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Interfacial fracture resistance of the joint of a solid oxide fuel cell glass–ceramic sealant with metallic interconnect

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HIGHLIGHTS

- Interfacial fracture energy of SOFC sealant/interconnect joint is determined.
- Interfacial fracture energy at 650 °C–800 °C is much larger than that at 25 °C.
- Maximum fracture energy takes place at 700 °C due to a crack bridging mechanism.
- A 1000-h thermal aging treatment enhances the fracture energy at 700 °C–800 °C.
- Chromate layer and glass–ceramic/chromate interface are the typical cracking path.

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ABSTRACT

Interfacial cracking resistance of a joint between a glass–ceramic sealant (GC-9) and interconnect stainless steel (Crofer 22 H) for planar solid oxide fuel cells is investigated. Interfacial fracture energy is measured at room temperature to 800 °C using a four-point bending test technique. A heat treatment of 100 h or 1000 h at 800 °C is applied for studying the thermal aging effect. Results show the variation trend of interfacial fracture energy with temperature is similar for all given material conditions. Interfacial fracture energy increases with temperature to reach a peak value at 700 °C and then drops at temperature above 700 °C. A 100-h aging treatment does not change the interfacial fracture energy significantly, compared to the non-aged condition. The 1000 h-aged joint, however, has greater interfacial fracture energy than the non-aged and 100 h-aged joints at 700 °C–800 °C. Two types of cracking path in the interior of fracture surface are identified. Firstly, delamination takes place at the interface between the glass–ceramic substrate and chromate layer. Secondly, cracking occurs within the chromate layer. However, for the 1000 h-aged joints tested at 700 °C–800 °C, fracture at the highly oxidized, peripheral regions takes place within the glass–ceramic layer.

1. Introduction

Solid oxide fuel cells (SOFCs) utilize solid ceramics as the electrolyte and electrode and operate at high temperatures. The high operating temperature enables SOFCs to have a superior efficiency of energy conversion and an advantage in flexibility of fuel needed, compared to other fuel cells. Two major configuration designs are being developed for SOFC, namely tubular and planar cells. Advantageous features of planar SOFCs (pSOFCs) over the tubular ones include easier fabrication, lower operation temperature, and higher power density. In particular, for anode-supported pSOFCs with a thinner electrolyte, the operation temperature can be lowered to less than 800 °C and the ohmic loss is also reduced, compared to the electrolyte-support configuration. In practical applications of pSOFC, multiple cells are assembled to form a stack and make a serial connection in the electric loop to generate a high voltage and power. As a result, interconnects play an important role in structural and electrical connection of unit cells. During the stacking process and operation, hermetic sealants are needed to maintain gas tight between components in pSOFCs. When a rigid type of sealing is applied to pSOFC stacks, joining glass–ceramic sealants to metallic interconnects is very common. Sealants are typically applied in a pSOFC stack at the following locations: (a) cell to metal frame; (b) metal frame to metal interconnect; (c) frame/interconnect pair to electrically insulating spacer; (d) stack to base manifold plate [1]. Seals at locations (b) and (d) can be regarded as a joint of glass–ceramic sealant and metallic interconnect.

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Significant thermal stresses can be developed in an SOFC system due to mismatch of coefficient of thermal expansion (CTE) between components and temperature gradients during cyclic operation [2,3]. Accordingly, thermal stresses are generated in the joint between glass–ceramic sealant and metallic interconnect in pSOFC stacks [1–3]. Thermal stresses at such a joint may cause failure of sealing with excessive deformation and/or debonding, leading to gas leakage and degradation of cell performance. Therefore, it is necessary to investigate the mechanical properties of such a joint for assessing the structural integrity and durability of a pSOFC stack. The mechanical properties in the interface of a joint between two dissimilar materials do not belong to those of either material. Any interaction between the glass–ceramic and metal may influence the mechanical properties of their joint. Although a few studies have investigated the mechanical properties of the joint of SOFC glass–ceramic sealant/metallic interconnect, they are mainly focused on the bonding strength and creep behavior [4–11]. Little literature, in particular experimental work, is related to the interfacial cracking resistance of such a joint in pSOFCs [12–14].

In terms of mechanical strength of a joint, the interface between dissimilar materials is where cracks usually initiate and propagate so that it may be the weakest part in a joint [12]. The interfacial cracking resistance is important particularly for the joints involving brittle materials such as glass–ceramic sealants because of the pre-existing defects [12]. In the studies of Malzbender et al. [13,14], interfacial fracture energy was investigated for the joint of SOFC components using a four-point bending test technique at room temperature in air. Sandwich specimens with glass–ceramic sealant between two interconnect steel strips were used to determine the interfacial fracture energy for the glass–ceramic/interconnect joint [13,14]. Their results revealed that the interfacial fracture energy increases with increasing annealing/aging time [13,14]. Those results of Malzbender et al. [13,14] were determined only at room temperature. However, pSOFC stacks work at high temperatures and there is lack of study related to the interfacial fracture energy of such joints at operating temperature. Thus, it is still needed to investigate the interfacial fracture energy of the glass–ceramic/interconnect joint at SOFC working temperature.

As hermetic sealants are usually weaker than other components in an SOFC system, a systematic investigation of mechanical properties of joints between glass–ceramic sealants and metallic interconnects at both room temperature and operating temperature is necessary for design of a reliable pSOFC stack. As part of a series of studies [10,11,15–21] on the mechanical properties of glass–ceramic sealants and metallic interconnects for pSOFCs, the aim of this study is to investigate the interfacial cracking resistance between a $BaO–B_2O_3–Al_2O_3–SiO_2$ glass–ceramic sealant (GC-9) and a ferritic-stainless-steel interconnect (Crofer 22 H) for pSOFC applications. Interfacial fracture energy of the glass–ceramic/metallic interconnect joint is evaluated at room temperature to 800 °C. In order to study the effect of thermal aging on the interfacial fracture energy, some joint samples are tested after aging at 800 °C in air for various lengths of time.

2. Experimental procedures

2.1. Materials and specimens

In order to investigate the interfacial fracture energy of glass–ceramic/interconnect joint, a notched sandwich specimen configuration for bending test is used in this study, as shown in Fig. 1. The glass–ceramic sealant, designated as GC-9, used to join the two metallic coupons is a novel $BaO–B_2O_3–Al_2O_3–SiO_2$ glass which has recently been developed at the Institute of Nuclear Energy Research (INER) for pSOFCs. Chemical composition of the patented GC-9 glass–ceramic in mol% includes 34 BaO, 9.5 B_2O_3, 4.5 Al_2O_3, 34 SiO_2, 12 CaO, 5 La_2O_3, and 1 ZrO_2 [22]. Relevant mechanical properties of the GC-9 glass–ceramic have been reported previously [15–18]. The GC-9 glass sealant shows good thermal properties, chemical compatibility and stability, and hermetic properties for use in pSOFCs [23–27]. The GC-9 glass has a glass transition temperature (T_g) and softening temperature (T_s) of 668 °C and 745 °C, respectively [15]. The GC-9 glass was made by mixing the constituent oxide powders followed by melting at 1550 °C for 10 h. After melting, it was poured into a mold preheated to 680 °C to produce GC-9 glass ingots. The GC-9 glass ingots were then annealed at 680 °C for 8 h and cooled down to room temperature. GC-9 glass powders were made by crushing the as-cast glass ingots and sieving with 325-mesh sieves. The average size of the glass powder is 45 μm. Slurries were then made by adding into the GC-9 powders the desired amounts of solvent (alcohol), binder (ethyl celluloid), and plasticizer (polyethylene glycol).

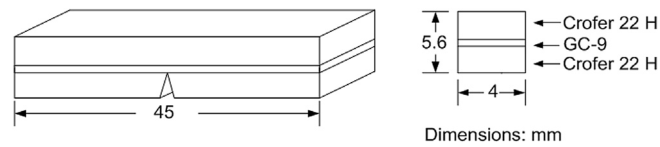

Fig. 1. Geometry of sandwich joint specimen for four-point bending test.

The metallic coupons of the joint specimens are made of a newly developed commercial ferritic stainless steel, Crofer 22 H (ThyssenKrupp VDM GmbH, Germany), which is a heat-resistant alloy developed for pSOFC interconnects. Chemical composition of the Crofer 22 H alloy in wt% includes 22.93 Cr, 1.94 W, 0.51 Nb, 0.43 Mn, 0.21 Si, 0.08 La, 0.07 Ti, 0.02 Cu, 0.02 Al, 0.014 P, 0.007 C, <0.002 S, and balance of Fe. Relevant mechanical properties of the Crofer 22 H alloy can be found in a previous study [20]. A large steel plate supplied by the vendor was cut into small ones having plane dimensions of 5 cm × 5 cm and a thickness of 2.5 mm for making sandwich joint specimens. No surface treatment is given to the steel plates such that their bonding areas remain as received surface condition. The arithmetical mean roughness (*Ra*) of the steel plate surface is around 0.25 μm, as measured by a surface roughness tester. Before joining process, each steel plate was cleaned with alcohol.

A slurry of GC-9 was spread on one side of each steel plate for making the metallic interconnect/glass–ceramic/metallic interconnect joint (Fig. 1). The as-assembled sandwich plates were then put into a furnace to dry the slurry at 80 °C. The sandwich plates were then sintered under a compressive load through appropriate heat treatments. In order to simulate a practical assembling process of a pSOFC stack, the applied compressive load is 12.25 kPa. In the sintering process, the joined plates were firstly held at 500 °C for 1 h to remove the binder and plasticizer, heated to 900 °C, and held for 4 h. The heating rate at each step is 5 °C min^{-1}. After the joining process, thickness of the glass–ceramic layer is about 0.6 mm. Each sandwich plate was then cut by a diamond saw into rectangular bars of dimensions of 4 mm × 5.6 mm × 45 mm (Fig. 1) for four-point bending test. Machining direction is along the 45-mm-length longitudinal direction. A spark-erosion wire cutting technique was used to generate a notch in one of the metallic coupons of each specimen. The notch tip is in the proximity of the interface. As the spark-erosion cutting wire has a diameter of 0.2 mm, the radius of the notch tip is around 0.1 mm. Some specimens were heat treated in air at 800 °C for 100 h or 1000 h to investigate the effects of thermal aging on the interfacial fracture energy.