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 (ΔT_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 (ΔT) 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 Al_2O_3–ZrO_2–SiO_2 and Al_2O_3–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 matter 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 ΔT_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.

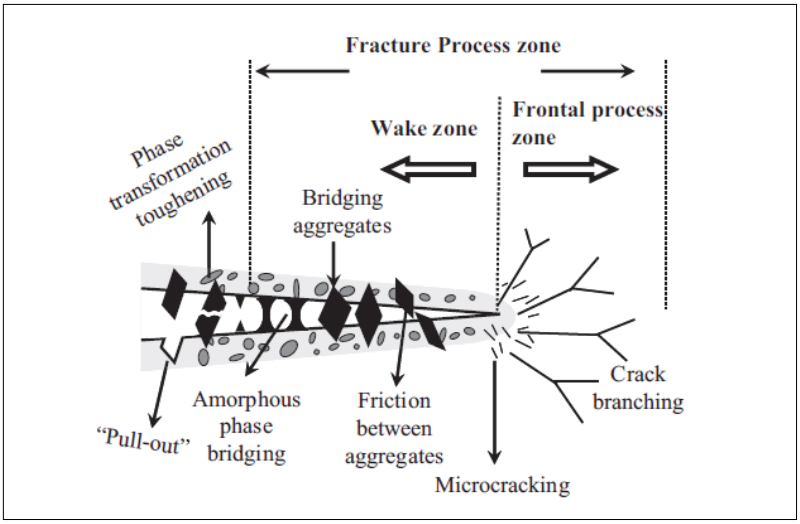

Fig. 1 Crack process zones [7]

J. Schnieder, N. Traon, S. Etzold, T. Tonnesen, R. Telle
RWTH Aachen University
Institute of Mineral Engineering
52070 Aachen
Germany

A. Tengstrand, A. Malmgren, E. Nylund
KTH Royal Institute of Technology
10044 Stockholm
Sweden

Corresponding author: *J. Schnieder*
E-mail: schnieder@ghi.rwth-aachen.de

Keywords: Refractories, high temperature thermal shock, eutectic aggregates, liquid phase bridging

Received: 01.12.2015
Accepted: 11.01.2016

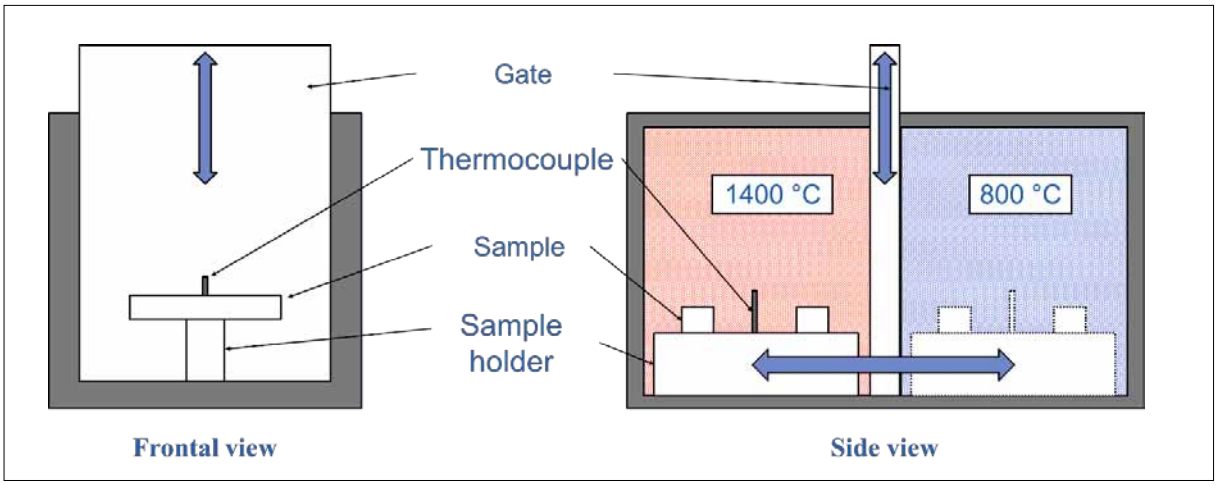

Fig. 2 New high temperature thermal shock furnace

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 microstructure of the aggregates [4–6].

Functional aggregates with eutectic composition (Al_2O_3–ZrO_2–SiO_2 and Al_2O_3–ZrO_2) 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 microcracks [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].

Tab. 1 Formulation of the castables

		Reference [mass-%]	Replaced Aggregates [mass-%]
CA cement	CA Secar 71	5	5
Reactive alumina	PFR	12,5	12,5
Tabular alumina	0–0,045 mm	10	10
	0–0,3 mm	10	10
	0,2–0,6 mm	10	10
	0,5–1 mm	17,5	17,5
	1–3 mm	35	23
Eutectic aggregates	2,24–3 mm		ca. 12
	Total	**100**	**100**
Water	H_2O	5	5
Deflocculant	FS 40	0,1	0,1
Retarder	Citric acid	0,03	0,03

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 Al_2O_3–ZrO_2–SiO_2 (AZS) and Al_2O_3–ZrO_2 (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 ΔT. 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.

The new high temperature thermal shock test is constituted of two separately heatable chambers connected through a gate (Fig. 2). The samples can be transferred within 2 s from one chamber to another

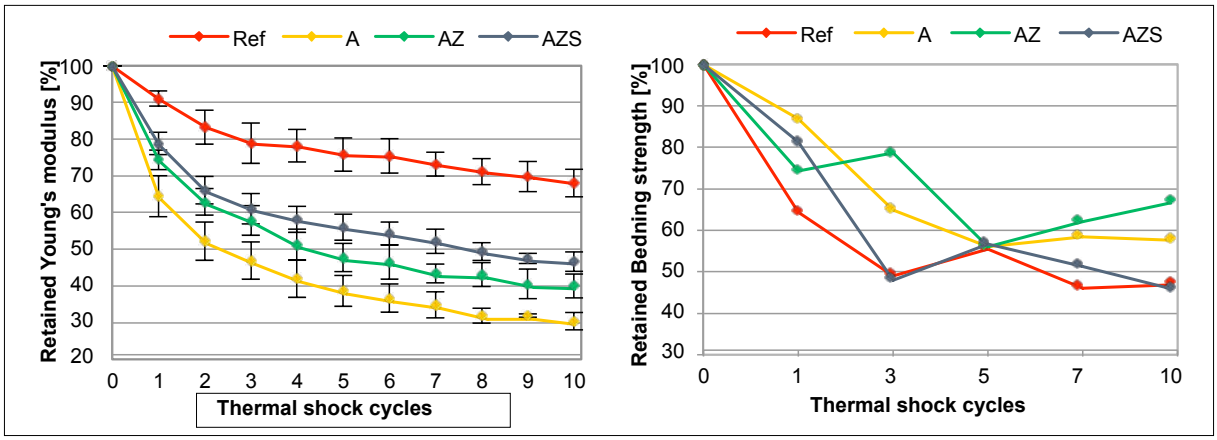

Fig. 3 Thermal shock at air according to DIN EN 993-11 [15, 16]

Tab. 2 Properties of studied compositions after sintering [16]

	Ref	A	AZ	AZS
Open porosity [%]	22,5 ± 1,1	21,5 ± 0,7	23,2 ± 0,7	21,1 ± 0,6
Young's modulus [GPa]	134,4 ± 4,0	41,5 ± 0,4	94,7 ± 3,0	145,5 ± 6,0
Modulus of rupture [MPa]	35,2 ± 0,8	9,8 ± 2,0	19,6 ± 0,8	36,1 ± 7,2

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 ZrO_2 phase of the Al_2O_3–ZrO_2–SiO_2 and Al_2O_3–ZrO_2 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_c. For refractories with functional aggregates, the

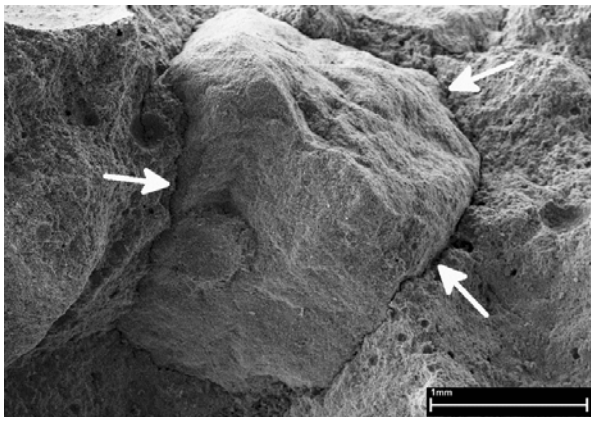

Fig. 4 Fracture surface AZ material after bending test [15]

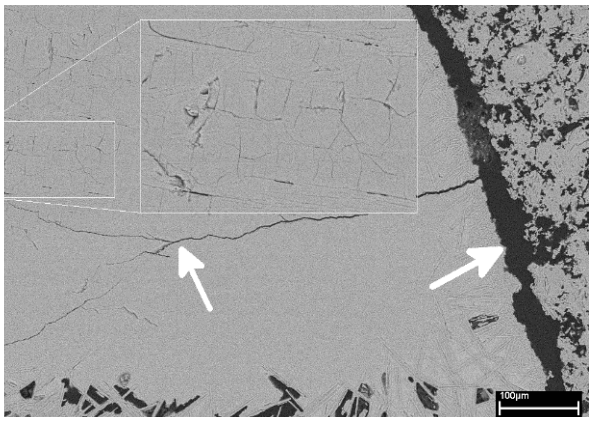

Fig. 5 Microcracking in andalusite sample after 10 thermal shocks [15]

authors showed (Fig. 6) specific ΔTs 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 ΔT = 600 K was selected. The slowing loss rate of mechanical strength stopped around this temperature difference and this ΔT is quite suitable to adjust. Two different temperature levels were chosen, namely 1000 – 400 °C, and 1400 – 800 °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.

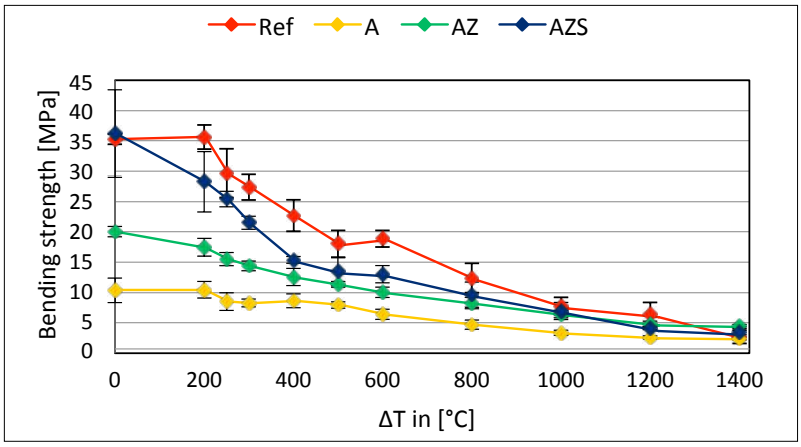

Fig. 6 Strength evolution after thermal shock with different ΔTs [17]

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-

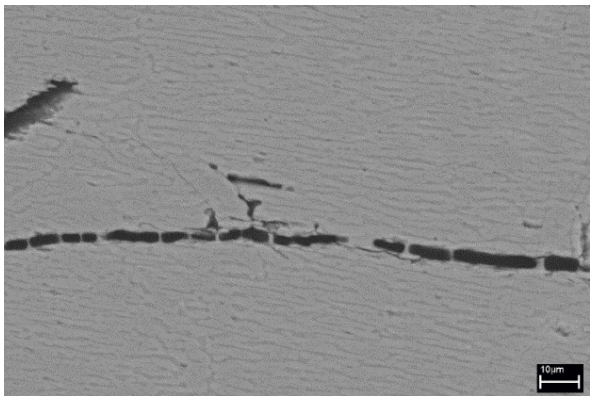

Fig. 7 A sample with liquid phase bridges [17]

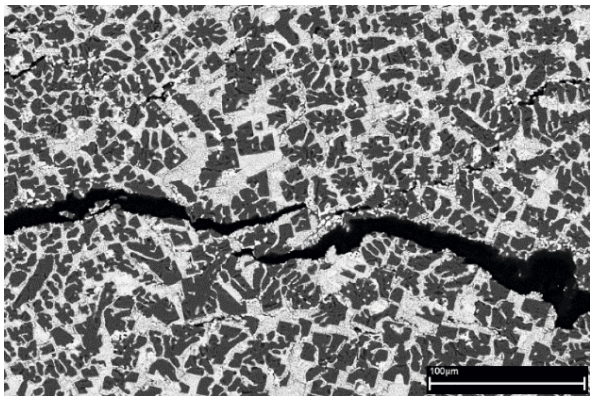

Fig. 8 AZ sample with crack bridging

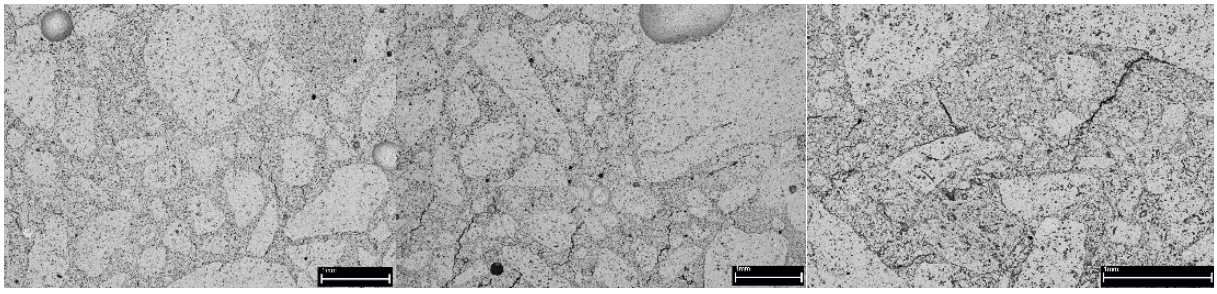

Fig. 9 Ref sample after zero and 10 thermal shocks

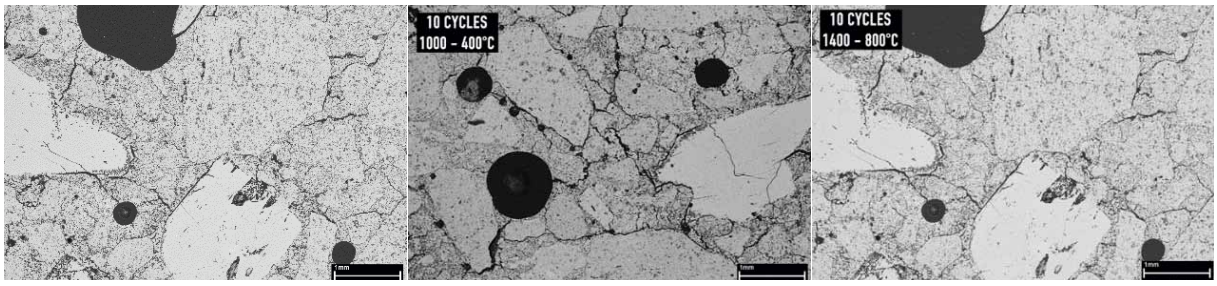

Fig. 10 Andalusite samples after zero and 10 thermal shocks

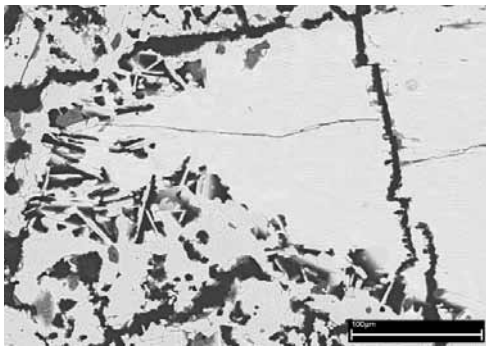

Fig. 11 Crack deflection in andalusite samples

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 ZrO_2/Al_2O_3 phase. Inside the pure Al_2O_3 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

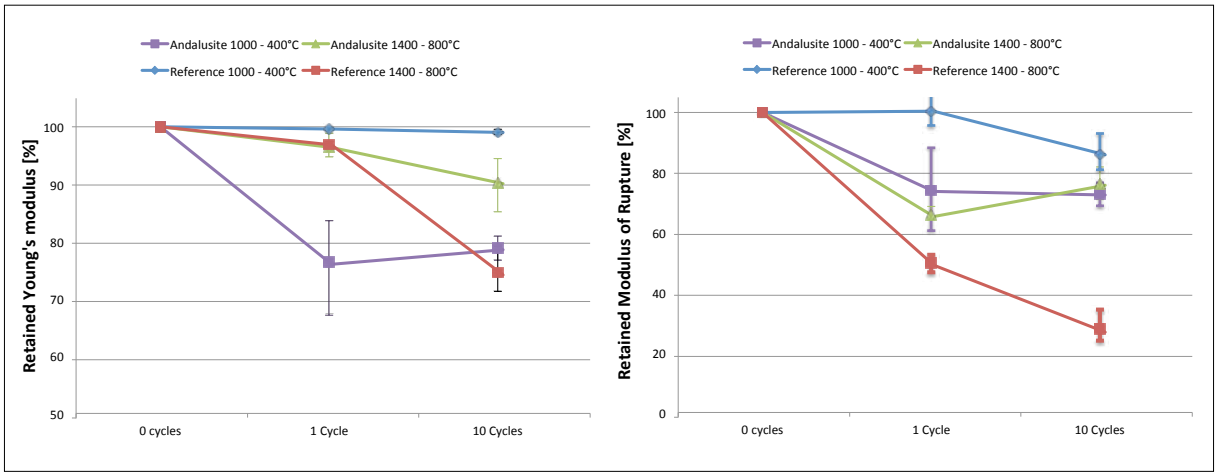

Fig. 12 Young's modulus and retained MOR after 1 and 10 thermal shocks

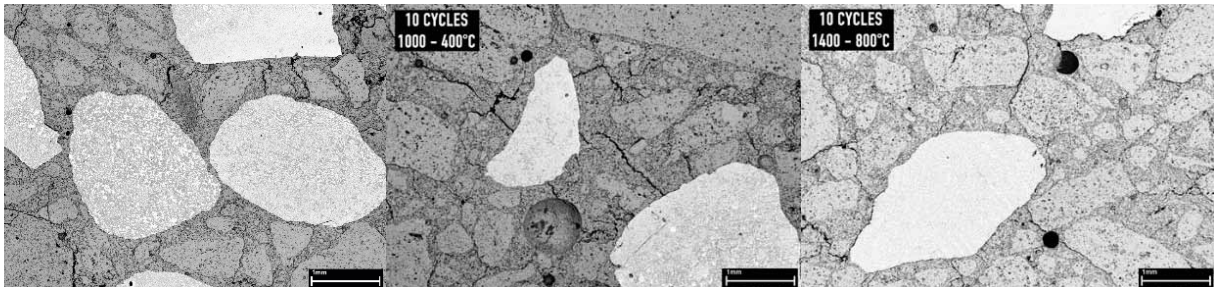

Fig. 13 AZ samples after zero and 10 thermal shocks

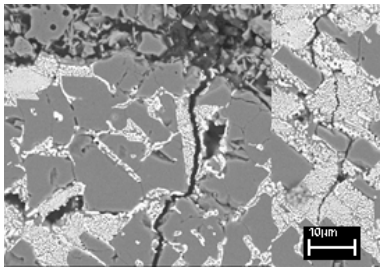

Fig. 14 Crack path in AZ aggregate mainly in ZrO_2-rich phase

vere damage at the level of the mullitized andalusite grains and the matrix. The thermal expansion mismatch of the andalusite

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

800 °C (Fig. 15). After the lower level thermal shock, Ref and AZ showed the same strength evolution. This did not correspond to the higher crack density in the AZ samples.

The AZS samples (Fig. 16–17) showed porous AZS grains. The amorphous silica diffused into the matrix leaving the porous grain and partially changed matrix composition around the aggregates. The expected CA6 formation could not be observed. A microporous structure with tabular alumina, pores and local silica-rich phases was found. After 10 thermal shock cycles

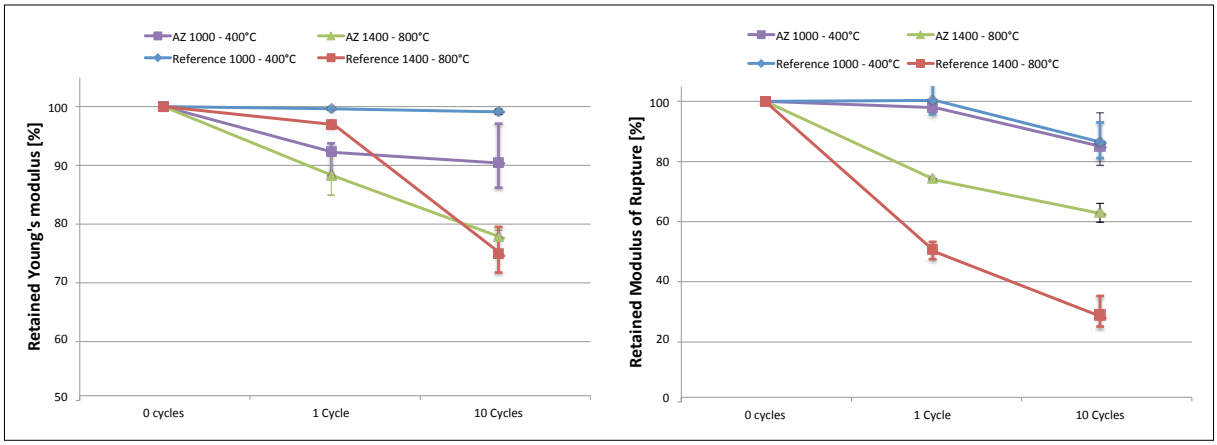

Fig. 15 Young's modulus and retained modulus of rupture after 1 and 10 thermal shocks respectively

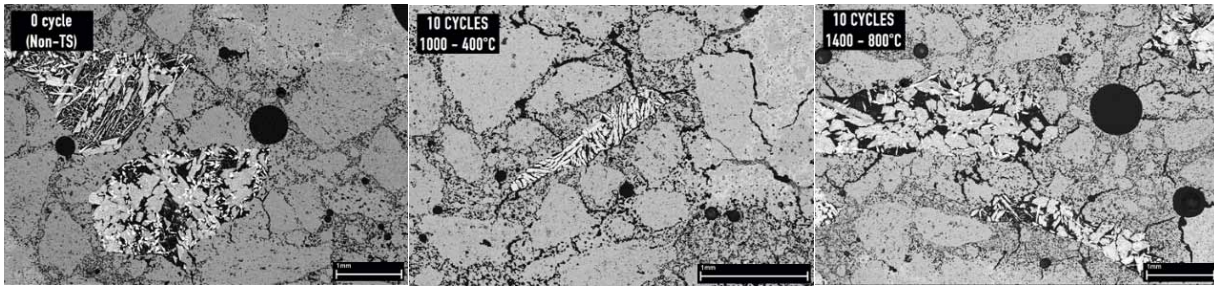

Fig. 16 AZS samples after zero and 10 thermal shocks

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-

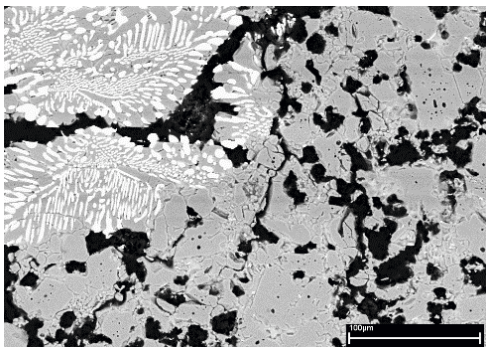

Fig. 17 AZS microstructure after 10 thermal shock cycles

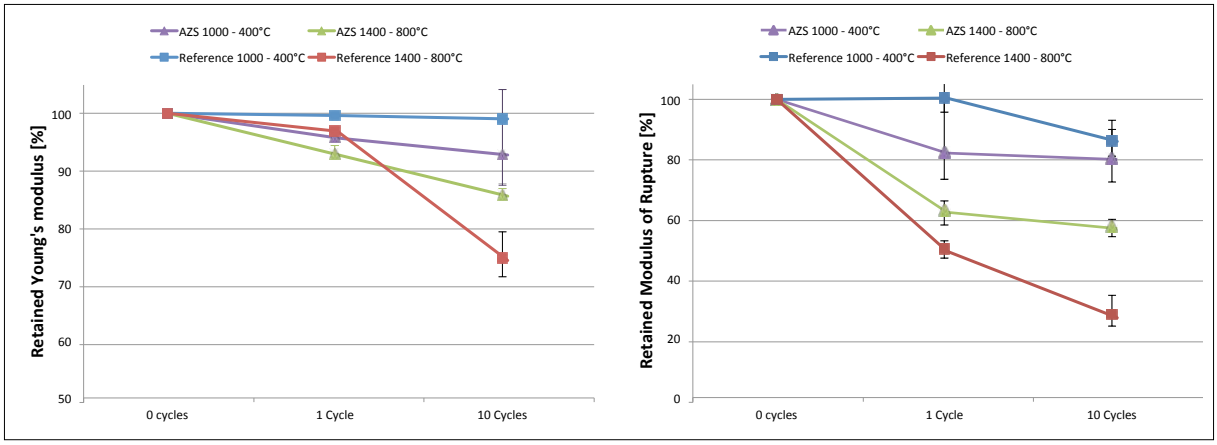

Fig. 18 Young's modulus and retained MOR after 0, 1 and 10 thermal shocks respectively, for Ref and AZS after high-temperature thermal shock

chanical 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], ZrO_2 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 according to Hasselman [3], critical temperature differences (ΔT_c) could be identified for Ref and A. After selecting $\Delta T = 600$ K, this temperature difference was chosen for the new high temperature thermal shock test. The 2 different temperature levels (1000 – 400 °C and 1400 – 800 °C) showed the importance of the selected level. Especially the Ref material exhibited different thermomechanical properties after the high temperature thermal shock test. To validate these results, the performance of 20 – 50 thermal shock cycles is projected.

Toughening mechanisms were mainly microcrack formation and changes in the matrix. Liquid phase bridges and crack bridging could be observed. Since these mechanisms occur very locally in the microstructure of the examined samples, the energy consuming effect [6] is considered rather small. To further examine these effects, formulations with larger grains were already designed and produced but not tested yet.

The fracture energy and the calculation of the crack density [20] is also an important parameter for a better understanding of the energy consumption by the different mechanisms.

Acknowledgements

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

References

[1] Boccaccini, D. N.; et. al.: Service life prediction for refractory materials. J. Mater. Sci. **43** (2008) 4079–4090

[2] Chandler, H. W.: Thermal shock of refractories, Refractories Appl. and News **10** (2005) [2]

[3] Hasselman, D. P. H.: Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics. J. Amer. Ceram. Soc. **52** (1969) [11] 600–604

[4] Bradt, R. C.: Fracture of refractories, in: Refractories Handbook, Ed. C.A. Schacht, Chapter 2, 11–38

[5] Bradt, R. C.: Crack extension in refractories. Proc. Unitecr '11; Kyoto, 30.10.-2.11.2011, Paper No. 2-D-5

[6] Harmuth, H.; Bradt R. C.: Investigation of refractory brittleness by fracture mechanical and fractographic methods. Refractories Manual 2010, 6–10

[7] Miyaji, D. J.; Tonnesen, T.; Rodrigues, J. d. A.: Eutectic aggregates containing refractory castables: What are their effects on fracture energy and thermal shock damage resistance? Proc. UNITECR '11, Kyoto, 30.10.–2.11.2011, Paper No. 2-D-3.

[8] Miyaji, D. J.; Otofuji, C.; Rodrigues, J. d. A.: The load-displacement curve of steady crack propagation: An interesting source of information for predicting the thermal shock damage of refractories. Proc. UNITECR '13, Victoria, Paper No. 17–10

[9] Garvie, R. C.: Zirconium dioxide and some of its binary systems, in: High-Temperature Oxides, Vol. 5-II., Ed. Alper, A.M., New York 1970, 117–166

[10] Pandolfelli, V. C.; et al.: Influence of mullite-zirconia aggregate addition on the thermomechanical properties of high-alumina refractories. Unitecr '93 Congress, São Paulo, 1993

[11] Pandolfelli, V. C., et al.: Evaluation of thermomechanical properties of alumina refractories containing a fused mullite-zirconia aggregate. Unitecr '95, Kyoto, Japan, 2, 1995

[12] Miyaji, D. J.; Tonnesen, T.; Rodrigues, J. d .A.: Fracture energy and thermal shock damage resistance of refractory castables containing eutectic aggregates. Ceramics Int. **40** (2014), 15227–15239

[13] Tessier-Doyen, N.; Glandus, J. C.; Huger, M.: Anisotropic untypical Young's modulus evolution of model refractories at high temperature, J. Europ. Ceram. Soc. **26** (2006) 289–295

[14] Kakroudi, M. G.; et al.: Anisotropic behaviour of andalusite particles used as aggregates on refractory castables. J. Europ Ceram. Soc. **29** (2009) 571–579

[15] Schnieder, J.; et al.: Crack formation and shape of fracture surface in tabular alumina based castables with addition of specific aggregates. J. of Ceramic Sci. and Technol. **5** (2014) [2] 131–136

[16] Schnieder, J.; et al.: Influence of eutectic aggregates in castables on the thermal shock resistance. Proc. Int. Coll. on Refractories 2013, Aachen

[17] Schnieder, J.; et al.: Influence of the thermal shock temperature difference on the microstructural damage and the crack propagation in modified high alumina refractory castables. Proc. Unified Int. Technical Conf. on Refractories 2015, Vienna, September 15–18

[18] Traon, N.; et al.: Influence of andalusite, Al_2O_3–ZrO_2–SiO_2 and Al_2O_3–ZrO_2 addition on elastic and mechanical properties of high alumina castables. Interceram Refractories Manual **11** (2014) 290–294

[19] Schnieder, J.; et al.: Microstructural damage of modified high alumina castables after several thermal shock cycles under specific experimental conditions. Proc. 57. Int. Coll. on Refractories Aachen, September 2014

[20] Salvini, V. R.; Pandolfelli, V. C.; Bradt, R. C.: Extension of Hasselmans thermal shock theory for crack/microstructure interaction in refractories. Ceramic Int. **38** (2012) 5369–5375