Development of ceramic tapes for thermal shock resistant calcium aluminate refractory materials with graded porosity

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Abstract

The ceramic tape casting technology is used for the development carbonless refractories. For the tape casting process an aqueous slip of alumina, calcium carbonate and organic binder system is developed. Cellulose fibres are also added to the ceramic slip to generate an adjusted pore volume after sintering of the ceramic which is very important for thermal shock properties of the material. For the tape casting slip aqueous binders are used. The organic binder has a great influence on the flexibility of the green tape and also on the further processing properties of the tape, for example the tape lamination. The tape casting slips are characterised by viscosity measurement. The orientation of the cellulose fibres can be influenced by the casting speed and casting thickness. Ion beam preparation and scanning electron microscopy are used for the characterisation of the green tape microstructure. The mechanical properties of the green tapes are estimated by tensile strength measurements in dependence on the casting direction and on the fibres orientation in x-y-layer.

1 Introduction

The presented results were gained within an applicable basic research project which targets to the development of thermal shock resistant and carbon-free refractory components. Carbon-free refractories are applied in the production of steel because of their high oxidation stability. These materials are exposed to high thermo mechanical stresses. Selective micro-structuring and gradient structures regarding porosity and phase composition are utilized to improved thermal shock properties of the materials. The ceramic tape technology and the multi-layer technology can be used for fabrication of thermal shock resistant microstructures and ceramic components. Via lamination of green tapes with same composition or with different composition a multilayer structure can be built up. The combination of ceramic tapes with different pore volume generates graded properties in the refractory component. The formation of pores leads to lines of tension in the material. This increases the resistance to cracks [1]. Another advantage is that the pores act as defects which can absorb the thermal shrinkage and expansion in the material. Thermal shock experiments shows that the mechanical strength of porous materials decreases less compared to initial state of strength than it is of dense materials. Furthermore the pore shape and the orientation of the pores are very important for the mechanical and elastic properties [1, 2].

The development of ceramic green tapes plays a key role within the whole process chain of development of multi-layer refractory components. Tape casting is an established technique for large-scale fabrication of thin ceramic substrates. [3, 4] Such essentially two-dimensional structures in x and y direction can be processed by laminating to multilayered structures and so an increase in z direction is possible. [3, 4] Tape laminating can yield to components with graded structure by using tapes with different composition for example different porosity. The tape casting process requires a homogeneous, de-agglomerated casting slip which is prepared by mixing and milling of the ceramic powder in a solvent with different organic additives (dispersing agent and binder system). [5] The homogenous, evacuated slurry is cast using a doctor-blade with

exactly adjusted casting gap on a smooth belt. During the subsequent drying the solvent is evaporated and simultaneously the tape thickness decreases. The composition of the tape casting slip and its rheological properties influence the casting and drying behaviour. Otherwise the casting speed and the casting gap affect the drying of the tape and the microstructure of the dried green tape. The majority of tape casting slips contains organic solvents as dispersing liquid. [4, 6] Today there is a trend to move away from organic solvents towards water-based systems with the objective of lower costs in combination with environmental and health aspects. A disadvantage of water-based tape casting slips is the longer drying time of cast tapes compared with organic solvents based slips. [6]
A plurality of water-soluble or water-dispersible binders exists for application in tape casting, for example derivates of cellulose ethers, polyvinyl alcohols, acrylic polymers and acrylic polymer dispersions. In the present study we consider the use of polyvinyl alcohol and acrylic polymer dispersions as binders for the tape casting. The aim of the study is to develop and characterise ceramic green tapes with different content of cellulose fibres for the fabrication of ceramic multilayer components for refractory application. The refractory ceramic is the composite material calcium-aluminate/ alumina which is formed during an reaction sintering process from the starting powders alumina and calcium carbonate. By addition of cellulose fibres to the tape casting slip a defined pore volume after sintering is aspired. The orientation of the fibres (= pores after sintering) has a great influence on the thermal shock behaviour. The orientation of the fibres in the tape shall be influenced by variation of casting speed and casting gap width. Also high solid volume content (inorganic powders) in the slip and pseudoplastic flow behaviour are aspired to obtain uniform tapes with high green density. The binders system was adapted with regard to the lamination behaviour of the tapes in further processing. For the lamination of the tapes it is necessary to have a flexible tape and the binder system has to ensure a good adhesive bonding between the tapes after lamination process. The green tapes were characterised by tensile strength measurements in dependence on the casting direction of the tapes. In this way it is possible to get information about the influence of fibres orientation on the strength of the green tapes.

2 Experimental Procedures

2.1 Materials and slip preparation

An alumina powder (A-16-SG from Alcoa) and calcium carbonate (M/Alfa) were used. The weight ratio of alumina to calcium carbonate was 9:1. Cellulose fibres (Fluka) with a length between 20 and 150 µm were used. The amount of cellulose fibres was 2, 4, 6 and 8 wt.-% refer to ceramic powder. As dispersing agent for the slip dispersing the product Dolapix CE64 (Zschimmer&Schwarz) was used. With this dispersant a homogenous, stable slip with high solids content is reached. For the development of the binder system binders and plasticizers in different amounts were tested: the polyvinyl alcohol Mowiol 20-98 (from Kuraray Europe GmbH), the acrylic polymer dispersion Primal™ ECO 8 (Rohm and Haas) and plasticizers glycerine and polyethylene glycol 400. In most cases a mixture of polyvinyl alcohol, acrylic polymer emulsion and plasticizer was used with an amount of 16 to 18 wt.-% refer to ceramic powder. Also defoamer and surfactant were used as further organic additives.

For slip preparation firstly the alumina and calcium carbonate powders were mixed and de-agglomerated in aqueous suspension in a planetary ball mill for one hour. Dispersant and defoaming agent were also added to the suspension. After the milling process the suspension is homogeneously and highly dispersed and it has a solid content of about 80 wt.-%. After addition of fibres, binders, plasticizer, surfactant and defoaming agent the suspension was treated in a ball mill for 15 hours. After this treatment the slip has a solid content of about 60 wt.-% and the pH is 9. The slip was de-aired by gently stirring under vacuum before casting.

2.2 Tape casting

For the tape casting experiments a laboratory equipment were used. This discontinuous tape casting machine has a moveable doctor blade and the slip is casted upon a stationary polymer carrier. During the drying it is possible to regulate temperature and humidity of the air flow over the wet film of slip. Thereby the risk of skin formation and cracking can be reduced, because the drying air has been saturated with solvent vapour when it meets the wet film of slip. The tape casting experiments were made at speeds from 3,5 mm/s to 27 mm/s. Casting gap width was varied in the range of 0,6 to 3 mm. The thickness of the green tapes was measured.

2.3 Characterisation methods

The viscosity of the tape casting slips was measured with the rheometer Physica Rheolab MC100 (Anton Paar GmbH) using the rotating measuring system Z3 DIN. The shear rate was stepwise altered between 1 s^{-1} and 100 s^{-1}. The shear stress under the blade gap during tape casting is to be expected also in this range.

The tensile strength of the green tapes was measured by using the tensile testing machine "inspect retrofit" (company Hegewald&Peschke). Tape samples with dimensions of 20 mm x 4 mm x tape thickness (length x wide x tape thickness) were used for these experiments. The given values are the real stress dimensions. The samples have an allowance for the clamping in the machine. The testing speed was 1 mm/min.

The correlation between the casting speed and the fibres orientation in the tape were was evaluated by scanning electron microscopic images. The specimens for SEM study were treated by ion beam preparation.

3. Results and discussion

3.1 Rheological measurements

The rheological properties of the different slips were characterized by viscosity measurements. Fig. 1 shows the influence of the fibres addition to the slip viscosity. The viscosity rises with increasing fibre content in the slip. All prepared slips exhibit pseudoplastic flow behaviour.

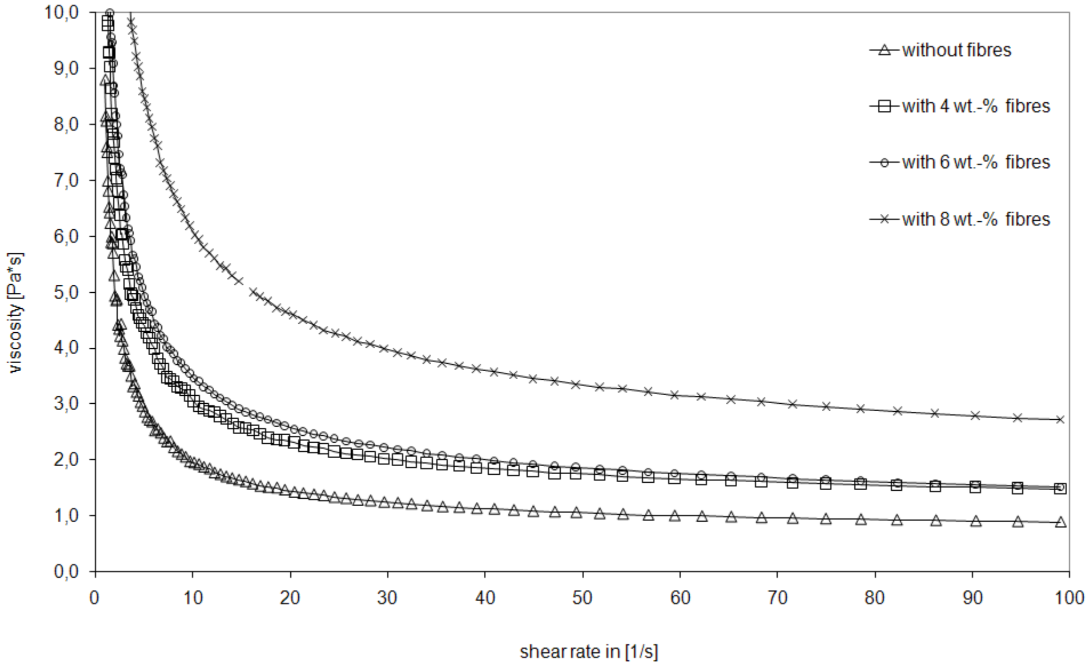

Fig. 1: Viscosity curves of tape casting slips with different content of cellulose fibres

3.2 Tape casting

In the tape casting experiments slips with binder systems in different contents were studied. Defect-free tapes are producible, both to the slips without fibres and to the slips with different fibre contents, with suitable content of binder system. The green tapes were easy to release from the carrier foil and they are flexible. The microstructure of green tapes is shown in Fig. 2. Both specimens were prepared vertical to the casting direction of the tape. The left image shows the tape which was cast with 3,5 mm/s and the right image with 27 mm/s. Both tape specimens were cast with gap width of 1,2 mm. The SEM images show that there is no significant influence of the casting speed on the orientation of the fibres. However it can be seen that the fibres are orientated mostly in casting direction. Only a few are orientated not along the casting direction. These fibres lie transversely in the matrix and they are cut in cross sectional area during ionic beam preparation.

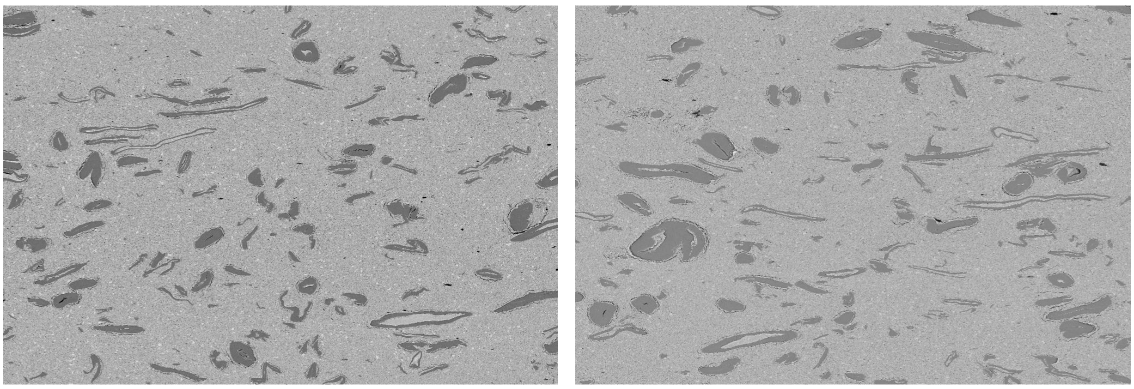

Fig. 2: SEM images of green tapes with different casting speeds (left: casting speed 3,5 mm/s, right: casting speed 27 mm/s)

3.3 Tensile testing

The strength measurements are evaluated by means of stress – strain – diagrams. In Fig. 3 the results of tensile tests of green tapes from one batch without fibres are demonstrated which were stressed in casting direction.

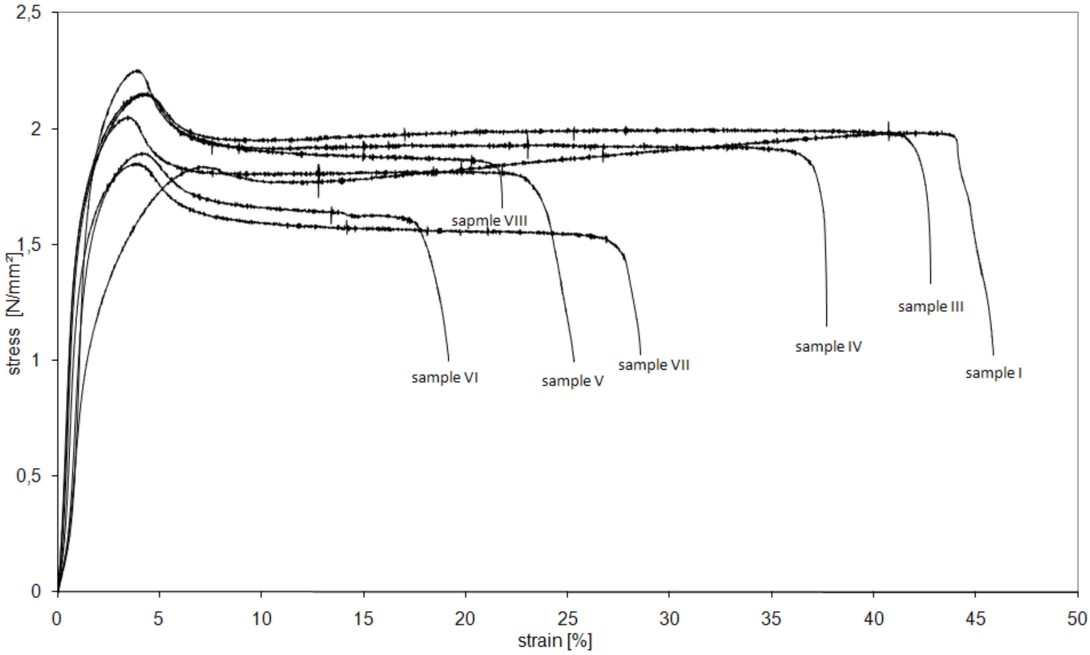

Fig. 3: tensile stress-strain-diagram of specimens stressed in casting direction without fibres

In the first section of stress-strain-curve the tapes show purely elastic properties. After initial elastic section the tapes reach the upper yield point/tensile strength and the specimen show plastic flow behaviour. This characteristic is determined by the binder system and conforms to the pure synthetic polymer material.

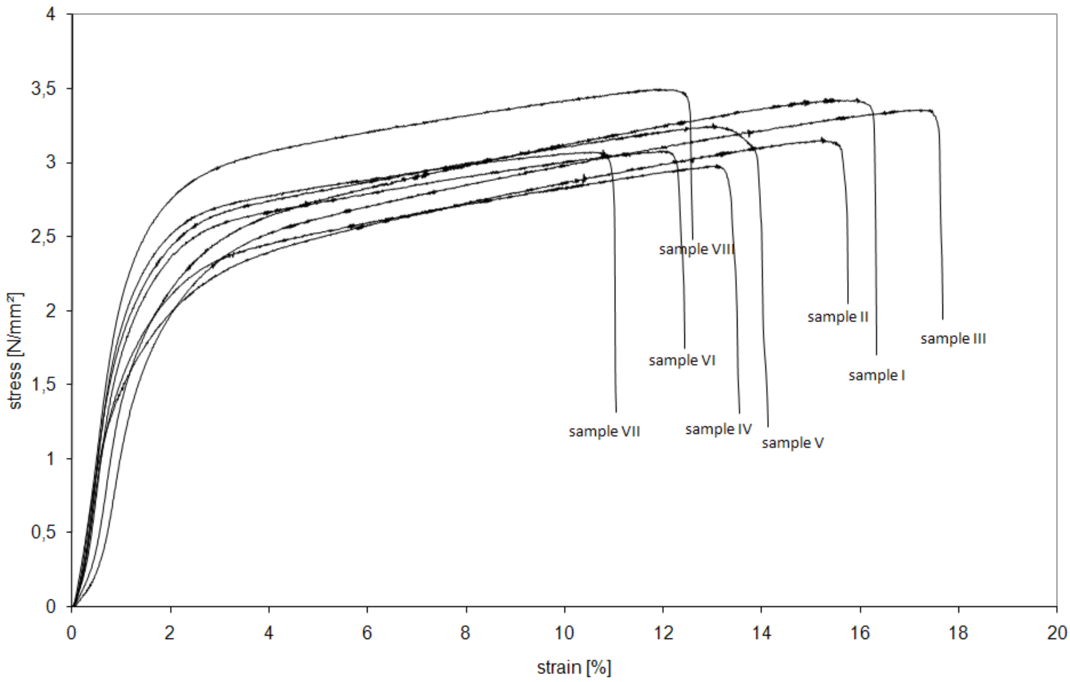

Fig. 4: tensile stress-strain-diagram of specimens stressed in casting direction with 8 wt.-% fibres

Fig. 4 shows the stressed specimens from one tape batch with 8 wt.-% fibres. The specimens were tested in casting direction. In comparison to the Fig. 3 the tape specimens show a stress increase. An explanation for this behaviour could be that the binder sticks at the fibres and therefore an additional force occurs. Due to the strength of the fibres the force constantly increases up to the crack of the tapes.

Fig. 5 shows the comparison of the tapes without fibres and tapes with 4 and 8 wt.-% fibres in the tensile stress measurements. A comparison between the specimens with 4 and 8 wt.-% fibres show that higher fibres content leads to higher strength (through resistance to cracking of fibre) and the strain decreases. For the specimens without fibres it can be seen that the polymer chains of the binder have a large influence to the behaviour of the tapes. Specimens with fibres are only limitedly elastic.

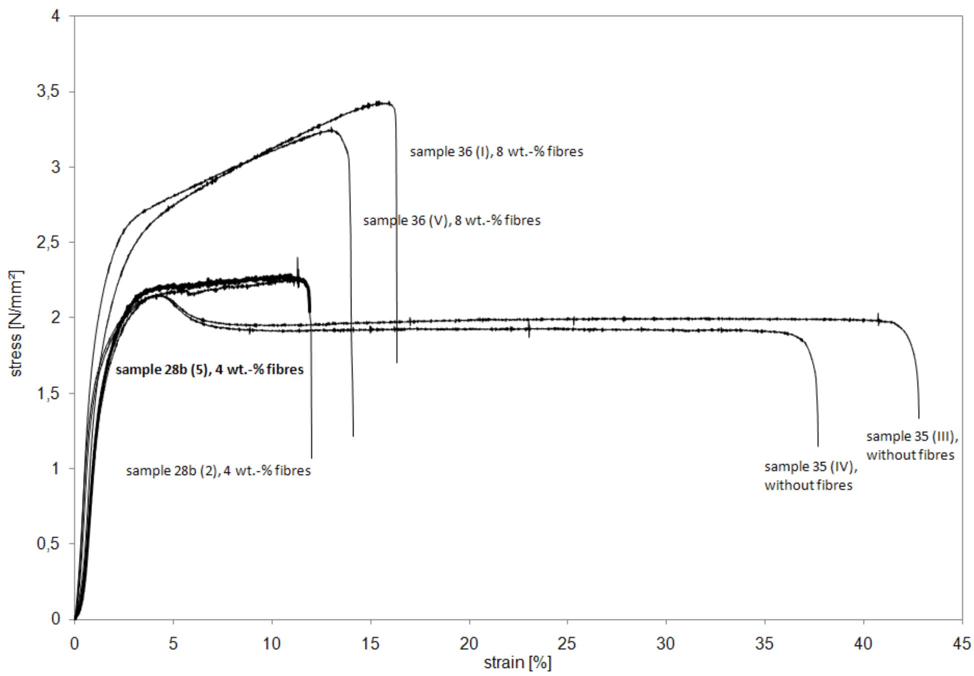

Fig. 5: tensile stress-strain-diagram of specimens stressed in casting direction; comparison between tapes without fibres and tapes with 4 and 8 wt.-% fibres

Furthermore green tapes were stressed across the casting direction. In Fig. 6 results of tensile testing of the tapes with 8 wt.-% fibres are represented. The behaviour of the tapes across the casting direction corresponds approximately to the behaviour of tapes without fibres. Fibres across to the casting direction have only a little influence to the strength of the tapes. The slightly increase of the strength is given through the orientation of few fibres also across to the casting direction.

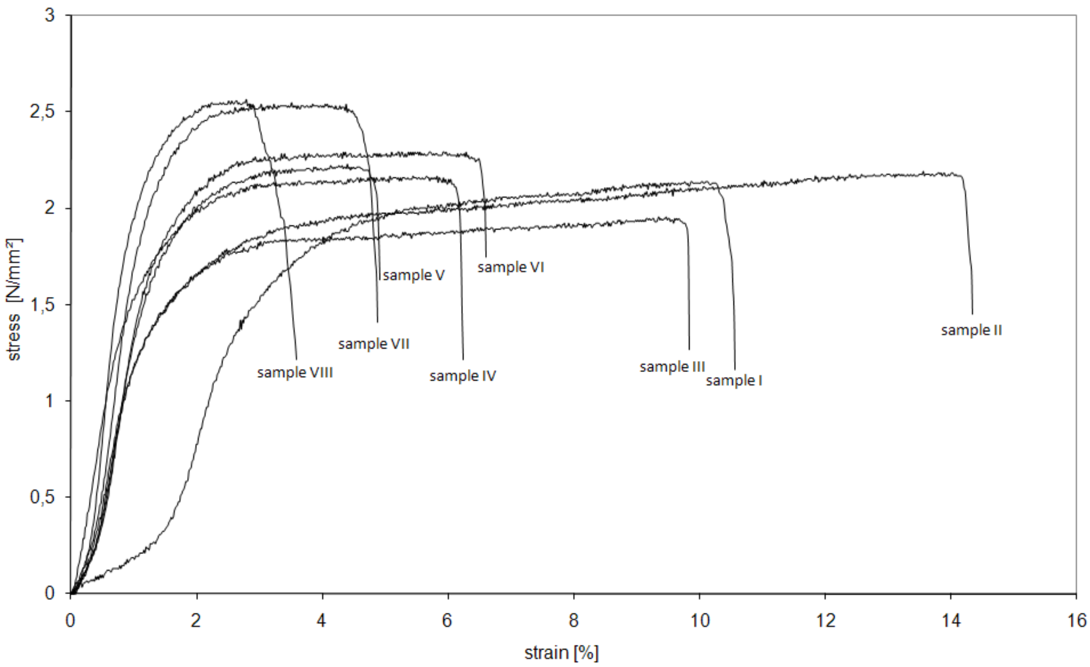

Fig. 6: tensile stress-strain-diagram specimens stressed across casting direction with 8 wt.-% fibres

Conclusion

With the tensile tests it could be shown that the fibre content influences the tensile strength in casting direction. Across the casting direction there is no significant impact to the tensile strength through the fibre in the tapes and this is comparable with tapes that contain no fibres. The tensile strength is extremely important in terms of the following process steps of the green tapes like lamination or deformation. Further investigations in this project will be the fabrication of laminates of green tapes to graded multilayer components which will be presented at this conference with the title "Lamination techniques for new multilayer for thermoshock resistant refractories based on the material system calcium-aluminate ".

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