SELF-HEALING MICROSTRUCTURE: THE UTMOST REFRACTORY TOUGHNESS MECHANISM

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ABSTRACT

Refractories are often exposed to thermal variations during their operational cycle, such as in torpedo cars and iron ladles, where molten metal is loaded and unloaded at a high frequency basis. Dealing with that aggressive thermal shock is not straightforward and the most common approach for these materials is to optimize the carbon sources, increasing the thermal conductivity of the bricks and reducing the thermal gradient between the hot and cold faces. If, on one hand, the material becomes more resistant to thermal shock damages, on the other hand, its higher conductivity imposes a negative consequence: higher thermal loss during operation. In this work, inspired by intelligent microstructures with the ability to adapt to the most severe environmental conditions, an innovative approach was evaluated, aiming at obtaining an Al2O3-SiC-C brick formulation designed to present a self-healing behavior, without variation in the carbon sources or content. The new developed structure successfully regenerated the cracks initiated during thermal cycles, resulting in an even tougher material after thermal shock tests. Other properties such as mechanical, oxidation, and corrosion resistance also showed promising results, pointing out the birth of a smart self-healing technology, able to completely change the role of refractories in thermal cyclic operations.

INTRODUCTION

The steel production chain has been going through a transition process towards a descarbonized future, where a large variety of actions are under consideration [1]. Although most of them are predicted to be fully implemented before no less than two decades, others are already in place in the ironmaking sector, involving both the use of different fuel mixes and the addition of new metallic charges. Additionally, steel producers have been looking for opportunities to reduce energy losses and CO_2 emissions in process beyond the Blast-Furnace operations [2].

The refractory lining is directly responsible to keep the heat inside the equipment and prevent any metal temperature drop. Nonetheless, in some cases, such role becomes challenging as the refractory material must also withstand very aggressive thermal cycles, as in the case of torpedo cars and hot metal ladles. A classical approach to reduce the thermal damage is by adding carbon sources, mainly graphite, in the refractories' structure so that the heat is easily transferred through the material and a lower thermal stress is generated. As a side-effect, however, more energy is lost by thermal conductivity by the refractory walls, which is undesirable for the sustainability commitments of steel producers [3].

In this scenario, where avoiding the cracks generated by thermal cycles are not straightforward, a different perspective is needed and the right question to be asked is: what if we could recover such cracks during operation?

Self-healing mechanisms are quite largely explored in the polymers field, where, for instance, small capsules containing a setting agent are included in the materials structure [4]. When a crack reaches them, the capsules are broken and a hardening reaction takes place between the base material and the additive which is now available, promoting the complete sealing of the crack area. Likewise, a new class of concretes for building construction was also developed with biomineralization ability. In these materials, bacteria are introduced so that they can metabolically produce minerals to help repair cracks and damage to the concrete [5].

Although those self-healing mechanisms are well-known and proved to work efficiently, they are still limited to room temperature conditions. At very high temperatures, such as the ones contemplated during the steel process operations, the usual components incorporated to induce self-healing mechanisms in those materials are no longer functional. The main purpose of this work was, then, to investigate and develop an entirely novel high temperature self-recovery mechanism, based on nature-like phenomena adapted to refractory structures, giving birth to the utmost toughness mechanism ever seen.

MATERIALS AND METHODS

Materials

The introduction of the new self-healing mechanism was evaluated in a Al_2O_3-SiC-C brick, frequently used as the torpedo car lining material. In order to mimic the healing behavior of living creatures, the regular ACS microstructure was reengineered in such a way that it could smartly interact with the just-generated crack and seal it, just like the human tissue heals a fresh wound with the formation of a new tissue layer. For this purpose, a combination of two non-organic recovery agent was added to the torpedo car formulation, as show in Tab. 1. The reference ACS recipe (SRB REF) was selected due to its benchmarking performance in the market.

Tab. 1: ACS brick formulations evaluated in this work, in wt%. SRB REF is the Shinagawa reference brick in the market. SRB SH stands for the newly developed SELF-HEALING technology.

Raw-material	SRB REF	SRB SH
Coarse Al_2O_3	55,0%	55,0%
Fine Al_2O_3	13,0%	13,0%
SiC + C	13,0%	13,0%
Binder	4,0%	4,0%
Anti-oxidants	2,0%	2,0%
Self-healing additives	-	5,0%

Self-healing evaluation

For a better observation of the presence of eventual self-healing mechanisms, cyclic thermal shock tests were conducted for both formulations, using three prismatic samples (160mm x 40mm x 40mm) of each composition, pre-fired at 1450°C for 5h at reducing conditions. Each cycle started with placing the samples originally at room temperature (30°C) into a pre-heated furnace (1200°C), leading to an aggressive heating shock. After leaving them there for 30 minutes, the cycle ended by returning the pieces to room temperature for more 30 minutes, inducing a cooling stress. This step was repeated for sixteen times and, every two cycles, the modulus of rupture (MoE) of the samples were measured to follow any variation in the material's structure along the test.

Once the recovering benefits could be proved, a scanning electron microstructural (SEM) analysis were performed to identify the presence of healed cracks in the damaged samples of the SRB SH composition. The cracks in the SRB REF material were also investigated for comparison's sake.

Performance evaluation

One of the project assumptions is that the introduction of a self-healing mechanism in the refractory's microstructure would not damage any of the other properties and, therefore, compromise the well-know performance of Shinagawa's bricks for torpedo car. The following properties were then evaluated for the two formulations (SRB REF and SRB SH):

- Open porosity and apparent density: evaluated by using the Archimedes technique in kerosene, following the ASTM Standard C380;
- Modulus of rupture: carried out under three-point bending tests (ASTMC 583) using prismatic samples (160 mm x 40 mm x 40 mm);
- Corrosion tests: conducted in a rotary furnace, in a two-cycle process, where a mix of blast-furnace slag and pig iron was used (80% slag + 20% pig iron);
- Oxidation resistance tests: carried out according to the following procedure → cubic samples of 50 x 50 x 50mm were 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 24h and, after cooling down, they were cut and the cross-sections were used for measuring the oxidized layer.

For all the above-mentioned tests, samples were previously fired at 1000°C or 1450°C, for 5h, at reducing atmosphere.

RESULTS AND DISCUSSION

The results obtained during the cyclical thermal shock tests are shown in Fig. 1. It is possible to observe that the reference material (SRB REF) confirmed its denomination as the benchmarking product, with a very good performance after 16 thermal cycles. A small decrease in the Modulus of Elasticity is perceived after the two first cycles (~15%), indicating the formation of minor damage in the structure, with no more further deterioration, which, in other words, means that the SRB REF composition was well designed to sustain the initial thermal shock damage and gurantee a stable performance. The new developed formulation (SRB SH) also presented the same initial behavior, with the generation of thermal cracks in its microstructure. Nonetheless, better than just supressing the damage propagation along the the test, its smart microstructure was able to interact with the new cracks and progressively seal them as further thermal cycles were applied to the samples. As the test was concluded, the last MoE measurement presented an amazing result: its value was entirely recovered to the level of the original, non-damaged structure.

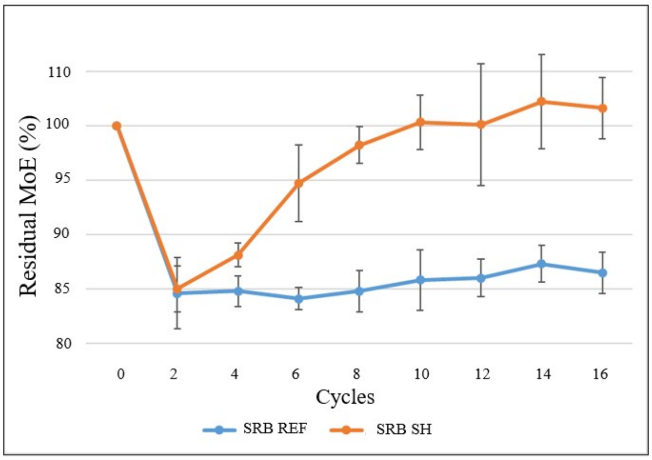

Fig. 1. Residual Moduli of Elasticity (MoE) as a function of thermal shock cycles for SRB REF and SRB SH formulations.

After the test, the samples of SRB REF and SRB SH were collected and used for a microstructural evaluation in order to identifiy and compare the cracks situation at both materials. Fig. 2 (a) shows the SEM image obtained for the SRB REF material using topographic effects, where it is easy to point out the generated crack between a coarse grain and the matrix. Due to a well designed grain size distribution and proper thermal properties, the crack was succesfully deflected and stopped, enabling a stable behavior along the thermal cycles, as seen in the previous graph. In the microstructure of the SRB SH material (Fig. 2 (b)), one may also observe the same crack pattern between the matrix and coarse grains. The main and most important difference is that such crack is visually sealed with a new phase that was formed during the following thermal cycles by the activation of the self-healing agents in the microstructure when they interacted with the propagating crack.

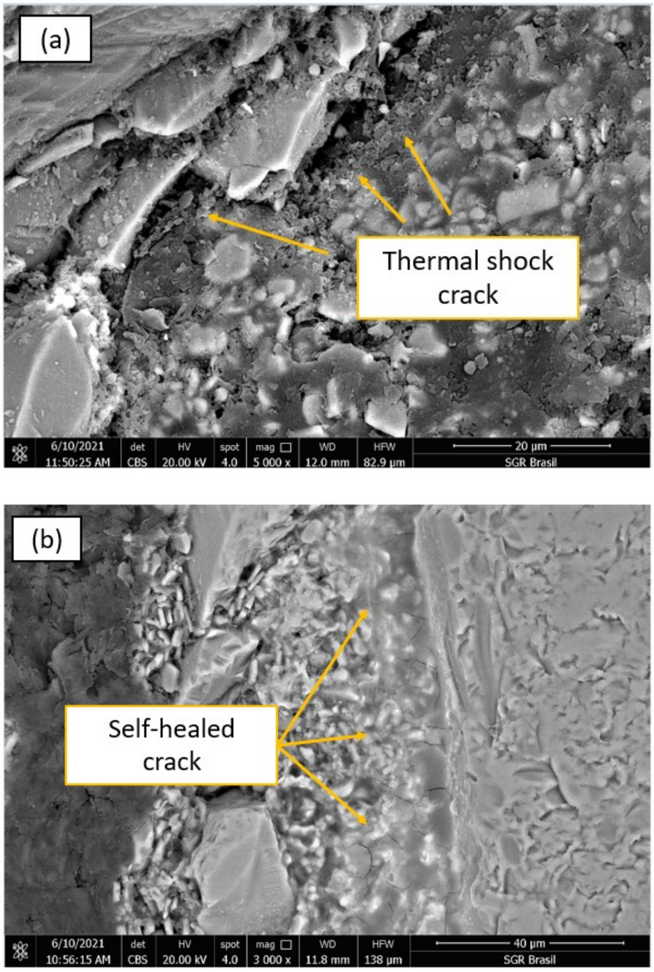

Fig. 2. Micrograph of (a) SRB REF and (b) SRB SH samples, obtained by SEM after sixteen thermal shock cycles.

This innovative smart mechanism was responsible to restore the microstructure original condition and, therefore, could be used to implement a new series of Al_2O_3-SiC-C bricks virtually inmunne to thermal cyclic damages. For that, it is also important to verify other important physical and chemical properties in order to check whether the introduction of such new structure could lead to a non-expected side-effect. Fig. 3, 4 and 5 presents, respectively, the apparent density, apparent porosity and hot modulus of rupture for both materials after firing at 1000°C and 1450°C for 5h at reducing atmosphere.

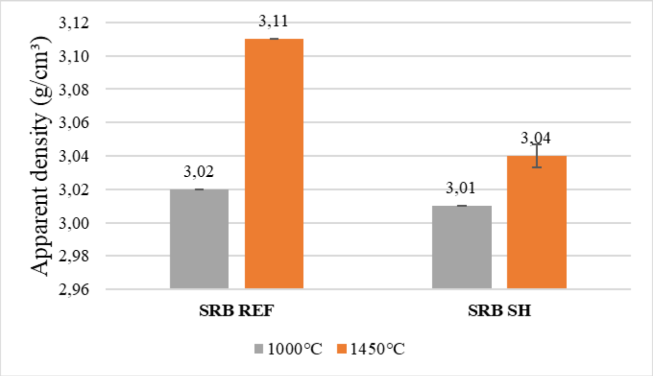

Fig. 3. Apparent density of SRB REF and SRB SH samples after firing at 1000°C and 1450°C.

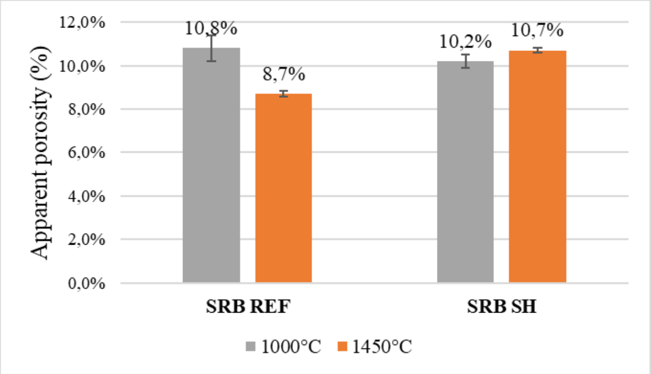

Fig. 4. Apparent porosity of SRB REF and SRB SH samples after firing at 1000°C and 1450°C.

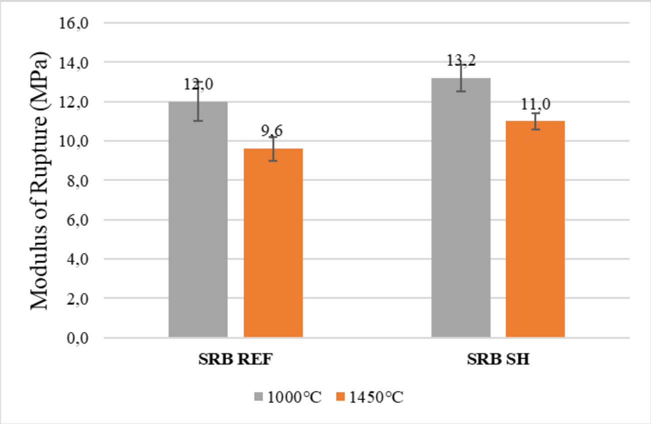

Fig. 5. Modulus of rupture of SRB REF and SRB SH samples after firing at 1000°C and 1450°C.

Due to the difference composition of the brick's matrix and, consequently, to the new phase structures which are formed at high temperatures, the new SRB SH samples presented slight differences in the density and porosity values after firing at 1450°C. However, it is relevant to note that, despite of those differences, the new self-healing material presented a cohesive and well bonded structure, as the MoR values were entirely compatible with the benchmarking reference ones.

Besides keeping almost the same values for the basic physical properties, the introduction of the smart self-healing mechanism in the SRB SH material also led to an improvement of the corrosion resistance, as observed in Fig. 6 and 7. As the refractory corrosion takes place via the infiltration of metal and slag through voids and deffects in the material, a high-temperature sealing system may clearly help to block possible infiltration paths and to prevent chemical dissolution inside the brick.

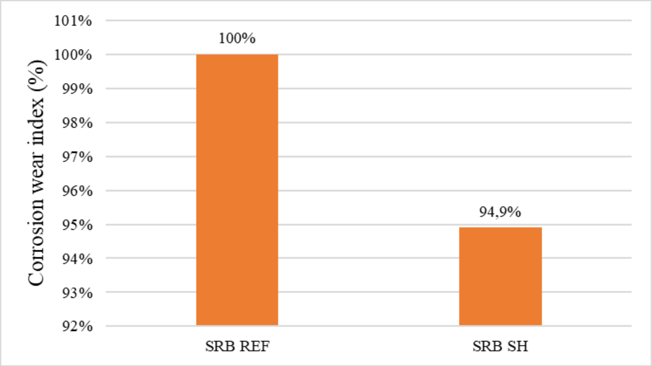

Fig. 6. Corrosion wear index of SRB REF and SRB SH samples.

Fig. 7. Cross-sextion of SRB REF and SRB SH samples after the corrosion test.

Finally, Fig.8 presents the measurements of the oxidized area of SRB REF and SRB SH samples after exposition of 6h and 24h in air. Once again, the presence of the self-recovery additives did not affect the material's oxidation resistance and, actually, the smart sealing process could again have helped to slightly decreased the oxidation process for the SRB SH material.

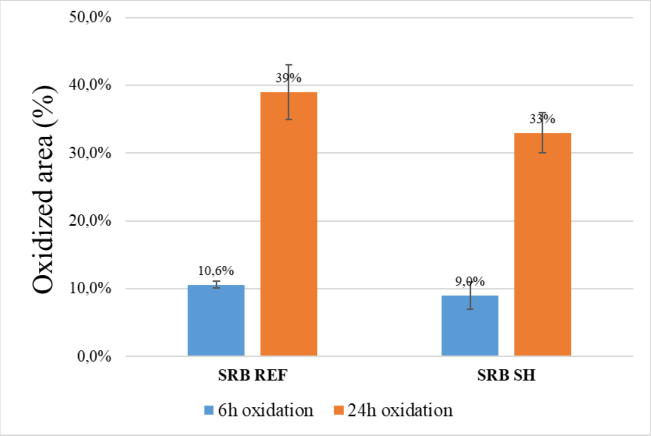

Fig.8. Oxidation resistance results after 6h and 24h for SRB REF and SRB SH samples.

CONCLUSIONS

Aiming at reducing the energy losses in the steel manufacturing process while also increasing the lifetime of refractories applied at high thermal cyclical areas, an exclusive smart self-healing structure was developed and introduced in a Al_2O_3-SiC-C torpedo car brick composition. The new mechanism was able to interact promptly with the cracks generated during thermal shock processes, activating the self-healing agents, and completely sealing the crack area. This innovative process induced a total recover of the original structure of the material and its modulus of elasticity returned to values as high as the pre-thermal shock condition. As neither the physical properties nor the corrosion and oxidation resistances were affected by this new smart structure, a very promising future is expected for refractories materials with the rise of such utmost and nature-inspired toughness mechanism.

REFERENCES

[1] Managi, S., Kaneko, S. Iron and Steel Indusry – Dialogue on European descarbonisation strategies. https://doi.org/10.4337/9781849803434.00015.

[2] Barati, M., Esfahani, S., Utigard, T. Energy recovery from high-temperature slags. Energy 36, 5440-5449. https://doi.org/10.1016/j.energy.2011.07.007

[3] Chen, E. S., Fréchette, M. H. Thermal and thermomechanical evaluation of high-strength insulation in steelmaking ladle, 79th Steel. Conf. Proc., ISS, 457-463 (1996).

[4] Yu, D.W., Meure, S., Solomon, D. Self-healing polymeric materials – a review. Progress in polymer science 33, 479-522 (2008).

[5] Wiktor, V., Jonkers, H.M. Quantification of crack-healing in novel bacteria-based self-healing concrete. Cement and concrete composites 33, 763-770 (2011).