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Phlogopite mica-based compressive seals for solid oxide fuel cells: effect of mica thickness

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Abstract

Commercially available Phlogopite mica papers of varying thickness, ∼0.1, ∼0.2, and ∼0.5 mm, were evaluated as potential solid oxide fuel cell (SPFC) seal materials. The micas were tested in two forms: plain and hybrid. The hybrid form involved the addition of glass interlayers between the mica and the adjacent components. For each sample, about 30 thermal cycles were conducted and the 800 °C leak rates were determined. The results showed an excellent thermal cycle stability of the Phlogopite micas in the hybrid design in that the leak rates remained almost constant after ∼10 cycles. In addition, the leak rate appeared to increase with increasing mica thickness in the hybrid design, but showed no thickness dependence for mica in the plain design. The Phlogopite micas also showed good mid-term (∼500 h) stability in both air and reducing environments. Microstructure characterization showed no distinct degradation such as fragmentation and particle formation after thermal cycle and the mid-term stability tests.

Keywords: Phlogopite mica; Solid oxide fuel cell; Leak rates; Thermal cycle

1. Introduction

The development of a suitable stack sealant or sealants is a very challenging task for the advancement of planar solid oxide fuel cells (SOFCs) because the requirements are stringent in multiple aspects: chemical compatibility, mechanical integrity, electrical properties, and thermal stability [1–4]. The seal task becomes more challenging because there are typically multiple sealing sections in planar SOFCs with metal interconnect; required seals may include electrolyte to metal frame, metal frame to metal interconnect, metal interconnect to ceramic spacer, and metal interconnect to manifolds. Up to now, the most stringent requirement for seals in SOFCs is the seal stability during repeated thermal cycles. The number of thermal cycles during the life service of SOFCs may be less than a few hundred for stationary power generation, but can reach multiple thousands if used as auxiliary power units for automobiles. Previous work on compressive mica seals was focused on Muscovite mica ($KAl_2(AlSi_3O_{10})(F, OH)_2$), which has a low CTE (∼7 ppm/°C) compared to components of the SOFCs such as the anode-supported cell and the metal interconnect, which have a coefficient of thermal expansion (CTE) of 12–13 ppm/°C [5–7]. The 800 °C leak rates for the Muscovite mica in the hybrid design were very low in the beginning ($\sim 2 \times 10^{-4}$ sccm/cm of seal length) [5]; however the leak rates abruptly increased by a factor of ∼l00 after a few thermal cycles [6]. Microstructure characterization after thermal cycling showed distinct degradation of the Muscovite mica adjacent to the sealed materials: fragmentation, micro-fracture, and particle formation. The degradation was mostly observed in the mica adjacent to the metal pipe where a large mismatch of CTE was present, rather than in the mica adjacent to the alumina substrate, where only a small mismatch of CTE was present [6].

One possible approach to minimize the abrupt increase in leak rate during thermal cycling is to use micas of higher CTE. In this study, we investigated Phlogopite mica ($KMg_3(AlSi_3O_{10})(OH)_2$), which has a higher CTE (∼10 ppm/°C), as the compressive seal material for SOFCs. The effect of mica thickness was examined on the thermal cycling on both the plain and the hybrid design. The plain design consists of a simple mica “gasket” placed between the materials being sealed, while the hybrid design involves the addition of glass interlayers between the mica gasket and the adjacent materials to be sealed [5]. In addition to thermal cycling tests, we also tested the stability of the Phlogopite mica in both air and the reducing environments for about 500 h. After the thermal cycling and mid-term

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stability tests, microstructures were analyzed with respect to the effect of mica thickness.

2. Experimental

2.1. Raw materials and characterization

The Phlogopite mica used in this study was in the paper form, instead of the naturally cleaved monolithic form. The paper form mica is composed of large and discrete mica flakes overlapping with each other and bonded with a few percent (∼3 wt.%) of organic binders. Fig. 1 shows the surface morphology (Fig. 1A) and the cross-section view (Fig. 1B) of the Phlogopite mica. The size of the mica flakes varies from a few hundred microns to a few millimeters. The thicknesses of the mica flakes are in the range of ∼2 to ∼10 μm. Phlogopite micas of three nominal thicknesses were used in this study: ∼0.1, ∼0.2, and ∼0.5 mm. The linear thermal expansion was conducted on micas pre-heat treated at 850 °C for 6 h in air. About seven layers of the mica paper (1 in. × 1 in. × 1/8 in.) were wrapped together for the CTE measurement in air using a dilatometer (Unitherm Model 1161, Anter Laboratory, PA). The surface morphology and the microstructure (cross-section) of the mica were characterized using the scanning electron microscopy (JOEL, JSM-5900LV). The crystal structure of the mica was determined using powder diffraction (Phillips XRG-3100).

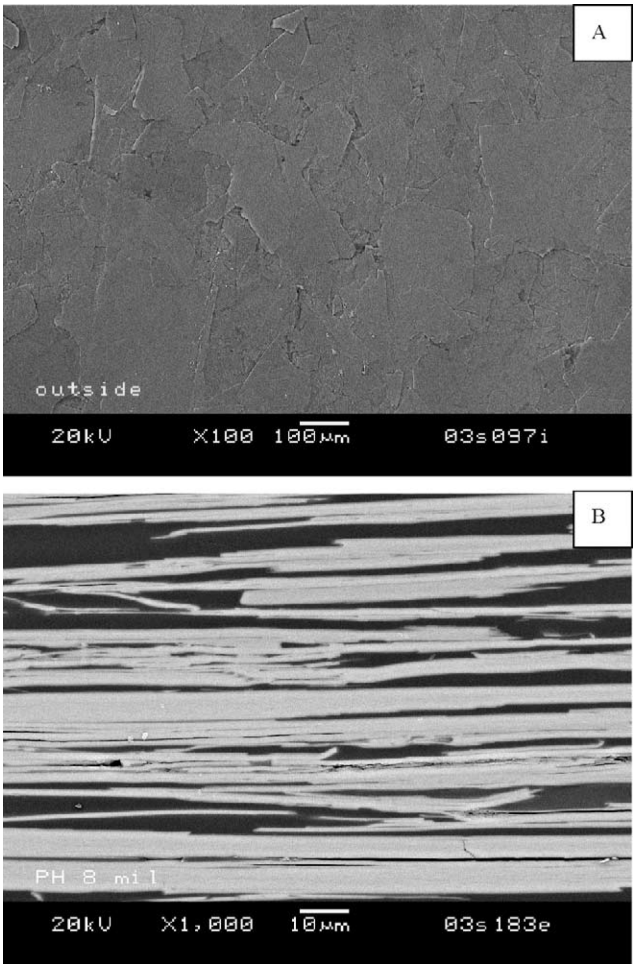

Fig. 1. Surface morphology (A) and cross-section view (B) of Phlogopite mica paper. The mica was heat treated at 700 °C for 4 h to burn out the organic binders.

2.2. Leak test, thermal cycling, and mid-term stability test

Leak testing was used in this study to assess the stability of the mica seal during the thermal cycling and the mid-term stability tests. The mica paper (about 1.5 in. × 1.5 in.) was tested in two designs: plain and hybrid, and pressed between an Inconel #600 pipe and an alumina substrate at 100 psi. The hybrid design involved adding glass interlayers at the mating interfaces, i.e. mica to metal pipe, and mica to alumina substrate [5]. The Inconel #600 pipe was surface finished with a #800 grit paper at the pressing section. The alumina substrate was used as received (Coors Tek, ADS-96-R) with a surface finish <0.89 μm. Thermal cycling was conducted in air for ∼30–50 cycles. The heating rate was ∼25 °C/min and the sample was held at 800 °C for 1 h before naturally cooling down to 100 °C. The mid-term stability tests were conducted at 800 °C in air and 700 °C in reducing environments (2.75% H_2/Ar+3% H_2O) for a period of ∼500–650 h. The detailed experimental setup and the determination of the 800 °C normalized leak rates are given in [5,6]. In this study, ultra-high purity helium was used to determine the leak rates at a gauge pressure of 2 psi. After the tests, mica samples were carefully removed from the test fixture and characterized with scanning electron microscopy.

3. Results and discussion

3.1. Linear thermal expansion of Phlogopite mica

As mentioned in the previous section, the mica paper was composed of large mica flakes overlapping with each other. Since each mica flake is considered a single crystal of monoclinic structure, one may expect anisotropy in CTE along and perpendicular to the basal planes (or the plane of the mica paper). For compressive seal applications, CTE along the basal plane is more important than that perpendicular to the basal plane, because the CTE mismatch along this direction was found to cause degradation of Muscovite mica seals during thermal cycling [6]. The measured thermal expansion along the basal plane of the Phlogopite mica is shown in Fig. 2. It is clear that the Phlogopite mica is stable in that no undesirable phase changes were evident. In addition, the expansion curve during the heating cycle coincided well with the cooling cycle. The average CTE from room temperature to 800 °C was calculated to be ∼10.3 ppm/°C. This is much higher than that of the Muscovite mica (∼7 ppm/°C).

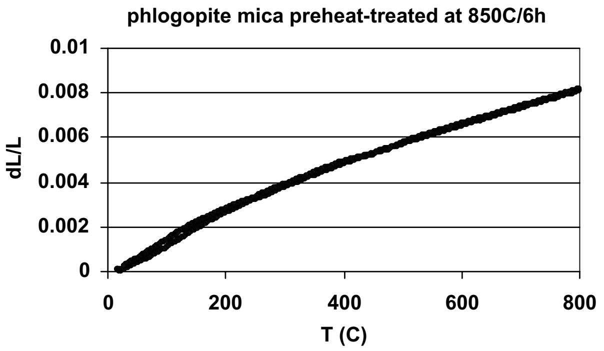

Fig. 2. Linear thermal expansion of Phlogopite mica (along the basal plane). Heating cycle data coincide with the cooling cycle data, indicating no undesirable phase changes. The average CTE (RT to 800 °C) was calculated to be 10.3 ppm/°C.

3.2. Thickness effect of plain mica on the 800 °C leak rates during thermal cycling

In this study, we tested the Phlogopite mica in three thicknesses: ~0.1, ~0.2, and ~0.5 mm. As shown in Fig. 3, there appears to be no dependence of leak rate on thickness; normalized leak rates were all about ~0.5 sccm/cm (standard cubic centimeters per minute per cm of seal length). The leak rates decreased slightly during ~30 thermal cycles; final leak rates were about 0.3–0.4 sccm/cm. Simmer et al. reported a leak rate of ~6 sccm/cm of the same Phlogopite mica (~0.5 mm) at the same compressive stress and helium gauge pressure [7]. The difference in leak rate is attributed to the different surface roughness and surface defects of the sealed materials. In the present study, the Inconel pipe was finished with a #800 grit paper, and the alumina substrate has a surface roughness <0.89 μm. In the other study [7], the Inconel was ground to a 32G finish and a ground Sr-doped $LaCrO_3$ disc was used as the other mating material which was found to have large and continuous grooves connected through voids, pores, and pull-out grains. Looking at the cross-section of the mica paper (Fig. 1B), one might expect that the leak rate would increase with the mica thickness. However, the results in Fig. 3 suggest that, consistent with earlier findings, the major leak paths for plain mica seals are from the interfaces between mica and the sealed materials, i.e. mica to Inconel pipe, and mica to alumina substrate [5].

3.3. Thickness effect of hybrid mica on the 800 °C leak rates during thermal cycling

In addition to the plain mica, the Phlogopite mica was also tested in the hybrid design. As mentioned in [5], the major leak paths for the compressive mica seals are from the interfaces with the sealed materials, rather than through the mica itself. Accordingly, it was found that insertion of a compliant (or wetting) layer such as silver or glass at these interfaces can greatly reduce the leak rates. In this study, a glass–ceramic developed for SOFC sealing applications was used as the interlayer. The glass is a Ba–Al–silicate glass with a small amount of B_2O_3 which crystallizes into a multiphase glass–ceramic upon heat treatment. Leak rates for the hybrid seals as a function of thermal cycles are shown in Fig. 4. It is evident that the leak rates were much less than those of the plain mica seals. For example, the leak rates were ~0.5 sccm/cm for the plain mica (~0.1 mm thick) and were ~0.04 sccm/cm for the hybrid mica of the same thickness.

In the hybrid design, the major leak paths at the interfaces are sealed with the wetting glass so the leakage is limited to the leak paths present in the mica itself (at least before the thermal cycles), i.e. through the voids between discrete mica flakes (Fig. 1B). Therefore, one might expect that the leak rates would increase with increasing mica thickness. The initial leak rates were ~0.08 sccm/cm for the thickest mica (~0.5 mm), ~0.05 sccm/cm for the intermediate thickness (~0.2 mm), and ~0.04 sccm/cm for the thinnest mica (~0.1 mm). The thickness effect appeared to be less signifi-

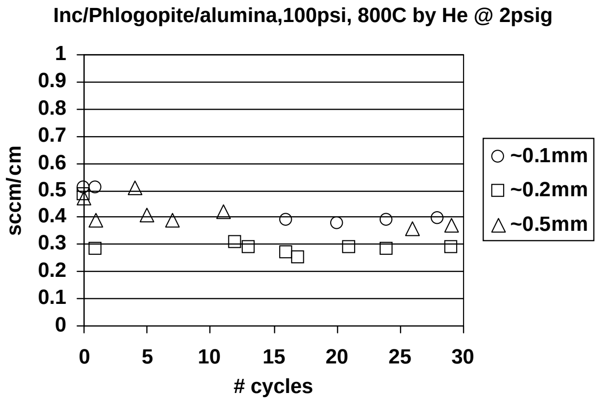

Fig. 3. Effect of thickness on the 800 °C leak rates of Phlogopite mica in the plain seal design (without glass interlayers) during thermal cycling in air. The mica was pressed between an Inconel pipe and an alumina substrate at 100 psi.

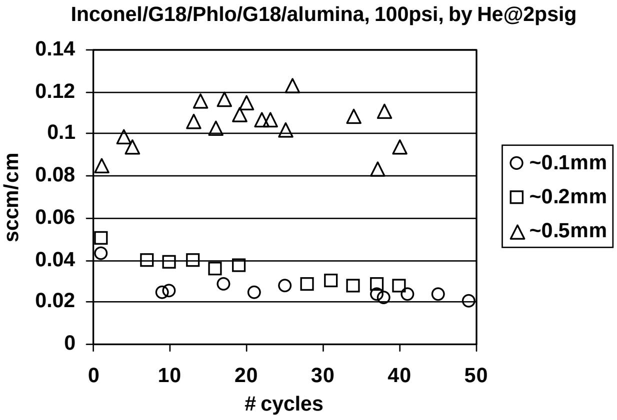

Fig. 4. Effect of thickness on the 800 °C leak rates of Phlogopite mica in the hybrid seal design (with glass interlayers) during thermal cycling in air. The mica was pressed between an Inconel pipe and an alumina substrate at 100 psi.

cant between the thinner micas (∼0.1 and ∼0.2 mm), as their leak rates were approximately constant after ∼25 thermal cycles with leak rates in the range ∼0.02 to ∼0.03 sccm/cm. While the leak rates for the thick mica (∼0.5 mm) showed more scatter during the thermal cycling, the leak rates were distinctly higher (∼3–5 times) than those of the thinner micas. It is interesting to note that the leak rates for the thinner micas actually decreased after the initial thermal cycles. The cause for the decrease is not clear, however, the stability of Phlogopite mica was evident during thermal cycling.

3.4. Microstructure characterization after thermal cycling

Figs. 5 and 6 show the surface morphology of the Phlogopite mica in the plain and the hybrid design after thermal cycling, respectively. For plain mica, indentations or impressions (Fig. 5B) were evident on the surface in contact with the adjacent metal, while the rest of the mica appeared to be intact (Fig. 5C). This damage is similar to that reported earlier on the natural cleaved monolithic Muscovite mica and can be attributed to the surface roughness of the two materials as well as mismatch in CTE. For the hybrid Phlogopite mica, no indentations or impressions were observed (Fig. 6A), likely due to the compliance of the glass interlayers. Traces of the glass penetrating into the mica paper through the voids were also evident (white phases in Fig. 6A). On higher magnification, the Phlogopite mica appeared to be intact, as no substantial and uniform micro-fracture, fragmentation and wear particles were found. The surface morphology of the mica which experiences the compressive stress is very similar to that of the mica in the free (unstressed) region (Fig. 6C). In addition, the morphology of the Phlogopite mica of other thicknesses (∼0.1 and ∼0.5 mm) was very similar to the mica shown in Fig. 6 (∼0.2 mm).

It is interesting to note that the lack of damage in the hybrid Phlogopite mica after thermal cycling is much different from the behavior of monolithic Muscovite micas, in which substantial damage, especially the formation of wear particles, was observed [6]. It is likely that the lack of damage can be related to the fact that the Phlogopite mica paper is composed of discrete mica flakes, so that no further micro-fracture and fragmentation need occur during thermal cycling, and hence no new leak paths are introduced. This explanation is consistent with the observed lack of dependence of leak rate on thermal cycling (Fig. 4). On the other hand, the Muscovite mica tested in [6] was a naturally cleaved “single crystal” in which the large mismatch in CTE resulted in fragmentation and formation of a substantial number of wear particles during thermal cycling, which caused a gradually increase in leak rate with repeated cycling.

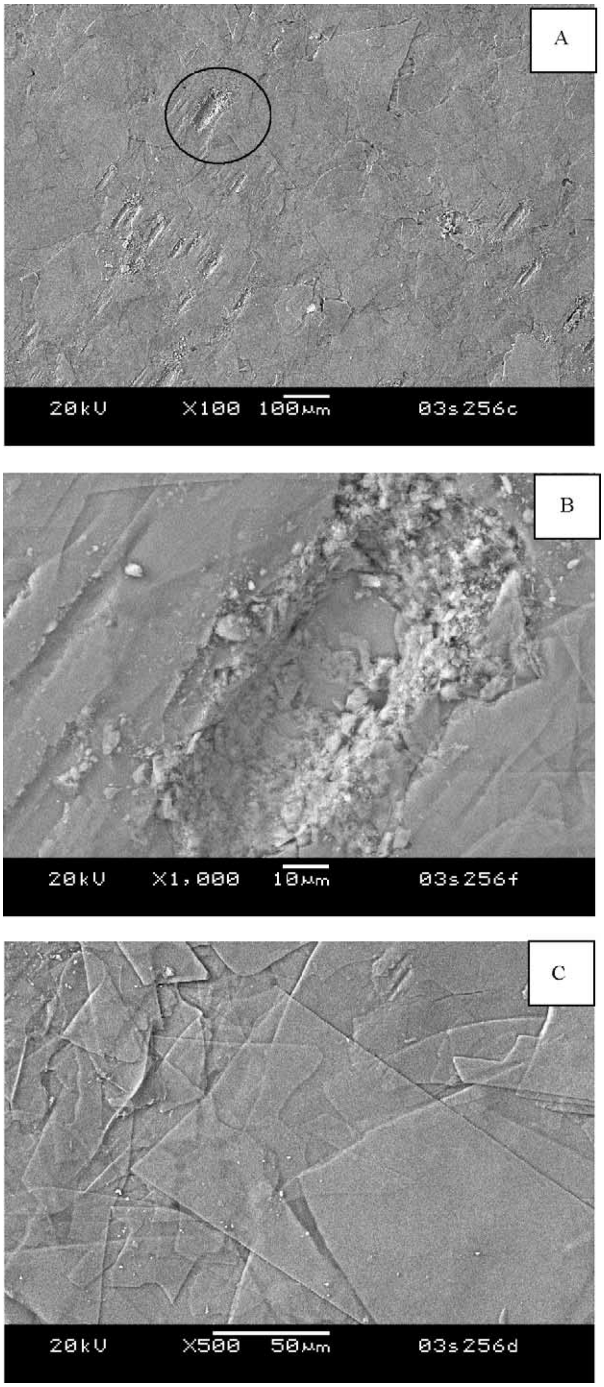

Fig. 5. Surface morphology of the Phlogopite mica (∼0.2 mm in plain design) after ∼30 thermal cycles in air: (A) low magnification of the mica, (B) high magnification of the circled region in (A), and (C) is of another region.

3.5. Mid-term stability test and microstructure characterization

Phlogopite mica ($KMg_3(AlSi_3O_{10})(OH)_2$) offers higher thermal stability than Muscovite mica ($KAl_2(AlSi_3O_{10})(F,OH)_2$) since it loses its chemical water at a much higher temperature (>950 °C) than the Muscovite (∼600 °C) [7]. To evaluate its thermal stability, the Phlogopite mica (∼0.1 mm thick in hybrid design) was tested for an extended period of time at 700–800 °C by monitoring the leak rate. Two environments were tested: air (800 °C) and reducing (700 °C). The results are shown in Fig. 7. The leak rates in the reducing

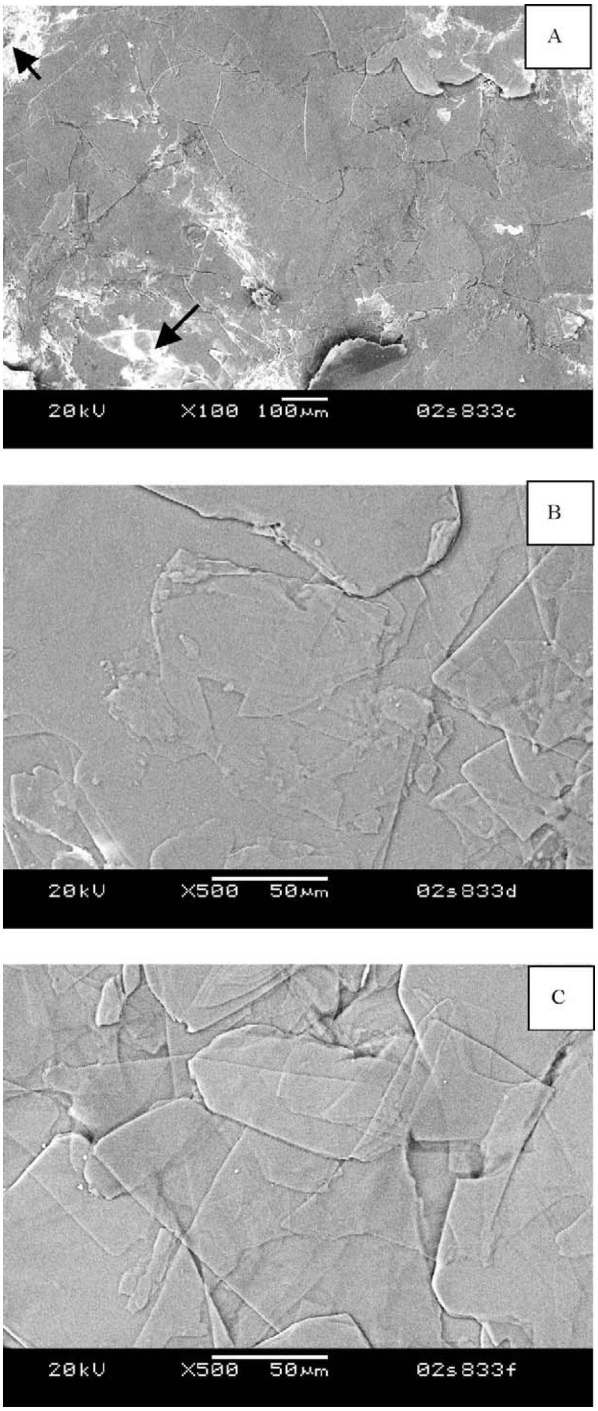

Fig. 6. Surface morphology of the Phlogopite mica (~0.2 mm in hybrid design) after 40 thermal cycles: (A) low magnification of the mica, (B) high magnification of (A), and (C) is from a region not located under the applied compressive stress. White phases (arrows in (A)) are glass from the glass interlayers that penetrated/wet through the voids between mica flakes.

environment were fairly constant in the range of ~0.01 to ~0.013 sccm/cm. The leak rates in the air environment were the same (~0.01 sccm/cm) as the reducing environment in the beginning; however, they decreased abruptly to <0.001 sccm/cm after about 100 h. This very low leak rate,

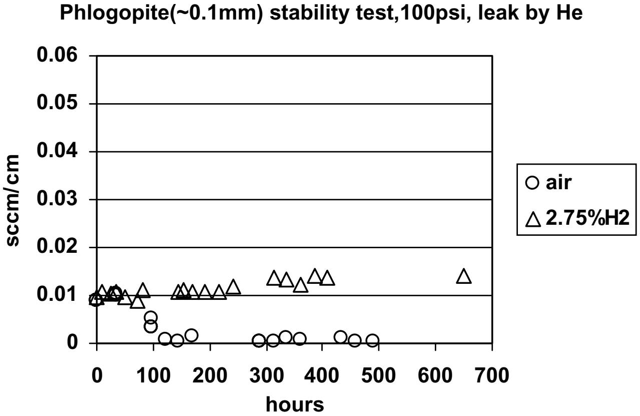

Fig. 7. Mid-term stability test of the Phlogopite mica in air (800 °C) and the moist reducing (2.75% H_2/Ar + 3% H_2O) environments (700 °C). The samples were pressed between an Inconel pipe and an alumina substrate at 100 psi.

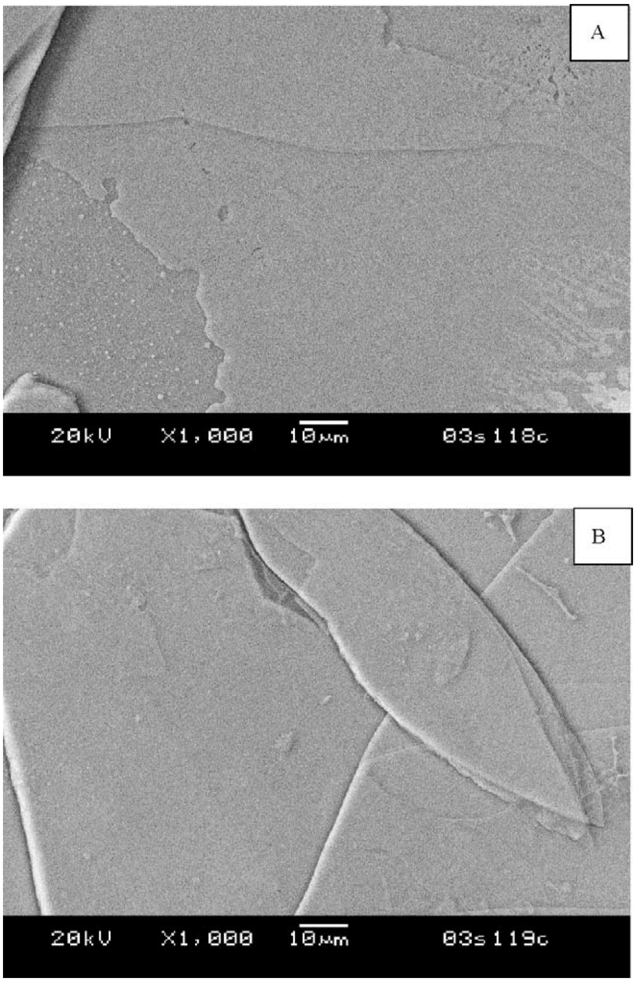

Fig. 8. Surface morphology of the Phlogopite mica (~0.1 mm thick) after the mid-term stability test: (A) in air for 490 h at 800 °C and (B) in the moist reducing environment (2.75% H_2/Ar+3% H_2O) for 649 h at 700 °C.

which is comparable to that of a rigid glass seal, suggests that the glass interlayers may have penetrated through the thickness of the mica (∼0.1 mm) through the voids between discrete mica flakes. The different behavior in the reducing environment was likely due to lower furnace temperature.

After the mid-term stability test at elevated temperatures, the surface morphology of the mica at the metal interface was characterized. For mica tested in air, the surface morphology was very similar to Fig. 6A with substantial evidence of glass penetration. As for the reducing environment, no substantial evidence of glass phase was observed on the mica surface. At higher magnification, no difference was found between the Phlogopite mica flakes tested in air (Fig. 8A) and in the reducing environment (Fig. 8B). Overall, the Phlogopite mica showed good stability in both the air and the moist reducing environments.

4. Conclusions

Phlogopite mica was tested as a compressive seal for solid oxide fuel cells. Phlogopite mica of three thicknesses (∼0.1, ∼0.2, and ∼0.5 mm) was tested in both the plain and the hybrid design for thermal cycling stability. The 800 °C leak rates of plain mica showed no thickness dependence upon thermal cycling, whereas the hybrid mica showed larger leak rates for thicker mica than for thin samples. The leak rates for the thinner micas (∼0.1 and ∼0.2 mm) were similar (in the range of ∼0.02–0.03 sccm/cm) after about 25 cycles. The thinner micas also exhibited a decreasing leak rate with increasing thermal cycles. Microstructure characterization of Phlogopite mica after thermal cycling showed no distinct degradation of the mica. The mid-term stability test of the mica in both air and the wet reducing environment demonstrated that Phlogopite mica is a viable compressive seal material for SOFCs.

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