Journal of Power Sources 245 (2014) 787–795

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Creep rupture of the joint of a solid oxide fuel cell glass–ceramic sealant with metallic interconnect

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H I G H L I G H T S

- Creep strength of SOFC glass seal/metal interconnect joint is assessed at 800 °C.
- Creep life time increases with a decrease in both tensile and shear loads applied.
- Prolonged constant tensile load degrades joint strength more than shear load.
- Creep fracture patterns of both shear and tensile joint specimens are similar.
- Creep crack growth occurs mostly along and around the chromate/glass interface.

A R T I C L E I N F O

Article history:
Received 1 May 2013
Received in revised form
8 July 2013
Accepted 9 July 2013
Available online 17 July 2013

Keywords:
Planar solid oxide fuel cell
Glass–ceramic sealant
Metallic interconnect
Creep
Joint strength

A B S T R A C T

Creep properties of sandwich joint specimens made of a newly developed $BaO-B_2O_3-Al_2O_3-SiO_2$ glass–ceramic sealant (GC-9) and a ferritic-stainless-steel interconnect (Crofer 22 H) for planar solid oxide fuel cells (pSOFCs) are investigated at 800 °C under constant shear and tensile loadings. The creep rupture time of Crofer 22 H/GC-9/Crofer 22 H joint specimens is increased with a decrease in applied load for both shear and tensile loading modes. The given metal/sealant/metal joint has a greater degradation of joint strength at 800 °C under prolonged, constant tensile loading as compared to shear loading. The tensile creep strength at a rupture time of 1000 h is about 9% of the average tensile joint strength, while the shear creep strength at 1000 h is about 23% of the average shear joint strength. Failure patterns of both shear and tensile joint specimens are similar regardless of the creep rupture time. In general, creep cracks initiate at the interface between the $(Cr,Mn)_3O_4$ spinel layer and the $BaCrO_4$ chromate layer, penetrate through the $BaCrO_4$ layer, and propagate along the interface between the chromate layer and glass–ceramic substrate until final fracture. Final, fast fracture occasionally takes place within the glass–ceramic layer.

1. Introduction

In recent development of solid oxide fuel cell (SOFC), planar SOFCs (pSOFCs) attract more attention than tubular ones as they are cost effective and have a lower Ohmic loss [1]. A pSOFC stack is generally a multi-layer structure composed of repeated units of ceramic anode–electrolyte–cathode assembly and metallic components. In particular, interconnects play a very important role in structural and electrical connection of unit cells. To maintain the operation and performance of a pSOFC system, hermetic sealants are needed to bond components and form gas-tight seals to separate both the oxidant and fuel chambers. When a rigid type of sealing is applied to pSOFC stacks, joining glass–ceramic sealants to metallic interconnects is very common. Locations of sealant applied in a pSOFC stack include: (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 [2]. Seals at locations (b) and (d) can be regarded as a joint of glass–ceramic sealant and metallic interconnect.

The high-temperature operation of SOFC could generate significant thermal stresses due to mismatch of coefficient of thermal expansion (CTE) between components and temperature gradients in the SOFC system [3–5]. Detailed configuration of the joint between glass–ceramic sealant and metallic interconnect in real pSOFC stacks is given in Refs. [2–4] to illustrate how and where thermal stresses are generated in such a joint. The thermal stresses

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http://dx.doi.org/10.1016/j.jpowsour.2013.07.047

may or may not cause an immediate failure of pSOFC structure, but they could generate creep damages in the components under a long-term high-temperature operation environment. Creep damages in the joint of a glass–ceramic sealant with metallic interconnect may eventually generate excessive deformation and/or cracking, leading to gas leakage and degradation of cell performance. Therefore, it is very important to investigate the creep properties of such a joint for assessing the structural integrity and durability of a pSOFC stack.

The high-temperature creep properties have been studied individually for glass–ceramic sealants [6–9] and metallic interconnects [10–13] for pSOFC applications. However, the mechanical properties of a joint do not belong to that of a single material while they are interfacial properties between two materials. Any interaction between the glass–ceramic sealant and metallic interconnect may influence the mechanical properties of the joint. Although a few studies have investigated the mechanical properties of the joint of SOFC glass–ceramic sealant/metallic interconnect [6,14–19], there is still lack of study on the long-term high-temperature creep behavior of such a joint. As a reliable pSOFC system is expected to operate steadily at elevated temperature for a prolonged period of time (at least 20,000 h for commercial systems), more studies are needed to investigate the creep behavior of joints between the glass–ceramic sealant and interconnect at high-temperature. As part of a series of studies [9–11,19–23] on the mechanical properties of glass–ceramic sealants and metallic interconnects for pSOFCs, the aim of this study is to investigate the high-temperature creep rupture behavior of the joint between a newly developed $BaO-B_2O_3-Al_2O_3-SiO_2$ glass–ceramic sealant (GC-9) and a ferritic-stainless-steel interconnect (Crofer 22 H) under both tensile and shear loadings.

2. Experimental procedures

2.1. Materials and specimens

As described above, glass–ceramic sealants bonding a metallic frame to a metallic interconnect and a stack to a base manifold plate are classified as a joint of glass–ceramic sealant and metallic interconnect. In order to simulate such a joint subjected to thermal stresses at operating temperature, two types of sandwich joint specimens (metal/sealant/metal) are applied to determine the tensile and shear creep properties of the joint. In consideration of interfacial fracture in a joint of two dissimilar materials, failure often occurs along the interface such that compressive loads normal to the interface are not expected to generate interfacial cracking or debonding along the interface. Therefore, only tensile and shear loadings are applied to the joint specimens for creep test in the current study. Details of the specimen geometry and dimensions are given in a previous study [19]. The metallic coupons of the joint specimens are made of a newly developed commercial ferritic stainless steel, Crofer 22 H (ThyssenKrupp VDM GmbH, Germany), for pSOFC interconnects. Chemical composition of 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 Crofer 22 H alloy can be found in a previous study [11]. In order to minimize bending and twisting effects during creep testing, the force is applied to the joint specimen by means of pin loading. The as-received, 2.5-mm-thick metal plates were cut into rectangular slices with dimensions of 95 mm (length) × 25 mm (width) × 2.5 mm (thickness). A pin hole was drilled in each steel slice. For shear test specimens, one edge of each steel slice was milled from the original thickness of 2.5 mm to 1 mm with an area of 8 mm × 25 mm to be spread with the glass–ceramic sealant. The nominal joining areas are 25 mm × 2.5 mm and 25 mm × 6 mm for tensile and shear test specimens, respectively.

In each joint specimen, a novel $BaO-B_2O_3-Al_2O_3-SiO_2$ glass–ceramic sealant (designated as GC-9), which was developed at the Institute of Nuclear Energy Research for pSOFC sealing, is applied to join the two metallic coupons. Chemical composition of the patent 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 [24]. Relevant material properties of GC-9 glass–ceramic have been reported previously [9,20–22,25–29]. After machining the steel slices, GC-9 glass paste was spread on the joining region of each steel coupon to make a half specimen. A joint specimen was assembled by placing a half specimen on another half specimen to form a metal/glass–ceramic/metal sandwich specimen through appropriate heat treatments. After the joining process was completed, the thickness of glass–ceramic sealant is of 0.5 mm for the shear test specimen and of 0.44 mm for the tensile test specimen. As the joint specimens were prepared and fabricated in a way similar to that of a previous study, details of materials and specimen preparation can be found in that study [19].

2.2. Creep test

Tensile and shear creep tests were conducted at 800 °C under a constant load using a direct-load creep test machine. Various weights were used as the loading source in the direct-load creep test machine. The stress level can be adjusted by changing the weights applied. For tensile creep tests, various constant loads of 180 N–280 N were applied, while constant loads of 60 N–100 N were applied for the shear creep tests. The values of the applied constant loads were selected to generate the magnitude of creep rupture time distributed in the orders of 10^0, 10^1, 10^2, and 10^3 h. In each test, the joint specimen was heated to 800 °C with a rate of 5 °C min^{-1} and held for 15 min to reach thermal equilibrium before applying the mechanical load.

2.3. Microstructural analysis

After creep testing, fracture surfaces were examined with an optical microscope to determine the true joining area for calculating the nominal tensile or shear stress. Scanning electron microscopy (SEM) was employed to examine the failure mode as well as the interfacial morphology between the glass–ceramic sealant and metallic interconnect. The energy dispersive spectrometer (EDS) module attached with the SEM was used for composition analysis to show the elemental distributions in selected regions on the fracture surfaces.

3. Results and discussion

3.1. Creep rupture behavior

For the given joint specimens, the shear joint strength has an average value of 6.6 MPa and 4.7 MPa at room temperature and 800 °C, respectively, while the average tensile joint strength is of 23 MPa at room temperature and of 12.7 MPa at 800 °C [19]. Creep rupture characteristics of the Crofer 22 H/GC-9/Crofer 22 H joint subjected to constant shear and tensile loads at 800 °C are shown in Fig. 1 by plotting the applied stress versus creep rupture time. Four constant loads (280 N, 200 N, 190 N, and 180 N) are applied to the shear test specimens, corresponding to constant shear stresses of 1.04 MPa–1.60 MPa (Fig. 1(a)). For tensile test specimens, the applied constant loads are of 100 N, 80 N, 70 N, and 60 N, corresponding to constant tensile stresses of 0.96 MPa–1.60 MPa (Fig. 1(b)). As shown in Fig. 1, the relationship between the applied