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PROCEEDINGS

THE CARBON CHALLENGE

Steps and leaps to master the future

IMPROVING THE REFRACTORIES SELECTION REGARDING THEIR THERMAL SHOCK RESISTANCE (TSR) BY USING PRACTICE-ORIENTED INVESTIGATIONS PROMOTING EXPERIMENTAL THERMAL LOADING CLOSE TO THEIR SERVICE CONDITIONS

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ABSTRACT
In service, refractories undergo thermal shocks, which magnitudes and ranges of temperature depend on the processes in which they are being used. The suitability of refractory products to serve in a given process, and more especially their ability to sustain thermal shocks, is, however, still widely established by using standardised testing methods that hardly represent their actual service conditions. As a result, refractory products may be selected despite not being the best fit for a given application. A refractory product could perform well at medium temperatures, even when faced with thermal shocks of high magnitude, but fail at higher temperatures despite experiencing thermal shocks of smaller magnitude.
A new testing system for thermal shock resistance (TSR) was used to assess the response of different refractory products (high alumina, andalusite and fused silica bricks) to different thermal cycling conditions. Different temperature ranges (moderate or high temperatures), different magnitudes of thermal shocks and different thermal shock modalities (ascending/descending) were investigated. The resulting damaging was assessed using ultrasonic measurements. For the investigated refractory products, the damaging was found to be more severe for thermal cycling applied at high temperature (above 900 °C) than at moderate temperature (below 900°C) despite having the same magnitude (ΔT of at least 580 K). Additionally, the resistance to thermal shocks was found to be dependent of the applied testing conditions, and even reversed in different temperature ranges.
Practice-oriented investigations, promoting experimental thermal loading close to their service conditions, lead to more relevant claims about the TSR of refractory products and help achieving better predictions of the lifetime of refractory linings.

INTRODUCTION
Depending on the processes in which they are being used, refractory products encounter different thermal loading conditions. For instance, in refractory linings of tunnel kilns in the tableware industry temperatures rarely exceed 1350 °C and mild, steady heat flow conditions prevail, whereas in the steel industry, linings in process units must withstand severe temperature changes with temperatures exceeding 1700 °C. Consequently, the response of refractory products to these thermal loading conditions, and the corresponding thermal stresses, vary considerably. A specific material might exhibit satisfactory performance at moderate temperatures when experiencing substantial temperature differences, but the very same material could fail when exposed to higher temperatures, even with smaller temperature differences and comparable heat transfers. Conversely, another material might behave differently, performing better at higher temperatures than at a lower temperature range.
In this regard, assessing the thermal shock resistance of refractory products using the common standardized testing conditions may result in inaccurate conclusions regarding the selection of the most suitable refractory solution for a specific application. Hence, there is a definite requirement for a testing approach that adjusts to the varied thermal shock conditions encountered by refractory products during their service.

DETERMINATION OF THE THERMAL SHOCK RESISTANCE OF REFRACTORY PRODUCTS
By the very nature of their function, refractory products, which serve as linings in high-temperature vessels and furnaces, are exposed to more or less severe transient or steady-state thermal gradients. One side of a refractory lining faces high temperatures as it comes into direct contact with the process heat that needs to be contained within the system. The opposite side of the lining remains at much lower temperatures, so that heat losses are minimized and the immediate vicinity of the structure is being protected. However, the presence of such a thermal gradient within a massive solid body is not without consequences, as thermal stresses arise that pose a threat to the material's structural integrity.
While, depending on the application, thermally-induced damage (thermal spalling) may not always be the primary wear mechanism, refractory materials will almost inevitably suffer from the formation of cracks. However, modern well-designed refractory materials and linings exposed to thermal stresses typically do not experience catastrophic failure but instead undergo a gradual wear process, maintaining their structural stability despite significant damage. Even severely cracked refractory linings do not disintegrate into fragments. Yet, the presence of cracks is very likely to increase the susceptibility to other wear mechanisms (corrosion and erosion), and the determination of the resistance to thermal-induced damage is therefore of particular relevance for many refractory applications.
Unfortunately, when it comes to testing the thermal spalling resistance of refractory products, more commonly referred to as their thermal stress/shock resistance (TSR), there is no such thing as a "one-size-fits-all" method [1]. The performance of refractory products exposed to thermal stresses is not an intrinsic material property [2]. Instead, the thermal stress resistance of refractory products is influenced by various factors, most of them varying significantly with the application. In addition to the thermomechanical and thermal properties of the material (thermal expansion coefficient, thermal conductivity, modulus of elasticity, mechanical strength, and specific fracture energy), which are highly dependent on temperature, the geometry of the refractory components (including shape, presence of edges, and dimensions) and the specific thermal conditions (process temperature, heat transfer coefficient, thermal cycling or steady-state) play a significant role.
Typically, a set of narrowly specified testing conditions are applied to test refractory pieces of well-defined geometry to evaluate the TSR of refractory products. The most common standardised test methods are DIN 51068, EN 993-11 and ASTM-C-1171. All these standardised procedures describe quenching cycles between either 950 °C (DIN and EN) or 1200 °C (ASTM) and room temperature with water (DIN) or compressed air (EN and ASTM). Such test conditions are relatively straightforward to perform in the laboratory and efficient in inducing thermal stresses and damage to refractory materials, but they are not particularly consistent with actual service conditions of refractory products and can therefore lead to misleading conclusions. As a result, testing procedures that are more focused on the refractory's service conditions have been developed over the last decades. In particular, the melt immersion test, in which test pieces are at least partially immersed in a melt (e.g. pig iron, steel, aluminium), is particularly proficient to simulating the service conditions encountered in steel and metal manufacturing processes [3]. Open flame burners are sometimes used to reproduce the heating process in tunnel kilns, rotary kilns or glass melting furnaces as well as to mimic the pre-heating process of metallurgical vessels for the steel production, or simply as heat source to provide more efficient heat transfer into a test piece as compared to a cold test piece that is simply placed into a hot laboratory furnace [4-5]. More exotic testing procedures are occasionally reported, such as the use of a laboratory furnace with two chambers at different temperatures to perform hot temperature cycling [6-7], or the direct irradiation of test pieces by focusing artificial light or by an intensively radiating susceptor that is induc-

tively heated to incandescence, [8]. However, these procedures are time consuming and labour intensive. In order to advance the testing procedures, Forschungsgemeinschaft Feuerfest e. V. has developed a new, fully automated thermal shock testing system.

PRACTICE-ORIENTED THERMAL SHOCK TESTING SYSTEM

Description of the new thermal shock testing device

A crucial aspect of the new system is to enable thermal cycling at different ranges of temperatures for both ascending and descending thermal shocks. To achieve this, the testing system uses three chambers, through which a test piece (50 x 50 mm cylinder) is conveyed (Fig. 1). The middle chamber serves as a standby furnace with the ability to heat or cool the test piece to a predetermined temperature (Fig. 1 (b)). Ascending thermal shocks are achieved in the upper chamber by transporting the test piece into a carbon ring which is inductively heated to incandescence (chamber 2). The intensive radiation emitted by the carbon ring (susceptor) is particularly efficient to raise the surface temperature of the test piece inside the carbon ring quickly up to 1800 °C (Fig. 1 (a)). Descending thermal shock takes place in the lower chamber by gas quenching (Fig. 1 (c)). A lifting device carrying a tube made of alumina assures the transport of the test piece through the three chambers that are stacked on top of each other. The system is continuously flushed with inert gas to protect the carbon ring in the chamber 2.

Assessment of the thermally induced damage

During the thermal cycling, stresses of sufficient magnitude to damage the test piece are generated. The impact of the thermal shocks is assessed quantitatively by measuring the decrease of the ultrasonic velocity inside the test piece, which reflects the deterioration of the mechanical properties of the test piece after having undergone a specified number of thermal cycling. Finally, for a better insight, the thermal damage is quantified using the dimensionless damage parameter according to Kachanov [9]:

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

where v is the ultrasonic velocity as it propagates through the test piece after thermal cycling and v_0 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 damage.

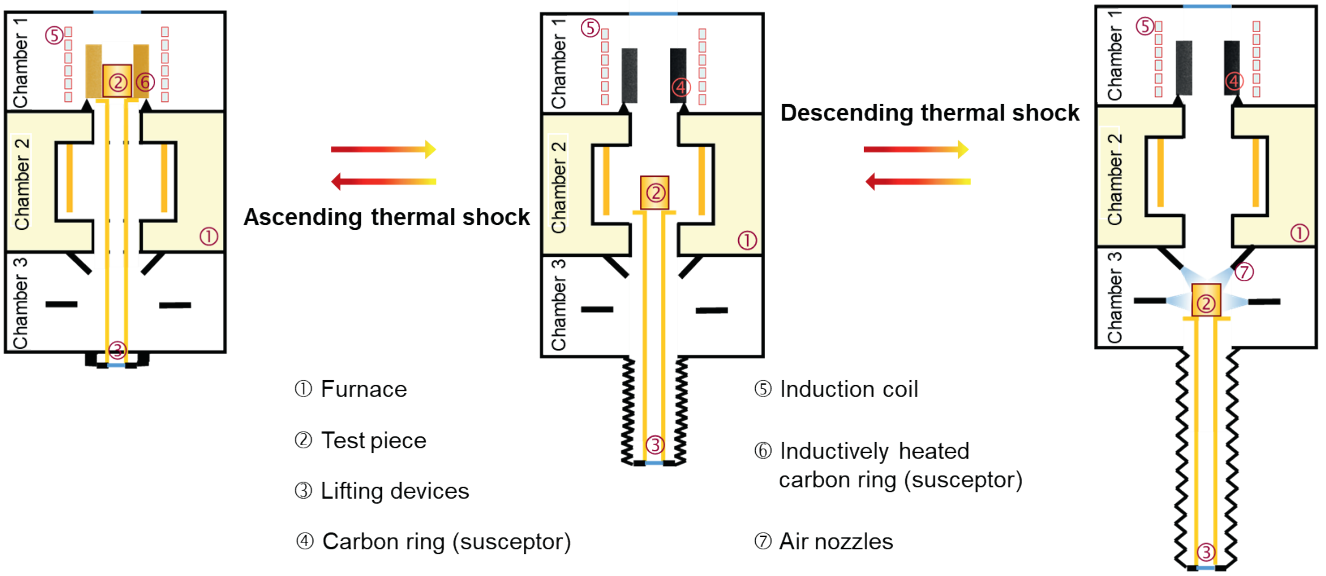

Fig. 1: Schematic representation of the new thermal shock testing system and the testing procedure. Preheating and tempering in the chamber 1 ***(b, middle)****, ascending thermal shock through driving the test piece into an inductively heated carbon ring in the chamber 2* ***(a, left)*** *or descending thermal shock by gas quenching in the chamber 3* ***(c, right)****.*

TESTING STRATEGY

Materials under investigation

Three refractory materials were investigated:

High-Alumina bricks with a content of Al_2O_3 above 99 % and ceramic bonded. Especially resistant to atmospheres containing CO and hydrogen up to very high temperature, they are typically used in the petrochemical and chemical industry (e.g. soot reactor).

Fused Silica bricks with a content of amorphous SiO_2 above 99 %. Because of their great resistance to acid environments, they are used in the chemical industry, as well as in the glass industry and as a hot repair material (for glass melters and coke oven plants).

Andalusite bricks with an Al_2O_3 content of 60 % and ceramic bonded. A versatile product presenting good resistance to creep, slag corrosion as well as to thermal shocks, and accordingly is a fitting solution for many applications in furnace engineering, iron and steel industry, waste incineration and glass melting furnace.

Thermal shock procedure

Either 5 or 10 ascending or descending thermal shock cycles were applied to test pieces as described above. A dwell time of 30 minutes in the middle chamber (chamber 2) was implemented to ensure the temperature homogeneity of the test pieces. Since thermal stresses tend to quickly reach a maximum during thermal shocking, which roughly corresponds to the maximal temperature difference in the test piece i.e. before its core starts to heat up and the thermal gradient inside of the test pieces gradually flattens out, there is no need to reach temperature homogeneity after applying the thermal shocks. Accordingly, a shorter dwell time (15 minutes) was used in the upper and lower chambers (chambers 1 and 3).

To quantify the resulting damage, the ultrasonic velocity inside the test pieces was measured at room temperature by pulse technique of ultrasonic (C.S.I. Concrete Tester, Type RBT 2-A) before and after the thermal cycling.

RESULTS AND DISCUSSION

On the whole and as expected, the damage increases with increasing temperature difference applied to the surface of the test pieces, i.e. increasing thermomechanical load. While small temperature differences (e.g. 380 K) cause little or no damage, large temperature differences (e.g. 880 K) almost systematically cause significant damage.

Tab. 1: Results from the TSR investigations with the new testing system on the test pieces made from high-alumina bricks.

Test	Temperature / °C Lower chamber	 Middle chamber	 Upper chamber	ΔT / K	Number of thermal shock cycles	D / -
1	RT (~20 °C)	900	-	880	10	0,24
2	RT	800	-	780	10	0,21
3	RT	600	-	580	10	0,04
4	RT	400	-	380	10	0,00
I		RT	900	880	5	0,00
II		RT	800	780	5	0,00
III		RT	600	580	5	0,00
A	-	900	1280	380	5	0,09
B	-	900	1480	580	5	0,27
C	-	900	1680	780	5	0,33
C*	-	900	1680	780	5	0,30
A'	-	900	1280	380	10	0,13
B'	-	900	1480	580	10	0,34
C'	-	900	1680	780	10	0,44

**Duplicate to check the repeatability*

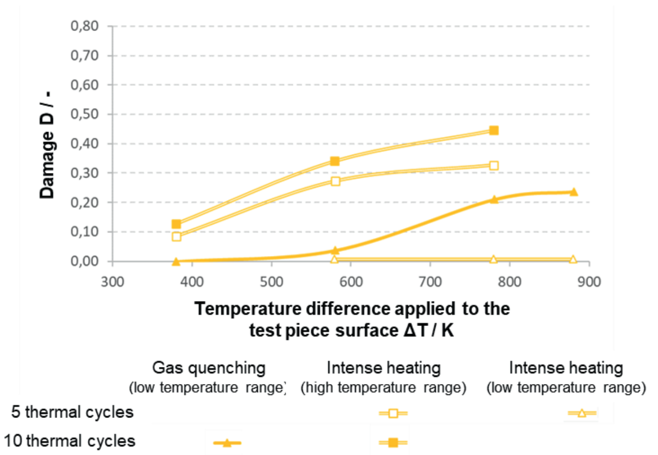

Fig. 2: Evolution of the damage for test pieces made from high-alumina bricks in function of the temperature difference applied to the surfaces of the test pieces for different testing conditions (low temperature range = below 900 °C, high temperature range = above 900 °C).

In the case of high-alumina bricks (Tab. 1 and Fig. 2), in the low temperature range (< 900 °C), gas quenching (descending thermal shocks) is more efficient to induce damage in the test pieces than intense heating with radiation (ascending thermal shocks). Quite surprisingly, no damage could even be detected as a result of ascending thermal shocks with intense radiation below 900 °C. Descending thermal shocks (quenching) on homogeneously heated test pieces promote more intense tensile stresses, to which refractory materials are notoriously more susceptible, while ascending thermal shocks promote initially more intense compressive stresses. Additionally, the applied gas quenching may lead to a more effective heat transfer than applying intense radiation.
However, in contrast, even a small applied temperature difference (380 K) resulted in significant damage during thermal cycling above 900 °C by means of intensive radiation. As expected, the extent of the damage increased with increasing applied temperature difference at the surface of the test pieces and with increasing the number of thermal cycles. Finally, significantly higher levels of damages due to thermal cycling were observed in the high temperature range than in the low temperature range, indicating a higher thermal shock sensitivity of the high-alumina bricks at high temperatures.

Tab. 2: Results from the TSR investigations with the new testing system on the test pieces made from andalusite bricks.

Test	Temperature / °C Lower chamber	 Middle chamber	 Upper chamber	ΔT / K	D / -
1	RT (20 °C)	900	-	880	0,13
2	RT	800	-	780	0,02
3	RT	600	-	580	0,03
4	RT	400	-	380	0,01
A	-	900	1280	380	0,18
B)	-	900	1480	580	0,53

Number of thermal shock cycles: 5

Tab. 3: Results from the TSR investigations with the new testing system on the test pieces made from fused silica bricks.

Test	Temperature / °C Lower chamber	 Middle chamber	 Upper chamber	ΔT / K	D / -
1	RT (20 °C)	900	-	880	0,00
2	RT	800	-	780	0,01
3	RT	600	-	580	0,00
4	RT	400	-	380	0,00
A	-	900	1280	380	0,05
B)	-	900	1480	580	0,76

Number of thermal shock cycles: 5

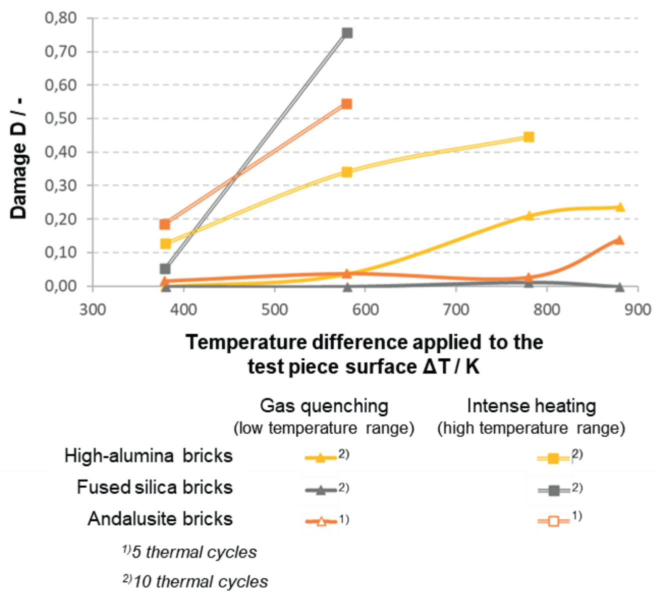

Fig. 3: Evolution of the damage for test pieces made from high-alumina bricks, fused silica bricks and andalusite bricks in function of the applied temperature difference to the surface of the test pieces for different testing conditions (low temperature range = below 900 °C, high temperature range = above 900 °C).

When comparing the three refractory materials, significant damage occurs as a result of gas quenching (i.e. low temperature range) for temperature differences applied to the test piece surface (ΔT) of 780 K and 880 K in the test pieces made from high-alumina bricks and andalusite bricks respectively. Test pieces made from fused silica bricks remained virtually undamaged by every gas quenching performed. Fused silica bricks are indeed well-known for their excellent thermal shock resistance up to approx. 1000 °C.
For ascending thermal shocks in the high temperature range (intense radiation heating), the previous classification is reversed, i.e. test pieces from fused silica bricks were already severely damaged

for a ΔT of 580 K (inhomogeneous transformation of quartz glass to cristobalite), andalusite bricks displayed slightly less damage and high-alumina suffered the least damage under these test conditions. Besides, these test conditions result in higher damage for all investigated materials compared to gas quenching in the low temperature range. This illustrates the great importance of TSR investigations that reflect the service conditions as much as possible to ensure a fair and application-oriented classification of the performance of refractory materials.

Visual inspection of the cut test pieces makes the extent of the damage even clearer. However, macrocracks could only be unequivocally detected in specimens whose dimensionless damage parameter D exceeded approximately 0,3 (Fig. 4). Furthermore, in materials such as andalusite bricks, which displays a network of cracks from the beginning (i.e. as a part of their microstructure), the increase and growth of the cracks is very difficult to assess visually. While helpful to gain an initial impression of the state of the test piece after thermomechanical loading, optical assessment does not allow an objective and quantitative assessment of the damage. However, the combination of optical inspection with ultrasonic measurements and calculation of the dimensionless damage parameter is particularly suitable for quantifying specific features and patterns resulting from thermomechanical loading.

CONCLUSIONS

In service and depending of their application, refractory products are subjected to thermal stresses and shocks of different magnitudes, and in different ranges of temperatures. Their suitability to sustain thermal stresses for a specific application is usually assessed using standardized testing conditions regardless of their actual service conditions, thus increasing the likelihood of coming to erroneous conclusions, or at least, to a suboptimal solution. On the contrary, thermal shock experiments tailored to the service conditions applied to refractory products are needed to obtain relevant information about the performance of refractories in their intended applications.

Thanks to a three chambers testing system, descending (gas quenching) as well as ascending (fast irradiation heating) thermal shocks of different intensity can be applied automatically and repeatedly to refractory test pieces previously heated to a defined temperature. Hence the temperature changes triggered at the surface of a test piece are controlled and a tailored automatic investigation of refractory product's resistance to thermal shocks in the application relevant temperature range is being achieved.

For the investigated products (high alumina, andalusite and fused silica bricks), the damaging was found to be more severe for thermal cycling applied at high temperature (above 900 °C) than at moderate temperature (below 900 °C) despite having the same magnitude (ΔT of at least 580 K). Additionally, while test pieces made of fused silica bricks outperformed the two other materials during descending thermal shocks in the lower temperature range, the classification obtained was completely reversed for ascending thermal shocks at high temperature.

As a result, the suitability of a given refractory product and/or the selection of refractory products for a given application can be assessed with enhanced reliability and a better prediction of the lifetime of refractory linings is expected.

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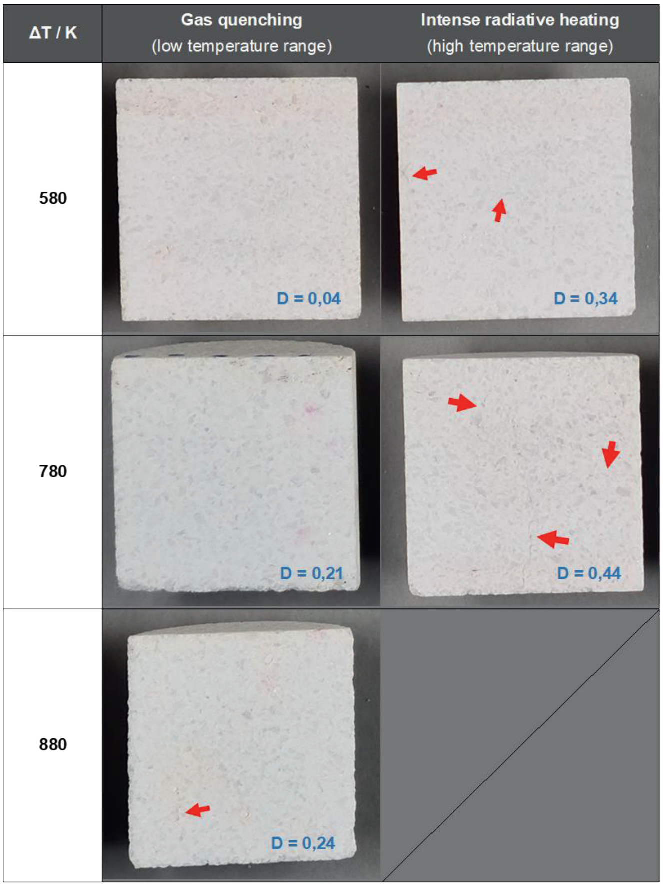

Fig. 4: Cross-sections of test pieces made from high-alumina bricks for different combinations of testing conditions after 10 thermal cycles (visible cracks are marked with arrows).

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