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Short communication

Mechanical performance of reactive-air-brazed (RAB) ceramic/metal joints for solid oxide fuel cells at ambient temperature

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ABSTRACT

Mechanical integrity of the sealants in planar SOFC stacks is a key prerequisite for reliable operation. In this respect joining with metals rather than brittle glass–ceramics is considered to have advantages. Hence, as one of the joining solutions for SOFCs of planar design, reactive air brazing of ceramic cells into metallic frames gains increasing interest.

Fracture experiments are carried out to characterize fracture energy and failure mechanisms of silver-based reactive-air-brazes, used for joining the zirconia electrolytes of anode supported planar cells with metallic Crofer22APU frames. The specimens are mechanically tested in notched beam bending geometry. In-situ observation in optical and SEM resolution reveals specific failure mechanisms. The influence of braze formulation and associated interfacial reactions on the crack path location is addressed. Discussion of the results focuses in particular on the role of oxide scale formation.

1. Introduction

The development of solid oxide fuel cells (SOFCs) is typically guided by progress in electrochemical performance, but with the utilization of SOFCs in the larger power unit of a stack also mechanical aspects receive rising interest. As an example solid oxide fuel cells in auxiliary power units (APUs) for vehicles [1] can be taken, where durable mechanical integrity and reliability under rapid thermal cycling conditions are key pre-requisites for satisfactory operation.

In principle planar SOFCs are ceramic composite sheets of anode, electrolyte and cathode layer. The cells are fixed and sealed in metallic housings and interconnected by metallic plates to form a stack. Bonding between the ceramic cell and the metallic interconnect is currently achieved by either glass–ceramics [2] or metallic brazing [4]. The joints are facing demanding conditions such as temperature gradients during steady state operation and superimposed transients during heating and cooling. As a consequence mechanical stresses are generated. Additional stresses can emerge from different coefficients of thermal expansion of the joining partners and chemical composition of the braze/interconnect and braze/ceramic interfaces as well as their changes during stack operation. Contrary to brittle glass–ceramics the ductile metal-based seals are assumed to be better suited and more promising to meet these requirements. However, only few characterization results of SOFC brazes are available from literature [2–5]. In particular information on failure mechanisms along the interfaces of metal-based SOFC sealants are still limited [3,4,5].

Four-point bending of notched bi-material beams (Charalambides et al. [6]) provides a convenient method to examine the fracture paths in sealants and to determine the interfacial fracture energy of layered composites. In the present paper this method has been adopted to mechanically characterize the adhesion of a metal-based braze seal between interconnect steel and the electrolyte layer of an SOFC. Special attention is given to the influence of braze formulation and oxide scale formation at the braze/interconnect interface on the crack path location.

2. Experimental

2.1. Sample geometry

The characterization of the interfacial fracture energy according to Charalambides et al. [6] is based on the generation of a crack which propagates from a notch tip along the interface of a multilayer specimen during bending (Fig. 1).

To provide the original stack-like joining situation the layered composite sample comprised a ferritic CroFer22APU steel strip as substrate (see Fig. 1: $h_2 = 2.5$ mm) and a SOFC half-cell as joined counterpart. The stiffness and flatness of the half-

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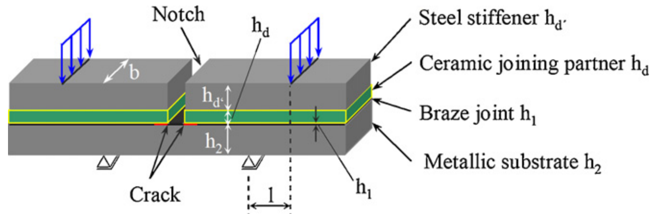

Fig. 1. Notched multi-layer sample for delamination experiment in four-point bending (schematic).

cells, comprising yttria stabilized zirconia (8YSZ) electrolyte and NiO/8YSZ-substrate, was increased by a second electrolyte layer on the opposite substrate surface. Thus the substrate was sandwiched between the electrolyte layers and had a total thickness of $h_d = 1.5$ mm.

If joint adhesion is stronger than the fracture resistance of the sandwiched SOFC half-cell the latter will fail. Thereby a characterization of the joint adhesion is not possible. For this reason a second sample version was developed. The SOFC half-cells of Forschungszentrum Jülich with porous anode substrate were substituted by thin dense TZ3Y-foils ($h_d = 0.1$ mm, Nippon Shokubai), of higher strength and toughness, as joined counterparts.

Steel substrate and the two ceramic joining partners were brazed into beams to investigate the joining system. Also additional steel stiffeners had to be attached to the specimens to prevent segmentation cracking of the brittle ceramic components; Fig. 1: $h_{d'} = 2.5$ mm). A narrow gap was kept between the ceramic bodies (Fig. 1) to represent the notch situation with the tip in close proximity to the braze/steel interface.

2.2. Sample preparation

A silver-based RAB (reactive-air-brazing)-alloy with a small amount of CuO [3] was used as standard joining material. The RAB-foils with a composition of Ag8CuO (mol%) were fabricated by electroplating of thin (0.1 mm) Ag sheets with Cu. In addition experiments were carried out with a CuO-free braze system.

The braze foils were positioned between the joining partners. All samples were joined in static air with specially designed brazing jigs applying a permanent load of 1.5 MPa without thickness limitation (h_1).

After joining one of the specimen's side faces was polished perpendicularly to the loading direction.

2.3. Mechanical testing

Delamination-testing was performed at room temperature using an Instron 1362 testing machine with ceramic four-point bending fixtures (45 mm specimen length, 40 mm/20 mm span ratio) applying a constant strain-rate of 0,33 μm s^{-1}. Supplementary in-situ tests were carried out in a scanning electron microscope (SEM, Zeiss Supra 50 VP) using a miniaturized deformation device system (DDS: four-point-bending equipment with 40 mm/10 mm span-ratio).

3. Data evaluation

The evolution of the interfacial fracture energy was based on measured load-deflection curves (Fig. 2). In principle the fracture energy values were derived from the difference between the strain energy in the un-cracked and cracked beam. Assuming that the strain energy in the beam portions above the crack is negligible, the fracture energy can be deduced from the difference in the elastic

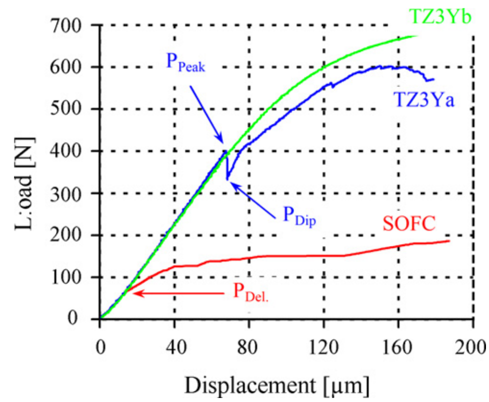

Fig. 2. Load-displacement curves typical for different delamination samples obtained by four-point bending.

energies of the un-cracked and cracked part of the lower beam. From Euler-Bernoulli beam theory the energy G_{SS} under plain strain conditions is [6]

$$G_{SS} = \frac{M_b^2(1-\nu^2)}{2 \times b \times EI}. \quad (1)$$

where ν refers to the Poisson's ratio and b to the specimen width. E is the Young's modulus, I the moment of inertia and $M_b = P_P l/2$ the bending moment with the load P_P and the distance l between outer and inner loading lines.

In the multilayer specimen the interfacial fracture energy between layer j and $j+1$ of n total layers can be derived from [7]:

$$G_{SS} = P_P^2 l^2/8 \times b \left(\frac{1}{\sum_{i=1}^{j} EI/(1-\nu_i^2)} - \frac{1}{\sum_{i=1}^{n} EI/(1-\nu_i^2)} \right) \quad (2)$$

As long as the crack remains within the inner loading regime of the four-point bending test, the crack front faces a constant moment, which is the driving force for crack-propagation. The load–displacement curve is expected to exhibit a constant load behavior. However, experimentally such steady-state characteristics were not frequently observed. Fig. 2 shows three typical curve types obtained by the tests. The delamination load P_P in Eq. (2) was determined in each case from the onset of major crack growth within the joining regime.

The fracture energy was calculated by Eq. (2) on the basis of the delamination load and the coefficients of elasticity ($E_{CroFer22APU} \sim 200$ GPa, $E_{SOFC} \sim 100$ GPa, $E_{TZ3Y} \sim 200$ GPa) of the layer materials.

The curve termed "SOFC" (Fig. 2) is typical for a specimen with sandwiched SOFC half-cells as ceramic joining partners. Due to the limited fracture toughness such samples generally failed within the highly porous SOFC anode-substrate. In these cases the delamination loads "$P_{Del.}$" were determined from the non-linear deviation of the curve.

Curves of the "TZ3Ya"-type (Fig. 2) are representative for specimens with TZ3Y-foils as ceramic joining partners and CuO-containing brazes. Faint but inevitable spreading of the braze into the notch-simulating slot between the TZ3Y-foils can reduce the notch stress and thus result in an overshoot in delamination load. Upon loading the starter crack has to penetrate the overlapping braze region when growing towards the steel substrate of the sample. Crack initiation (at "P_{Peak}") and propagation dissipate stored elastic energy, what becomes visible in a load drop. Upon further deflection of the specimen the crack is deflected into the joining regime where it proceeds along a path of weakest material resistance. According to Zhang and Lewandowski [8] the delamination

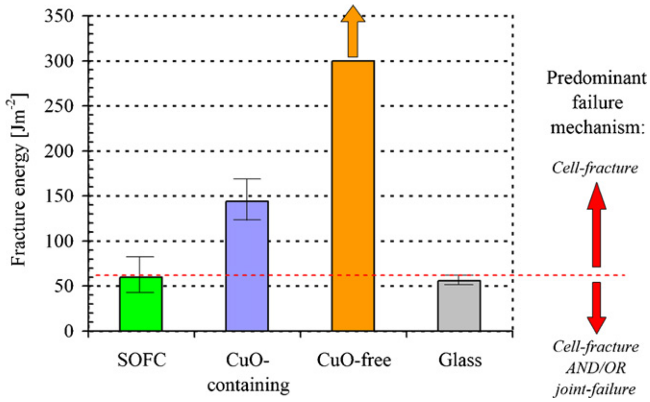

Fig. 3. Fracture energy results of SOFC-stack components and prevailing failure mechanisms of the joining systems based on the fracture resistance value of Forschungszentrum Jülich SOFC half-cells as a comparative level.

load is best represented by the stop-value of the starter crack "P_{Dip}" (Fig. 2).

Advanced, CuO-free braze systems often showed a behavior corresponding to the graph "TZ3Yb" in Fig. 2. In this case delamination testing was restricted by both the sample geometry and the material properties. In the given testing geometry the yield strength of the metal substrate (~200 MPa at room temperature) limited the characterization of the fracture energy to an upper value of about 300 J m^{-2}. Specimens that revealed plastic deformation of the metallic substrate beam exhibited curves of the "TZ3Yb"-type. Crack formation could not be obtained within the elastic loading regime of the test. Therefore, the upper elastic limit of the testing method was employed as a lower limit of fracture energy of the joint.

4. Results and discussion

Fig. 3 gives the fracture energies of the metal-based joining systems in the as-brazed state in comparison to the fracture energy of the anode material of the SOFC and a well established glass–ceramic seal [2].

With respect to safe stack-operation the comparison of the fracture energy of the SOFC and the brazing variants is certainly of higher practical importance, rather than discussing the obtained maximum delamination resistance. For this reason the fracture energy value of Forschungszentrum Jülich SOFC half-cells of ~60 J m^{-2} will serve as a comparative level in the following assessment of braze systems.

The CuO-free braze exhibited a fracture energy value exceeding the testing limits, thus only a lower limit of >300 J m^{-2} can be given for this joining variant. The CuO-containing braze failed at a lower resistance level. However, both the CuO-containing and the CuO-free joining variants exceeded the fracture energy of the Forschungszentrum Jülich SOFC standard substrate. This is quite important since in consequence the joining system as a whole is more likely to fail within the SOFC-substrate than within the brazing regime under excessive thermo–mechanical loading. Vice versa crack formation and propagation within the brazing regime itself is only critical if the delamination resistance of the braze is equal or lower than the fracture energy of the SOFC. Note that the fracture resistance value of the glass–ceramic seal [2] displayed in Fig. 3 is in this critical regime. Table 1 summarizes the fracture energy results.

All tested metal-based joints outbalanced the SOFC in fracture resistance. Crack formation within the brazing regime is therefore less likely in the as-brazed state. In consequence – since mechanical performance of the tested joining systems with metallic brazes is limited by the fracture resistance of the SOFC – improvement of the joining system as a whole can only be accomplished by enhancing the fracture resistance of the SOFC.

Table 1
Fracture energies of SOFC-stack components.

Component	Fracture energy (J m^{-2})
SOFC	60 ± 20
CuO-containing braze	144 ± 23
CuO-free braze	>300
Glass–ceramic seal	56 ± 3 [2]

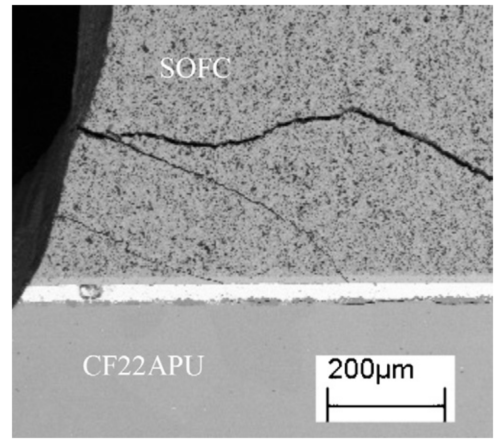

Fig. 4. Samples containing SOFC half-cells as ceramic joining partners. Typical fracture predominantly within the porous SOFC anode substrate.

On the other hand glass-seal variants exhibited fracture energies slightly below the comparative SOFC level [2]. Hence both, the glass-seal and the SOFC, are equally prone to crack formation in this joining system.

The SEM-micrographs in Figs. 4–6 illustrate failure locations and mechanisms related with the macroscopic interfacial fracture energy results.

Fig. 4 shows a typical fracture pattern in the anode substrate of samples comprising SOFC half-cells as the ceramic joining partners (see also corresponding curve "SOFC" in Fig. 2). At the interface of braze and ferritic steel mixed Cu/Fe/Cr/Mn – oxides are observed which have been formed due to the reaction of the CuO-containing silver braze with the steel surface. This reaction zone becomes failure relevant when the SOFC half-cell is substituted by a TZ3Y-foil to characterize the braze joint by itself (curve "TZ3Ya" in Fig. 2).

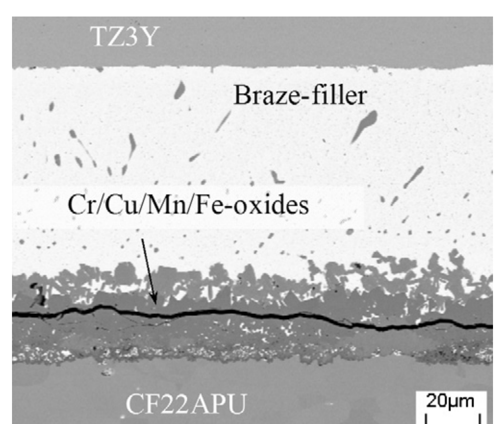

Fig. 5. Samples with TZ3Y-foils as ceramic joining partner (braze: Ag8CuO): typical failure within the reaction zone of braze and ferritic steel.

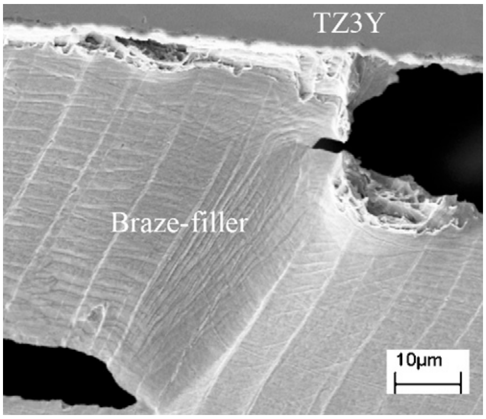

Fig. 6. CuO-free joint. Delamination originated from pores in the vicinity of the interfaces (not visible in the micrograph). Ductile deformation of braze filler where counter-directed delamination of opposite interfaces meets.

Accordingly, fracture then occurs within the reaction zone (Fig. 5). A typical crack path in the brittle reaction oxides is shown, what supports the need to control the oxide formation. In the case of CuO-free joints the reaction zone mainly consisted of thin chromia and chrome–manganese spinel layers, which obviously provide better interfacial adherence. Thus delamination is not exclusively restricted to the braze/ferritic steel interface but may also occur at the interface of braze and TZ3Y ceramic. An example, where delamination had originated from distant pores at both interfaces and had progressed from there towards the same location is shown in Fig. 6. Rather than by further crack growth the plastic deformation of the silver matrix compensates the increasing separation of the TZ3Y from the steel substrate in the mechanical test.

5. Conclusion

Two metal-based brazes (with and without CuO) for joining SOFCs and metallic housings were examined by delamination testing at ambient temperature. Both brazes exceeded the fracture energy of the SOFC anode substrates currently used at Forschungszentrum Jülich. The cell material by itself turned out to limit the overall joint performance. In this respect both metallic brazes can be considered to be applicable advantageously compared to established glass–ceramics. However, the full mechanical potential of silver based brazes will only be utilized, if cells with higher fracture resistance of the anode substrate are joined and sealed in the stacks.

Failure in the bending tests was observed to be dominated by interfacial phenomena. The fracture tests highlighted the unfavorable role of brittle oxide layers formed on the steel surface as reaction products during brazing. Failure preferentially occurred between these scales. Plastic deformation of the braze matrix only occurred in CuO-free joints.

Although the brazing method needs to be further elaborated, e. g. towards avoiding long-term interfacial degradation effects under stack service conditions, the obtained results, in particular those from CuO-free brazes, appear very promising for joining tasks in SOFC applications.

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