



## Short communication

## Elevated temperature effects on the mechanical properties of solid oxide fuel cell sealing materials



Yilin Zhao, Jürgen Malzbender\*

Forschungszentrum Jülich GmbH, IEK-2, 52425 Jülich, Germany

## H I G H L I G H T S

- Partially crystallized sealants showed viscous effects above  $T_g$  ( $\sim 700$  °C)
- Partially crystallized sealants had drop in elastic modulus and strength above  $T_g$ .
- Fully crystallized material shows stable properties ( $T_g \sim 900$  °C).
- Polishing increases the fracture stress by 30%.
- Critical flaw size is a factor of  $\sim 10$  larger for partially crystallized material.

## A R T I C L E I N F O

## Article history:

Received 24 July 2012

Received in revised form

22 March 2013

Accepted 7 April 2013

Available online 19 April 2013

## Keywords:

Solid oxide fuel cells

Sealant

Mechanical properties

Fracture

Viscosity

## A B S T R A C T

A promising candidate to fulfil the solid oxide fuel cell sealant requirements with respect to gas tightness, high temperature stability and electrical insulation appear to be glass-ceramic sealing materials. However, the reliable operation of solid oxide fuel cell stacks depends strongly on the structural integrity of the sealing materials. In this respect failure and deformation are aspects which need to be assessed in particular for glass ceramic sealant materials. Bending tests were carried at room temperature and typical stack operation temperature for glass ceramic sealants with different degree of crystallization. Elastic moduli, fracture stresses and viscosity values are reported. In addition to sintered bars bending testing were carried out for steel specimens that were head-to-head joined with the glass ceramics similar as in a stack application, where the ceramic particle reinforced sealant material was screen printed onto the steel. The results reveal a decrease of the strength for the partially crystallized sealant at operation relevant temperatures that can be associated with the viscous deformation. Fractographic analyses based on a combination of optical, confocal and scanning electron microscopy gave insight into the failure origin.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The reliability and robustness of sealants are a prerequisite for the commercialization of planar solid oxide fuel cells (SOFCs). Approaches to join and seal stacks have been based on glasses, glass-ceramics, glass-composites and metallic materials [1–4]. The sealant should separate anode and cathode gas compartment hermetically and not show any unwanted chemical interactions to other component materials or gaseous species and furthermore, possess a sufficient bonding strength to withstand operation induced stresses. Glasses and glass-ceramics have better resistance to the oxidizing and reducing atmospheric in the stack than

metallic sealants and appear to fulfil most SOFC specific requirements. Glass-ceramics are cheaper than related metallic sealing materials and can be applied to the sealing surfaces as a powder dispersed in a paste, as tape casted sheets or by screen printing. Furthermore, they typically exhibit better wetting behaviour than metallic sealants, are electrically insulating and can be engineered to exhibit similar coefficient of thermal expansion (CTE) as the adjacent SOFC components, thereby minimizing thermally induced stresses [2,5]. Another most important criterion for the sealant design and development is the glass transition temperature  $T_g$ , above which the materials behaviour changes from brittle to ductile [6,7]. Viscous stress relaxation or occurrence of structural instabilities coupled with strength reduction might be expected above  $T_g$ .

During the joining process, the initial glass might partially or fully crystallize and react with the metallic interconnect materials

\* Corresponding author. Tel.: +49 2461 616964; fax: +49 2461 613699.  
E-mail address: [j.malzbender@fz-juelich.de](mailto:j.malzbender@fz-juelich.de) (J. Malzbender).

or any existing oxide layer. The resulting interaction phases might thicken with increasing operation times and become porous, yielding weak interfaces that can be susceptible to thermo-mechanically induced cracking [8,9]. The crystallized materials are typically mechanically stronger. However the final joint can expect to be brittle and fracture susceptible when exposed to tensile stresses that might result of components CTE mismatches or simply thermal cycling operation induced temperature gradients [8]. As an alternative to fully crystallized glass-ceramics, particle or fibre reinforcements might be considered as means to optimize the fracture toughness by crack stopping and deflection mechanism [10,11]. A brittle filler material with high elastic modulus and toughness can dissipates energy during pull out or by a change in crack path.

In the present work, results of the mechanical characterization of two glass-ceramic sealants are reported. One ceramic filler particle reinforced sealant with a rather low level of crystallization (abbreviated H, 80% glassy phase) and one without reinforcement which is almost fully crystallized (B, <10% glassy phase). The materials are characterized with respect to elastic and viscous behaviour, and strength. Tests are carried out for sintered bars or in a head-to-head joined geometry.

## 2. Experimental

The partially crystallized glass-ceramic sealant (H) was based on a glass matrix of the BaO–CaO–SiO<sub>2</sub> ternary system with addition of small amounts of Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and ZnO [12]. The raw materials were obtained from Merck KGaA, Darmstadt and had a purity grade higher than 99%. Each batch was prepared by mixing an appropriate mole fraction of oxide ingredients and melting at 1480 °C in an induction furnace in a platinum crucible [3]. For a better homogenization, the melting procedure was carried out twice. For subsequent powder preparation, 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 32 µm size mesh. The chemical composition of the material was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) yielding BaO – 48.2, SiO<sub>2</sub> – 29.8, and CaO – 6.1 wt.% with minor additions of Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, and ZnO. To obtain sintered rods, a conventional sintering process was carried out, powders were mixed with YSZ particles (sizes 1–40 µm) and pressed and sintered on a wavelike curved platinum foil at 850 °C for 10 h and then cooled down to room temperature (RT). Heating and cooling rates were 5 K min<sup>-1</sup>.

The almost fully crystallized glass-ceramic sealant (B) is also based on BaO–CaO–SiO<sub>2</sub> system, however with addition of only Al<sub>2</sub>O<sub>3</sub> and received otherwise the same processing as the H series [12]. Chemical composition of the material was also analyzed by ICP-OES, yielding a composition of BaO – 36.7, SiO<sub>2</sub> – 46.8, and CaO – 15.8 wt.%, with minor additions of Al<sub>2</sub>O<sub>3</sub>. The powder was pressed and sintered at 950 °C for 10 h. Heating and cooling rate was also 5 K min<sup>-1</sup>.

The head-to-head joined specimens were prepared using an in-house developed sealing jig [13]. Similar as in SOFC stacks [8], Crofer22APU was used as steel for the joint, with a surface preparation equivalent to that typical for stack application. The sealant was deposited by screen printing. Specimens dimensions were 52 mm × 6 mm × 4 mm with a sealant thickness of <0.2 mm. The uncertainty for dimensions and parallelism for head-to-head joined specimens and sintered bars was 0.05 mm.

Five specimens of each variation were tested in four-point bending in the as-joined state and after additional polishing of either the tensile side or of all sealant surfaces. The fracture stress of the head-to-head joined specimens was determined after ASTM C1161[see also [14–16]. In addition viscous deformation was

investigated in bending tests for bars and head-to-head joined specimens. The viscous bending rupture was investigated only for material H (3 specimens) in the as-joined state at typical operation temperatures. The tests were carried out up to failure at 800 °C in air with the heating rate of 5 K min<sup>-1</sup>. The viscosity was determined as outlined in Ref. [13]. The elastic modulus of the sintered bars was determined using impulse excitation (Grindosonic, Lemens KG, Belgium).

## 3. Results and discussion

The CTE of material B [17] and H (non-aged and aged) [18] (non-aged and aged) are compared in Fig. 1 to the values of the interconnect steel Crofer22APU and the NiO/YSZ anode substrate [18]. The CTE has been determined for sintered bars; experimental details are given in Refs. [17,18]. The CTE of sealant H in the glassy state shows a strong increase when the glass transition state ( $T_g$ ) of about 640 °C is approached. The softening temperature ( $T_s$ ) of ~750 °C can be seen as peak of the CTE curve. The obtained glass transition temperature for material B is ~700 °C. Overall the values are higher than for H material. The softening is observed around the same temperature. Details on the crystallization temperature (differential thermal analysis), softening temperature (“sinking dilatometer”) [19] and transformation temperature (dilatometer) can be found in Ref. [18]. Since the CTE of glass-ceramic H is smaller than that of metallic parts and cermet, compressive stresses are induced into the material on cooling, which is advantageous for ceramic materials. It has been verified in numerous stack tests [8] that the sealant survives stack operation and moderate thermal cycling and that in fact in the case of thermal cycling stresses generated by in-plane temperature gradients that are not related to CTE differences appear to be the main problem [8].

For the stack typical as-joined state (Fig. 2), it might be suggested on the basis of the curves in Fig. 1 that the glass transition temperature is reduced to about 600 °C for sealant H. Such reductions in the transition temperature associated with a different composition of the remaining glassy matrix after the crystallization process have been discussed in Ref. [20]. It has been suggested that when the concentration of crystalline phases is low, the cross-linking density of the remaining glass will decrease, resulting in a decrease of the glass transition temperature [20]. Sealant B

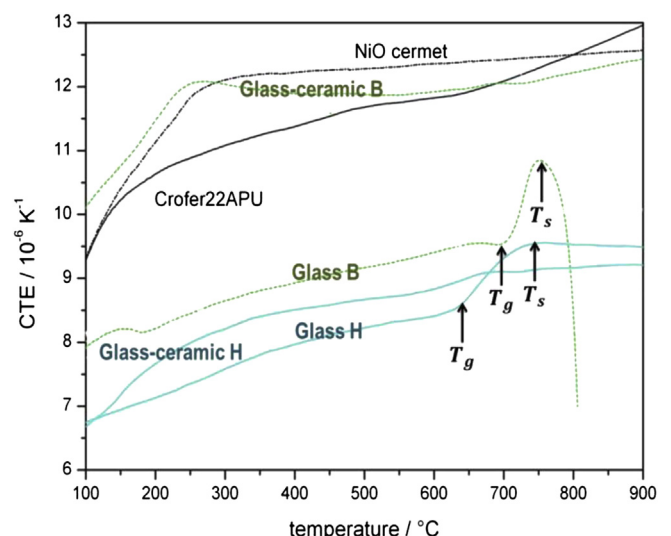


Fig. 1. CTE of material B and H in the glassy and crystallized state.

Download English Version:

<https://daneshyari.com/en/article/7740193>

Download Persian Version:

<https://daneshyari.com/article/7740193>

[Daneshyari.com](https://daneshyari.com)