional wear indicator, kilogram of refractory per ton of transported pig iron has shown a higher rise, according to figure 5, preventing a better prediction of lining performance.



Source: Effect of Metallic Antioxidants and the fenolic resin in Al_2O_3-C-SiC refractory properties, Master Thesis , MAJELA, de Sá, Geraldo April /2007

Figure 4 – Campaign evolution of refractory lining for torpedo cars between January 1998 and April 2006.



Source: Effect of Metallic Antioxidants and fenolic resins in Al_2O_3-C-SiC, Master Thesis, MAJELA,de Sá, Geraldo, April 3007
Figure 5 – Specific Consumption Evolution of refractory materials for torpedo cars between January 1998 and April 2006.

Considering Figures 4 and 5, throughout 1998 there was a rise in lining life span. 1999 was characterized by a transition period. From this date, there was a decline in lining performance along with a tendency to stabilize refractory materials consumption from 2000. Considering an average lining performance of about 500,000 tons of transported pig iron in early 1999, i.e., a life span of about 4 years in operation, the assembly of this lining would have occurred early 1995. Considering now the average lining performance of about 300,000 tons of transported pig iron early 2001, i.e., an equivalent life span of about 2 years, the assembly of the lining would have occurred early 1998. In this light, it could be inferred that the decline in lining performance for torpedo cars was influenced by permanent alterations of a variable or a group of variables between 1995 and 1999. The operational variables analyzed and regarded as the most important ones and which refer to this transition period are:

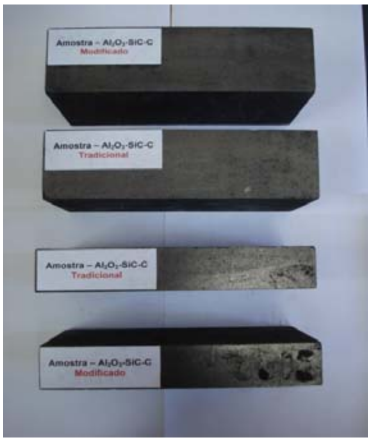
- Gradual transfer of pig iron desulphurization from torpedo cars to ladles in the steel plant, which reduces the desulphurization index in the torpedo car from about 90% to about 30%. This means reduction in crust formation on the lining in the last few years. It is believed that crust can act as a lining protector, decreasing its thermal loss and direct contact of atmospheric air with the bricks. Furthermore, multiple thermal cycling, stemming from the unloading(steel plant) and pig iron loading (high blast furnace), would be less rigorous.
- Increase in pig iron average temperature and, consequently, refractory lining surface from 1999, as a consequence of new operational practices. This could broaden phase transformation along lining thickness.

11 METHODOLOGY FOR THE IMPROVEMENT OF Al_2O_3-C-SiC REFRACTORY MATERIALS USED IN TORPEDO CAR LININGS

The adopted methodology for the improvement of alumina-carbon-silicon-carbide products traditionally used in the lining of torpedo cars was through laboratory re-evaluation of physical and chemical properties considered relevant after micro-structural changes in the materials, aiming at the decrease in elasticity modules, without compromising resistance to slag corrosion and oxidation.

12 TESTS

In order to demonstrate the performance of alterations carried out in the laboratory in the traditional structure of Al_2O_3-C-SiC in comparison with the modified structure, thermal and physical tests were necessary.
Figure 6 below shows the preparation of samples (traditional and modified Al_2O_3-C-SiC structure) before being subjected to tests.



Samples dimensions:
P229x114x63mm
P229x114x32mm

Burned in reducing atmosphere at 1450ºC.

Figure 6- Sample preparation for laboratory tests.

13 RESULTS AND DISCUSSION

Table 4 below refers to the results of comparative tests, as previously mentioned, between traditional and modified Al_2O_3-C-SiC bricks. It may be noticed that in the tests carried out porosity, for the modified type, had a significant reduction, which is considered beneficial as it decreases liquid pig iron infiltration in the refractory material and, consequently, decreases slag attack and metal infiltration. The results found in the creep-test, which indicates hot deformation under a given compression tension over a long period of time, show that the modified material had more hot deformation, indicative of the formation of a viscous and thermoplastic liquid phase, which contributes to the decrease in the elasticity module under a given tension. Although it may seem contradictory, the biggest hot deformation did not compromise the structural stability of the lining in this kind of application.

Table 4 – Comparative tests between traditional and modified Al_2O_3-C-SiC bricks.

TEST / MATERIAL	Traditional	Modified
M.E.A (g/cm³)	**3,04**	**3,01**
Apparent porosity (%)	**11,02**	**8,65**
R.F.T.A (MPa)	**13,63**	**13,84**
R.C.T.A. (MPa)	**53,31**	**54,21**
Dimensional linear variation (%)	**0,00**	**0,00**
Hot rupture module 1200ºC (MPa)	**4,4**	**6,85**
Creep Test (1450ºCx15hx0,3 MPa) Deformation (%)	**- 0,60**	**-1,80**
Oxidation Test at 1000ºCx5h (%)	**62,87**	**55,85**
Thermal shock resistance at 1000ºC x 1h and water cooling	**22 cycles**	**30 cycles**

Note: Samples burned in reducing atmosphere at 1450ºC.

The results achieved in this improvement were valid under applied tests and later the approved product was adopted as standard lining, whose advantages include:

- greater availability of the torpedo car;
- greater operational reliability for conduction of pig iron pre-treatment;
- reduction in the wear rate and,
- increase in torpedo car campaigns (about 450,000 tons of transported pig iron).

14 CONCLUSION

The temperature gradient along lining thickness and the exposure time of these refractory materials in industrial conditions have been a reason for concern if we take into consideration that the main wear mechanism is crack spreading and chipping of refractory materials hot face (structural thermal shock). The changes in micro-structure of the new material, which consisted of percentage increment of fixed carbon, quality adequacy and amount of antioxidant agents and induction to form a vitreous phase, thermoplastic in the typical temperature of the process, were the main measures which contributed to enhancing the campaigns of refractory linings for torpedo cars.

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