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Original article

Creep rupture of the joint between a glass-ceramic sealant and lanthanum strontium manganite-coated ferritic stainless steel interconnect for solid oxide fuel cells

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ABSTRACT

Creep rupture is investigated at 800 °C of a joint between a glass-ceramic sealant and a ferritic stainless steel interconnect coated with lanthanum strontium manganite for solid oxide fuel cell application. Results reveal the shear and tensile creep strength of the as-joined, non-aged joint at a rupture time of 1000 h is about 42% and 3% of the average shear and tensile bonding strength, respectively. A thermal aging of 1000 h at 800 °C enhances the creep strength. For both non-aged shear and tensile specimens with a short creep rupture time, fracture mainly takes place in an oxyapatite interlayer which is formed in the joining process. For a medium creep rupture time, fracture site changes to a mixed $BaCrO_4$/oxyapatite layer. Oxyapatite and $BaCrO_4$ dominate the creep failure mechanism for 1000 h-aged shear specimens, while $(Cr,Mn)_3O_4$ spinel plays a role in the creep failure of 1000 h-aged tensile specimens.

1. Introduction

In order to increase power density and fulfill the requirement of electrical application, several unit cells are connected in series by interconnects and sealants in a typical planar solid oxide fuel cell (pSOFC) system. Interconnects in a pSOFC stack serve as the electrical connection between cells as well as the separation of fuel and oxidant gas. Thanks to a reduction in operating temperature to the range of 600–800 °C, ferritic stainless steels with high Cr concentration have been commonly used for interconnect in pSOFCs due to lower cost, better manufacturability, higher electrical conductivity, and high mechanical strength [1,2]. However, Cr-containing alloys have two major challenges, namely rapid chromium oxide (Cr_2O_3) scale growth and evaporation of Cr^{6+} species from interconnect into cathode [1]. The rapid Cr_2O_3 scale growth at high temperature leads to an increase of area specific resistance and/or spallation of interface between interconnect and other components [1]. On the other hand, volatile Cr^{6+} species deposited on the surface of cathode also increases the electrical resistance, which is called Cr poisoning [1]. These phenomena could result in degradation of cell performance and long-term durability of pSOFC stack. One of the approaches to address these limitations is applying a protective coating on the metallic interconnect to prevent Cr poisoning and improve the long-term durability of pSOFC [1–20]. Among the coating materials developed, lanthanum strontium manganite ($La_{1-x}Sr_xMnO_3$, LSM) has been practically applied on the metallic interconnect [15–20], as LSM is commonly used as cathode in pSOFC.

The hermetic sealant is another crucial part in pSOFC. Sealant must be stable in both fuel and oxidant gas sides and prevent from leakage and mixing. Glass and glass-ceramic seals are practically and favorably used in pSOFC stacks as they are hermetic and may crystalize during operation to form a more rigid glass-ceramic seal [21]. During thermal cycles of SOFC operation, thermal stresses are generated due to temperature changes and gradients as well as mismatch of coefficient of thermal expansion (CTE) between adjacent components [22,23]. Thermal stresses may generate creep damage in the components under a long-term high-temperature operating condition. In particular, undesired chemical reaction and creep damage in the joint between glass-ceramic sealant and metallic interconnect in pSOFC stacks may cause failure of sealing with excessive deformation, debonding, and/or cracking and lead to gas leakage and degradation of cell performance. Therefore, study on the chemical compatibility and creep properties of such a joint is necessary for assessment of the structural integrity and durability of a pSOFC stack.

Although mechanical properties of the joint between SOFC glass-ceramic sealant and metallic interconnect have been investigated in several studies [24–36], very few of them are focused on the long-term

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high-temperature creep behavior of such a joint [34]. In particular, there is still lack of study on the mechanical properties of the joint between SOFC glass-ceramic sealant and LSM-coated metallic interconnect. However, it is very important to study the influence of the interaction between glass-ceramic sealant, metallic interconnect, and LSM protective coating on creep behavior of such a joint. For these reasons, the purpose of this study is to investigate the creep properties of a joint between a SiO_2–B_2O_3–Al_2O_3–BaO glass-ceramic sealant and an LSM-coated ferritic stainless steel interconnect for pSOFC applications. In addition, the effect of thermal aging on the creep behavior of such a joint is also investigated. It is hoped that results of the present study and previous work [33–36] can provide an insight for assessing the long-term structural stability of pSOFC stacks.

2. Experimental procedures

2.1. Materials and specimens

As indicated in previous work, the joints of glass-ceramic sealant/metallic interconnect in a pSOFC stack are subjected to thermal stresses at operating stage [22], and it is expected that compressive loads normal to the interface in the joint would not induce interfacial fracture. Accordingly, only tensile and shear loadings are considered and applied in the present study to characterize the creep properties of such a joint. As shown in Fig. 1, two types of sandwich joint specimen (LSM-coated metal/glass-ceramic sealant/LSM-coated metal) are designed and made for mechanical test. By applying a pin loading, the interfaces of the joint are subjected to either shear stress (Fig. 1(a)) or tensile stress (Fig. 1(b)). A commercial ferritic stainless steel for pSOFC interconnect, Crofer 22 H (ThyssenKrupp VDM GmbH, Werdohl, Germany), is used for the metallic parts of the sandwich joint specimens. Chemical composition, mechanical properties, and high-temperature creep behavior of Crofer 22 H alloy have been characterized in previous studies [37,38]. Note that the content of Cr in the Crofer 22 H alloy is 22.93 wt% [37,38]. Details of preparing and machining the bare metallic coupons can be found in Refs. [33,34]. After machining, a thin $La_{0.67}Sr_{0.33}MnO_3$ layer was sputtered on the joining area before spreading the glass-ceramic sealant. The LSM coating was deposited onto the steel slices using a pulsed direct current magnetron sputtering system [39]. The LSM-coated Crofer 22 H slice was then calcined at 850 °C for 4 h to form a perovskite protecting layer. The thickness of the LSM layer coated on the Crofer 22 H slice is about 3 μm.

The glass-ceramic sealant used to join the two LSM-coated steel coupons is a SiO_2–B_2O_3–Al_2O_3–BaO glass and is designated as GC-9. With good thermal properties, chemical compatibility and stability, and hermetic properties, GC-9 glass-ceramic sealant has been proved to be suitable for application in pSOFCs [40–43]. Its major composition includes 34 mol% SiO_2, 9.5 mol% B_2O_3, 4.5 mol% Al_2O_3, 34 mol% BaO, 12 mol% CaO, 5 mol% La_2O_3, and 1 mol% ZrO_2 [40]. Mechanical properties and high-temperature creep behavior of GC-9 have been studied previously [44–47]. After the LSM coating process, GC-9 glass paste was spread on the joining region of each steel slice to make a half-specimen. A joint specimen was then assembled by placing a half-specimen on another to form a Crofer 22 H/LSM/GC-9/LSM/Crofer 22 H sandwich specimen through designed heat treatments. The final thickness of the glass-ceramic sealant layer is about 0.50 mm and 0.44 mm for the shear test and tensile test specimens, respectively. As the sandwich joint specimens are made in a way similar to that of previous studies, details of preparation procedures can be found in those studies [33,34]. For investigating the effects of long-term operation in an oxidizing environment, some joint samples were thermally aged in air at 800 °C for 1000 h before conducting mechanical test.

2.2. Creep test

The interfacial bonding strength of the given joint specimens in both shear and tensile loading modes at 800 °C in air was firstly determined by conducting uni-axial tensile test in a commercial closed-loop servo-hydraulic material test machine attached with a furnace. For each loading mode, about 3–5 specimens were repeatedly tested and the average bonding strength was determined. After that, tensile and shear creep tests were conducted at 800 °C in air under a constant load using a direct-load creep test machine. Based on the results of bonding strength test, various stress levels were selected for applying constant loads to generate the creep rupture time distributed in the orders of 1, 10, 100, and 1000 h. These mechanical and creep testing techniques have been

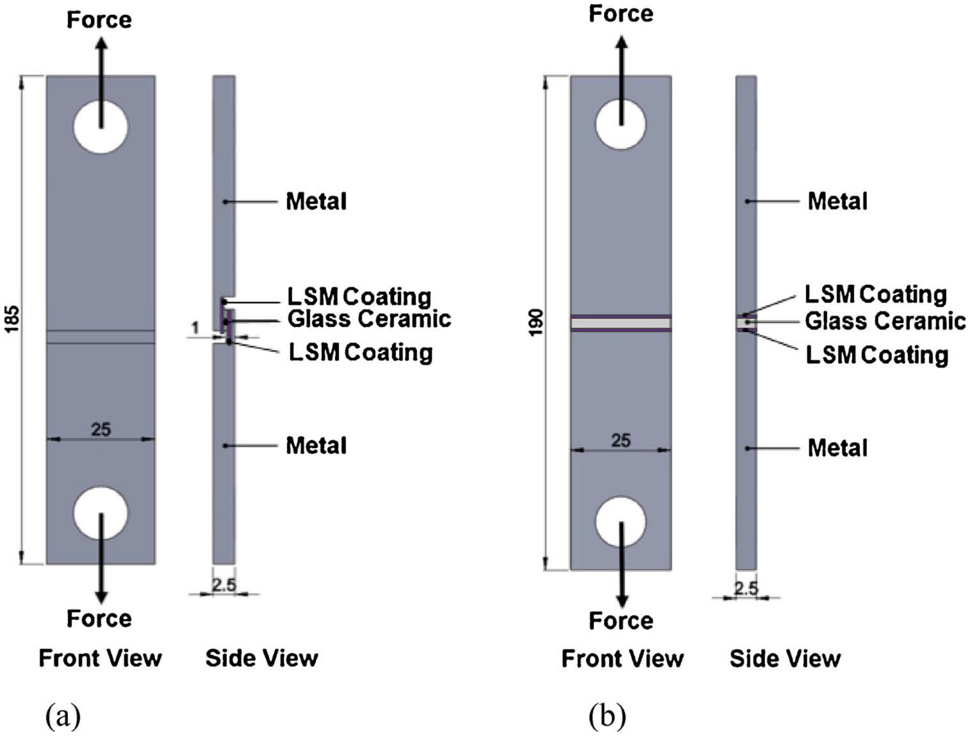

Fig. 1. Schematic of two types of joint specimen: (a) shear specimen; (b) tensile specimen. (Dimensions: mm).