A CONTRIBUTION TO THE UNDERSTANDING OF THE FAILURE MECHANISM OF HIGH ALUMINA REFRACTORY CASTABLES UNDER PRACTICE-ORIENTED THERMAL SHOCK CONDITIONS

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ABSTRACT

In service, refractory linings endure steady and/or transient thermal loading, inducing thermal stresses that may cause serious damage, even leading to the failure of the refractory linings. The assessment of the thermal shock resistance (TSR) of refractories is therefore of central concern for both refractory manufacturers and users.

When considering refractory castables, it is additionally important to keep in mind that this type of refractory system is highly heterogeneous over the thickness of the lining, where only the first few centimetres can develop a ceramic bond, followed by a dehydrated and thus mechanically weak transition zone. Finally, at the cold face, even hydrate phases may still be found. For reasons of practicality, classical approaches to investigate their TSR largely ignore this key feature. Test pieces made from castables are, on the contrary, usually completely and homogeneously pre-fired before testing for TSR.

Thanks to an innovative testing device, which enables thermal cycling at high temperatures, the TSR of high alumina refractory castables was investigated under practice-oriented thermal shock conditions and compared to the behaviour of test pieces from high alumina bricks.

Sintering processes during the thermal shock strongly impact the TSR behaviour of the castables tested. While in test pieces made from fired bricks the damaging was found to be more pronounced and concentrated near the hot face, the damages in test pieces made from unfired castables tended to occur at first in the weak bonded “cold part” of the test pieces, while sintering occurred near to the hot face. After increasing the number of thermal cycles, damaging near the hot face increased. Pre-fired castable test pieces basically behaved like refractory bricks.

Keywords: *thermal shock, refractory castable, spinel forming*

INTRODUCTION

Refractory products basically make high technology processes requiring high temperature, such as the steelmaking, cement production or waste incineration, possible. They contain the process-inherent generated or supplied heat, where most other class of materials would inevitably fail. Thereby refractory linings play the double role of ensuring the structural stability of furnaces, reactors or other processing units, and protecting the immediate environment and workers from intense heat. As a direct consequence, important steady and/or transient thermal gradients arise within the refractory linings, which result in thermal stresses.

Under typical operating conditions, process related rapid and/or repeated temperature changes at the hot face of the refractory lining, i.e. thermal shocks, are responsible for particularly intense thermal stresses that initiate damages within the refractory linings and may cause premature breakdown of the lining. In order to ensure reliable operation and extended operating time, refractory suppliers strive to develop products with constantly improved thermal shock resistance (TSR). However, the pragmatic development of such products is closely linked to the sound understanding of the material behaviour and accordingly its characterisation under practice-relevant conditions. Especially for refractory castables, there is a noticeable lack of practice-oriented knowledge on their thermal shock behaviour. Testing Standards for investigating the TSR of refractory products and most of the investigation results reported on the TSR of refractory castables imply homogenously pre-fired test pieces whereas, in practice, refractory castables usually endure their first heating up from their green state during their first use. Consequently, refractory castables in industrial linings develop a highly heterogeneous sintering profile and behaviour, hardly comparable with homogenously pre-fired test pieces.

The present work aims at improving the understanding of the behaviour and failure mechanism of hydraulic bonded high alumina refractory castables submitted to thermal shocks.

FUNDAMENTAL CONSIDERATIONS

Investigation of the thermal shock resistance (TSR) of refractory products

Ongoing efforts are being made to develop testing methods and establish standards that enable a proficient assessment of the TSR of refractories at the laboratory scale. These testing standards and specific tests are technological testing methods, and, in a metrologically rigorous way, only allow a relative comparison of the TSR behaviour of materials for the testing conditions given in the standards or specified for the test [1].

Although most of them are quite simple to perform, they are rarely consistent with industrial operating conditions. Especially, the main testing standards still in force describe “descending” thermal shocks, either by means of water quenching (DIN 51068) or air quenching (EN 993-11 and ASTM-C-1171) from 950 °C to room temperature (in case of the DIN and EN standard). The resulting heat transfers and thermal stress distribution are not comparable to typical refractory applications. In practice, ascending thermal shocks are usually more severe and decisive for most refractory linings (contact with molten metal, slag or hot aggregates, burning process…). Furthermore, the thermo-mechanical properties of refractory products greatly vary from brittle to kind of elastic/plastic behaviour with increasing temperature.

Some specific tests have been developed to adapt the thermal stress testing conditions to the refractory service conditions [1-2]. In order to perform thermal cycling at high temperatures, some laboratories proposed to build experimental furnaces with two chambers set to different temperatures [3]. However, only very mild heat transfers are achieved under these conditions that are therefore barely able to initiate significant thermal damages on the test pieces. The use of open flame burners as heat source is also reported [2-4], providing more efficient heat transfers but still far from the most prominent service conditions. By melt immersion tests, test pieces are at least partially immersed into a melt (e. g. pig iron, steel, aluminium) [5-6]. Thereby, the test conditions, especially the heat transfer, are close to those occurring in the metal making industry. However, melt immersion tests are intrinsically expensive and laborious.

Thermo-mechanical behaviour of hydraulic bonded refractory castables

As most materials, refractory products display a significant temperature-dependant behaviour, being rather brittle at room temperature and developing a kind of elastic/plastic behaviour with increasing temperature. In contrast to shaped products, refractory castables are usually not fired before being placed in furnaces, reactors or other processing units. In the best case, a recommended heating up schedule (usually provided by the refractory castable's supplier) is being applied at their hot face during the first heating up before operations start. As a consequence, only the part of the castable close to the hot face is able to develop a ceramic bond once a sufficient temperature is reached. With increasing distance from the hot face, the temperature in the castable lining drops and becomes insufficient to efficiently promote sintering, while still high enough to dehydrate and thus weaken the hydraulic bond. Accordingly, linings made of refractory castables are highly heterogeneous over their thickness, which strongly influences their thermo-mechanical behaviour, far beyond the simple effect of temperature on a pre-existing (ceramic) bond such as by shaped products.

MATERIAL AND TEST METHODS

Within the framework of the present work, a testing system that is able to reproduce the thermal shock under practice-oriented conditions and realistic temperature cycling was developed and the behaviour of high alumina model castables was examined.

Model castables

Starting from a reference calcium aluminate (CA) bonded high alumina castable (Al_2O_3 > 98 wt.-%), 4 % of spinel precursors, either sintered magnesium oxide (Nedmag DIN70; Nedmag Industries Mining & Manufacturing B.V, Nederland) or raw magnesite (magnesium carbonate $MgCO_3$, Magnesia GmbH, Germany), were added to the formulation to obtain spinel forming formulations (Tab. 1). Nedmag and magnesite partially substituted the fine fraction of tabular alumina (0,0-0.045 mm). The deflocculation of the model castables was achieved with a polycarboxylate ether based additive (0.15 wt.-%). The use of microsilica (MS) was necessary in conjunction with Nedmag to avoid the formation of cracks caused by the brucite formation during the curing of the test pieces. The formulation with magnesite was microsilica free and allowed therefore, to a certain extent, to assess the impact of microsilica on the thermal shock resistance of spinel forming castables.

Tab. 1: Composition of the model castables [wt.-%].

Castable	**MCA_MS0_M0**	**MCA_MS0,5_M4 (Nedmag)**	**MCA_MS0_M4 (magnesite)**
Tabular alumina			
1.0-3.0 mm	25	25	25
0.5-1.0 mm	21	21	21
0.2-0.6 mm	11	11	11
0.0-0.2 mm	12	12	12
0.0-0.045 mm	9	4,5	0,5
Calcined alumina	10	10	10
Reactive alumina	7	7	7
Microsilica (MS)	**0**	**0.5**	**0**
CA cement (Secar 712)	5	5	5
Nedmag	0	**4**	0
Magnesite	0	0	**4**

After casting, the tests pieces were stored in their mould for 24 h in a climatic chamber at 20 °C and a humidity of 95 %. Then they were demoulded to be stored another 24 h in the climatic chamber before being dried at 110 °C for 24 h. Finally, in order to prevent explosive spalling during their characterisation at elevated temperature, the test pieces were carefully heated to 450 °C with a heating-up rate of 2 $K.min^{-1}$ and kept at this temperature for 5 h.

A high alumina brick (Al_2O_3 > 99 wt.-%) was also investigated for comparison purposes.

Thermal shock testing system

Traditional methods and techniques to investigate the TSR of refractory systems still strongly rely on rather unrealistic testing conditions (e.g. descending thermal shocks, low temperatures) when compared to typical industrial applications.

The proposed technological testing method was therefore developed to tackle the main drawbacks of the commonly used testing methods to assess the TSR of refractory products, and therefore enforce the following features:

1. Apply an ascending thermal shock, comparable to contact with molten metal or burning process, followed by natural convection cooling.
2. Cycling at high temperature to simulate filling and emptying of metal making vessels, leading to temperature at the hot face oscillating between 1000 °C and 1700 °C.
3 Trigger a quasi-linear thermal gradient, since the heat flow occurring in most parts of industrial refractory linings stretches out perpendicular to its hot face, promoting the occurrence of a quasi-linear thermal gradient within the lining thickness.

The thermal shock testing system consists of a high-temperature laboratory furnace, into which a lifting system for test pieces (cylinder Ø 50 x 100 mm) is accommodated. During the heating up of the laboratory furnace, the test piece is maintained in a lower position (Fig. 1 (a)) so that its upper surface, while heated up, is kept at a temperature below that of the furnace. In the furnace itself a heat accumulator is heated to the temperature of the furnace.

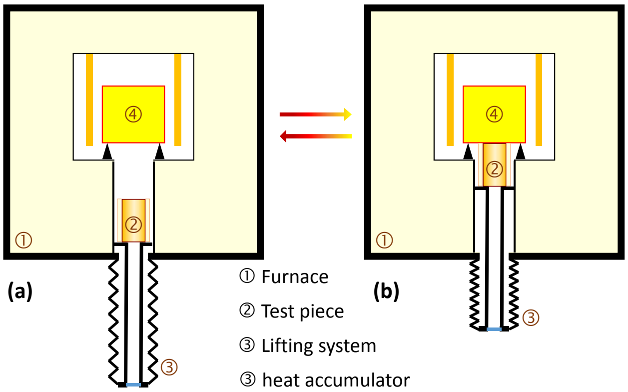

Fig. 1: experimental testing device a) test piece in the lower position, b) test piece in contact with the heat accumulator

The thermal shock is initiated by pushing the test piece into contact with the heat accumulator (Fig. 1 (b)). Due to the high heat capacity of heat accumulator and the good heat transfer coefficient, a strong thermal exchange is induced between test piece and heat accumulator. As lateral sides of the test piece are thermally insulated, the induced heat flow is almost unidirectional. For the thermal cycling, the test piece is moved back to the colder zone of the furnace to cool down. Thus, thermal cycles where the hot face of the test piece experiences temperature changes between 1000 °C and 1600 °C, can easily be achieved. During the thermal cycling, stresses of sufficient magnitude to damage the test pieces arise. The impact of the thermal shocks is appraised quantitatively by measuring the decline of the ultrasonic velocity within the test piece, reflecting the degradation of the test piece’s mechanical properties after the thermal cycling. The thermal damage is finally quantified with the dimensionless damage parameter according to Kachanov [7]:

$$D = 1 - \left(\frac{v}{v_0} \right)^2 \tag{1}$$

where v [m/s] is the ultrasonic velocity as it propagates through the test piece after thermal cycling and v_0 [m/s] is the initial ultrasonic velocity as it propagates through the undamaged test piece before thermal cycling. D = 0 means therefore no damage, while the value of D increases with increasing damaging.

Testing strategy

Two different thermal pretreatments were applied to the test pieces before being submitted to thermal cycles. They were either homogenously pre-fired at 1600 °C, or pre-fired in a quasi-linear thermal gradient (hot face at 1000 °C) to simulate the pre-heating of refractory linings in practice. The ultrasonic velocity of the test pieces was measured lengthways, i.e. in the direction of the heat flow, to assess the global damaging, and widthways, i.e. parallel to the hot face, to evaluate the damaging locally as a function of the distance to the hot face.

Each thermal cycling consisted of a contact of 15 minutes between the test piece and the heat accumulator at 1600 °C, followed by a cooling down period of 15 minutes in the lower part of the furnace. After a series of ten thermal cycles, the test piece was cooled down to room temperature for ultrasonic velocity measurements. In total three series of ten thermal cycles were performed for each test pieces.

RESULTS

Just like for most of industrial refractory linings, a thermal gradient arose during the initial heating of the test piece, reaching 600 °C before the start of the thermal cycling. The thermal cycling caused a moderate but rapid increase of the thermal gradient. The first cycles/shocks were found to be the most severe, namely producing the higher temperature difference (up to 900°C) within the test pieces. 15 minutes cooling period turned out to be insufficient to bring the test piece back to equilibrium. Consequently subsequent thermal shocks were slightly milder, as heat became stored in the test pieces.

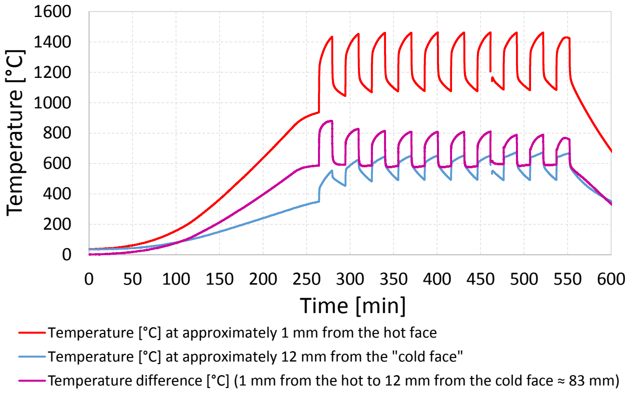

Fig. 2: Temperatures measured with thermocouples placed on test pieces during the thermal cycling of the reference model castable MCA_MS0_M0 (See Tab. 1)

With regards to the *global* damaging of the test pieces (Fig. 3), the high alumina brick and the pre-fired model castables appeared to be the more sensitive to thermal shocks, displaying higher level of damage after thermal cycling (D > 0,2). In comparison, the model castables pre-fired at lower temperatures in a thermal gradient (which is similar to the thermal gradient that the test pieces experienced before the beginning of the thermal cycling in the thermal shock testing system) presented lower stiffness before the thermal shock, i.e. lower values of ultrasonic velocity, and an apparently better thermal stress damage resistance, i.e. lower values of D. Even negative values of D were assessed for the spinel forming model castables, suggesting that the test pieces were "healed" during the thermal cycling. This behaviour, contradictory at first, was further examined by assessing the *local* damage as a function of the distance to the hot face (Fig. 4).

For the high alumina brick and the pre-fired model castables, the damaging profile follows the thermal gradient (Fig. 4 (a), (b) & (d)). The damages measured were found to be more severe near to the hot face, where the high temperatures tend to weaken the ceramic bond and the thermal stresses usually display a maximum under ascending thermal shock. At the cold face, only minimal damage was assessed. As expected, the damaging of the test pieces accumulated with increasing number of cycles, whereby the first thermal cycles usually caused the most significant damage. In contrast, the stiffness of the model castables which were pre-fired at lower temperature in a thermal gradient increased at first, resulting in negative values of D (Fig. 4 (b), (c) & (d)). As previously mentioned, the microstructure of castables undergoes significant changes while being heated. Especially at high temperatures the sintering process leads to the formation of stiff ceramic bonds, which explains the increase of the ultrasonic velocity and the negative values of D near to the hot face after the first series of ten thermal cycles. In the middle of the test piece and near to the cold face, damages may still occur as substantial thermal stresses arise, but the temperatures are not high enough to promote the efficient sintering of the weakened hydraulic bond. After the subsequent series of ten thermal cycles, the ultrasonic velocity decreased, and accordingly the values of D increased. For the reference model castable (MCA_MS0_M0, Fig. 4 (b)), the "positive" effect of the sintering near to the hot face even was nullified and the values of D became positive after the second series of ten thermal cycles. Spinel forming model castables still benefitted from the positive effect of the sintering after three series of ten thermal cycles (Fig. 4 (c) & (d)). This explains the, at first sight, surprising negative values of D previously mentioned for the global damaging of the test pieces (Fig. 3) and testifies the expected improved thermal shock resistance of spinel forming systems. The use of magnesite and absence of microsilica seemed to even further enhance the TSR of spinel forming castables.

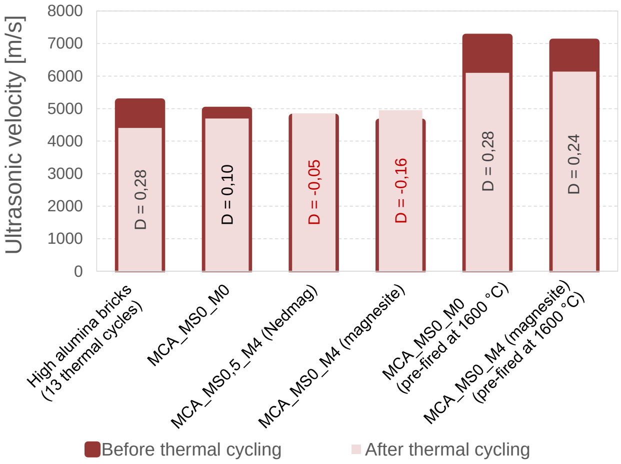

Fig. 3: Thermal shock results: *global* damaging of the test pieces after three series of ten thermal cycles

DISCUSSION

The failure of refractory castables seems to result from the competition between two antagonist processes: on the one hand, the thermal stresses promote the damaging of the refractory, on the other hand the high temperatures trigger the sintering process able to mitigate, and even counteract, the damage caused by the thermal stresses. Test pieces with limited or without sintering potential, such as bricks or materials pre-fired at high temperatures, directly suffer from the consequence of the thermal shocks and get globally damaged. Of course, damages are higher near to the hot face due to the combination of maxima in the thermal stress field and the weakening effect of the temperature. In contrast, test pieces with high sintering potential tend to improve their mechanical resistance in a thermal gradient as long as enough sintering activity can be ensured. After high numbers of thermal cycles, and presumably too intense thermal shocks, thermal damages accumulate and inevitably lead to the failure of the material. Considering this, the optimization of the sintering activity of refractory castables stands as an innovative lever to improve their thermal shock resistance and shed new light on the potentials of spinel forming castables. Not only the thermal expansion mismatch between the newly formed spinel and alumina grains may account for their improved thermal shock resistance, but also their higher sintering activity at moderate temperature compared to pure high alumina castables.

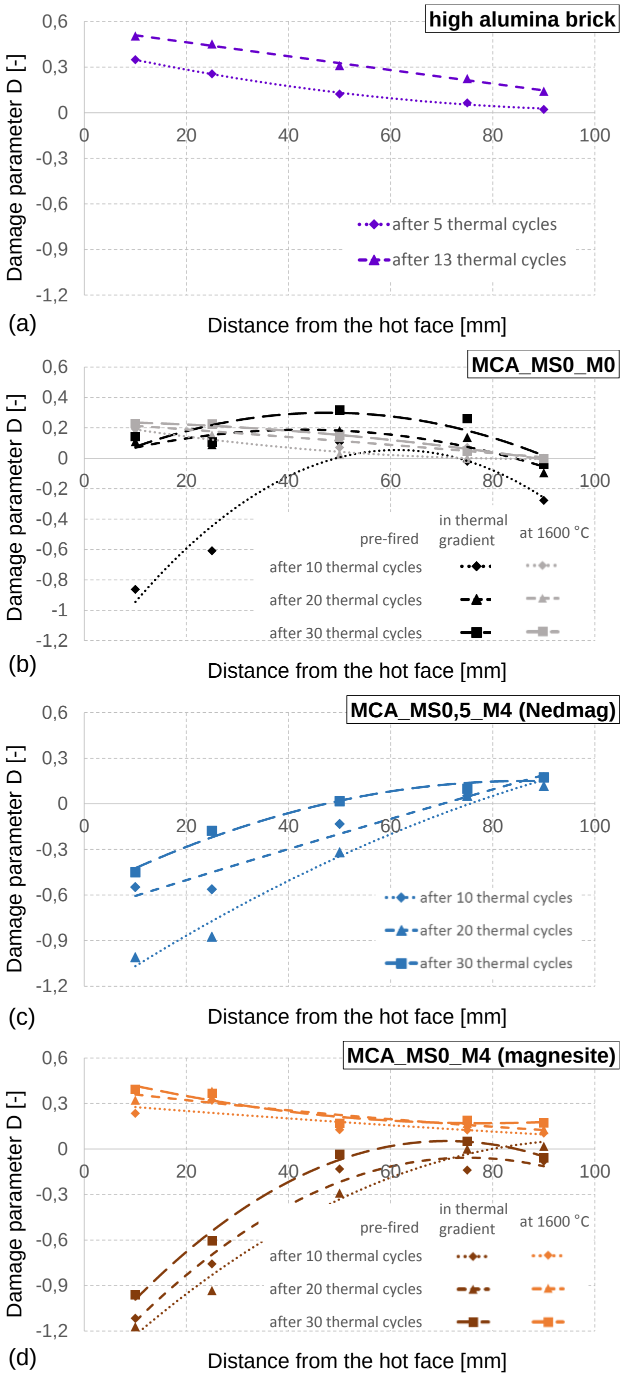

Fig. 4: Thermal shock results: *local* damaging of the test pieces as a function of the distance to the hot face after each of the three series of ten thermal cycles

CONCLUSION

Thanks to an innovative thermal shock testing system, practice oriented thermal cycles were applied to model castables for use in the steelmaking industry. The strong thermal gradient led to important changes in the microstructure of castables and an original behaviour when compared to refractory bricks. The thermal stresses induced damages within the refractory castable microstructure, especially in the dehydrated weak zone, while near the hot face, the sintering process promoted a reinforcement of the mechanical resistance. Accordingly, a high sintering potential seemed to mitigate, or at least delay, the impact of thermal shocks. Indeed, the model refractory castables pre-fired at 1600 °C behaved like fired shaped refractory bricks and suffered straightaway from damages after the first series of thermal cycles. The characterisation of the thermal shock resistance of refractory castables traditionally performed on pre-fired test pieces was therefore questioned. Additionally, the use and optimization of the sintering potential of refractory castables could be a seriously underestimated way of improving their thermal shock resistance.

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