

Manufacture of Refractory Multilayer Composites with Optimised Thermal and Chemical Properties Via the Tape Casting Process

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Multilayer refractory structures have been manufactured by means of cast green tapes to improve their thermal and corrosive properties. Using different grain size distributions, the packing density could be controlled and thus, dense and porous tapes could be generated with variable properties. For processing, conventional Al_2O_3 , ZrO_2 and MgO powders have been used. Residual stresses were incorporated in multilayer structures via differences in shrinkage or thermal expansion behaviour in order to improve the thermal shock resistance. In addition, a glass layer has been introduced between ceramic layers, which softens at higher temperatures, and therefore deflects or stops cracks. Finally, a green tape was joined with a traditional refractory brick in order to improve the surface of conventional refractories. The influence of these attempts on thermal shock behaviour has been demonstrated for sintered planar tape laminates.

1 Introduction

Multilayer ceramics have been an emerging field for decades in the field of functional ceramics [1–4]. Since several years many publications are using the multilayer

concept to improve mechanical properties [5–9]. This paper discusses the use of the ceramic multilayer technology for applications at high temperatures. Traditionally, the refractory industry uses monolithic bricks. In terms of a clean steel technology which focuses on the reduction of greenhouse gases, the carbon content in refractories should be reduced. Additionally, the unwanted incorporation of carbon in steel, which decreases several properties, e.g. like ductility, is another motivation to eliminate carbon from refractory materials. However, carbon is typically added in order to increase the thermal shock resistivity. Therefore, concepts have to be developed to compensate for this disadvantage. Based on tape cast green tapes the ceramic multilayer technology offers the possibility to overcome this disadvantage because it can combine beneficial properties in different layers. A roadmap, based on market analysis and research activities, predicts potential for such multilayer composites in the field of refractories [10].

Tape casting is a large scale production method to obtain planar green tapes as a basic intermediate product to manufacture multilayer composites. In multilayer device processing the cast and dried green tapes are cut, stacked, and laminated, followed by thermal treatment like binder burnout and co-firing [11]. Tape casting is typically limited to thin substrates and fine-grained slurries. To cast coarse-grained refractory powders with particle sizes up to 1 mm, the casting process was adjusted by increasing the blade height, by decreasing the casting speed and by using restriction bars at the edges of the tape, the latter to prevent any side flow effect at higher blade gaps. By these measures homogeneous tapes based on refractory material systems like Al_2O_3 , MgAl_2O_4 and MgO with thicknesses up to approximately 6 mm could be manufactured [12, 13]. By use of appropriate powder mixtures fired tapes with a wide range of properties could be achieved; e.g., porosities between 1 – 36 % could be produced. Lamination and co-firing of these tapes was successful, which is a prerequisite for multilayer device processing. In order to be able to classify these tapes as suitable for refractory applications, static corrosion tests were conducted using a lime based steel works slag. By heating the slag above its melting point, the penetration and dissolution behaviour was analysed. It was found, that pore sizes under 20 μm in diameter will not be infiltrated. In coarse-grained tapes, the gaps between particles are typically larger, but by using specific powder mixtures, these voids can be filled with fine particles, which make such tapes resistant against corrosion [13]. In order to avoid stresses exceeding the strength of interfaces between materials with high difference in thermal expansion, thin gradient tapes were introduced successfully to reduce thermal stresses during cooling [12]. In order to introduce layers

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of even higher porosity of up to 40 %, the ceramic tapes were combined with preceramic papers via lamination and co-firing [14]. On the basis of planar and cylindrical structures, composed of defect-free, porous or dense structures, the flexibility and versatility of this manufacturing method was demonstrated.

In another approach, the thermal shock behaviour was improved via generation of weak interfaces. This was demonstrated by manufacture of rotational-symmetric structures for application as submerged entry nozzle. These nozzle structures were manufactured via spiral winding of green tape strips and subsequently fired.

Flexibility of the green tapes is a mandatory property for winding; the thickness of tapes which are suitable for winding is limited to about 600 μm . The nozzles consisted of about ten layers; monolithic and graded structures were manufactured and characterised. After firing the nozzles exhibited moderate defects like partial delamination effects, which caused weak interfaces between the layers. This kind of structures stops cracks improving the thermal shock behaviour, whereas the wound spiral structure of the nozzle prevented catastrophic failure.

The corrosion behaviour was dominated by the kind of defects, which allow a steel slag to penetrate in the inner layers of the spiral structure and spread along interfaces. Nevertheless, only slight dissolution of material was observed at these interfaces, which confirms the application potential of such multilayer nozzle structures [15, 16]. Beside weak interfaces, the incorporation of residual stresses offers another possibility to increase thermal shock resistance. One way to generate such stresses is to combine layers of different material systems, which exhibit different coefficients of thermal expansion (CTE). This results in temperature-dependent stresses, which are highest at room temperature, as they are generated during cooling after firing.

On the other hand, shrinkage differences can be used to induce internal stresses. These stresses are permanent, as far as the temperature will not be exceeded, above which layer softening causing stress relaxation. Combining layers with a moderate shrinkage difference, an increase in bending strength of 60 % could be achieved, com-

Tab. 1 Powder mixtures of the slurries for tape casting (A: Alumina, M: Magnesia, Z: Zirconia in [mass-%])

Tape	Powder Fraction Finest Powder ($d_{50} \sim 1\text{--}3 \mu\text{m}$)	Powder Second Finest Powder ($d_{\text{max}} < 45 \mu\text{m}$)	Powder Fraction Second Coarsest Powder (d: 0,2–0,6 mm)	Powder Fraction Coarsest Powder (d: 0,5–1 mm)
A1	100	0	0	0
A2	45	55	0	0
A3	30	70	0	0
A4	15	85	0	0
A5	25	25	50	0
A6	10	25	40	25
M	20	35	0	45
Z	10	25	40	25

pared to a single layer of the same composition as the top layer, which is loaded in the composite structure [17].

Another approach to improve thermal shock behaviour, which will be demonstrated in this paper, is to introduce a softening layer, which transfers the kinetic energy of the propagating crack into plastic deformation at elevated temperatures and thereby stops this crack.

2 Experimental procedure

2.1 Tape casting and tape characterization

All multilayer laminates used in this study were based on cast green tapes. The required slurries were based on fine- and coarse-grained alumina (CT1200 SG and T60, Almatix GmbH/DE), magnesia (Luvomag MI, Lehmann & Voss & Co. KG/DE and Nedmag 99 DBM, Nedmag Industries/NL) and yttria-stabilized zirconia powders (13 % Y-Zirconia, UCM Advanced Ceramics GmbH/DE).

These powders cover a wide range of particle sizes with medium particle sizes d_{50} from about 1 μm up to a maximum size of around 1 mm. The powder compositions of all cast tapes are listed in Tab. 1. Tapes A1 and S are so-called monomodal tapes based on only the finest powder fractions, which are therefore expected to be dense sintering.

All other tapes consist of at least two powder fractions and will remain porous after firing due to the low specific surface area of the coarser powders. The composition of the tri- and tetramodal tapes A5, A6, M and Z has been optimised concerning particle packing efficiency using the theory of

Dinger and Funk [18] based on the grain size distribution of the powders.

In order to prepare homogeneous slurries, the powders were deagglomerated in a solvent mixture (azeotropic mixture of ethanol and toluene) using the dispersant Hypermer (Croda/US; 1,0 mass-% of solids). Homogenization was carried out in a tumbling mixer (Turbula, WAB AG/CH) for 24 h.

In order to introduce shear forces for deagglomeration, alumina milling balls were added to the bimodal slurries. The tri- and tetramodal slurries were prepared without milling balls, as the coarsest particles are heavy enough to generate adequate shear forces. Then, polyvinylbutyral binder (BUTVAR, Solutia/US) and plasticizer (Santicizer, Ferro/US) were added and homogenised for another 24 h. For all prepared slurry compositions, the binder to plasticizer ratio was 1:1. Before tape casting, the slurries were screened using a wire cloth with an aperture size of 244 μm to retain the milling balls and other large contaminations. These slurries were degassed for 20 min using underpressure of 230 mbar in a rotary evaporator under slow rotation. The tri- and tetramodal slurries were not degassed in order to avoid settlement of the coarse particles. The tapes were cast on a tape casting machine of 4 m length using a thin PET tape with a thickness of 100 μm as a carrier and a fixed casting head with a blade gap of 2,0 mm (bimodal tapes) or 5,0 mm (other tapes), respectively. For the thick tapes, side bars were placed behind the casting head in order to prevent lateral flow of the slurries to the edges. The bars were mounted parallel in a lateral distance of 210 mm, which corresponds to

the width of the used casting head. For the bimodal tapes, the casting speed was set to 2,4 m/min, resulting in a shear rate of 20 s^{-1} . The other tapes were cast with the lowest possible speed of 0,4 m/min in order to give the highly viscous slurry enough time to flow and thus to ensure the formation of a homogeneous green tape. After drying in ambient air, the green tape was carefully lifted off the carrier tape. The dried bimodal tapes had a green thickness of approximately $900 \mu\text{m}$, whereas the other multimodal tapes exhibited a thickness of around 4 mm after drying.

For characterization, 20 squared samples of each type of tape with the size of $35 \text{ mm} \times 35 \text{ mm}$ were cut out of the bimodal green tapes by means of a hot knife (Groz-Beckert KG/DE) at a temperature of $60 \text{ }^\circ\text{C}$. The thicker tri- and tetramodal tapes had to be cut by means of a plate shear (HM Machinery/DK).

The specimens were fired in air at $1700 \text{ }^\circ\text{C}$ with a dwell time of 5 h (HT 16/17, Nabertherm GmbH/DE). For alumina samples, alumina setters were used, whereas zirconia-coated alumina plates were applied for zirconia samples and magnesia setters for magnesia samples.

Debinding was conducted slowly with a heating rate of $0,25 \text{ K/min}$ up to $500 \text{ }^\circ\text{C}$, followed by a heating rate of 3 K/min to the peak temperature. The in-plane shrinkage of the samples was determined via geometrical measurement before and after firing. Young's moduli were measured via ultrasonic impulse reflection (USD 10, Krautkramer/DE) in water. The CTE was determined via dilatometry (DIL 402C, NETZSCH GmbH/DE) using a sintered piece of tape (dimensions $\sim 5 \text{ mm} \times 15 \text{ mm}$). Using a heating rate of 3 K/min up to $1600 \text{ }^\circ\text{C}$, the CTE was evaluated in a low-temperature regime from room temperature up to $600 \text{ }^\circ\text{C}$ and a high-temperature regime $>600 \text{ }^\circ\text{C}$.

2.2 Manufacture of multilayer laminates

In this paper all laminates were manufactured via thermo compression (Polystat 200T, Servitec Maschinenservice GmbH/DE). The laminates were pressed at $80 \text{ }^\circ\text{C}$ at a pressure of 25 MPa for 60 min in a die of the dimensions $60 \text{ mm} \times 100 \text{ mm}$. In order to ensure a homogeneous pressure distribution, the laminate was removed from the

die after 30 min, turned upside down and pressed for another 30 min.

To acquire information about the ability to join such multilayer structures with traditional, already fired refractories, a tape A6 was fabricated and laminated onto a conventional chamotte brick with a high alumina percentage.

The aim is to be able to grade up fire-bricks or to repair corroded refractory material. Before joining, a grid-like pattern was cut into a segment of the brick (size $\sim 30 \text{ mm} \times 50 \text{ mm}$) by means of a diamond saw. The slurry, on which tape A6 is based, was chosen as a kind of glue which etched the green tape in order to achieve a sufficient contact between the roughened surface of the chamotte and the green tape. The slurry was applied onto the surface of the brick and the tape was pressed onto it manually. Thereby, parts of the slurry are pushed into the grid pattern increasing the cohesion between tape and brick. The joint structure was dried 24 h at ambient atmosphere.

All laminates were fired according to the above given sintering profile for the individual tapes. The composite of tape and brick was fired with the tape facing downwards. The weight of the chamotte brick loads the tape with a pressure of about 550 Pa preventing delamination. Cross section and plane view images have been generated using a macroscope (M420, Leica Camera AG/DE).

In order to implement a layer into the multilayer composite structure, which softens at higher temperatures and thereby deflects and absorbs crack energy, a glass layer was introduced between monomodal layers of alumina tape A1. A coverglass based on borosilicate (Schott AG/DE) of $300 \mu\text{m}$ in thickness was chosen with a CTE of $7,2 \times 10^{-6} \text{ K}^{-1}$ and a glass transition temperature of $557 \text{ }^\circ\text{C}$.

This coverglass was stacked together with tapes A1 of 2 mm thickness, which had already been fired and subsequently ground parallel. For joining, the stacks were loaded with a pressure of 380 Pa and heated above the glass transition temperature of the according glass without melting it. This resulted in laminates with a total thickness of around 4 mm. After keeping the top temperature of $1100 \text{ }^\circ\text{C}$ constant for 1 h, another holding time was introduced in the

glass transition region at $550 \text{ }^\circ\text{C}$ for 1 h to ensure defect-free laminates. The heating and cooling rate was 5 K/min each.

2.3 Thermomechanical behaviour of ceramic-glass composites

To investigate the thermo-mechanical behaviour of ceramic-glass composites by four-point bending tests, each laminate was cut into bars with a length of around 50 mm and a width of about 3,5 mm by means of a diamond saw in accordance with DIN EN 843-1.

The experiments were carried out at room temperature and elevated temperatures (Instron 4204, Instron Wolpert/DE). The distance between the upper loading pins of the four-point bending test assembly was 20 mm whereas the downside supporting pins had a distance of 40 mm. The flexural strength was determined with a low feeding rate of $0,1 \text{ mm/min}$. After keeping the temperature constant at 500, 600, and $700 \text{ }^\circ\text{C}$, respectively, for 30 min, the load-displacement curve was recorded. After fracture, the crack propagation was analysed via optical and scanning electron microscopy.

2.4 Thermal shock testing

In order to investigate the impact of rapid temperature changes on the layer cohesion, three-layer multilayer laminates of tape A5 were manufactured and fired, which resulted in an overall thickness of around 10 mm. By means of a diamond saw, they were cut into dices with an edge length of around 10 mm. After measuring Young's modulus of each dice, the sample were placed in a cold furnace (LM412.27, Linn High Term GmbH/DE) and heated up to temperatures of 200, 400, 800, 1000 or $1200 \text{ }^\circ\text{C}$, respectively, with a heating rate of 3 K/min .

After holding the peak temperature for 30 min in order to ensure a homogeneous temperature distribution inside the laminates, the furnace was opened and all samples were immediately quenched in cold water.

This procedure was repeated 10 times for each sample. After each shocking event, the in-plane Young's modulus was measured via the impulse reflexion method in order to acquire information about the occurrence of defects, e.g. delaminations and cracks. The loss in elastic modulus was recorded in relation to the original value and addition-

ally, the number of samples, which failed owing to complete interface delamination was counted. The compound of tape and conventional refractory brick was shocked in the same manner at all above mentioned temperatures in ascending order. After each shock, the cohesion of the interface was documented via macroscopic images.

3 Results and discussion

3.1 Tape characterisation and lamination

Casting of thin and thick tapes for refractory applications was in general possible. By means of side bars, which prevent lateral flow, thick tapes could be cast with a thickness of several mm, up to 6 mm [13]. In this study, the highest green tape thickness used was 4 mm.

Fig. 1 depicts shrinkage and Young's modulus of the investigated tapes. The monomodal tape A1 exhibits a very high shrinkage of around 17 % and therefore a remaining porosity of less than 2 %. The bimodal alumina tapes A2, A3 and A4, which differ in their amount of coarse grained powder, show a shrinkage dependence on the coarse grain fraction.

Tape A4 with the highest percentage of coarse grains (85 %, Tab. 1) shrinks least due to the low specific surface area of the coarse particles. As a consequence this results in a high porosity of 14 % in case of tape A2 and 29 % for A4. Comparing the multimodal tapes A5, A6, Z and M, the highest shrinkage values occur in tapes A5 and M. A5 does not include the coarsest fraction with the lowest specific surface area; tape M exhibits a higher amount of the two finer powders compared to the other multimodal tapes.

The lowest shrinkage values of about 1 % occur for tapes A6 and Z, which have an identical composition concerning the ratio of the four powder fractions, but differ in their basic material system. The same trend is visible for the Young's moduli, which decrease with increasing porosity and therefore increasing amount of course grains. In general, zirconia has a very low elastic modulus, which causes the lowest Young's modulus of 26 GPa for tape Z.

The Coefficients of Thermal Expansion (CTE) determined for all involved material systems can be found in Tab. 2. While alumina exhib-

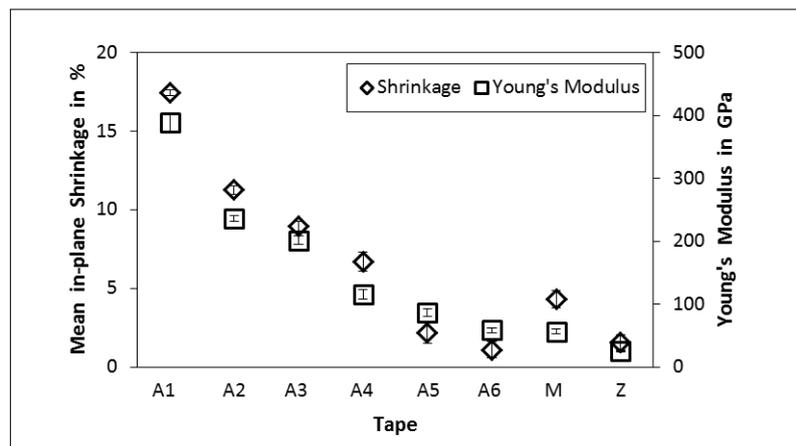


Fig. 1 Mean in-plane shrinkage and Young's modulus of several investigated tapes

Tab. 2 Linear thermal CTE for all investigated material systems determined via dilatometry

Material System	CTE (RT–600 °C)	CTE (>600 °C) [10 ⁻⁶ K ⁻¹]
Al ₂ O ₃	8,0	10,2
MgO	13,9	18,8
ZrO ₂	10,0	13,0

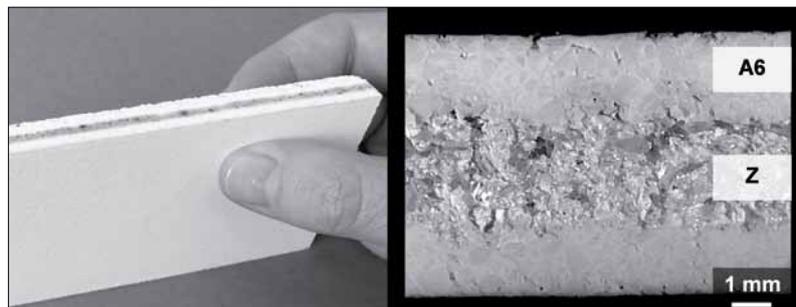


Fig. 2 Side view of a laminate with the layer sequence A6-M-A6 (l.); cross section of three-layer laminate with the layer sequence A6-Z-A6 (r.)

its a typical ceramic expansion behaviour, the CTE of zirconia and especially magnesia is higher. Hence, suitable tape combinations for generation of residual stresses via CTE differences of adjacent tapes in a multilayer composite, is alumina combined with a zirconia or magnesia layer, respectively.

As examples, Fig. 2 shows defect-free laminates consisting based on an alumina/magnesia layer sequence (left) and an alumina/zirconia assembly (right). In case of the material combination alumina and magnesia, it was necessary to implement one or more thin intermediate layers of an alumina-magnesia powder mixture to bridge the gap in thermal expansion behaviour between the layers to reduce stresses preventing failure during firing [12].

In order to generate residual stresses via shrinkage differences, mono- or bimodal tapes can be arranged in a multilayer composite between multimodal tapes, as far as layers do not delaminate. An eleven-layer symmetric alumina laminate with the layer sequence A6 – 3 × A4 – 3 × A2 – 3 × A4 – A6 is shown in Fig. 3. This graded structure is based on coarse-grained low-shrinkage tapes A6 at the outside, followed by three layers of the medium-shrinking bimodal tape A4 and three layers of the high-shrinkage tape A2 in the centre. In the cross section micrograph, the edge of the laminate exhibits a slightly concave shape, which indicates constrained sintering in the inner layers, resulting in residual stresses.



Fig. 3 Side view of an eleven-layer laminate with the layer sequence A6-3*A4-3*A2-3*A4-A6

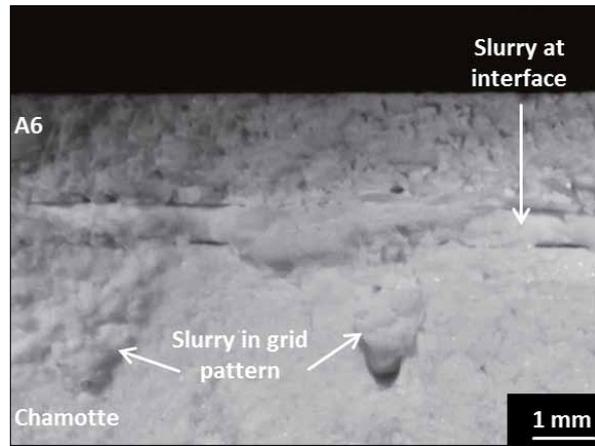


Fig. 4 Side view of the joined interface between traditional chamotte brick and coarse-grained alumina tape A6, joined via slurry, after firing

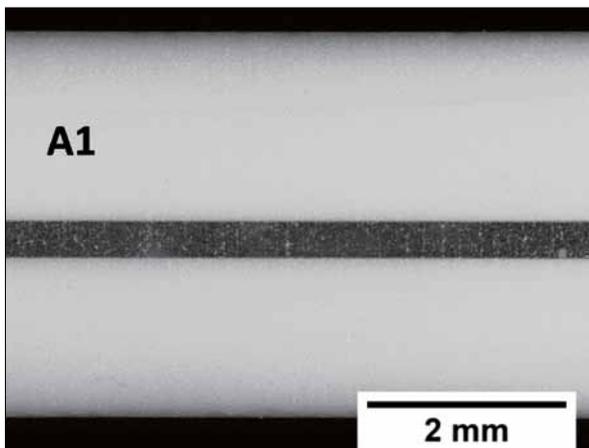


Fig. 5 Joined ceramic-glass laminate with a defect-free glass-layer surrounded by dense sintering alumina layers

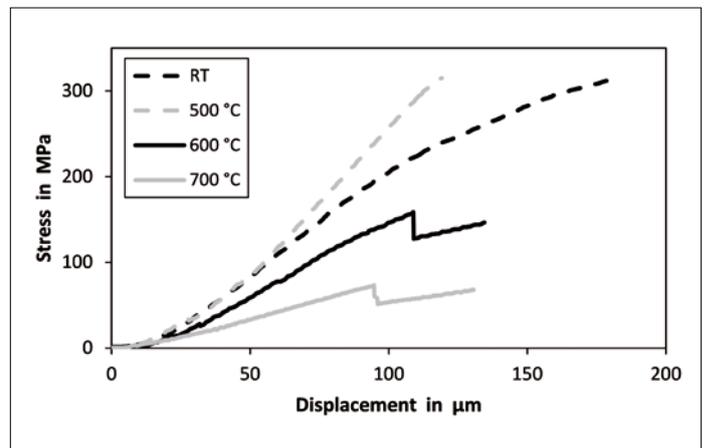


Fig. 6 Stress-displacement curve of alumina-glass composite at different temperatures

Bimodal tapes can also be used to manufacture cylindrical structures via winding processes. Spiral winding has been demonstrated as a well-suited method to generate layered nozzle structures based on ceramic green tapes which exhibited good thermal shock behaviour due to controlled defect structures based on either strong [19] or weak interfaces [15, 16]. In combination with preceramic papers, which typically have porosities of more than 30 %, defect-free multilayer structures could be achieved. Depending on the kind of applied tape, open porous structures as well as almost dense structures were obtained; in case of dense outer layer, the open pore structure of the paper layer could be enclosed [14]. In order to combine such tapes with already fired traditional refractory materials, the low-shrinkage tape A6 was chosen to minimise stresses during constrained sinter-

ing of such composite structures. The slurry, which had the function of a glue penetrated well into the cross-pattern during the joining process (Fig. 4) and generates an excellent cohesion towards the tape. Without the grid, the drying and sintering shrinkage caused complete delamination between glue and brick. Due to the grid, the anchoring of the glue on the surface of the brick is improved which keeps the composite together despite of the stresses occurring during drying and firing. Fig. 4 shows the good cohesion between ceramic tape and chamotte brick after firing.

3.2 Thermomechanical behaviour of ceramic-glass composites

Due to the properly adjusted glass substrate, all alumina-glass laminates could be joined without defects (Fig. 5). Additionally, the wettability of the glass on sintered alu-

mina was high enough to ensure sufficient interface cohesion. The stress-displacement curves (Fig. 6) show a different behaviour in dependence on temperature at which the flexural strength measurement is carried out. At temperatures up to 500 °C, which is below the glass transition region, a brittle fracture of the entire laminate occurs with flexural strength values between 300 – 350 MPa. Exceeding the glass transition temperature of 557 °C, the flexural strength decreases significantly, but a step-wise progression of the stress-displacement curve is observed. As the glass layer softens, the energy of the propagating crack is completely transferred into plastic deformation and therefore only the bottom layer under tension breaks. After further increase of the load, fracture of the remaining second ceramic layer occurs. The measured flexural strength decreases with increasing tem-



Fig. 7a–c Optical microscope images of fractured surfaces of ceramic-glass laminates after four-point bending test at: a) room temperature, b) 600 °C, and c) 700 °C

perature. As only one layer breaks, the fracture strength is significantly lower at temperatures above the glass transition region. In this temperature regime, the flexural strength ranged between 70–170 MPa depending on temperature and statistical flaw distribution of the individual specimens.

The fractured surfaces (Fig. 7) clearly state, that brittle fracture of the entire laminate occurs when the glass layer is in a rigid condition at temperatures below the glass transition temperature (Fig. 7a). When heated above the glass transition region the intermediate glass layer stops crack propagation and delays catastrophic failure which requires a further increase in load to initiate the crack through the second layer (Fig. 7b–c). Fig. 8 gives a more detailed view of a crack path in a composite, where loading has been stopped immediately after fracture of the first layer. In this case, the crack has entered the glass layer and is deflected inside this soft layer, before reaching the second ceramic layer. Therefore, such an intermediate glass layer is suitable to delay fracture, which can increase the life time of such a refractory structure. At higher temperatures, i.e. at lower viscosities, the glass layer could heal cracks or suppress crack propagation completely.

3.3 Thermal shock behaviour of laminates

Most of the monolithic multilayer dices endured multiple shocking at temperature differences up to 1200 °C. Every drop out of a sample was caused by interface delamination; all observed cracks were located near to the surface and did not lead to complete failure of the samples. Fig. 9 shows such laminates after four cycles of quenching from 1000 °C to room temperature in water. Beside samples without visible dam-

age and completely delaminated ones, also partial delamination occurred. This partial delamination always started at the edges and in many cases, these laminates dropped out by interface delamination some cycles later. At low temperature differences, no drop outs were observed up to 400 °C temperature difference (Fig. 10). By quenching at higher temperatures, the number of drop outs via interface delamination increases with increasing temperature. After quenching samples from 1200 °C to

temperature, the dropout rate decreased to 26 % in comparison to a temperature difference of 1000 °C, where about 42 % of all samples delaminated. Therefore, it can be assumed, that stresses which are generated during thermal shocking are partially released during the next heating cycle at such high temperatures.

The determination of Young's modulus after each thermal shock cycle also gives information about the damaged structure of the laminates after each shocking event.

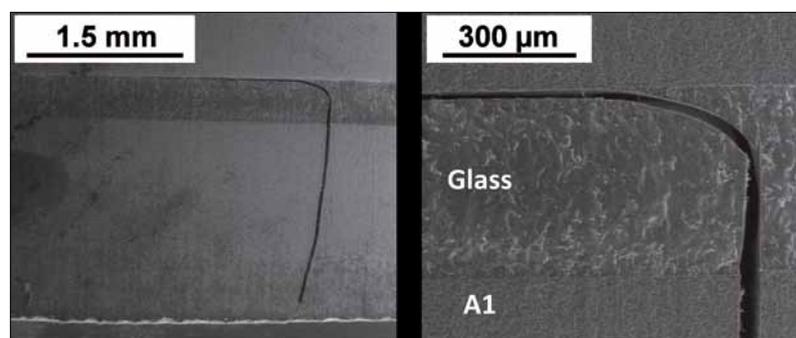


Fig. 8 Crack path in a ceramic-glass composite after flexural bending at 600 °C, where the sample has been removed immediately after fracture of the bottom layer



Fig. 9 Three-layer alumina laminates (A5) after fourfold downward thermal shock ($\Delta T = 1000$ °C, quenching in water): no visible damage (l.), partially delaminated sample (middle), completely delaminated laminate (r.)

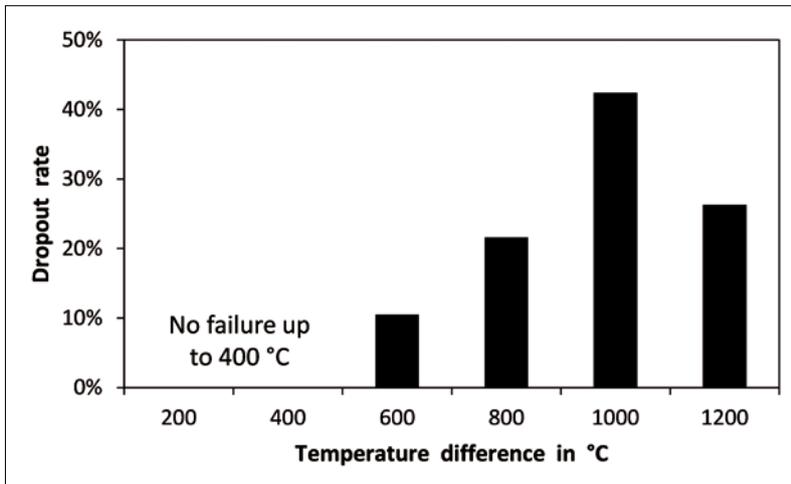


Fig. 10 Dropout rate of three-layer alumina samples (A5) after ten cycles of quenching in water with different temperature differences

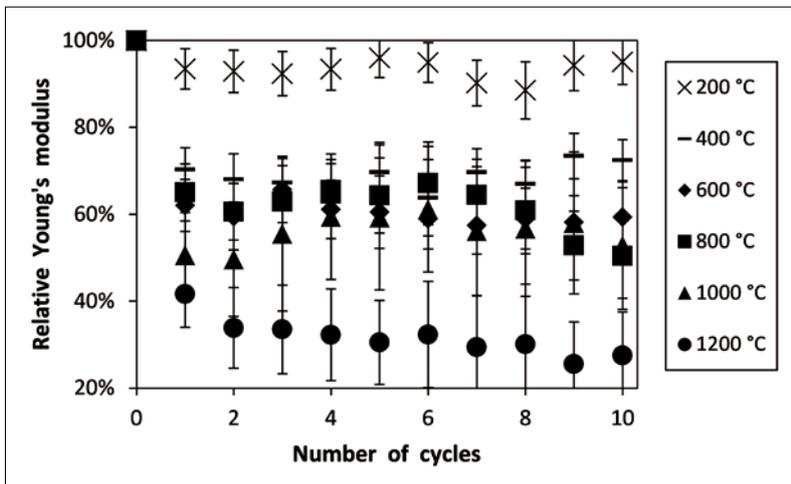


Fig. 11 Relative Young's modulus in in-plane direction of three-layer alumina laminates (A5) after up to 10 cycles of quenching in water with different temperature differences

Fig. 11 shows that the elastic modulus does not drop to less than 90 % of the original value when exposed to thermal shock with a temperature difference of 200 °C. At higher temperature differences between 400 – 1000 °C, similar values of relative Young's modulus between 50 – 60 % were

obtained. If the laminates are quenched after heating to 1200 °C, the relative elastic modulus ranges between 20 – 40 %. Comparing this result with the diagram of Hasselman [20], who measured the remaining strength of alumina samples after thermal shock at various temperature differences,

such a drop of properties can also be seen in Fig. 11. Following Fig. 11, the critical temperature difference, at which cracks are generated and partially propagate, causing a decrease in strength and also Young's modulus, is situated between 200 – 400 °C. Hasselman located this critical temperature difference between 300 – 350 °C for alumina. After the significant decrease in strength above this temperature difference, there is a regime with lower but constant strength where the present cracks behave subcritical and do not grow.

This area can also be found in this study at temperature differences between 400 – 1000 °C, where similar levels of Young's modulus were determined.

Above 1000 °C, a significant decrease in Young's modulus was observed which also corresponds to the strength curve of Hasselman. In this region, the crack length is too high and therefore the cracks can propagate and cause such a decline in strength and Young's modulus, respectively. These tests were conducted with monolithic laminates, which therefore do not contain residual stresses. The introduction of residual stresses would increase the thermal cycling capability.

The composites of traditional refractory brick and ceramic tape endured thermal shocking up to 800 °C without visible damage (Fig. 12). It is obvious, that partial delamination phenomena are present between the grid structures, but that the channels of the grid structure caused a form-locked joint with a strong cohesion between the layers. After quenching from 1000 °C to room temperature, this strong contact is partially lost and more delaminations appear, but the tape layer and the brick still stick together. After shocking at 1200 °C, the contact got lost completely and the tape layer fell off. The remaining parts clearly demonstrate the

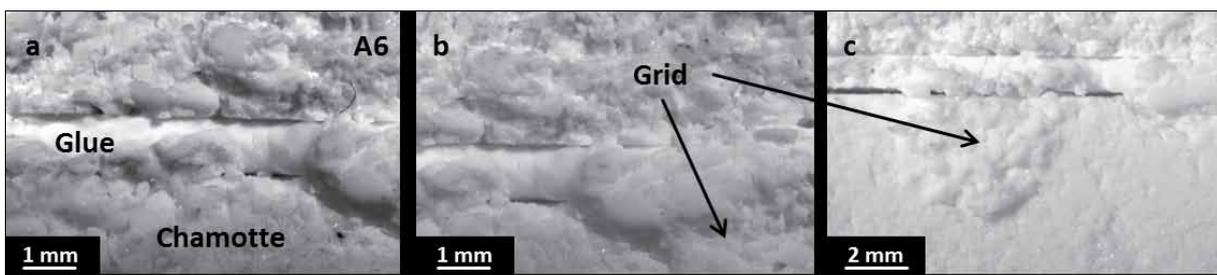


Fig. 12 Interface of a composite between alumina tape A6 and chamotte brick joint by means of a grid and a ceramic slurry as a glue, after quenching with temperature difference of: a) 400 °C, b) 800 °C, and c) 1000 °C

important role of the grid pattern for the strength of the joint between brick and tape (Fig. 13). On the one hand it is the form-lock joint of the slurry in the channels of the grid in the brick and on the other hand it is the good joining of the slurry with the tape which is responsible for the good interface cohesion. This concept of joining a fired brick with a green tape has potential for renovation of corroded refractories.

4 Conclusion

Using the tape casting process, fine and coarse-grained green tapes have been manufactured in thicknesses up to several millimetres. Dense sintering tapes as well as porous ones can be generated via intentional variation of the slurry composition concerning grain size distribution. By using four fractions of alumina, magnesia or zirconia powders with a maximum grain size of up to 1 mm, thick and highly porous tapes could be cast with very low shrinkage values between 1 – 2 %. Tapes with porosities up to 35 vol.-% exhibit low Young's moduli, which makes them interesting for high temperature applications where thermal shock resistance is a requirement. In order to manufacture thick laminates for refractory applications, multilayered structures of such tapes have been produced. The absence of carbon reduces the thermal shock behaviour; this can be compensated via residual stresses by introducing tapes of different thermal expansion or shrinkage behaviour in the multilayer structure. Investigations of the thermal shock behaviour show the potential of such multilayers. The thermal shock tests with monolithic 3-layer laminates revealed that the interface is the weakest point in such multilayer structures. On the other hand, such an interface can stop or deflect a crack propagating through the structure and therefore prevent catastrophic failure. This phenomenon was demonstrated by means of a glass layer between ceramic tapes. When the temperature increases above the glass transition temperature, this layer softens. In a 4-point bending test, a step-wise fracture of the laminate could be observed at elevated temperatures of 600 °C and higher. Macroscopic images showed that the crack entered the glass layer and that it was deflected at the interface on the opposite side, where it stopped after a few millimetres. Thus, such a structure offers the

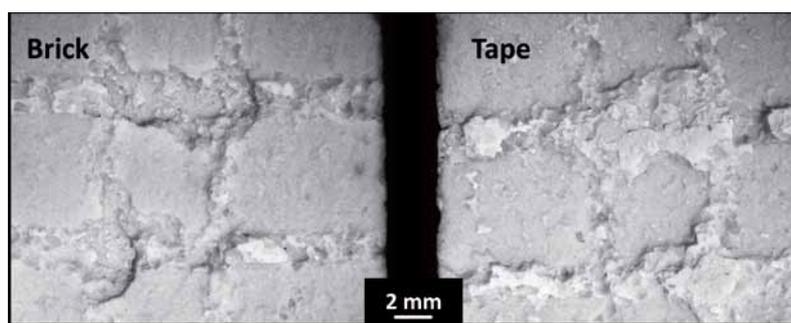


Fig. 13 Delaminated brick-tape composite after quenching at 1200 °C, left side: top view of brick, right side: top view of tape. The residues of the dried and fired slurry used as glue stick to the brick inside the grid pattern, at other positions the glue remained in contact with the tape

possibility to delay or even prevent catastrophic failure.

In order to evaluate the applicability of such novel planar refractories in combination with traditional refractory materials, an alumina tape has been joined with a chamotte brick using the corresponding alumina slurry as glue. A form-locked joint was generated via a grid-like pattern, which had been cut into the brick in advance. This laminate endured quenching without delamination up to 800 °C. A temperature difference of 1000 °C lead to partial delamination whereas the interface cohesion was completely destroyed after quenching from 1200 °C to room temperature.

In general, such novel multilayer structures have a great potential as refractory materials, because their assembly can consider the profile of requirement by placing tapes with the desired properties at the appropriate position in the multilayer stack.

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