Eco-friendly zero carbon Al_2O_3-SiC brick for hot metal ladle (HML)

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Abstract

For many years, hot metal ladles (HML) have been lined with Al_2O_3-SiC-C (ASC) bricks due to their excellent resistance to acidic slag in the ironmaking process. Although these bricks present standard performance for this application, increasing demands for extended equipment lifetime, simplified and easy recycling (no AOX), and zero fume emissions emerge as key points for new technological advances in the steelmaking industry. A novel tempered C-free Al_2O_3-SiC (AS-K) brick with engineered microstructure and special binder was developed to reach these environmental requirements. This work presents a comparison of the microstructural, physical, mechanical, and thermomechanical properties of AS-K and ASC technologies and evaluates the field trial followed by a 3D laser scanning technology to measure the wear rate and the performance of this new product concept.

Keywords: Hot metal ladle (HML); C-free brick; Al_2O_3-SiC; 3D laser scanning.

1 Introduction

The evolution of the steelmaking industry, which accounts for the largest worldwide refractories consumption, triggers the current demand for increasingly high-performance and sustainable steel. To overcome the current challenges, the refractory industry must innovate and provide a complete solution package tailored to the specific needs of its customers. This includes adjusting product formulations and manufacturing processes to improve refractory properties at high temperatures and implementing campaign monitoring solutions to inspect lining wear and prevent refractory failures, thereby promoting safer operations. This scenario leads to a novel global refractories' requirement: eco-friendliness and easily recyclable products, displaying low CO_2 footprint and no-fume emissions. Consequently, the refractory industry needs to pursue solutions based on engineered microstructures which result in their lifetime increase, intensifying the equipment available at the customer's site and delivering a complete solution package capable of measuring the refractory's wear rate and its thickness, contributing with a safe operation during the production process. The hot metal ladle (HML) in the steelmaking shop is associated with various hazardous activities and has traditionally been lined with high alumina refractories because of their compatibility with highly acidic slag and excellent resistance to thermomechanical stress.

Unlike the standard resin-bonded technology (Al_2O_3-SiC-Carbon bricks), which provides improved thermal shock and corrosion resistance by the carbon sources addition [1], C-free tempered bricks [2], that takes benefit of the first HML heating for fast sintering and properties evolution, emerge as an alternative to fulfill the current requirements for no fume, high performance, and joint closing. This study presents a new concept of C-free Al_2O_3-SiC (AS-K) technology for use in hot metal ladle (HML) applications, which was compared to a standard-shaped resin-bonded brick. The impact of this new material was evaluated through a field trial, in which a fully lined HML was monitored using 3D laser scanning [3], except for the impact pad.

2 Experimental procedure

2.1 Materials and methods

Comparative evaluations were carried out on commercially shaped bricks manufactured in plant-scale production, and the tests were conducted in the R&D department. Table 1 illustrates schematic compositions that highlight the differences between the recipes.

For purposes of comparison, both ASC and AS-K bricks were tempered at 200 °C and afterward exposed to coking at 1000 °C, 1400 °C, and 1500 °C for 5 hours each (using an electric furnace with a heating rate of 10 °C/min). Comparative chemical analysis was conducted using the X-ray fluorescence (XRF) technique with Magix Pro – Philips equipment.

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To evaluate permanent volumetric changes (PVE), the dimensions of the bricks were measured before and after each heat treatment using digital calipers.

Archimedes' principle was conducted to measure bulk density and apparent porosity using kerosene as the liquid medium (in accordance with NBR-6220 standard). Cold Crushing Strength (CCS) was assessed using a Kratos ECC (Brazil) machine equipped with a 100 kN load cell (following JIS, R-2206, Brazil) on 50 x 50 x 50 mm3 specimens. Microstructure analysis was performed using optical microscopy (Carl Zeiss – Model: AXIO-Imager. A1m). A thermal shock resistance test was conducted using pre-coked samples on a one-side water refrigerated plate, simulating the first HML heat (1000 °C / 5h) on nickel-wrapped 160 x 40 x 40 mm3 bars. The drop in elastic modulus was monitored for 20 thermal shock cycles ($\Delta T = 1025$ °C) (in accordance with ABNT – NBR 13202) using the ultrasound velocity method (James Instrumental Inc). A corrosion test was performed using octagonal prismatic samples in an induction furnace at 1500 °C / 3h with samples coked at 1000 °C / 5h to eliminate any volatile. Specimens were immersed in hot metal (pig iron) with synthetic Blast furnace slag and restored every 30 minutes to avoid slag saturation.

3 AS-K development - Discussions

3.1 Chemical, physical and thermomechanical properties

To evaluate the chemical differences between the ASC and AS-K bricks, the chemistry results are showed in Table 2.

The results indicate that both products are similar in composition, except for the carbon content. Both bricks concept was based on the same raw material additions, and the SiC usage was due to its high endurance characteristics, which impart high abrasion and thermal shock resistance [1]. Regarding the AS-K brick, the purpose of incorporating MgO in the AS-K brick is to promote joint closure during operation by promoting controlled spinelization through the binder system, which helps to prevent hot metal infiltration between the assembled bricks [2,4]. Additionally, the main change of those two-technology concepts is in the binding system. The ASC brick uses a resin binder, whereas the new AS-K brick technology utilizes a special hydraulic binder that can provide faster sintering due to its higher reactivity at lower temperatures. Figure 1 shows the microstructure of the AS-K brick after being cooked at 1000 °C.

Table 1. Schematic compositions of ASC and AS-K bricks

Component	Fixed carbon	Free-C	SiC	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	Others
ASC	2.16	5.53	7.21	11.90	75.67	1.32	3.23	0.05	0.62
AS-K	1.70	0.00	5.68	8.54	77.98	1.08	3.17	3.11	0.44

Table 2. Schematic compositions of ASC and AS-K bricks

Component	Fixed carbon	Free-C	SiC	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	Others
ASC	2.16	5.53	7.21	11.90	75.67	1.32	3.23	0.05	0.62
AS-K	1.70	0.00	5.68	8.54	77.98	1.08	3.17	3.11	0.44

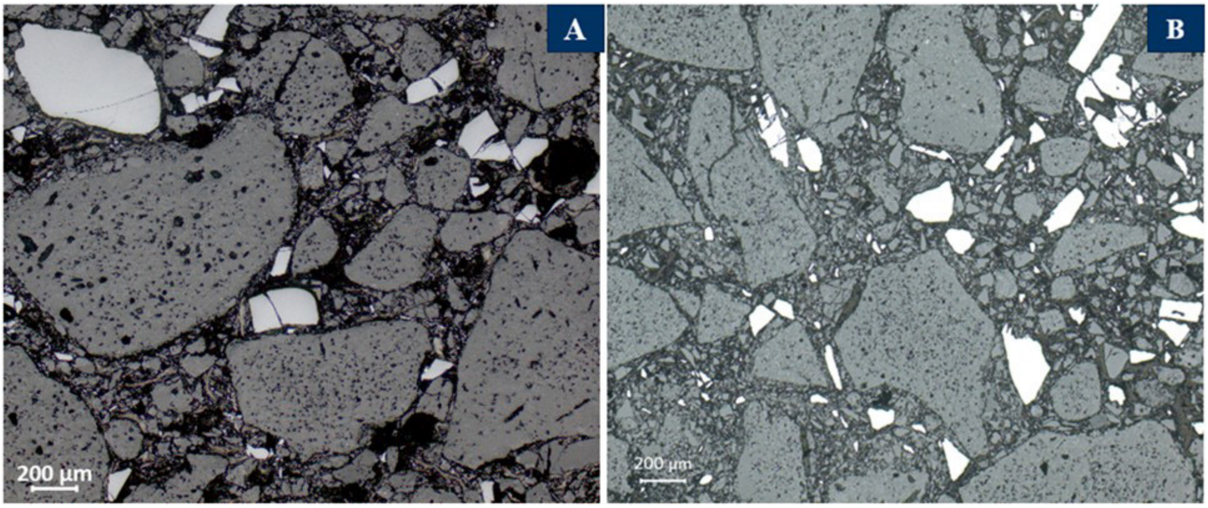

Figure 1. Microstructures after coked at 1000 °C of A) ASC and B) AS-K brick.

According to the microstructures, it is noted that the difference between the bricks is mainly because of the absence of C-sources and the binder system. It is possible to observe an early reaction in the C-free brick, that provides special properties in the first heats of the equipment campaign. Table 3 presents a comparative analysis of the physical and mechanical properties of ASC and AS-K bricks as a function of different heat treatments, in order to assess the impact of the two different binding systems and product concepts on the microstructure.

The AS-K brick showed a consistently higher bulk density compared to the standard ASC brick among all evaluated temperatures. This difference is likely due to the replacement of graphite with bauxite and magnesia in the AS-K composition.

However, the C-free brick exhibited a higher apparent porosity after tempering. Nevertheless, after temperatures ranging from 1000 °C to 1500 °C, the values remained stable at around 13.0%. This behavior is attributed to the fast-sintering binder system, which generates a homogenous porosity in the microstructure through the new technology, thereby imparting more flexibility to the brick. The elastic modulus corroborated with higher flexibility in the AS-K system, noticing that, in the pre-heating (33 GPa instead of 50 GPa in the resin-bonded system).

The AS-K brick exhibits a unique trend of permanent volumetric expansion (PVE) that shifts from retraction at lower temperatures to expansion beyond 1400 °C. Conversely, no expansion is observed in the counterpart system. The expansion behavior is desirable to mitigate the threat of molten hot metal infiltration through the brick joints, and it is attributed to the high-speed in-situ spinalization facilitated by the system's high reactivity. However, the absence of carbon content leads to better sinterability results after coking at 1400 °C and 1500 °C, which improves the brick's cold crushing strength (CCS) when using a new binder. Figure 2 illustrates this sintering behavior in AS-K bricks coked at 1400 °C and 1500 °C.

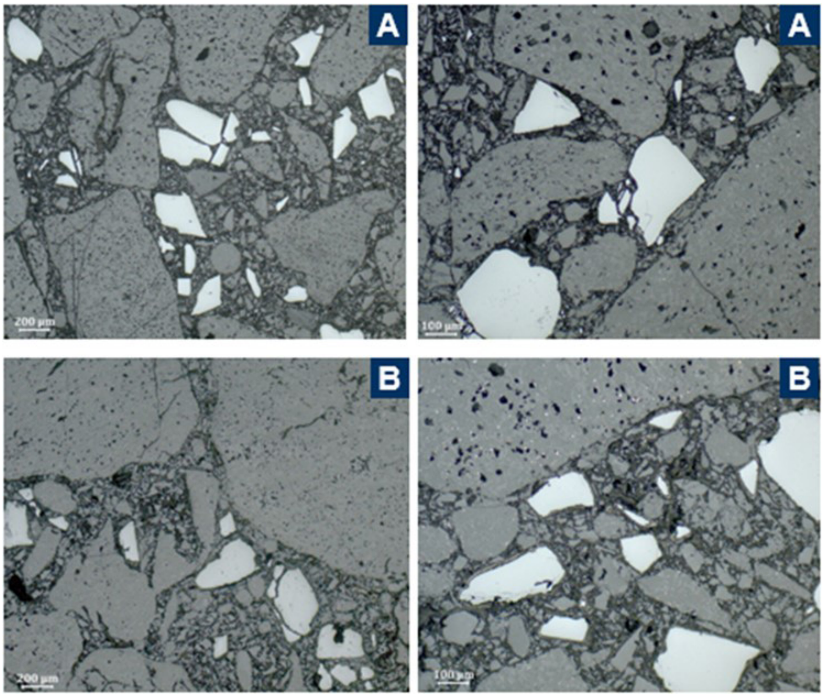

Figure 2. Microstructures of AS-K brick: A) coked at 1400 °C and B) coked at 1500 °C.

Table 3. Physical and mechanical properties of ASC and AS-K bricks

Thermal treatment	Tempered at 200 °C		Coked at 1000 °C		Coked at 1400 °C		Coked at 1500 °C	
Evaluated Properties	ASC	AS-K	ASC	AS-K	ASC	AS-K	ASC	AS-K
Bulk Density (BD) [g/cm^3]	2.89	3.00	2.90	2.96	2.90	2.94	2.90	2.95
Apparent Porosity (AP) [%]	5.03	9.33	9.87	13.59	10.27	13.33	11.43	13.60
Permanent vol. expansion (PVE) [%]	0.17	-0.31	-0.46	-0.17	-0.72	0.94	-0.95	1.17
Cold Crushing Strength (CCS) [MPa]	56	52	44	40	42	62	40	58
Elastic modulus (EM) [GPa]	80	35	50	33	43	38	39	45
Metal line wear (%)	-	-	0.52	0.64	-	-	-	-
Slag line wear (%)	-	-	9.91	9.58	-	-	-	-

Figure 3. Images after corrosion test: A) ASC brick and B) AS-K brick.

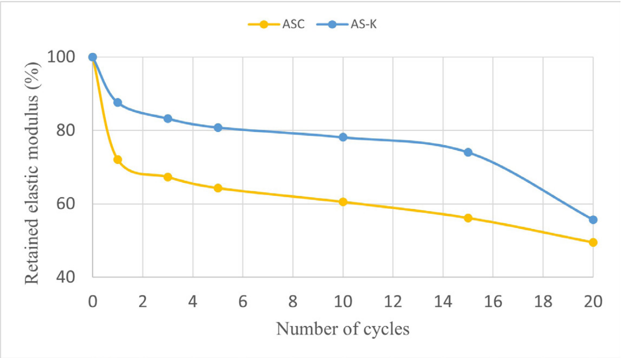

Figure 4. Retained elastic modulus (EM) values as a function of thermal shock cycling for bricks coked at 1000 °C for 5 h with one subjected to a temperature variation (ΔT) of 1025 °C.

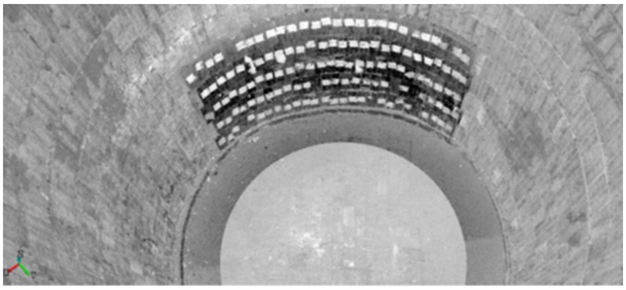

Figure 5. HML assembled with AS-K brick in the wall in a 3D view.

The corrosion resistance of both materials was nearly identical, indicating that the distinct microstructure with a small pore distribution created by the new binder system effectively prevents slag infiltration. Figure 3 represents images of the ASC and AS-K samples after metal and slag attack following the corrosion test.

To comprehend the impacts of these two distinct product concepts on the microstructure, both were subjected to coking at 1000 °C (simulating the initial heating process and removing volatiles), followed by testing for thermal shock damage resistance (TSR) for a ΔT of 1025 °C to room temperature. The results of the thermal shock resistance trend are illustrated in Figure 4.

Both profiles exhibited vastly different behavior, with the most substantial decrease in elastic modulus in the ASC concept occurring during the first cycle (~ 30%), followed by a continuous decline observed in all subsequent cycles. In the carbon-free AS-K brick, there was an initial decrease of approximately 10.0% during the 1st cycle, followed by a gradual reduction until the 15th cycle. Conversely, the ASC displayed a significant decrease in the retained elastic modulus (~25.0% in first cycle), indicating that it has lower thermal shock resistance.

4 Steel shop trial

The new carbon-free AS-K brick was installed on the wall of an 80-ton capacity hot metal ladle, with a working lining thickness of 127 mm, while the standard material was maintained for the impact pad. To ensure accurate trial result measurements and a safe environment for the customer during the trial, a 3D laser scanning tool [3] was utilized to closely monitor wear and optimize ladle durability during its operation. Figure 5 illustrates the AS-K brick assembly in a 3D view of the equipment generated by laser scanning.

During this field trial, no fumes or abnormalities were observed during installation and pre-heating, which was vastly different from the resin-bonded brick [5]. Figure 6 illustrates the measured wear profile (62.2 mm) in a transversal (a) and longitudinal (b) 3D view, with a

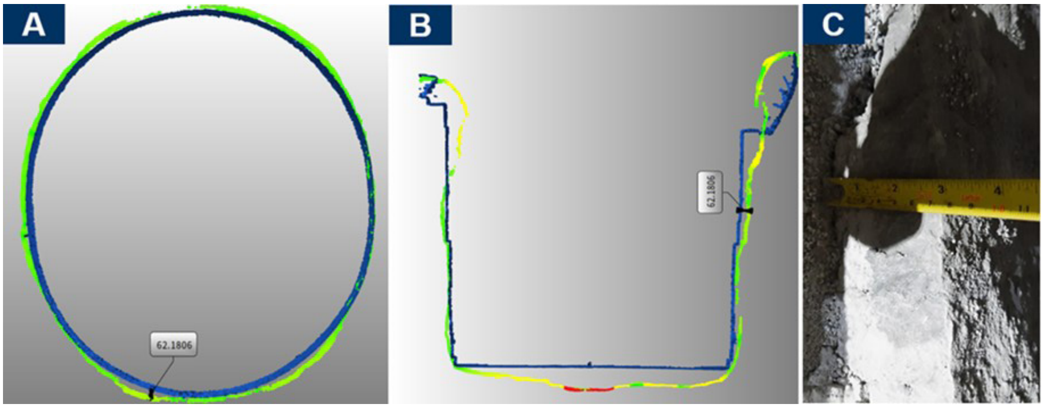

Figure 6. Overall wear rate comparison between the initial and residual thickness promoted by the 3D laser scanning after 1303 heats (a) transversal, (b) longitudinal view and (c) residual thickness.

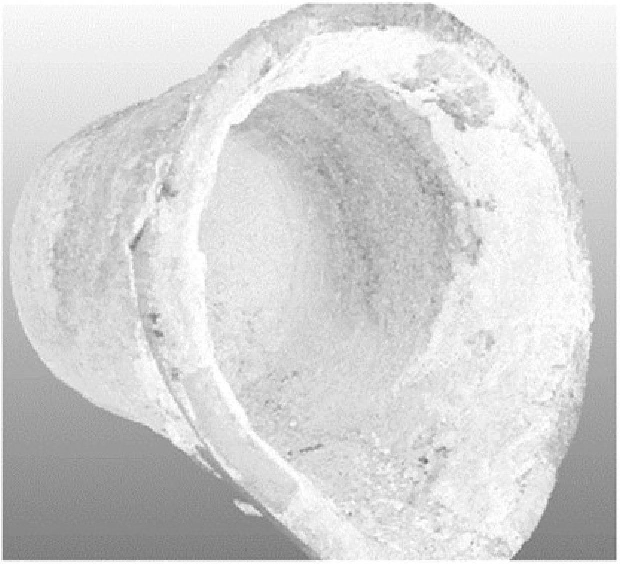

Figure 7. Overral wear rate produced by the 3D laser scanning after 1303 heats.

focus on the AS-K brick linings. The figure also displays the wear rate generated by the scanning tool, considering the initial (127.0 mm) and residual thickness (c) (65.0 mm) after 1303 heats. During the campaign, frequent 3D scans were conducted to confirm that the wear was in line with expectations and below the wear limit.

Based on the 3D scanning tool, the minimum thickness found (~ 62.0 mm) in the side wall area of the hot metal ladle needs to withstand its potential throughout the entire campaign with almost no maintenance. This field trial ended after 1303 heats due to the heavy wear rate in the impact pad area caused primarily by intermittencies in the operational campaign.

However, considering the lowest residual region and this feature, the potential campaign of AS-K bricks could be 1828 heats, exceeding the average lifetime of 1700 heats. For elucidation purposes, it is worth noting that the visual inspection and the 3D scan image generated after the end of the campaign (Figure 7 below) indicated the integrity of the wall where the new AS-K brick was applied, showing a well-preserved residual brick with no cracks, spalling, or any other relevant damage. No hot metal infiltration was observed, confirming the material's efficiency in closing the brick joints.

5 Conclusions

A new clean technology has been developed in the form of a C-free AS-K brick with a special binder designed for HML applications. This material was compared with the standard ASC brick and presented suitable properties for this application. To validate this new technology, a field trial was conducted with the customer, during which no fumes were observed during pre-heating.

According to these results, AS-K brick lining demonstrated outstanding behavior in severe operational conditions, showing a potential of 128 heats above the average lifetime in this Brazilian customer. Consist extra remaining thickness may lead to higher campaign heats or optimization in the brick profile increasing the internal volume of the HML.

In conclusion, the new C-free AS-K brick, along with the implementation of 3D laser scanning technology, offers numerous advantages for the steel and refractory industry. These solutions optimize equipment campaigns, enhance steel shop safety, and meet environmental demands, thereby providing a more sustainable approach to the industry.

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Referencies

1. Nag M, Nag B, Gangopadhyay S, Panigrahi P, Singh B. Exploration of new quality refractory to improve hot metal ladle refractory performance. Engineering Failure Analysis. 2021;125:105384.
2. Pagliosa C. Novel unburned alumina-magnesia bricks for ULC steel: zero-carbon and zero-fume refractory. In: Proceedings AISTech 2016; Pittsburgh. Warrendale: Association for Iron & Steel Technology; 2016. p. 1339-1346.
3. Macedo JF, Ribeiro AS, Nonaka F, Guimaraes BF, Morais VL, Avila HC. How 3D scan is adding value and performance to refractory lining inside Steel Industry. In: AISTech Technology Conference, Pittsburgh. Warrendale: Association for Iron & Steel Technology; 2022.
4. Sardelli JAP, Borges OH, Pagliosa C, Pandolfelli VC. In-situ Al2O3-MgO and Al2O3-ZnO spinel formation: the Kirkendall effect on physical and mechanical properties. Aachen: ALE; 2022.
5. Mukhopadhyay S, Chatterjee S, Kanda MK. Eco-friendly smokeless Al2O3-SiC brick for hot metal ladle. China's Refractries. 2008;17(1).

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