Fracture Process Zone in Refractory Castables after High-Temperature Thermal Shock

J. Schnieder, N. Traon, S. Etzold, T. Tonnesen, R. Telle, A. Tengstrand, A. Malmgren, E. Nylund

Thermal shock damage is an important issue for the refractories industry. To understand the microstructural behaviour and with it the thermoelastic properties during thermal shock treatment are key topics for high performance refractory materials and their development. Most ceramic materials exhibit a critical temperature difference ($\Delta T_c$) as a minimum temperature required for fracture initiation. Refractories exhibit within their heterogeneous structure already pores, aggregates of different size and cracks. To understand the influence of the temperature difference ($\Delta T$) and the temperature level, a new high temperature thermal shock furnace was designed and constructed. Unlike standard thermal shock tests with compressed air or water, the new furnace's two separately heatable and interconnected chambers enable the transfer of samples between two high temperatures without exposing them to the surrounding atmosphere at room temperature. To understand the effect of rapid temperature changes, the natural aggregate andalusite and the synthetic aggregates $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$-$\text{SiO}_2$ and $\text{Al}_2\text{O}_3$-$\text{ZrO}_2$ are incorporated in a model low cement castable formulation based on tabular alumina. The influence of these aggregates on the elastic and thermomechanical properties is examined and correlated to the microstructure.

1 Introduction

The degradation of the thermo-mechanical properties of commercial refractories resulting from thermal shock is an important mater for the refractories industry. Therefore, it is very important to understand, predict and validate the mechanisms involved in high temperature processes [1]. Refractories technology is still under constant development but the fundamentals and factors influencing thermal shock resistance in refractories are well-known, e.g. elasticity, strength and size of aggregates, debonded grains or thermal mismatch [2]. Hasselman presented a theory for crack propagation in dense ceramics subjected to thermal shock and furthermore defined new thermal shock parameters as well as a critical $\Delta T_c$ as a minimum temperature required for fracture initiation [3]. However, this temperature difference is very low in most cases and hardly avoidable in practical applications, especially when refractories already exhibit cracks after sintering.
2 Experimental procedure

A standard Low Cement Castable (LCC) formulation was defined as reference material. The castable was composed of 82,5 mass-% tabular alumina aggregates, 12,5 mass-% fine reactive alumina and 5 mass-% calcium aluminate cement (Tab. 1). The granular fraction 2,24–3,0 mm of tabular alumina from the reference formulation was separated by sieving, approximately ca. 11 mass-% of the mixture, and replaced by the same amount of eutectic aggregates Al₂O₃–ZrO₂–SiO₂ (AZS) and Al₂O₃–ZrO₂ (AZ) or andalusite (A). Respecting the following geometry, 125 mm × 25 mm × 25 mm or 160 mm × 40 mm × 40 mm prismatic bars were cast. Each composition was cast after mixing, subsequently cured in a humid environment for 48 h at room temperature and dried at 110 °C for 24 h. The samples were sintered for 6 h at 1500 °C with a heating and cooling rate of 2 K/min. The elastic properties were determined by using a Resonant Frequency Damping Analyzer (RFDA) according to ASTM C 1548-02 (2012). The Modulus of Rupture (MOR) was measured after heat treatment and after 1 – 10 thermal shock cycles according to DIN EN 993-6. The thermal shock tests were performed according to DIN EN 993-11 in water with different ∆T. Those results were compared with those obtained after high temperature thermal shock with the help of the equipment illustrated below in Fig. 2, not in accordance to standards standard.

2,24–3 mm ca. 12

Total 100 100

Water H₂O 5 5

Deflocculant FS 40 0,1 0,1

Retarder Citric acid 0,03 0,03

Fig. 2 New high temperature thermal shock furnace

In the last years, the focus switched from the examination of the damaging mechanisms occurring at the crack tip to the following wake region. Mechanisms at the crack tip like crack branching and crack deflection are already well-known [4]. The effects in the process wake depend on different mechanisms (Fig. 1). They were defined as crack bridging and bridging of liquid phases at higher temperatures as well as friction between aggregate and matrix. These effects mainly depend on the shape, size and micro-structure of the aggregates [4–6]. Functional aggregates with eutectic composition (Al₂O₃–ZrO₂–SiO₂ and Al₂O₃–ZrO₂) were employed to investigate the effects of their specific inner structure [7, 8]. The substitution of alumina aggregates by eutectic aggregates resulted in changed thermo-elastic properties and crack networks with transgranular and intergranular cracks. Additionally, effects like pull-out as well as bridging mechanisms could be observed. The zirconia phase transformation (tetragonal – monoclinic) [9] and the thermal expansion coefficient mismatch between the aggregates and the matrix caused microcracking. Cracks generated by thermal shock load interacted with these micro-cracks [10–12].

An aggregate with similar effects on the microstructure is andalusite. This material is already noted for its resistance to thermal shock damage. Debonding and microcrack generation were observed in a model system containing glass. The anisotropic behaviour of andalusite and the occurring mullite transformation during heat treatment are causing the shown effects [13, 14].
without contact to the surrounding atmosphere at room temperature. The temperature difference and level of the thermal shock is adjustable. The samples were shocked between 1000 – 400 °C and 1400 – 800 °C with a dwell time of 45 min in each chamber for temperature adjustment. 1 – 10 thermal shock cycles were performed.

### 3 Results and discussion

High-temperature thermal shock is a new method to determine thermal shock damage under conditions closer to industrial praxis. In this survey the elastic and mechanical properties after high-temperature thermal shock tests are considered and compared to previous studies with thermal shocks according to standard and with different ΔTs. The authors [15–16] showed the effect of functional aggregates reducing the Modulus of Rupture (MOR) and the Young's modulus after sintering caused by microstructural effects (Tab. 2). Andalusite decreases the stiffness of the material when added to a castable formulation induced by thermal expansion mismatch and its transformation into mullite at elevated temperatures [13, 14]. The ZrO₂ phase of the Al₂O₃–ZrO₂ and Al₂O₃–ZrO₂–SiO₂ aggregates with a characteristic volume change [9] leads to the formation of a microcrack network. Thermal shock testing methods according to DIN EN 993-11 (Fig. 3) showed the same evolution for all materials. The first three thermal shocks had the strongest impact on the stiffness and strength. Ref exhibited a comparatively very high retained Young’s modulus but loss of strength exceeded the values observed with addition of andalusite, AZ and AZS.

Performing quenching tests in water on the studied formulations showed a difference in the severity of the damage. For this thermal shock, two groups of materials could be distinguished: Ref and AZS characterized by a drastic depletion of the toughness up to the third TS cycle. As for A and AZ, those materials with low initial strength values showed in direct comparison only a slight decrease in strength values. Debonding (Fig. 4) and severe microcracking (Fig. 5) were observed [15].

In the 1960ies, Hasselman [3] introduced the catastrophic decrease of strength for dense ceramics after thermal shock tests within a certain temperature difference ΔT. For refractories with functional aggregates, the
authors showed (Fig. 6) specific $\Delta T$s with no effect and with a decreasing strength loss rate. Effects in the wake region of the crack like liquid phase bridging (Fig. 7) or crack bridging (Fig. 8) could be observed. According to those results, the $\Delta T = 600$ K was selected. The slowing loss rate of mechanical strength stopped around this temperature difference and this $\Delta T$ is quite suitable to adjust. Two different temperature levels were chosen, namely $1000 - 400 \, ^{\circ}$C, and $1400 - 800 \, ^{\circ}$C because of the transformation temperature of unstabilized ZrO$_2$ [9] and for the higher temperature to favour the formation of liquid phase bridges.

The Ref samples (Fig. 9) exhibit almost no cracks after sintering. With increasing number of thermal shock cycles the crack length increased.

The crack path was intergranular and partial crack deflection was observed at tabular alumina grains. Between the different temperature levels the microstructure showed almost no distinction. In comparison to Ref, andalusite samples (Fig. 10) showed se-

![Fig. 6 Strength evolution after thermal shock with different $\Delta T$s [17]](image)

![Fig. 7 A sample with liquid phase bridges [17]](image)

![Fig. 8 AZ sample with crack bridging](image)

![Fig. 9 Ref sample after zero and 10 thermal shocks](image)

![Fig. 10 Andalusite samples after zero and 10 thermal shocks](image)
grains during sintering and the following volume expansion due to mullitisation were responsible for this damage [13, 14]. With increasing number of thermal shocks, the crack network extended especially intergranular but also transgranular with crack deflection (Fig. 11) inside of andalusite grains. After 10 thermal shock cycles between 1000 °C–400 °C the andalusite (A) microstructure showed more cracks than the samples between 1400 °C–800 °C. The evolution of Young’s modulus is confirming length increased. The cracks continued to be mainly intergranular. After 10 TS cycles partially damage of the AZ aggregates could be observed. AZ (1400–800 °C) exhibited distinct long cracks through the samples (>10 mm) but less density of microcracks. The crack path (Fig. 14) inside the aggregate is mainly along the weakened precipitated ZrO2/Al2O3 phase. Inside the pure Al2O3 phase, crack bridging could be observed. In contrast to the Ref samples AZ samples exhibited a high level of retained strength after thermal shocks between 1400 °C and

this statement. The higher level of temperature difference exhibited a lower loss. In contrast to this, the bending strength evolution showed no difference between both temperature levels. The andalusite material showed the same strength after the thermal shock cycles. Ref (1400 – 800 °C) exhibit a high loss in strength with ca. 70 % after 10 thermal shocks. AZ samples (Fig. 13) showed cracks and a partially debonding after the sintering. The cracks were short (200 – 600 µm) and intergranular. With increasing thermal shock cycles the number of cracks and the crack density increased. The cracks continued to be mainly intergranular. After 10 TS cycles partially damage of the AZ aggregates could be observed. AZ (1400–800 °C) exhibited distinct long cracks through the samples (>10 mm) but less density of microcracks. The crack path (Fig. 14) inside the aggregate is mainly along the weakened precipitated ZrO2/Al2O3 phase. Inside the pure Al2O3 phase, crack bridging could be observed. In contrast to the Ref samples AZ samples exhibited a high level of retained strength after thermal shocks between 1400 °C and

Fig. 11 Crack deflection in andalusite samples

Fig. 12 Young’s modulus and retained MOR after 1 and 10 thermal shocks

Fig. 13 AZ samples after zero and 10 thermal shocks

Fig. 14 Crack path in AZ aggregate mainly in ZrO2-rich phase

evere damage at the level of the mullitized andalusite grains and the matrix. The thermal expansion mismatch of the andalusite
both temperature levels exhibited enlarged cracks in length (several millimetres) and width (up to 15 µm). The cracks partially stopped in AZS grains and pores.

After thermal shock treatment AZS material showed relatively high strength values (Fig. 18). The porous aggregates and the microporous matrix could function as crack stopper reducing the stresses. Both mechanisms are active at the crack tip. The thermal shock between 1400 – 800 °C was more severe than the thermal shock between 1000 – 400 °C. The samples for both thermal shock types showed after 10 thermal shock cycles a stabilization decreasing strength.

4 Conclusions

The tests in the new high temperature thermal shock furnace showed the importance of realistic thermal shock conditions. Not only was the temperature difference important but also the temperature level. With the application of functional aggregates, the influence of these thermal shock conditions on the elastic and thermome-

---

**Fig. 15** Young’s modulus and retained modulus of rupture after 1 and 10 thermal shocks respectively.

**Fig. 16** AZS samples after zero and 10 thermal shocks.

**Fig. 17** AZS microstructure after 10 thermal shock cycles.

**Fig. 18** Young’s modulus and retained MOR after 0, 1 and 10 thermal shocks respectively, for Ref and AZS after high-temperature thermal shock.
mechanical properties was examined under different thermal shock conditions, correlated to the microstructure and compared to testing methods according to DIN EN 993-11. Eutectic and andalusite aggregates with a grain size of 2.24 – 3.00 mm had a strong impact on the initial elastic and thermomechanical properties of the low cement castables [15–17]. Responsible for this, were thermal expansion coefficient mismatches [18], ZrO₂ transformation and the resulting generation of microcracks. The addition of smaller aggregates e.g. 0.2–0.6 mm exhibited a decreased crack density and higher strength values [19]. Inducing thermal shock by quenching ac-
density and higher strength values [19].0,2–0,6 mm exhibited a decreased crack
The addition of smaller aggregates e.g.
the resulting generation of microcracks. The crack density [20] is also an important
the examined samples, the energy consum-
ction for predicting the thermal shock damage
of fracture surface in tabular alumina based
castables with addition of specific aggregates.
[16] Schnieders, J.; et al.: Influence of eutectic ag-
gregates in castables on the thermal shock re-
sistance. Proc. Int. Coll. on Refractories 2013, Aachen
shock temperature difference on the micro-
structural damage and the crack propagation
in modified high alumina refractory castables. Proc. Unified Int. Technical Conf. on Refrac-
tories 2015, Vienna, September 15–18
ZrO₂–SiO₂, and Al₂O₃–ZrO₂ addition on elastic and mechanical properties of high alumina
[19] Schnieders, J.; et al.: Microstructural damage of
modified high alumina castables after several
thermal shock cycles under specific experimen-
tal conditions. Proc. S7. Int. Coll. on Refrac-
tories Aachen, September 2014
ension of Hasselmans thermal shock theory for crack/microstructure interaction in refrac-
tories. Ceramic Int. 38 (2012) 5369–5375

References
tories Handbook, Ed. C.A. Schacht, Chapter 2, 11–38
[6] Harmuth, H.; Bradt R. C.: Investigation of re-
fractory brittleness by fracture mechanical and fractographic methods. Refractories Manual
2010, 6–10
[9] Garvie, R. C.: Zirconium dioxide and some of
its binary systems, in: High-Temperature Ox-
[10] Pandolfelli, V. C.; et al.: Influence of multilite-
zirconia aggregate addition on the thermomechanical properties of high-alumina
refractories. Unitecr ’93 Congress, São Paulo, 1993
 mechanical properties of alumina refractories containing a fused multilite-zirconia aggregate. Unitecr ’95, Kyoto, Japan, 2, 1995
[16] Schnieders, J.; et al.: Influence of eutectic ag-
gregates in castables on the thermal shock re-
sistance. Proc. Int. Coll. on Refractories 2013, Aachen
shock temperature difference on the micro-
structural damage and the crack propagation
in modified high alumina refractory castables. Proc. Unified Int. Technical Conf. on Refrac-
tories 2015, Vienna, September 15–18
ZrO₂–SiO₂, and Al₂O₃–ZrO₂ addition on elastic and mechanical properties of high alumina
[19] Schnieders, J.; et al.: Microstructural damage of
modified high alumina castables after several
thermal shock cycles under specific experimen-
tal conditions. Proc. S7. Int. Coll. on Refrac-
tories Aachen, September 2014
ension of Hasselmans thermal shock theory for crack/microstructure interaction in refrac-
tories. Ceramic Int. 38 (2012) 5369–5375

Acknowledgements
The authors would like to express their thanks to the German Research Founda-
tion. This project is supported in the frame-
work of the Priority Program 1418 Micro-
structural Processes in the Wake Region of
the Crack in Castables Containing Eutectic
Aggregates at High-Temperature Thermal
Shock. The authors are also grateful to Al-
teo, Kerneos, DAMREC, REFEL and BASF for
supporting this work with raw materials.

The authors would like to express their
thanks to the German Research Founda-
tion. This project is supported in the frame-
work of the Priority Program 1418 Micro-
structural Processes in the Wake Region of
the Crack in Castables Containing Eutectic
Aggregates at High-Temperature Thermal
Shock. The authors are also grateful to Al-
teo, Kerneos, DAMREC, REFEL and BASF for
supporting this work with raw materials.