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Short communication

Mid-term stability of novel mica-based compressive seals for solid oxide fuel cells

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Abstract

A novel mica-based compressive seal concept was examined at elevated temperatures under compressive stress to evaluate its stability. The "hybrid" mica compressive seals, composed of cleaved Muscovite mica and two compliant inter-layers, were reported earlier to have very low leak rates at 800 °C. In the present study, we examined the mid-term (~350–700 h) stability of the mica-based compressive seals with three different inter-layers: a low melting borosilicate glass, a glass ceramic material, and a metallic material. The 800 °C leak test results showed excellent stability for the three different inter-layers in air at a compressive stress of 100 psi as the leak rates remained almost unchanged during the test. Microstructural characterization of the interfaces showed very limited interfacial reaction or glass penetration at the glass/8YSZ substrate interface. The results clearly demonstrate the applicability of the mica-based compressive seals for solid oxide fuel cells.

Keywords: Mica-based compressive seal concept; Solid oxide fuel cells; Muscovite mica

1. Introduction

The development of a suitable stack sealant or sealants is a very challenging task for the advancement of solid oxide fuel cells (SOFCs) [1–4]. The requirements for the sealants are stringent due to the high operating temperatures (typically 700–1000 °C) and the very harsh environments (oxidizing, reducing and humid). The sealant needs to provide sufficiently low leak rates that any leaks (e.g. H_2 into the air stream) will not cause undesirable local heating which can lead to the structural or functional failure of the stack. The sealant also has to survive many thermal cycles during routine operation; this appears to be the most challenging part of the seal development. Finally, the sealant needs to have long-term stability, and must not cause severe degradation of the materials with which they are in contact (e.g. stabilized zirconia, interconnect, and/or electrodes) under the SOFC operating conditions.

Currently, most SOFC seal development has focused on glass and glass–ceramic seals, although other approaches such as cement seals, mica glass–ceramics, and braze seals have been proposed [5–9]. Recently, mica-based compressive seals were reported as alternative sealants for SOFCs that do not require a stringent CTE match with the materials being sealed [10–13]. Chou and Stevenson developed a "hybrid" mica-based compressive seal, composed of cleaved Muscovite mica and two compliant inter-layers, and reported a very low leak rate of $\sim 1.6 \times 10^{-4}$ sccm/cm at 800 °C and 100 psi [11]. Thermal cycling of the hybrid mica seals in air showed a rapid increase in leak rates during the initial couple of cycles, with a tendency for the increase in leak rate to saturate after 20–30 cycles [12]. In this paper, we report further evaluation of the hybrid mica seals in terms of their stability at elevated temperature. The primary objectives were to examine the stability of the mica material, as well as stability of the electrolyte in contact with the inter-layer. Three different inter-layers were tested: a low melting borosilicate glass, a glass ceramic material, and a metallic material. Results of 800 °C leak tests are reported. Also, scanning electron microscopy was used to characterize the microstructural changes at the interface, and the observed degradation is discussed.

2. Experimental

2.1. Raw materials, characterization, and leak test

The mica investigated in this study was natural cleaved single crystal Muscovite mica ($KAl_2(AlSi_3O_{10})(F, OH)_2$) in

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the thin sheet form (~100 μm thick). For the hybrid seal, which involves adding an inter-layer between the mica and the materials to be mated, three materials were used as the inter-layer: a low melting borosilicate glass (designated G6), a Ba–Al–Si glass–ceramic (G18), and silver foil. Further details of these materials are given in [11,12]. After assembling the mica sheet with the inter-layers, they were pressed between a metal pipe and an 8YSZ substrate. The assembly was then heated in a clamshell furnace to 800 °C under a constant stress of 100 psi for the desired time to test the leak rates. The details of the experimental setup and the calculation of the normalized leak rates (in standard cubic centimeter per minute per unit length of seal, i.e. sccm/cm) are given in an earlier paper [11].

3. Results and discussion

3.1. Hybrid mica seal with silver as the inter-layer

Earlier testing of the hybrid mica seals was focused on glass or glass–ceramic as the compliant inter-layers [11,12]. The same concept was also tested using metallic inter-layers and was proved effective in reducing the leak rates substantially [13]. Silver was selected among other precious metals due to its stability in oxidizing environments, relatively low cost, and availability in a variety of forms, although silver is not stable in reducing environments at high temperatures. Improvements in SOFC materials and designs over the past 10 years have resulted in lowering of the operating temperatures from as high as 1000 °C to below 800 °C; at these lower temperatures, silver may offer long-term stability, especially when placed under compression with a relatively small exposed area. The 800 °C leak rates of the hybrid seal with silver as the compliant inter-layer are shown in Fig. 1 as a function of time. The initial leak rate was about 0.003 sccm/cm. The leak rate doubled to about 0.006 sccm/cm after ~80 h and remained almost constant for 324 h. The reason for the leak rate increase was not clear and may be due to limited micro-fracture of the adjacent mica sub-layers; however, it is evident that the hybrid mica seal with silver inter-layer appears to be stable. The equilibrium vapor pressure of silver at 800 °C is about 6×10^{-8} atm and about 2.4×10^{-9} atm at 700 °C [14]. The material loss by vaporization may not be substantial for silver in air as long as the exposed area is minimized; however, the stability in reducing environment must be considered for SOFC applications.

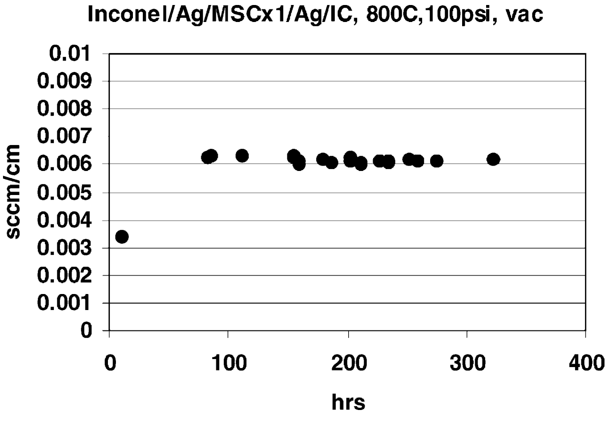

Fig. 1. Mid-term stability test of the hybrid mica seal with silver as the inter-layer material at 800 °C in air under a stress of 100 psi.

3.2. Hybrid mica seal with a glass or glass–ceramics as the inter-layer

Two glasses were selected as the inter-layers for the hybrid mica seal: a low melting borosilicate glass (G6) and a glass ceramics (G18). The glass (G18) is a Ba–Al-silicate glass which crystallizes at 700–800 °C into a rigid ceramic containing multiple crystalline phases. The CTE of the G18 glass was carefully tailored to match that of the anode materials (i.e. Ni-8YSZ cermet). It is evident that the leak rates remained fairly constant during the whole period of time at 800 °C for both glasses, as shown in Figs. 2 and 3. The 800 °C leak rates were <0.001 sccm/cm for the

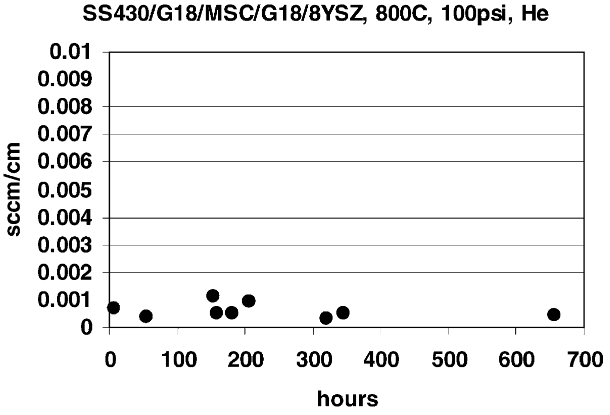

Fig. 2. Mid-term stability test of the hybrid mica seal with a glass–ceramic as the inter-layer material at 800 °C in air under a stress of 100 psi.

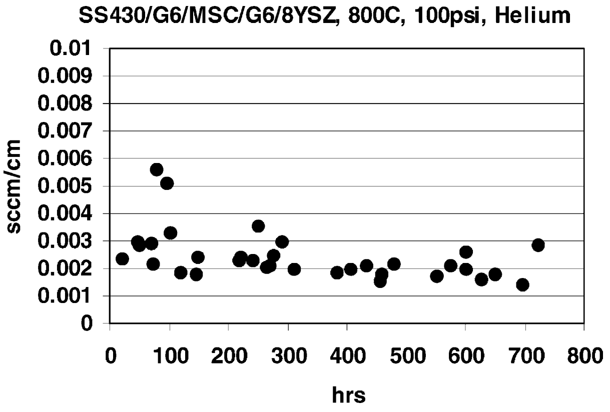

Fig. 3. Mid-term stability test of the hybrid mica seal with a low melting borosilicate glass as the inter-layer material at 800 °C in air under a stress of 100 psi.

glass–ceramic (Fig. 2) and were about 0.002–0.003 sccm/cm for the borosilicate glass (Fig. 3). The difference between these two glasses is likely due to the Muscovite mica itself that the cleavage into multiple sub-layers may be different from sample to sample and resulted in minute changes in leak paths.

3.3. Materials degradation

Although the hybrid seals exhibited very low leak rates, there are two major concerns with the inter-layers used: will the inter-layers degrade the mica (e.g. through melting or chemical reaction), and will the inter-layers damage the other adjacent materials. After the mid-term stability tests were concluded, the hybrid mica assemblies with the three different inter-layers could be easily separated from the adjacent metal pipe and the 8YSZ substrate; only a couple of mica sub-layers were mechanically or chemically bonded to the mating surfaces. As mentioned in an earlier paper [10], at elevated temperatures the Muscovite single crystal mica loses about 4% of its weight due to volatilization of chemical water. The mica will then separate along the basal planes into multiple parallel sub-layers of thickness about 2–10 μm. Except for the few sub-layers on each side which were bonded to the adjacent materials surfaces, the rest of the mica appeared to be intact and showed no damages from the inter-layers. For the glass–ceramic (G18) and the borosilicate glass, no melting of the mica was observed despite the fact that the Muscovite mica is an alumino-silicate material. For the silver inter-layer, some diffusion of silver into the mica was evident based on discoloration that was observed on the adjacent sub-layers (Fig. 4A). This is not surprising since silver melts at 960 °C and would be rather mobile at 800 °C; however, the diffusion was limited to a few adjacent sub-layers so that the interior of the mica was not affected (Fig. 4B). The current observations imply good chemical compatibility of the mica with the different inter-layers at elevated temperatures and compressive stresses,

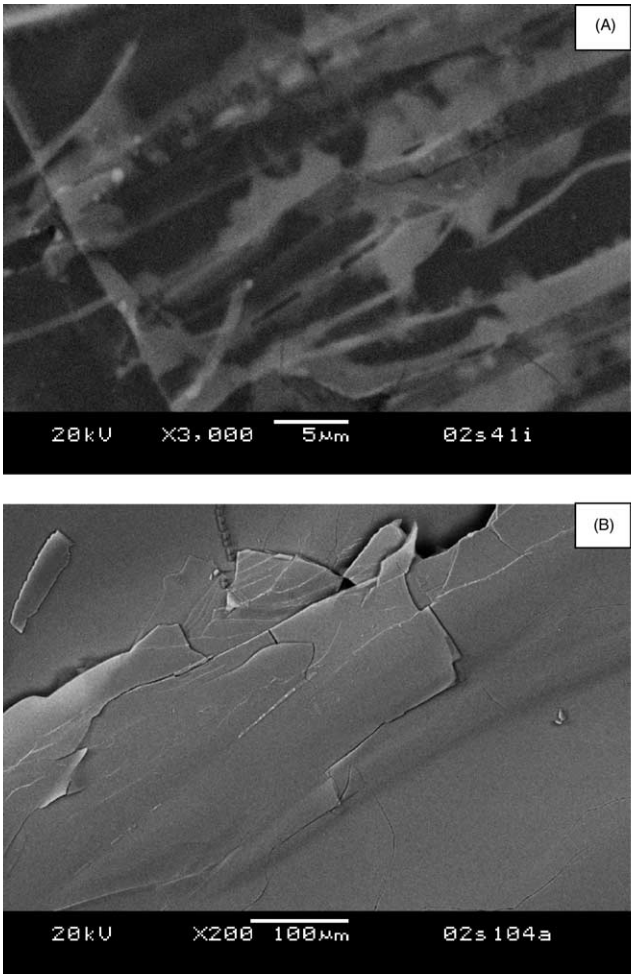

Fig. 4. Interfacial microstructure of the hybrid mica seal with silver inter-layers pressed between a metal pipe and an 8YSZ substrate at 800 °C, with an applied load of 100 psi for 324 h in air. The section under compression (A) clearly shows the diffusion of Ag into the mica and caused discoloration as compared to the section not under compression (B).

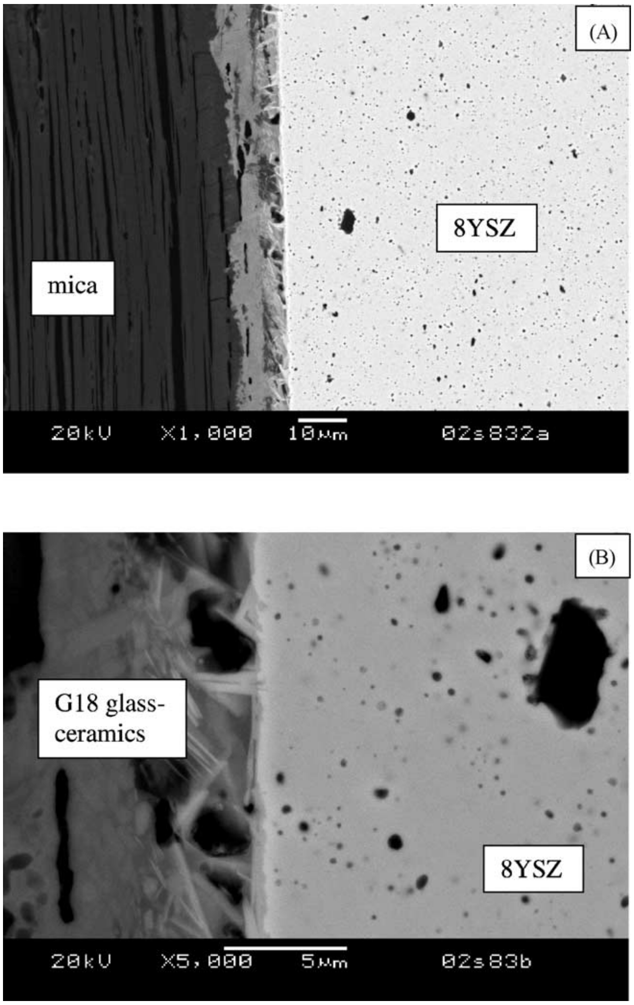

Fig. 5. Interfacial microstructure of the hybrid mica seal with G18 glass–ceramic inter-layers pressed between a metal pipe and an 8YSZ substrate at 800 °C, with an applied load of 100 psi for 650 h in air: (A) a low magnification, and (B) a high magnification at the interface.

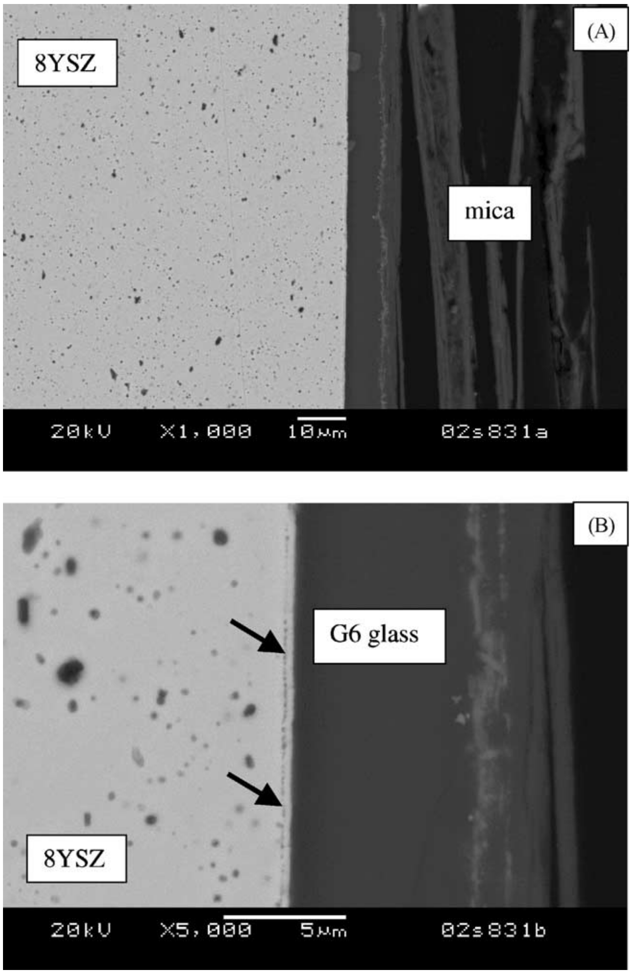

Fig. 6. Interfacial microstructure of the hybrid mica seal with a borosilicate glass as the inter-layer material pressed between a metal pipe and an 8YSZ substrate at 800 °C, with an applied load of 100 psi for 724 h in air: (A) a low magnification, and (B) a high magnification shows the glass penetration near the interface.

although the stability in humid and reducing environments remains to be determined.

The other concern regarding the hybrid seal was the potential degradation of the 8YSZ ceramic electrolyte (8YSZ) by the glass inter-layers. The 8YSZ directly under the seal area in the stack will not contribute to the electrochemical performance of the cell, however undesirable reactions with the inter-layer materials such as melting or glass penetration along the grain boundaries should be minimal to assure long-term stability in SOFC environments. Fig. 5 shows the interfacial microstructure between the 8YSZ, the glass ceramic (G18) and the cleaved mica sub-layers at low (Fig. 5A) and high magnification (Fig. 5B). Clearly, the glass crystallized into multiple phases along the interface, likely $BaSiO_3$ or $BaAl_2Si_2O_8$ [9]. It is evident that there was no severe "melting" of the 8YSZ into the glass–ceramic, nor any glass penetration into the electrolyte through grain boundaries. For the case of the borosilicate glass, no distinct crystallization was observed in the glass (Fig. 6A), which appeared to remain amorphous after holding at 800 °C for 724 h. However, this glass did penetrate into the 8YSZ (as shown by arrows in Fig. 6B) uniformly to a depth of approximately 0.5 µm, forming discrete minute droplets with sizes less than ~0.2 µm. The degradation by this penetration and discrete tiny droplets formation should cause no concern regarding the mechanical strength that the intrinsic flaw sizes of the electrolyte are much larger.

4. Conclusions

The stability of a novel mica-based hybrid compressive seal was examined in air at 800 °C under a compressive load. Three different inter-layers were studied: a low melting borosilicate glass, a Ba–Al-silicate glass ceramic, and a thin silver foil. The 800 °C leak test results showed excellent stability for the hybrid mica with all three inter-layers in air at a compressive stress of 100 psi, as the leak rates remained almost unchanged during the test. Leak rates less than 0.001 sccm/cm were obtained using the glass ceramic as the inter-layer. Microstructural characterization of the interface showed very limited reaction or glass penetration at the 8YSZ substrate interface as well as no severe degradation to the mica by these inter-layer materials. The results clearly demonstrate the applicability of the mica-based compressive seals for solid oxide fuel cells.

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