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Short communication

Reinforced composite sealants for solid oxide fuel cell applications

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ABSTRACT

Glass–ceramic sealants are commonly used as joining materials for planar solid oxide fuel cells stacks. Several requirements need to be fulfilled by these materials: beside of electrical insulation and appropriate thermal expansion, a good adhesion on the ceramic and metallic components of a SOFC stack is necessary to form a gas-tight joint. Even though the joining process might have been successful, failures and leaks often occur during the stack operation due to fracture of the brittle material under thermal stresses or during thermal cycling of the components. This study focusses on composite materials consisting of a glass matrix based on the system of $BaO–CaO–SiO_2$ and various filler materials, e.g. yttria-stabilized zirconia fibres or particles and silver particles. In order to evaluate a possible reinforcing influence of the filler material of the composite, tensile strength tests were carried out on circular butt joints. The highest strength values were found for the composite material with addition of silver particles, followed by the glass matrix itself without any filler addition and the lowest values were measured for the composite with YSZ particles. SEM investigations of cross-sections of the joints elucidated these results by the microstructure of the glass-ceramic sealants.

1. Introduction

When progressing from a SOFC stack test with a limited amount of repeating units to a system with submodules of several kilowatts, the need for a reliable and hermetic sealing material obtains a high priority. Glass–ceramic sealants have proven to be a good choice to fulfill the requirements of adaptation of thermal expansion, electrical insulation and chemical stability in oxidizing and humid reducing atmospheres [1,2], but the brittle behaviour and the weak interfaces to the joining partners are still a significant disadvantage of the concept. A leakage of a stack often would not stand out, as the joining and initiation might take place in the similar electrically heated furnace before the long-term operation of the stack starts. Many test benches does not monitor the gas tightness and a small leakage of hydrogen would burn in the furnace atmosphere without a noticeable increase of the stack temperature or a decrease of the open cell voltages. Problems arise when transferring the stack to be adapted to a system that allows only a limited leakage rate [3]. It was demonstrated that the thermal stresses induced by the stack operation conditions of the Juelich F20 stack design lead to cracking of the glass–ceramic sealants. Therefore the need of an improved glass sealing becomes obvious and from material scientific point of view a reinforcement of the sealing material seems to be an appropriate option to solve the problem. The glass sealant as the weakest part of the stack could be improved using a composite material. Several filler e.g. YSZ ceramic powder and fibre, silver powder as ductile material are investigated as additives for a glass matrix based composite in this study. These materials have proven the applicability as sealing material for SOFCs by joining and thermal cycling tests, but it was not possible to evaluate the influence of the filler addition by these tests. The aim of this study is to differentiate between the composite materials and to substantiate a possible reinforcement mechanism by the addition of fillers to the glass–ceramic sealing materials. The chosen filler materials offer diverse possibilities for a reinforcement of the brittle glass material. The YSZ particles are expected to behave as a crack deflecting barriers, while the YSZ fibres will change the crack pattern due to the different length-to-diameter ratios and a possible fibre pull-out mechanism. The ductility of silver particles can help by bridging microcracks and stopping of crack propagation.

2. Scientific approach

Conventional analytical techniques for the evaluation of joining behaviour of glass–ceramic sealants do not allow a distinct classification of different materials concerning their ability to withstand thermal stresses. As it is not possible to test each material combination in a real stack test, a simple test method needs to be set up to evaluate the strength of glass–ceramic joints with a high sensitivity of the method and good reproducibility of the results. The difficulties of tensile strength measurements of brittle joints

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Table 1
Chemical compositions of the investigated glass composition in wt.%.

	BaO	SiO_2	CaO	Additions
Glass H	48.2	29.8	6.1	Al_2O_3, B_2O_3, V_2O_5, ZnO

are the prevention of any bending moment or shear force in the testing equipment and an exact sample preparation allowing to obtain a set of uniform samples. For that reason, new adapters were constructed with a flexible wire allowing the axial adjustment of the circular butt joint sample. The sealants were applied by screen printing to the metallic surfaces and it was possible to gain a homogenous and final form-fitting layer.

3. Experiments

The composite materials used in this study consist of an amorphous glass matrix with YSZ powder or YSZ fibres as ceramic fillers and silver particles as ductile metal filler. The zirconia powder was distributed by Unitec Ceramics (Stafford, UK) and was an yttrium stabilized zirconium oxide with small impurities of hafnium oxide. The powder had a median particle size of 15 μm. The fibre material used was produced by Zircar Zirconia Inc. (Florida, USA) and was distributed under the name ZYBF-2. It was modified by milling in an agate ball mill to shorten the fibre length before preparing the composite material. The silver powder was an Alfa Aesar product with a grade of purity of 99.9% and an average particle size between 0.5 and 1 μm. The glass matrix was based on the ternary system BaO–CaO–SiO_2. The glass was molten from a batch of pure carbonates and oxides in an inductively heated platinum crucible at 1480 °C. The raw materials were distributed by Merck KGaA (Darmstadt, Germany) and had a grade of purity higher than 99%. After a dwell time of 2 h the melt was quenched by pouring into ice water, rinsed with acetone and dried in a heat chamber at 60 °C. For a better homogenization of the glass, the melting procedure was carried out twice. The glass frits were wet-milled in acetone in an agate ball mill to a median particle size of 10–13 μm. The chemical composition was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES), the results are shown in Table 1. Compared to commonly used glass–ceramic sealants, Glass H is a typical invert glass and has a rather low silica content with additions to decrease the viscosity and to improve the wetting behaviour.

For the composite material, three mixtures were prepared of the glass with 20 wt.% of YSZ powder, 13 wt.% modified YSZ fibres or 20 wt.% silver powder. For better homogenization, the mixtures were agitated in a mechanical shaker for 30 min.

In order to investigate the tensile strength properties, circular butt joints of two steel plates of an outer diameter of 36 mm were joined with the composite sealants. High chromium containing ferritic steel was used in this study (in wt.%: 20–24 Cr, 0.3–0.8 Mn, 1–3 W, 0.2–1 Nb, 0.04–0.2 La, 0.02–0.2 Ti, bal Fe, produced by Thyssen Krupp VDM under the name Crofer22H [4]). The steel circles were ground using BN grit (125 μm), and both of them had an internal thread of 8 mm in the centre. For the application of the glass, the powder was blended to a paste, using ethyl cellulose as binder in terpineol. The paste was then dispensed by screen printing to the steal surface. Before dispensing the glass, the steel samples were cleaned in ethanol in an ultrasonic bath for 10 min and subsequently rinsed with acetone. The glass paste was applied with a ring contour of 32 mm external diameter and 12 mm internal diameter to one of the metallic circles. In order to maintain a minimal joining gap, small zirconia chips of a thickness of 0.14 mm were put on the uncoated outer part of the steel plate. The joining of the sample was carried out by placing a dead load of 1000 g on top of the second steel plate and heating up to 850 °C in a resistance heated chamber furnace in air. The samples were cooled to room temperature at a rate of 2 K min^{-1}. For the tensile strength measurement, ten samples of each materials combination were positioned by wire adapters to a universal testing machine with a maximum test range up to 500 kN and were disrupted with a load sensor of 10 kN and a traverse of 2000 μm. One of each sample combination was epoxy-mounted and sectioned. The cross sections were analyzed by optical and scanning electron microscopy (Cambridge Stereoscan 360) with energy dispersive X-ray analysis (Oxford) at an operating voltage of 20 kV. In order to analyze the gas-tightness, sandwiched samples of two steel plates of the size 50 mm × 50 mm were joined with the glass itself and the composite materials. One of the steel squares had a drill hole of 10 mm in the centre, allowing to check the gas tightness by He-leakage detection (UL200, Inficon) at a difference in pressure of 1000 mbar.

4. Results

4.1. Joining tests and microstructure characterization of the joints

For a straight-forward approach to evaluate sealing materials, sandwiched samples with two square steel plates allow a macroscopic overview on the applicability of a glass–ceramic material. It is possible to assess the gas-tightness, adhesion, viscous flow during joining and electrical insulation of the sealant, offering the possibility to evaluate the microstructure in a follow-up examination on the cross-section. Many glass–ceramic sealants failed even with this simple test set-up. But for the successfully inspected materials of this experiment the question arises, of which of them is better than the other. For that reason, strength measurements were planned and knowing that tensile stresses are most detrimental for glass–ceramics, focus was given on tensile strength measurements of joined samples.

All the four materials reported in this study showed low helium leakage rates smaller than 10^{-9} mbar l s^{-1} for the sandwiched samples joined at 850 °C for 10 h. The measurement of such a low value has proven an excellent gas tightness of the sealants. All of the materials would fulfill the requirements for stack operation with a relative leakage rate of hydrogen below 1% of fuel utilisation.

Microstructural analysis was carried out with scanning electron microscopy on cross-sectioned and polished samples together with energy dispersive X-ray analysis.

The microstructure of a joined sample of Crofer22H with the glass matrix without any filler addition is presented in Fig. 1. The remaining porosity of the sample was low, showing the compaction of the material during the viscous sintering process. The formed pores were not round, which was a consequence of the crystallization of the glass starting early during the viscous sintering process. Crystallites growing close to the pores tend to fill the voids and the compression of the partially crystallized fluid during the joining resulted in a flattened or elliptical form of the pores. With higher magnifications the microstructure of the glass–ceramic could be analyzed more in detail, showing a high degree of crystallization. The residual glass phase in light grey contrast was filling a network of barium aluminium silicates formed by the dark grey needles. The binary barium silicates formed small white blocks of a size between 5 and 10 μm and with a median grey contrast the ternary Ca–Ba-silicates agglomerated to spheres of a size of 10–40 μm.

The cross-sections of a YSZ particle reinforced composite on basis of glass H are presented in Fig. 2. An increased porosity with large voids up to 30 μm in diameter was noticeable. The pores were of a spherical shape, allowing the conclusion that the viscosity of the glass matrix was sufficiently low at the joining temperature. The crystallization of the glass matrix was at an early stage after 10 h heat treatment at 850 °C. Against the common expectations of adding nucleation sites by the filler material, the zirconia parti-

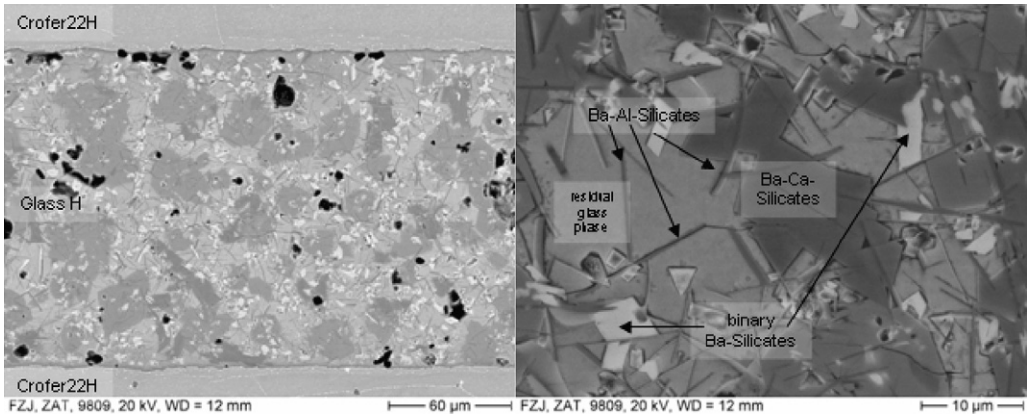

Fig. 1. SEM image of cross-sections of circular butt joint of Crofer22H with glass matrix H after a heat treatment at 850 °C for 10 h. Overview on the left and magnification on the right.

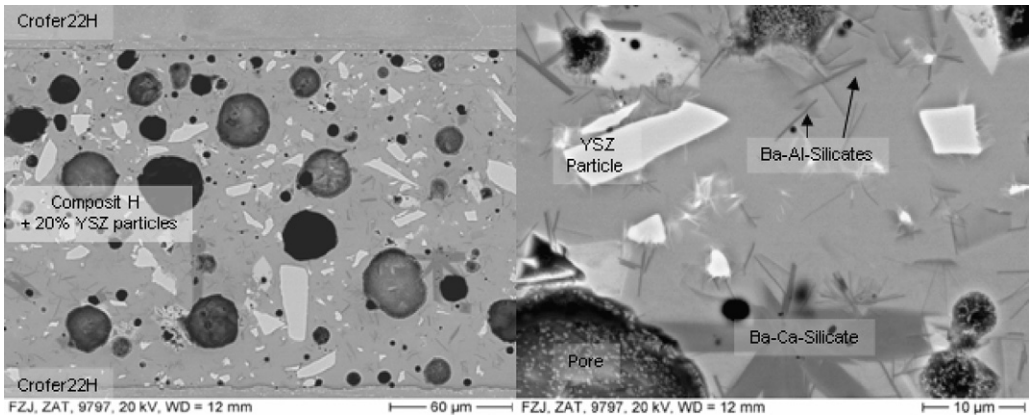

Fig. 2. SEM image of cross-sections of circular butt joint of Crofer22H with a composite of glass H and 20% YSZ particles after a heat treatment at 850 °C for 10 h. Overview on the left and magnification on the right.

cles (sharp white blocks) suppressed the crystallization. Small dark needles of barium aluminium silicates were formed, the amount of binary Ba-silicates or ternary Ba–Ca-silicates was very low and in correlation to these findings, and the amount of residual glass phase was high. These findings were in good correlation to previous tests reported in [5].

The YSZ fibre reinforced composite material of glass H is presented in Fig. 3. The overview on the left shows some microcracks in the joint, which probably have been formed during the metallographic preparation of the joint. Although the samples were carefully embedded in epoxy resin and cut by diamond wire saw, cracking of the glass–ceramic cannot be avoided in all cases. Compared to the particle reinforcement, the porosity was lower and comparable to the macrostructure of the glass matrix without filler addition. The cross-section showed the anisotropic orientated fibre materials sectioned lengthwise and crosswise. The original fibre material was a fine-grained, hollow and fibrillar material, which was infiltrated by the glass matrix. The crystallization of the glass matrix was at a similar stage like the YSZ particle reinforced sample with beginning crystallization of celsian phases and binary Ba-silicates and high amount of residual glass phase.

The cross-section of a sandwiched sample of Crofer22APU with a silver particle reinforced glass H is presented in Fig. 4. The overview showed a moderate porosity of the joint. The spherical shaped silver particles were partly agglomerated, pinpointing the possibility of optimization of paste preparation. Similar to the above mentioned reinforced composites, the amount of residual glass phase was high. In contrast to the composites with YSZ filler, no dark needles of barium aluminium silicates were formed, but a comparatively higher amount of block like crystals of binary Ba-silicates. Good wetting of the silver particles by the amorphous glass was observed.

In theory, the addition of a rigid filler material should increase the viscosity of a fluid. Thus it can be expected that the viscous sintering process of the composite sealants will be affected by the additives. Comparing the joining gap of the glass matrix without filler (154 μm) and the gap of composite with YSZ particles (163 μm) and with YSZ fibres (241 μm), an increase of viscosity for the fibre reinforced material could be observed. A minimum gap of 140 μm thickness was given by the experimental set up and it can be assumed that the glass matrix was blocked by the distance spacers. The particle reinforcement with rather small particles of a median particle size of 15 μm seemed not to influence the viscous settling as much as the fibre material, which could cause a sterical hindering of the viscous flowing. The gap of silver particle reinforced composite could not be directly compared to the above values as the sample set-up differs and the comparable data were not yet available.

4.2. Tensile strength measurements

Glasses and glass–ceramic materials are well-known to be easily destroyed when suffering tensile stresses. When using glasses as sealing materials, reaction layers are formed along the interface to the steel or cell components, which can also influence the stiffness of the joint. In order to estimate the overall strength of the connection between glass and steel, a set-up of two metal rings was

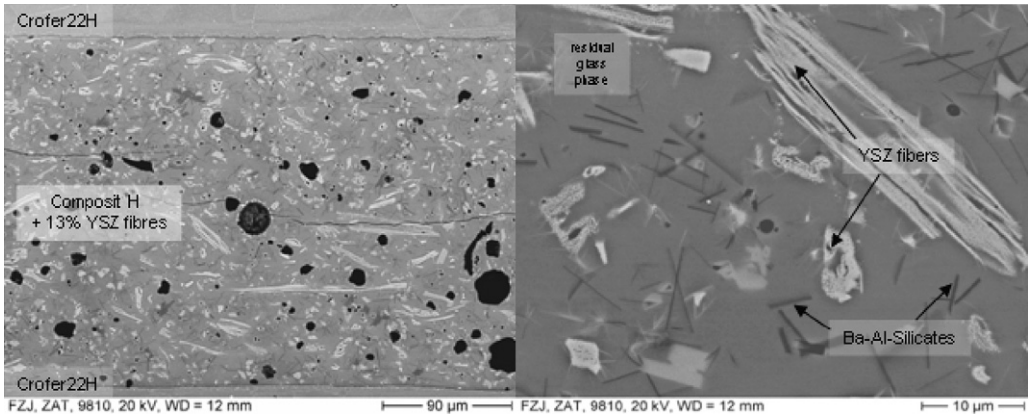

Fig. 3. SEM image of cross-sections of circular butt joint of Crofer22H with a composite of glass H and 13% YSZ fibres after a heat treatment at 850 °C for 10 h. Overview on the left and magnification on the right.

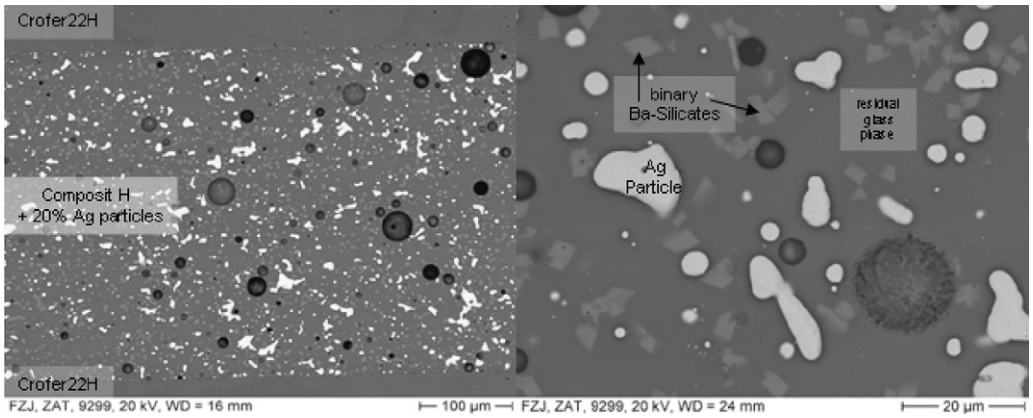

Fig. 4. SEM image of cross-sections of sandwiched samples of Crofer22APU with a composite of glass H and 20% silver particles after a heat treatment at 850 °C for 10 h. Overview on the left and magnification on the right.

Table 2
Arithmetic mean of tensile strength of ten circular butt joints of Crofer22H with glass matrix and three different reinforcement additives after heat treatment at 850 °C for 10 h.

	R_m (N mm^{-2})	Standard deviation	Rel. std. deviation
Glass matrix H	3.80	0.03	0.8%
Composite H + 20% YSZ powder	2.90	0.03	1.1%
Composite H + 13% YSZ fibres	3.18	0.03	0.8%
Composite H + 20% Ag particles	5.2	0.29	5.6%

chosen, which we re joined with the glass–ceramic sealants. For the first set of experiments the joined area was kept very small to resemble the original width of joints used for sealing of SOFC stacks and to keep the length to cross section area as large as possible [6]. Unfortunately the results of these tests had shown a rather high relative standard deviation of about 25% of their mean strength values, not allowing to significantly distinguish the strength of different materials. The set-up was improved by increasing the joining area and by reducing the bending moment of the sample adapter to the testing machine. The latter was achieved by inserting a wire rope of 4 mm in diameter between the fixing units of the sample and the testing machine. The wire rope was brazed by a nickel based hard solder to the stainless steel adapters.

The results for the improved tensile strength measurements are summarized in Table 2. The smallest values for the tensile strength R_m were obtained for the composite of glass H with YSZ particle addition, closely followed by the data for YSZ fibre reinforcement. The highest tensile strength was achieved for the silver particle reinforced composite with a significantly higher value compared to the glass matrix H without filler addition. The increased standard deviation of the silver reinforced composites can be explained by the need to change the testing set-up during the measurement of this series. The metal brazed joints of the wire rope of the adapter failed during the strength measurements and a short term improvisation lead to a more rigid testing set-up at the expense of reproducibility of strength values. Nevertheless the results allowed a significant statement on the increased strength values of this material.

5. Discussion and conclusion

When interpreting the tensile strength values for the four different sealing materials, it is astonishing that the strength for the glass matrix without any filler is higher in comparison to the ceramic reinforced composites. The expectation would have been a small value for the matrix and an increase of strength by the addition of filler material. These findings can be explained by the microstructural characterization of the joints. All the four sealants were

subjected to the similar heat treatments and joining conditions and should resemble the status "as joined". However, the resulting microstructure of the joints was dissimilar. The glass matrix showed a highly crystallized state and a low porosity. Due to this the joint had different possibilities to deflect micro cracks compared to the joints with ceramic fillers with a high amount of residual glass phase allowing an unhindered crack growth. Therefore a higher strength value for the glass matrix could be explained by the difference in crystallization progress. For a distinct clarification of this phenomenon, further experiments will have to be carried out on thermally treated and fully crystallized glass–ceramic composites. The differences between the two different types of ceramic reinforcement can be interpreted by two different explanations. The slight differences of the strength value can be ascribed to the reinforcement by the fibre material or to a weakened joint due to the increased porosity of the YSZ powder reinforced material. To increase the density of the joint and to avoid the porosity, the particle size of the powder materials and the temperature and time for joining would need to be changed, which would also affect the crystallization progress of the glass matrix and as consequence, results would not be comparable anymore. The expectation to increase the strength by addition of ductile filler particles like silver was fulfilled by the measured data. During crack growth the tensile ductility of the filler particles could stop the progress and partially absorb the stresses.

To assess the results of this study, the silver reinforcement showed the highest values for tensile strength and good joining properties concerning a low porosity and slow crystallization behaviour. Future experiments will focus on tensile strength measurements of thermally aged samples, furthermore the influence of thermal cycling will be investigated.

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