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Symmetric shear test of glass-ceramic sealants at SOFC operation temperature

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Abstract Glass-ceramics of the $BaO–CaO–Al_2O_3–SiO_2$ system are frequently used in planar solid oxide fuel cells (SOFC) stacks to seal the fuel and air compartments and to join non-conductively the individual components. Due to the thermal mismatch of the ceramic and metallic materials in the stack, the seals experience predominantly shear stresses. A symmetric shear test has been developed to characterize the critical shear stress of the glass-ceramic at SOFC operation temperature. Specimens representative for the seal situation in an SOFC stack were prepared, using the glass-ceramic to join a center piece of a NiO-YSZ anode covered by yttria-stabilized zirconia (YSZ) electrolyte layers on both surfaces between two Crofer22APU interconnect steel blocks. Shear stress and based on a rheological model, shear modulus and viscosity of the sealant were determined. The investigations showed that the sealant exhibits viscous shear deformation at 800 °C, a temperature typical for SOFC operation. The influence of increasing crystallization on the shear deformation is demonstrated.

Introduction

Solid oxide fuel cells (SOFC) are highly efficient energy conversion devices, producing electricity by the controlled electrochemical reaction of oxygen with a fuel gas, such as hydrogen or methane. Efficiencies of more than 50% render SOFCs very promising for stationary power plants as well as for auxiliary power units in mobile applications [1]. Research and development activities on SOFCs at Forschungszentrum Jülich (FZJ) concentrate on a planar design concept that offers high surface, volumetric and gravimetric power densities. Standard cells to be used for SOFC stacks comprise thick anode substrates of Ni/yttria-stabilized zirconia (YSZ) cermets, thin YSZ electrolytes and lanthanum-strontium-iron-cobalt or lanthanum-strontium-manganite cathodes. These cells are embedded in metallic frames of a high chromium (22 wt.%) ferritic steel and are stacked in serial mode using bipolar metallic interconnects of the same ferritic steel [1].

In the FZJ-SOFC design frames and interconnects are joined by a hermetically gas-tight and electrically insulating seal. Glass-ceramics have proven to be appropriate materials for this application. Currently variants of the BCAS ($BaO–CaO–Al_2O_3–SiO_2$) system are used for joining the dissimilar and similar materials, i.e., ceramic cells, metallic manifolds, and metallic interconnects. Besides electrical insulation and gas-tightness, these sealants should also possess a satisfactory matching of the thermal expansion coefficient (CTE) with the ceramic cell and steel components [2].

The slight differences in thermal expansion $\Delta\alpha \sim 10^{-6}$/K) of the materials and components comprising the planar SOFC arrangement of a stack generate residual stresses in all stack components. The residual and operation stresses endanger the mechanical integrity of the sealant, which ultimately might terminate the stack lifetime. In order to characterize mechanically seals of planar SOFC stacks (Fig. 1), shear deformation tests appear to have highest relevance. Note that other deformation and failure modes

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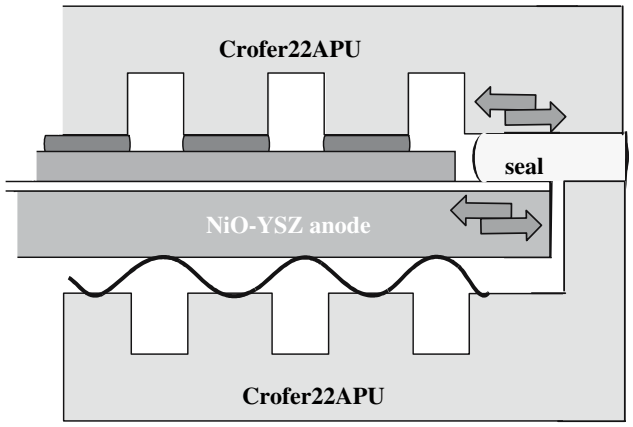

Fig. 1 Schematic drawing of the seal geometry in a planar design of SOFC stacks at FZJ. Shear stresses develop between interconnect steel and cell

have less importance, since the stacks and seals are kept under predominantly compressive load during operation.

It is the goal of the present work to characterize a specific glass-ceramic sealant used for SOFCs with respect to shear behavior at operation temperatures (~800 °C). The tests were carried out with a specially developed symmetric shear test specimen. Shear stresses are given for specimens as joined and after additional crystallization time of the glass-ceramic. In addition, on the basis of a rheological model, shear modulus and viscosity are determined.

Experimental

The sealants used for the investigations are based on the BaO–CaO–SiO_2 system [2]. The glasses were melted in an inductively heated platinum crucible at 1,480 °C from batches of pure carbonates and oxides. The raw materials (Merck, Darmstadt) had a grade of purity higher than 99%. After two hours, 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 15 μm [2]. The chemical composition was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The glass (SiO_2—34.7%, CaO—8.6%, BaO—41.4%) also contained minor additions of transition metal oxides, such as ZnO, PbO, and/or V_2O_5 to adjust the SOFC relevant physical and chemical properties [2]. The glass powders were blended to a paste, using ethyl cellulose as binder in terpineole.

A schematic drawing of the symmetric shear test specimen developed for mechanical seal characterization is shown in Fig. 2. A ~ 1.5 mm thick NiO-YSZ anode substrate with a thin (~10 μm) YSZ electrolyte layer on both surfaces was joined to Crofer22APU (Thyssen-Krupp) interconnect steel blocks ($1.5 \times 10 \times 10$ mm^3) using the as prepared glass paste. After joining the typical thickness of the seals was ~200 μm. With the materials and the seal thickness selected a test representative for the sealant behavior in a SOFC stack was designed. The pieces of the symmetric shear test specimens were aligned and joined using a special jig. Standard joining was carried out at 850 °C for 10 h. Also some of the joined specimens were given an additional heat treatment at 800 °C for 30 h. After joining, the side faces and the bottom face were polished to correct small misalignments and to permit in-situ observation of the specimens during the experiment. All shear tests were carried out at 800 °C using an electro-mechanical universal testing machine (INSTRON 1362) with digital fast track control.

Rheological model of shear deformation

In general, shear testing can be performed in different modes (Fig. 3), which apply (a) constant loading rate, (b) constant displacement rate, (c) constant load or (d) constant displacement. The experiments carried out in the present study refer to two of the four modes (a and b).

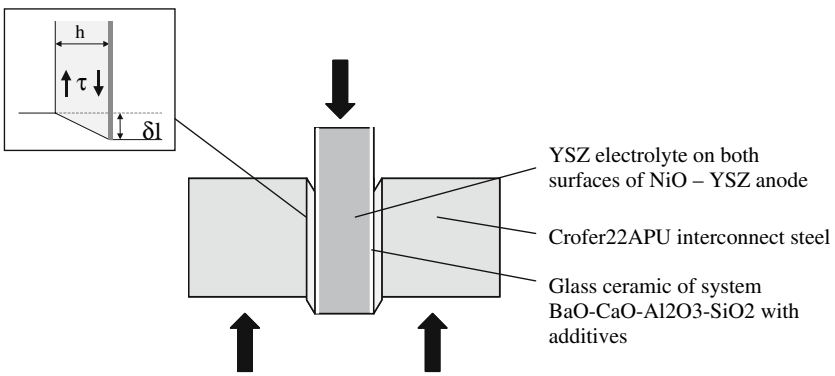

Fig. 2 Schematic drawing of the symmetric shear test

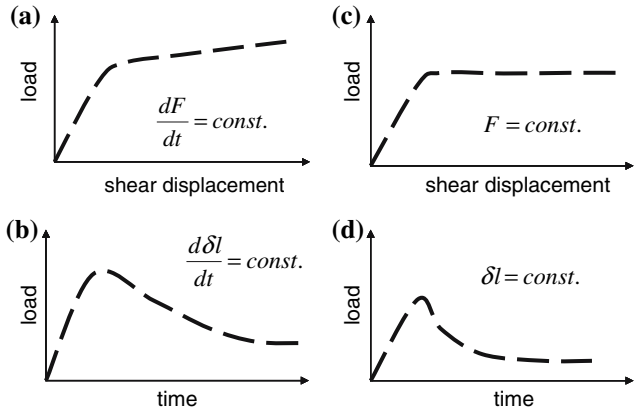

Fig. 3 Possible shear test procedures, (**a**) Constant loading rate, (**b**) constant displacement rate, (**c**) constant load and (**d**) constant displacement

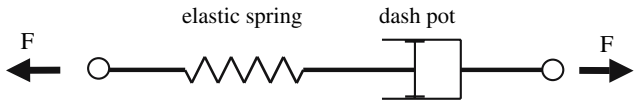

Fig. 4 Rheological model of viscoelastic shear deformation

A simple rheological model of viscoelastic shear deformation (Fig. 4) considers the total displacement being the sum of an elastic and a viscous (Newtonian behavior [3]) contribution:

$$\delta l_{\text{tot}} = \delta l_{\text{elast.}} + \delta l_{\text{visc.}} \tag{1}$$

The elastic displacement is given by:

$$\delta l_{\text{elast.}} = h\frac{\tau}{G} \tag{2}$$

and the viscous displacement by:

$$\delta l_{\text{visc}} = h\frac{\tau}{\eta}\delta t \tag{3}$$

where τ is the shear stress, G is the shear modulus and η the viscosity.

In the case of crystallizing glass-ceramics, the viscous flow is likely to be hindered by physical contact and interlocking of the crystalline phases. To obtain the shear deformation this additional material resistance (internal shear resistance τ_i) has to be compensated. Note that both the amount and morphology of the crystalline phases influences τ_i. Thus, in an extension of the rheological model of viscoelastic shear deformation (Fig. 5), the viscous displacement has been modified by the τ_i contribution [4]:

$$\delta l_{\text{visc}} = h\frac{\tau - \tau_i}{\eta}\delta \tag{4}$$

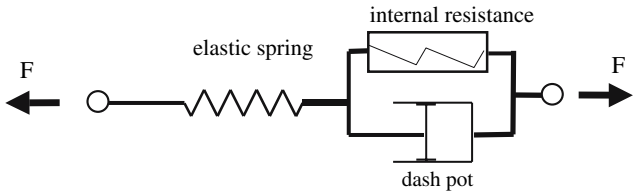

Fig. 5 Rheological model of viscoelastic shear deformation considering internal stress [4]

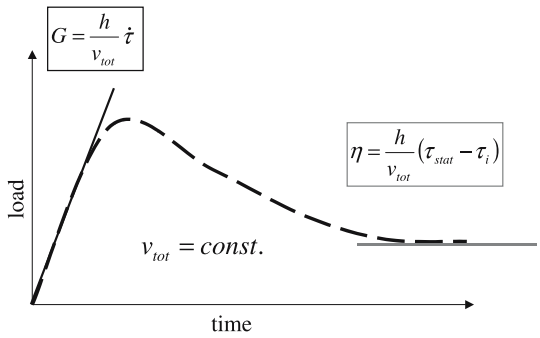

Fig. 6 Example for the determination of the parameters from the relaxation curve

As outlined in Fig. 6 for an experiment with constant displacement rate, the shear parameters can be determined directly from:

$$v_{\text{tot}} = \frac{\delta l_{\text{tot}}}{\delta t} = h\frac{\dot{\tau}}{G} + h\frac{\tau - \tau_i}{\eta} = const. \tag{5}$$

The initial slope allows the determination of the shear modulus since the viscous displacement results only in a constant load term and hence does not change the slope. The regime of the final steady state load provides the information necessary to evaluate values for the viscosity and the internal stress, if tests with different displacement rates are carried out.

The shear modulus can also be determined in experiments carried under constant loading rate (Fig. 3a) since:

$$G = \frac{h}{v_{\text{tot}}}\dot{\tau} = \frac{h\,dt}{ds}\frac{d\tau}{dt} = h\frac{d\tau}{ds} \tag{6}$$

Results and discussion

A comparison of load–shear displacement curves obtained at 800 °C for specimens as joined and additionally crystallized is shown in Fig. 7. Two curves for the as joined condition are given in Fig. 7 which can hardly be discriminated. It can be seen that the load to initiate a shear displacement is approximately a factor of ten higher for

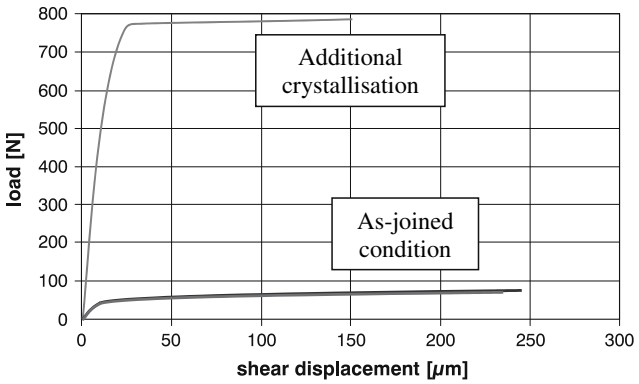

Fig. 7 A comparison of load/shear displacement curves. The as joined specimens were annealed at 850 °C for 10 h. The additionally crystallized specimens received an additional heat treatment at 800 °C for 30 h

specimens that received the additional thermal treatment of 30 h at 800 °C. This increase in load is a result of the crystallization taking place during the annealing time and is reflected in a change in the microstructure of the sealant material (Fig. 8). The significant amount of amorphous phase present in the as-joined state, has disappeared after the additional thermal treatment and the microstructure is then dominated by crystalline phases.

An example of the initial and final state of a shear test is shown in Fig. 9. The shear stress determined at 800 °C using a constant loading rate (Fig. 4a) is ~0.3 MPa for the as-joined and ~4 MPa for the additionally annealed state. The additional annealing, which also takes place during stack operation at 800 °C, leads to a sealant of improved mechanical stability. Note that an increase from 12 J m^{-2} to 56 J m^{-2} has also been observed for the fracture energy [5, 6].

In order to determine the viscosity in as joined condition, shear tests with constant displacement rate (Fig. 4b) were carried out. As a result of experimental limitations, partly related with measurement at low displacement rates, the internal resistance parameter and viscosity at 800 °C can only be derived for the as joined sealant. An example with three constant shear displacement rates (5, 50, 500 μm/h, Fig. 10), shows the proportionality of loading rate and relaxation time.

Shear modulus, internal stress and viscosity are determined according to Eq. (5) for the as joined sealant on the basis of experimental curves with eight constant displacement rates (2, 5, 20, 50, 100, 200, 400, 500 μm/min). Solving simultaneously the relationships given in Section 'Rheological model of shear deformation', yields average values of the viscosity: $\eta \sim 5$ MPa s, shear modulus: $G \sim 1$ MPa and internal shear resistance: $\tau_i \sim 0.18$ MPa, at 800 °C. As shown in Fig. 11 the viscosity value agrees well with results obtained previously, using beam bending viscosimeter, rotation viscosimeter and dilatometer techniques for the non-crystallized sealants [7].

Experiments were also carried out at 800 °C under constant loading rate. Although the displacement rate was not kept constant in these tests (Fig. 3a), it was possible to determine the shear modulus using Eq. (6).

In agreement with the measurements under constant displacement rate, a shear modulus of ~1 MPa is derived. Shear experiments under constant loading rate were also

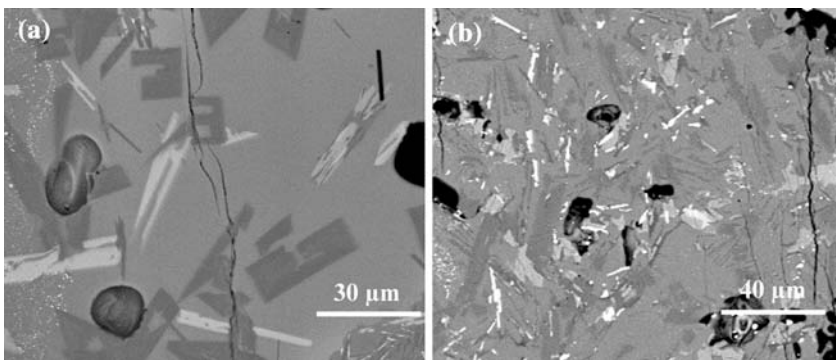

Fig. 8 Morphology of (**a**) as joined sealant and (**b**) sealant after additional crystallization. The as joined specimens were annealed at 850 °C for 10 h. The additionally crystallized specimens received an additional heat treatment at 800 °C for 30 h

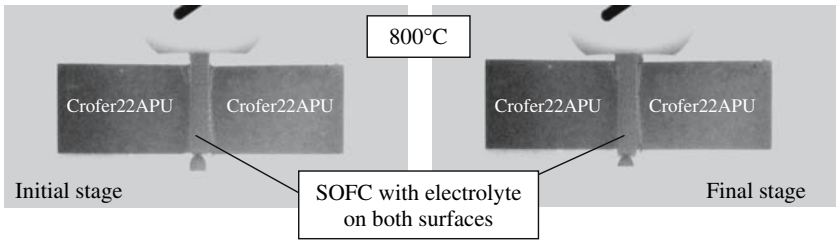

Fig. 9 Initial and final stage of a symmetric shear test

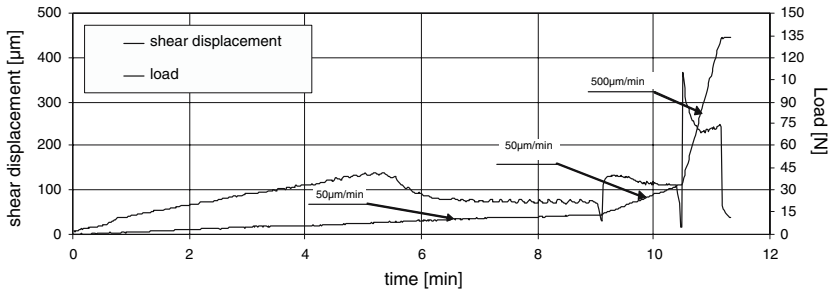

Fig. 10 Example of test with different constant displacement rates (5, 50, 500 µm/min) for an as-joined specimen

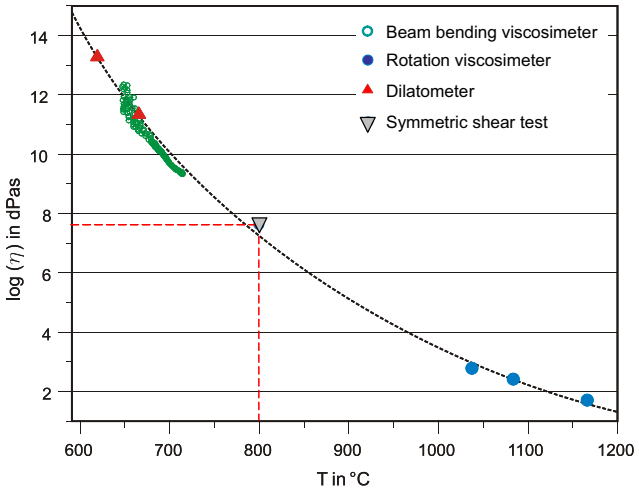

Fig. 11 Comparison of the viscosity of the as joined sealant with results obtained previously for the non-crystallized sealants [7]. The lines represent only a guide to the eye

performed for the additionally annealed sealing condition yielding a shear modulus of ~15 MPa. Hence similar to the shear strength, the shear modulus increases by a factor of ~15 as a result of the additional heat treatment of 30 h at 800 °C.

The results obtained for the internal shear resistance τ_i cannot be further discussed to date. Independent measurements are not known to the authors. Future systematically increased heat treatment times at 800 °C should be investigated to correlate the changes in amorphous and crystalline microstructure with τ_i values.

Conclusions

A symmetric shear test has been used to characterize at 800 °C shear stress and, based on a rheological model, shear modulus and viscosity of a sealant used for SOFC stacks. The critical shear stress increased from $\tau \sim 0.3$ MPa for the as-joined to ~4 MPa for the additionally annealed condition. Similarly the shear modulus $G \sim 1$ GPa increased by a factor of 15 for the heat treated specimens. The higher shear strength and shear modulus show that the additional annealing leads to a sealant of improved mechanical stability.

At the typical SOFC operation temperature of 800 °C, the as joined glass-ceramic sealant exhibits initially viscous shear deformation. Viscous shear becomes more difficult with increasing crystallization. A rheological model has been introduced which considers this mechanical aspect assuming a hinderence of viscous shear deformation by interaction of crystalline phases. Further experiments to correlate microstructural features with the shear deformation parameters are in preparation.

References

1. Blum L, Buchkremer H-P, Gross SM, de Haart LGJ, Quadakkers WJ, Reisgen U, Steinberger-Wilckens RW, Steinbrech RW, Tietz F (2005) SOFC IX, Electrochem Soc PV 2005–2007, 39
2. Gross SM, Koppitz T, Remmel J, Reisgen U (2005) Ceram Eng Sci Proc 26:239
3. Uhlmann DR, Kreidl NJ (eds) (1986) Glass science and technology 3: viscosity and relaxation. Academic Press, Orlando, FL
4. Kleist G (1995) Internal report. Research Center Jülich, FZJ
5. Malzbender J, Steinbrech RW, Singheiser L (2003) J Mater Res 18:929
6. Malzbender J, Steinbrech RW, Batfalsky P (2005) Ceram Eng Sci Proc 26/4:285
7. Pisit G (2003) PhD Thesis, RWTH Aachen