THERMOMECHANICAL BEHAVIOR OF HIGH-ALUMINA REFRACTORY CASTABLES CONTAINING PARTIALLY STABILIZED ZIRCONIA WITH DIFFERENT GRAIN SHAPES

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ABSTRACT

In many industrial processes refractory materials are exposed to considerable mechanical stresses at high temperatures. The wear resistance of refractories against these conditions is crucial to the service life of industrial aggregates. Therefore, an increased flexibility at elevated temperatures constitutes a desirable properties for refractory materials. The formation of interlocking structures contributing to this behavior can be found in nature; for instance itacolumite, a material based on interlocked quartz grains exhibiting large intergranular decohesions. This particular microstructure, reminding of a puzzle, enables itacolumite to resist large strains before failure when exposed to thermomechanical stresses. Inspired by this very special material behavior, this study attempts to create refractory castables which are capable of resisting higher thermal shock stresses and show an improved flexibility. As a first step of this study, two chemically identical high-alumina castables were designed, which differ in the shape of the added Y-PSZ (Partially Stabilized Zirconia doped with 3 mol.-% yttria; size 0.2 - 1 mm) grains only: The first formulation mainly includes anisometric Y-PSZ particles, whereas the second formulation predominantly contains isometric Y-PSZ grains of the same production lot. Thereby, two different methods of material reinforcement, namely transformation toughening and the formation of interlocking structures, are intended. To evaluate their impact on the high temperature performance of the castables, the applied testing methods include Resonant Frequency Damping Analysis up to 1500 °C as well as Refractoriness under Load (RuL) and Creep in Compression (CiC), Hot Modulus of Rupture (HMOR) tests between room temperature and 1500 °C and a post mortem SEM analysis of the microstructure. The examined castables showed a very similar behavior under compressive load, but considerable difference in bending behavior. Both the HMOR measurements and SEM analysis indicated that the grain shape has a strong influence on the condition of the matrix. Since heating as well as the sudden volume change of the martensitic transformation particularly lead to expansion in axial direction in case of the elongated Y-PSZ grains, a different crack network is introduced into the surrounding matrix compared to the castable containing isometric zirconia particles which expand approximately uniform in radial direction.

Keywords: thermomechanical properties, elastic properties, particle shape, thermal shock resistance, resonant frequency damping analysis, transformation toughening

INTRODUCTION

The wear resistance of refractories against mechanical and thermal stresses is crucial to the service life of industrial aggregates. Hence, refractories exhibiting an increased flexibility and mechanical strength at high temperature constitute an interesting research topic. Examples of beneficial effects like the formation of interlocking structures contributing to this behaviour can be found in nature: Itacolumite, a material based on interlocked quartz grains exhibiting large intergranular decohesions. Its extraordinary puzzle-like microstructure enables itacolumite to withstand large strains before failure when exposed to thermomechanical stresses [1]. In previous studies conducted by Babelot et al. [2], the creation of flexible ceramic materials inspired by the special behaviour of itacolumite are capable of resisting higher thermal shock stresses and may show an improved flexibility.

This study continues based on prior results that have focused on the grain shape influence on the thermomechanical behavior of refractory castables exhibiting identical compositions under constant bending stress [3]. It has been shown, that within the mentioned experimental conditions, splintery Y-PSZ grains tend to shorten the service life but enable larger deflection values compared to rather isometric particles of the same production lot. To expand the existing characterization, the present study focuses on the thermomechanical behavior under a constant bending rate as well as compressive stress and the thermoelastic properties via Resonant Frequency Damping Analysis up to 1500 °C accompanied by a post mortem SEM analysis of the microstructure.

EXPERIMENTAL PART

Three different refractory castable formulations are analysed within the framework of this study whose compositions are shown in table 1. To characterise the influence of partially stabilized zirconia (Y-PSZ) on the overall behaviour of the analysed formulations in the applied test methods, a reference castable mainly based on Tabular Alumina has been designed. The two formulations completing this survey contain each 13.75 wt.-% Y-PSZ with the same grain fraction and chemical composition (0.2 - 1 mm, 3 mol.-% Y_2O_3) but exhibit different particle shapes. The castable formulation "Anisometric Y-PSZ" primarily contains splintery zirconia grains, while the formulation marked as "Isometric Y-PSZ" mainly includes less splintery particles of the same zirconia production lot.

The presorted zirconia materials are provided by *Imerys*, the alumina raw materials are contributed by *Alteo* and the CA Cement *Secar 71* is supplied by *Kerneos*. The deflocculant *FS 40* by *BASF* and citric acid are dissolved in water to prepare the solution needed for the mixing process of these three Low Cement Castables.

Each of these formulations is used for the casting of both rectangular bars (150 mm x 25 mm x 25 mm) and prismatic blocks (230 mm x 65 mm x 55 mm) using steel moulds prepared with mould release agent *Panolin Form Synth*. Subsequently, all samples are cured for 48 h in a humid chamber, dried at 110 °C for 24 h and sintered at 1500 °C for 6 h.

To determine the difference in particle shape of the added presorted Y-PSZ grains, a characterization of their aspect ratio (width / length) is carried out on the basis of Dynamic Image Analysis (DIA) via shadow projection of the particles (Type *Camsizer P4, Retsch,* Germany). An aspect ratio of 1 refers to a perfect circle or square, whereas a value converging to 0 represents an elongated, needle-like particle [4, 5]. The elastic properties, namely dynamic Young's modulus and damping, are determined via Resonant Frequency Damping Analysis (RFDA) according to *ASTM C1548-02* using devices by *IMCE* (Belgium)

Tab. 1: Compositions of the tested castable formulations

Material	Specification	Ref	Anisometric Y-PSZ	Isometric Y-PSZ
		wt.-%		
CA Cement	CA Secar 71	5	5	5
Reactive Alumina	PFR	12.5	12.5	12.5
Tabular Alumina	0 – 0.045 mm	10	10	10
Tabular Alumina	0 – 0.3 mm	10	10	10
Tabular Alumina	0.2 – 0.6 mm	10	5	5
Tabular Alumina	0.5 – 0.1 mm	17.5	8.75	8.75
Tabular Alumina	1 – 3 mm	35	35	35
Anisometric ZrO_2 (3 mol.-% Y_2O_3)	0.2 – 1 mm		13.75	
Isometric ZrO_2 (3 mol.-% Y_2O_3)	0.2 – 1 mm			13.75
Total		100	100	100
Water	H_2O	5	5	5
Deflocculant	FS 40	0.1	0.1	0.1
Retarder	Citric acid	0.03	0.03	0.03

for characterization at room temperature (Type *RFDA system 23*) and high temperature (Type *RFDA HT1750*), both in flexural mode. Therefore, the prepared rectangular bars are excited by a slight mechanical impulse which causes the emission of an acoustic signal due to the vibration of the samples in one or more of their resonant frequencies. To obtain the elastic properties, the emitted signal is received via a microphone and evaluated by a software-based analysis. In case of the high temperature characterization, the samples are excited in an interval of 60 seconds while heating up to 1500 °C and cooling down to room temperature (2 °C / min each) which allows an adequate evaluation of the elastic properties over the whole analyzed temperature range.

Hot Modulus of Rupture (HMOR) tests are performed on rectangular bars of the same geometry as the RFDA measurements at 25 °C, 500 °C, 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C and 1500 °C on a universal testing system with bending device (*Instron*, Germany) applying a constant loading rate of 0.15 MPa/s until rupture (according to *DIN EN 993-7*).

Refractoriness under load (RuL) and Creep in Compression (CiC) tests are performed according to *DIN EN ISO 1893* and *DIN EN 993-9* respectively. Therefore, cylindrical samples (50 mm diameter, 50 mm height, internal bore diameter 12.5 mm) are drilled out of the castable blocks. Their deformation is measured while they are subjected to a constant compressive load of 0.2 MPa and heated up with 2 °C / min. In case of the CiC tests, the heating is stopped at 1500 °C and the samples are kept at this temperature level for 25 h.

RESULTS AND DISCUSSION

After sintering, the samples of the "Anisometric Y-PSZ" castable exhibit Young's modulus values of 94.0 ± 7.0 GPa whereas the formulation predominantly containing isometric Y-PSZ grains shows a slightly higher stiffness of 108.6 ± 8.5 GPa. The measured damping values after firing are $(1.55 \pm 0.56) \cdot 10^{-3}$ as well as $(0.85 \pm 0.20) \cdot 10^{-3}$ for the formulations marked as "anisometric" and "isometric" respectively. This correlates with a differently developed crack network observed in the Scanning Electron Microscopy (SEM) analysis of these formulations, which will be shown more detailed in the microstructure analysis section, caused by the considerably differing grain shape of the added zirconia particles. The corresponding mean aspect ratios measured via DIA are mentioned in table 2. Regarding the reference castable, the stiffness values after sintering (147.1 ± 2.3 GPa) are higher due to the absence of zirconia as well as its reversible volume changes caused by the martensitic transformation. Furthermore, the reference castable exhibits the lowest damping values are $(0.42 \pm 0.04) \cdot 10^{-3}$ in the comparison of the three tested formulations.

Tab. 2: Particle shape values determined via DIA

Material	Mean aspect ratio
Isometric Y-PSZ (3 mol.% Y_2O_3)	0.67
Anisometric Y-PSZ (3 mol.% Y_2O_3)	0.56

Thermoelastic characterization via HT-RFDA

Rectangular samples of all three castable formulations are examined via HT-RFDA after firing. The thermoelastic behavior of the reference castable is plotted in figure 1. During heating the dynamic Young's modulus decreases to approximately 75 % of its value at room temperature, but returns to its initial state after cooling again. The occurring hysteresis between the heating and cooling curve is attributed to the slightly different thermal expansion coefficients (CTE) of the tabular alumina grains compared to the surrounding calcium hexa-aluminate (CA_6) matrix. However, no relevant change of the elastic properties is implied after finishing the HT-RFDA measurement despite the observed behavior.

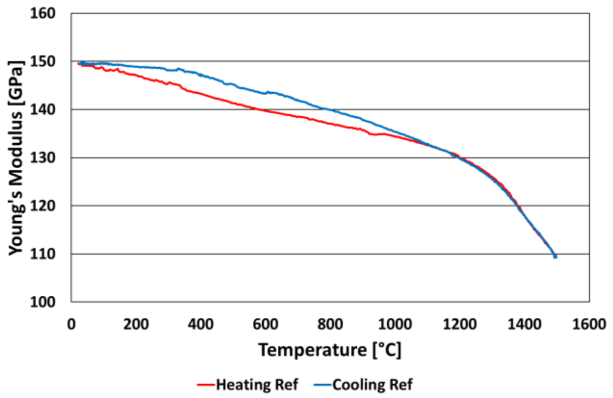

Fig. 1: Stiffness development of the reference castable formulation based on tabular alumina

Since both of the other examined castable formulations exhibit a more complex stiffness development with varying temperature, the shown graphs in figure 2 are subdivided in several heating and cooling segments (H1 – H4 and C1 – C2 respectively). The first region is located between room temperature and 550 °C. Both Y-PSZ castables show a comparable stiffness decrease of approximately 20 % in this segment, that is also considered to be a CTE mismatch effect, but more distinct compared to the reference castable since the thermal expansion of Y-PSZ is significantly higher than the CTE values of both tabular alumina and CA_6. Thus, the detected lowering of the Young's modulus is caused by the widening of pre-existing microcracks originated during firing and additional microcracks induced by zirconia grains expanding into the matrix. The second heating section (H2, 550 °C – 800 °C) is introduced by the transformation of the monoclinic zirconia particles into the tetragonal modification. The abrupt contraction of the zirconia grains leads to a debonding of these grains from the surrounding matrix which interrupts the decrease of stiffness. Nevertheless, thermal expansion of the all constituents proceeds due to the ongoing temperature increase while a stagnating Young's modulus level is measured. Since the zirconia particles exhibit larger thermal expansion compared to the other components, they gain contact to their surrounding again during heating and thereby stiffness increases (H3, 800 °C – 1250 °C). Above 1250 °C (H4), this healing effect changes into the opposite again and pressure is applied by the zirconia grains which leads to additional damaging. The subsequent increase of Young's modulus may be evoked by the appearance of small amounts of an amorphous phase but has to be examined in detail by future studies. During cooling (C1) the Young's Modulus increases which is explained by the closure of the previously induced cracks due to shrinkage of the specimen. The Young's modulus features an approximately constant level in this temperature range, especially between 1000 °C and 400 °C, which might be relevant to practical application. In segment C2 the reverse zirconia transformation, tetragonal to monoclinic, takes place and has a beneficial effect on the stiffness since the occurring volume expansion strengthens the Young's modulus increase during cooling. In this segment the most obvious difference in the stiffness development can be noticed: After passing the effects triggered by the transformation of the isometric grains (appr. 300 °C), the Young's modulus keeps its value until room temperature, whereas the more splintery grains lead to a peak followed by a subsequent decrease of stiffness until 200 °C. Remarkably, both materials return to their initial stiffness despite the mentioned effects. In future studies, cycling HT-RFDA tests could reveal if this behavior still occurs after several heating and cooling cycles.

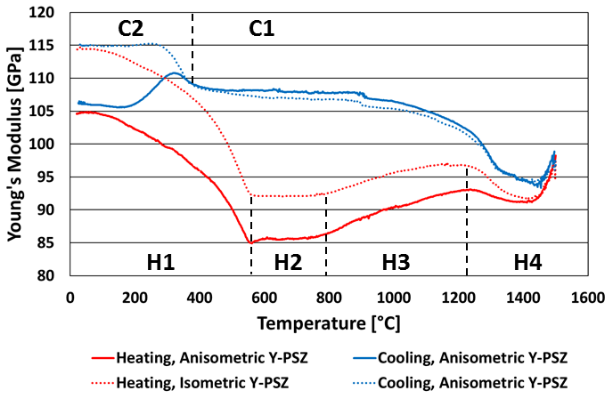

Fig. 2: Thermoelastic behavior of the castable formulations additionally including differently shaped Y-PSZ

Thermomechanical behavior under bending conditions

Figure 3 and Figure 4 present the results of the bending tests in terms of MOR and maximum deflection of all three castable formulations. Both diagrams show a similar arrangement of the material performance. The reference castable without added zirconia exhibits the highest values of both flexural strength and bending, while the addition of Y-PSZ grains causes a lowering of the mentioned properties.

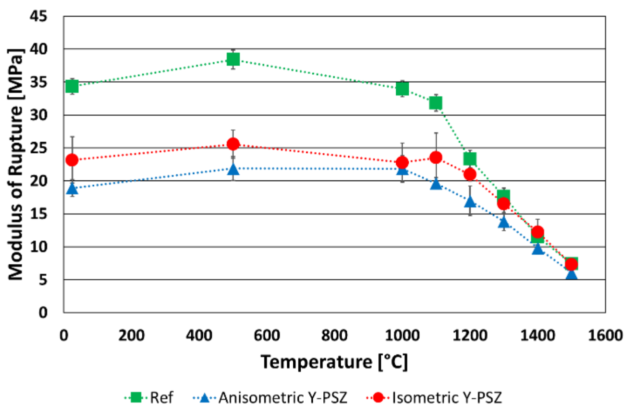

Fig. 3: Development of the flexural strength with rising temperature up to 1500 °C

It is noticed that the MOR values seem to be less affected by the grain shape than the relative deflection of the samples. The addition of Y-PSZ itself provokes a considerable loss of bending strength, whereas the grain shape influence on this thermomechanical property is of comparably low extent. However, slightly higher MOR values are detected in the testing of the castable containing less splintery grains. Comparing the MOR results to the maximum deflection values it becomes obvious that the latter property is affected stronger by the grain shape of the added zirconia particles. With both Y-PSZ containing castables less deflection is achieved compared to the reference material but the particle shape influence is more pronounced in this correlation. Whereas the formulation containing more splintery grains substantially deviates from the other tested castables, these two materials show comparable results which implies that rather isometric grains of the given grain size contribute to the flexibility of the tested materials under these experimental conditions.

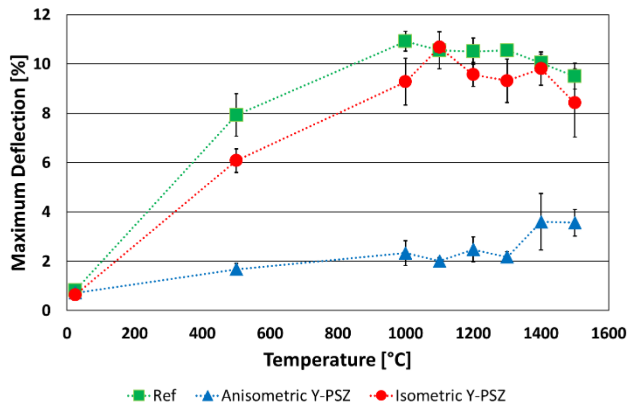

Fig. 4: Maximum deflection detected during HMOR tests up to 1500 °C

Thermomechanical characterization under compressive load

In addition to the thermomechanical measurements under flexural load, CiC and RuL tests are performed to examine the thermomechanical behavior under compressive stress. The relative expansion of all three castables obtained in the CiC tests are plotted in figure B and the corresponding RuL and CiC parameters are composed in table 3.

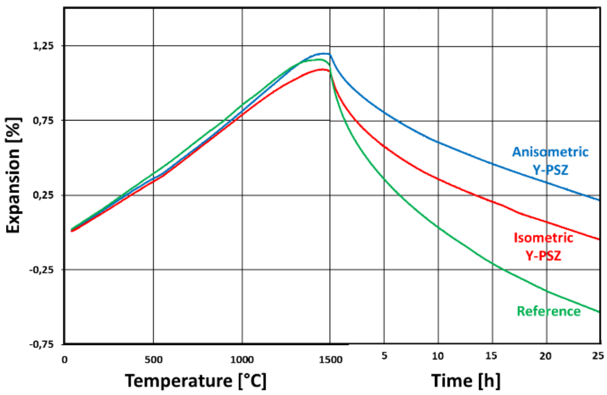

Fig. 5: Relative expansion via Creep in Compression test of all tested castable formulations

In contrast to the mentioned behavior under flexural load, both test methods applying compressive stress do not reveal different material performance related to the particle shape. Nevertheless, a considerable improvement of the creep rate (CiC) as well as $T_{0.5}$ and T_1 parameters (RuL) is observed due to the zirconia addition, regardless of their grain shapes. In both cases, the creep rate between the 5th and 25th hour after reaching a testing temperature of 1500 °C is decreased by approximately 60 %. Regarding the RuL parameters, both temperature values correlated to a deformation of either 0.5 % or 1 % are raised by 20 °C and 10 °C respectively. Even so, the measurement accuracy does not enable an exact determination of the particle shape influence on these properties.

Tab. 3: Determined RuL and CiC parameters

Castable	Creep rate (5-25h) [ε%/hour]	$T_{0.5}$ [°C]	T_1 [°C]
Reference	-0,074	1610	1654
Isometric Y-PSZ	-0,031	1632	1666
Anisometric Y-PSZ	-0,030	1631	1663

Microstructure analysis via Scanning Electron Microscopy

As observed in figure 6 and figure 7, no interlocking structure is achieved by the addition of zirconia grains due to a lack of contact between the included zirconia. This is considered to be caused by an insufficient amount or particle size of the Y-PSZ grains.

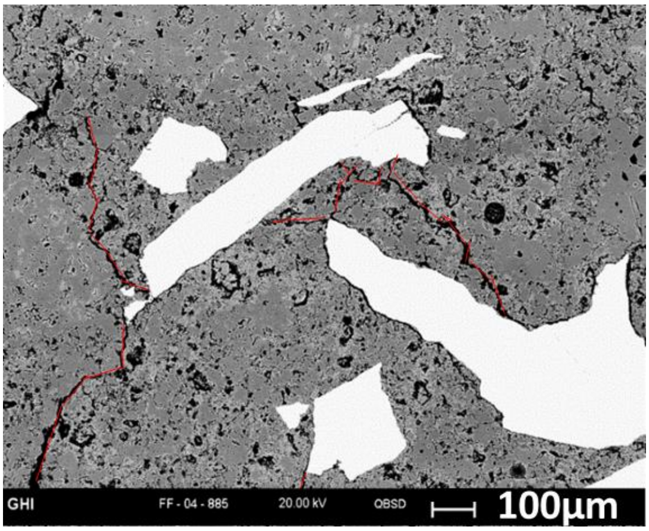

Fig. 6: The microstructure of the castable containing rather needle-like Y-PSZ grains mainly exhibits cracks located at the sharp-edged grain tips

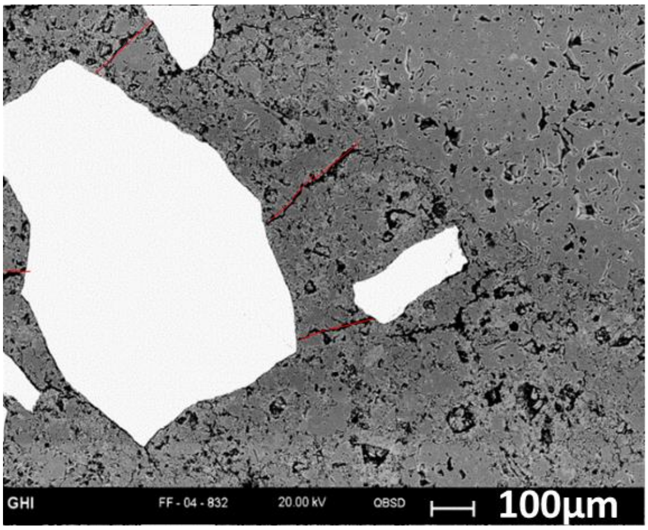

Fig. 7: Crack initiation mainly observed at Y-PSZ grain angles in the microstructure of the castable formulation containing less splintery zirconia grains

Therefore, it is assumed that the differences observed in the mentioned results of the applied test methods are an effect of a differently developed crack network in the microstructure of the Y-PSZ containing castables. Whereas the needle-like Y-PSZ grains mainly initiate cracks at their sharp-edged tips (figure 6), the less splintery zirconia particles mainly introduce cracks at their angles (figure 7).

CONCLUSION

To conclude, this study has contributed to the overall understanding of the particle shape influence on the thermomechanical and thermoelastic properties of refractory castables and highlights the impact of even small changes in their composition on the performance under different loading conditions.

Whereas constant compressive stresses do not allow a sufficient determination regarding the particle shape impact, bending conditions reveal considerably deviating behavior. In contrast to the achievement of larger deflections under constant bending load mentioned in [3], a constantly increasing flexural stress seems to reduce the possible bending of the samples including anisometric Y-PSZ grains. This implies a time-dependent behavior that could be an interesting subject for future studies, especially in correlation with the observed effects on the microstructure due to grain shape variations.

Since rather isometric grains appear to contribute to the flexibility under the given experimental conditions, presorting by grain shape could help to improve materials applied under similar conditions.

To separate the grain shape impact from the transformation effects caused by Y-PSZ, presorted alumina materials will be used in the next steps of this survey.

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