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Room and elevated temperature shear strength of sealants for solid oxide fuel cells

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ABSTRACT

The shear strength of glass-ceramic sealants was measured in torsion to aid the developments of robust sealants that can withstand the combined complex stress situation typical for solid oxide fuel cell stacks. The specimens consisted of hour-glass-shaped samples, with the sealant layer in typical application relevant thickness between two steel plates. Partially crystallized sealant materials with either silver particles or 8YSZ fibers as filler material were tested and compared with respect to their shear strength and failure behavior at room and elevated temperatures up to 800 °C. The results emphasize the importance of interfacial bonding as well the effect of creep properties of sealant and steel substrates onto the testing results. An outlook on improvements of testing procedure and specimens' geometry is given.

1. Introduction

Solid oxide fuel cells (SOFCs) are promising energy supply options. Their potential operation in electrolysis mode and their coupling to metal oxide storage devices [1,2] enhance their prospective for energy supply and networks. Their potential has been verified by stack tests with low degradation rates being operated under laboratory conditions for more than 70.000 h [3].

Most current works concentrate on planar designs. Contrary to mobile application, where metallic sealants are used [4], stationary designs are typically based on glass or glass-ceramic sealants [5,6]. Hence, robustness of the sealant material and in particular bonding to the interconnect steel are critical for a reliable long-term operation of stacks [7]. The sealant will be exposed to strains mainly caused by differences in thermal expansion of different stack component materials. In general, these strains increase with decreasing temperature and are therefore largest at room temperature (RT); however, it has been verified that large strains can also be generated by in-operation temperature gradients in stack planes [5]. Several studies have been published on RT mechanical properties of brittle sealant materials [8–14], indicating also the relevance of creep deformation at operation relevant temperatures [15,16].

Recent finite element simulations of stacks revealed that the sealant material will be exposed to tensile and shear stresses [5], hence requiring also a characterization under shear loads [17] in addition to the frequent characterization under tensile loads [18], which is sometimes realized via bending tests [15,16]. Whereas bending tests have also been carried out at elevated temperatures, shear tests of sealant materials concentrated onto the RT behavior [17].

It has been verified that a torsion test is the most appropriate shear testing technique [19]. Hence, the torsion test has been used in the current work to characterize two partially crystallized sealant materials with either silver particle or 8YSZ fiber reinforcement [20,21], using a newly developed torsion test set-up which permits characterization up to 1000 °C [22]. Results of the silver enhanced material are compared to previously derived room and high temperature bending test fracture stress data [20].

2. Experimental

The studied composite sealant is based on a glass matrix of the $BaO-CaO-SiO_2$ ternary system, with addition of small amounts of Al_2O_3, B_2O_3, V_2O_5, ZnO (see [21]). The raw materials were obtained from Merck KGaA (Darmstadt, Germany) and had a purity grade of more than 99%. Each batch was prepared by mixing an appropriate mole fraction of oxide ingredients and melting at 1480 °C in a platinum crucible in an induction furnace [23]. For a better homogenization of the glass, the melting procedure was carried

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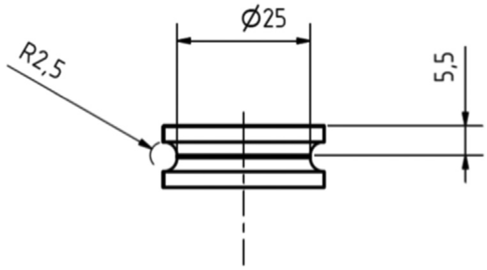

Fig. 1. Specimen dimensions used for the torsion test.

out twice. The frits were wet-milled in acetone in an agate ball mill to a median particle size of 10–13 μm, dried and then sieved through a mesh size of 0.32 μm to collect powders. To obtain a bulk glass sample, the melt was poured into a graphite mold and transferred to a preheated (750 °C) chamber furnace as soon as it was dimensionally stable, followed by a slow cooling down to RT. The powders were mixed either with silver particles (abbreviated H-Ag) or 8YSZ fibers (resulting material abbreviated H-F), respectively.

The specimens consisted of hour-glass-shaped samples, where the sealant was deposited by screen printing in a round geometry on 25×25 mm^2 Crofer22APU specimens (see Fig. 1). The specimens were joined at 850 °C for either 10 h or 100 h and then cooled down to RT. Heating and cooling rates were 5 K/min. In addition, tests were carried out to assess the elevated temperature behavior of the steel materials using specimens fabricated entirely of Crofer22APU and the more creep resistant CroferH [24]. Experiments from RT up to 800 °C were carried out using an in-house built torsion test set-up (Fig. 2).

In the torsion test, a joined plate-shape specimen was twisted by two loading arms until fracture occurred. The rotational speed was ~4 °/min. The maximum torque that might be used in the set-up is 220 Nm. A horizontal folding oven was used for the high temperature tests. The shear stress could be calculated by following equation [17]:

$$\tau = \frac{16\boldsymbol{T}}{\pi \boldsymbol{d}^3} \quad (1)$$

where τ is the shear stress, T the applied torque, and d the diameter of the joining area, here is 25 mm. The torques was calculated at specimens' fracture.

The test series consisted of 7 test (3 at elevated temperatures) with sealant H-Ag and 12 with H-F (4 at elevated temperatures). The sealant thickness was ~300 μm as estimated from the specimens' thickness and the deposited materials' amount. The fractured specimens were examined using an optical microscope (MA 705EC-REV-005, CSM, Switzerland).

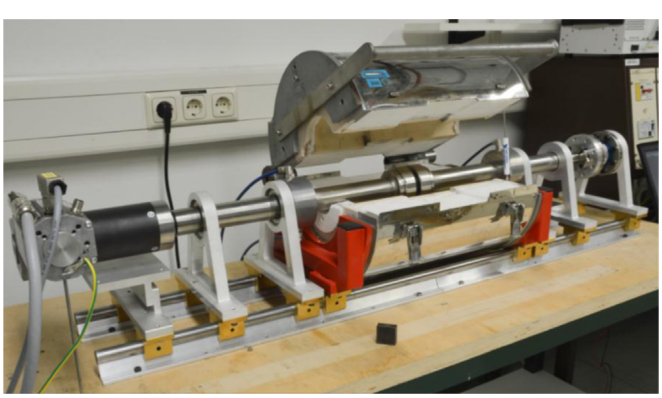

Fig. 2. Torsion test set-up.

3. Results and discussion

The following sections summarize the experimental results. Furthermore, they are compared and discuss with respect to literature reports. Microstructural details on the sealant materials can be found in previous publications [20,21].

3.1. Sealant H-Ag

Torsion tests of sealant H-Ag at RT (10 h joining at 850 °C) yielded a similar average shear fracture stress (61 ± 4 MPa, see Table 1 and Fig. 3) as obtained previously from bending tests on head-to-head specimens (55 ± 6 MPa [20]). Two tests that were carried out at 600 °C resulted in a similar shear stress of 64.1 ± 0.3 MPa, indicating that residual stresses induced by thermal mismatch of sealant and steel, which are maximum at RT, do not affect the torsion test result, for the considered materials combination. A single test at 800 °C revealed a non-linear loading behavior (see Fig. 4) of H-Ag specimens and a significant decrease in shear fracture stress (13 MPa). A similar effect was previously observed for a head-to-head joined bending test specimen (7 MPa [20]). This decrease in the fracture stress can be associated with the softening of the sealant due to residual glassy phases as reported also for head-to-head joined bending specimens [21].

In fact, as a guideline for the softening, transition and softening temperatures of the sealants might be used, experimental evidence for similar compositions published in [25,26] suggest a temperatures in the range of 650–700 °C. However, it has to be considered that softening and transition temperature are typically assessed for the glassy state and due to crystallization the composition of the remaining glassy phase changes and hence also the apparent softening and transition temperature, an effect that cannot be assessed then anymore for typically used dilatometer techniques. Hence, the currently used test might be the more accurate means to assess the apparent softening of the material.

To simulate the effect of longer stack operation a test was performed for a specimen after 100 h joining process at 850 °C, yielding a lower RT shear failure stress (14 MPa, see Table 1 and Fig. 3). Again, a similar effect has been reported for annealed H-Ag head-to-head joined bending test specimens [21]. Such a decrease in fracture stress has obvious implications for the sealant application in stacks.

Note, failure in bending tests appeared to be predominant via

Table 1
Shear test results.

Sealant	Joining [h]	Temp. [°C]	Shear stress [MPa]	Average shear stress [MPa]
H-Ag – Crofer22APU	10	RT	59.2	61 ± 4
		RT	57.0	
		RT	65.3	
		600	64.4	64.1 ± 0.3
		600	63.8	
		800	12.5	12.5
	100	RT	14.0	14.0
H-F – Crofer22APU	10	3 Test, RT	> 68.6	> 68.6
		800	17.1	17.1
	100	RT	48.6	58 ± 8
		RT	50.1	
		RT	57.4	
		RT	> 68.6	
		RT	65.9	
		600	58.9	58.9
		760	15.2	15.2
		800	16.5	16.5