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High-Temperature Seals for Solid Oxide Fuel Cells (SOFC)

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A functioning solid oxide fuel-cell (SOFC) may require all types of seals, such as metal-metal, metal-ceramic, and ceramic-ceramic. These seals must function at high temperatures between 600 and 900 °C and in the oxidizing and reducing environments of fuels and air. Among the different types of seals, the metal-metal seals can be readily fabricated using metal joining, soldering, and brazing techniques. However, metal-ceramic and ceramic-ceramic seals require significant research and development because the brittle nature of ceramics/glasses can lead to fracture and loss of seal integrity and functionality. Consequently, any seals involving ceramics/glasses also require significant attention and technology development for reliable SOFC operation. This paper is prepared to primarily address the needs and possible approaches for high-temperature seals for SOFC and seals fabricated using some of these approaches. A new concept of self-healing glass seals is proposed for making seals among material combinations with a significant expansion mismatches.

Keywords glass, high temperature, seals, solid oxide fuel cells (SOFC)

1. Introduction

Among the many fuel-cell technologies, the solid oxide fuel-cell (SOFC) functions at much higher temperatures (650-900 °C) and offers unique advantages of utilization of the more abundant fossil-derived fuels (hydrocarbons) as well as hydrogen. Additionally, much higher efficiencies than the low-temperature fuel cell are possible for the SOFC when integrated with the combined cycle utilizing the waste heat. SOFC technology has progressed to a stage where some of the problems associated with the electrochemically active cell components, such as electrolyte and electrode, have been adequately addressed. The remaining issues of technology needs, such as the cost and long-term performance goals, are being addressed through several government- and industry-supported programs. One area that currently needs more attention is related to the seals for SOFCs. Reliable seals are essential to the long-term performance and reliability of the SOFC because a poor seal will degrade cell performance, lead to wastage of fuels, and possibly pose danger to the safety of the fuel-cell stacks. Consequently, SOFC seals are important and are in need of significant additional attention (Ref 1-3).

A variety of seals, such as metal-metal, metal-ceramic, and ceramic-ceramic, are required for a functioning SOFC. These seals must function for long times (5000-40,000 h) at high temperatures (between 600 and 900 °C). Among the different type of seals, probably the metal-metal seals can be readily fabricated using metal joining, soldering, and brazing techniques; however, the issue of oxidation at these high-temperatures needs to be considered for long-term survivability of all metal seals as well. This ease in fabricability is not yet possible for the metal-ceramic and ceramic-ceramic seals because the brittle nature of ceramics/glasses can lead to fracture and loss of seal functionality. Consequently, any seals involving ceramics/glasses require significant attention and technology development for reliable SOFC operation.

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1.1 Current Status of SOFC Materials Selection

A search for reliable seals for SOFCs must start with considerations of the selection of materials based on their stability in the severe environments of SOFCs. SOFCs operate over a range of temperatures from 600 to 900 °C in a reducing potential of fuels (anode) and in an oxidizing environment of the oxidant (cathode). The fuels for SOFCs could be based on diesel, gasoline, hydrogen, propane/natural gas, coal-derived gases, and methanol, to name just a few, which provide an important advantage for SOFCs over the low-temperature fuel cells because the latter cannot tolerate these fuels except for the purest of hydrogen gas. The oxidant can be simply air. Therefore, the sealing materials must be selected based on their survivability in both oxidizing and reducing environments. This may involve selection of metals, ceramics, glasses, and, possibly, brazing alloys that can survive the severe environment of SOFCs. Figure 1 shows a unit cell of a SOFC and locations of possible seals. The current materials system for the SOFC may consist of 8%-YSZ (yttria-stabilized zirconia-electrolyte), Ni-YSZ anode, doped lanthanide perovskite cathode, doped chromites/alloys as interconnects, insulating seals, and manifolds made of heat-resistant metallic alloys.

Selection of a suitable metallic material for the seal's development is very important so that the seals can join a realistic metallic component to the electrolyte-electrode assembly by ceramic-ceramic-metal seals. To this end, a variety of metallic materials are under consideration for use in SOFC. These may include ferritic alloys such as Crofer, E-Brite (26 Cr-1 Mo), and 430-stainless steel, to name just a few. These alloys form chromia scales and have been studied for their oxidative sta-

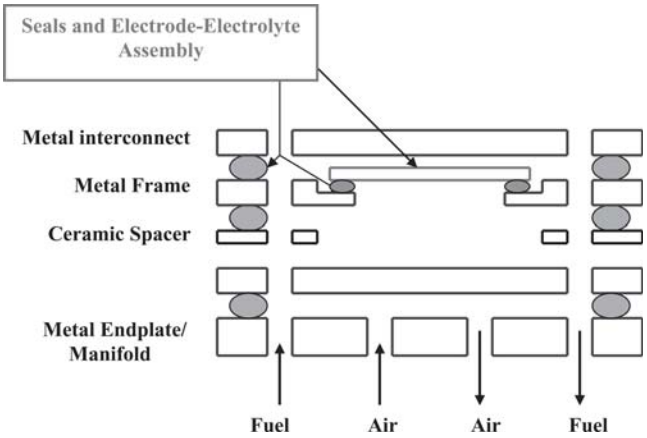

Fig. 1 Schematic of a SOFC and possible seals and their locations

bility and conductive scale-forming ability for the interconnect applications (Ref 4). An external coating of $LaCrO_3$ on T446 stainless steel offered oxidation resistance via reduced chromia scale growth.

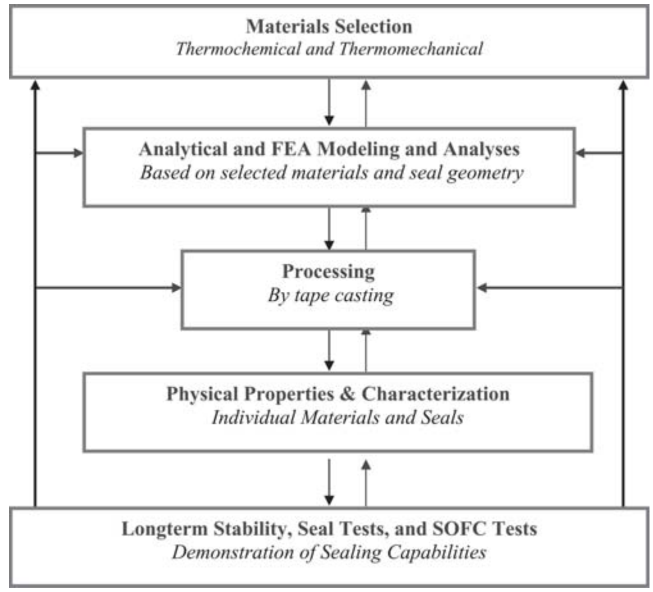

Fig. 2 Flow chart of the integrated approach of seals for SOFC

1.2 Status of Seals for SOFC

The most delicate component in a SOFC is the electrode-electrolyte assembly due to the brittle electrolyte, which can be as thin as 10-15 μm. Some designs use an anode-supported electrolyte while other approaches use a cathode-supported electrolyte. The delicate electrolyte-electrode assembly requires a seal to separate the anode from the cathode both physically and electrically (insulating) in a SOFC functioning at ~650-800 °C (Fig. 1). Consequently, a sealing system must not only transmit the lowest possible stresses to the ceramic components but also be stable at temperatures between 650 and 850 °C over a long period.

Weil et al. (Ref 5) used alloys like FeCrAlY (Fe 22% Cr, 5% Al, 0.2% Y) as a model metal for sealing by brazing to YSZ. In this study, Ag-CuO braze materials were used. However, additional work is required to determine the effects of interdiffusion and durability of the brazed joints at high temperatures in the oxidizing environment of a fuel cell.

A number of more novel sealing concepts are also possible for seals in SOFC. Lewinsohn et al. (Ref 6) presented an idea of using polymers of Si-C-N to make seals to SOFC components. Potentially these polymers can be used as a paste to join two surfaces, but these materials are inherently unstable against oxidation in air at high temperatures or in moist air. They also suggested using ceramic and metallic fillers to control the coefficient of thermal expansion (CTE) to match expansion of SOFC components. Loehman (Ref 7) has suggested using viscous seals for attaching SOFC components. Chou and Stevenson (Ref 8-10) used a novel approach of mica and mica-glass hybrid compressive seals with promising results, but these seals require compression loads, and issues related to interface reactions and crystallization of some of the glasses were also of concern. One glass composition was 58% SiO_2, 9% B_2O_3, 11% Na_2O, 6% Al_2O_3, 4% BaO, and ZnO, CaO, and K_2O in trace amounts. Chou (Ref 11) presented research on infiltrated mica for seals with promising results after infiltration with Bi, B-, and glass-forming materials, but these seals still require loads and may pose stability issues (evaporation) at high temperatures when used over extended times. Brow (Ref 12) and his group are developing promising glasses and glass-ceramics for SOFC seals with properties quite suitable for fabrication.

Taniguchi et al. (Ref 13) reported using a combination of glass/YSZ and Fiberfax (essentially alumina fiber) fiber matte to seal the SOFC components. The fiber layer was porous and compliant and provided stress reduction on the electrolyte-electrode assembly via compliance of the fiber layer. It was not apparent from the paper as to how the porous Fiberfax was made impervious or reduced leak rates when in contact with the electrolyte. Donald (Ref 14) provided a general review of the glasses and glass-metal seals that can be used as a reference for guiding materials selection for seals.

2. Possible Approach of Seal Development for SOFC

The results from the literature clearly indicate that promising sealing concepts and materials are available for use as seals in SOFCs. Table 1 lists the CTEs for a variety of realistic metallic, ceramic, and glass materials of interest as seals for SOFCs. A seal must somehow accommodate a large mismatch in CTE between metallic and ceramic materials. However, most of the seal work to date has not used an explicit integrated approach for selecting materials based on stability considerations, thermophysical properties, modeling of residual stresses upon sealing and during cell operation, and the geometrical aspects of seals toward improved reliability. Most of the seals developed so far have been rigid in nature, which is expected to create detrimental stresses to the delicate electrolyte-electrode assembly, leading to fracture of the ceramic components or of the seal itself. New concepts that minimize internal stresses under both steady-state and thermal transients are needed to develop reliable seals for SOFCs.

An integrated approach/concept for seal development is shown in Fig. 2. It consists of materials selection, analytical modeling, processing, property measurements, and seal testing. Because the seals for SOFCs must function in an oxidizing environment, it is desirable to select sealing materials that are thermochemically stable in air between 600 and 1000 °C. Most

Table 1 Coefficient of thermal expansion (CTE) for some useful metallic, ceramic, and glass materials

Materials	Possible use in SOFC	Temperature range, °C	α, ppm/°C
Inconel 600	Metallic hardware	25-1000	16.7
SS 430	Metallic hardware	25-1000	13
Haynes	Metallic hardware	25-1000	14-15
Ceramic Perovskite	Interconnect	25-1000	10.6-11.1
Alumina	Insulator	25-1000	8.8
ZrO_2 (stabilized)	Ionic conductor	25-1000	10.0
8-YSZ	Electrolyte	25-1000	11
Soda glass	Sealant	25-800	9.0
Li_2O-ZnO-Al_2O_3-SiO_2 (glass-ceramic)	Sealant	25-900	5.5-12, depending on ZnO content
Cao-SrO-ZnO-SiO_2-B_2O_3 glass/glass-ceramic	Sealant	25-900	10-12, depending on composition

Source: Ref 1, 2, 12-14

suitable sealing materials may be crystalline oxides, oxide glasses, or materials that, upon active oxidation, form stable crystalline oxides or oxide glasses. The second most important requirement on the materials is that they should be thermochemically compatible with the YSZ-electrolyte and the metal-cermet-ceramic-electrodes-current collectors. In addition, the selected sealing materials must have a reasonably close match to the CTE (thermomechanical compatibility) with the components being sealed to avoid significant residual stresses that can lead to premature seal failures.

The selected materials must be analyzed for residual stresses using sealing materials and the components being sealed, such as the electrolyte-electrode assembly with the metallic components. Analytical and finite element analysis (FEA) models can be readily used for this purpose so that the candidate materials can form a seal with the least amount of the stress. This analysis must be done using materials properties, realistic processing temperatures, and thermal transients encountered upon cell operation. These steps can lead to selection of the most appropriate materials for seal development, which may then be used to develop processing methods for making seals between selected components. A variety of sealing concepts can be used at this point to develop appropriate processing methods for making seals, such as rigid, viscous, wet, and/or flexible seals. The sealing materials, thus processed, must be characterized for physical, mechanical, and thermophysical properties over a range of temperatures. These properties can then be used as inputs into the analytical models for assessing residual stresses in the seals and adjoining components. These inputs can then be used as feedback mechanisms to select better materials for creating reliable seals for SOFCs. Long-term stability of the sealing materials and the seals themselves need to be evaluated at elevated temperatures to assess stability of the materials systems and seals. Subsequent to these steps the seals should be evaluated with respect to a working SOFC to determine the functionality and long-term survivability of the seals. This integrated approach for seal development for SOFCs is expected to create successful seals in a functioning SOFC.

2.1 Approach of Self-Healing Glass Seal Development for SOFC

Although the approach outlined earlier is required for selecting appropriate materials for a promising seal, it may require additional new concepts because it is very difficult, if not impossible, to minimize the expansion mismatch among the various materials forming a seal. A novel concept of self-healing glasses can help alleviate some of the expansion mismatch and still form a functioning seal between materials with a significant expansion mismatch. The rationale behind this novel concept is that at the SOFC operating temperature, a sealing glass with appropriate properties can heal cracks created during thermal transients. The advantage of this approach is that materials with dramatically different expansion can potentially be used for seals, because at the cell operating temperatures, induced thermomechanical stresses can be relaxed. However, there are a number of challenges to making a functioning seal by employing self-healing glasses. The first challenge is the glass must demonstrate self-healing properties near the cell operating temperature of ~800 °C, remaining stable for long-times while maintaining sealing capability. These solutions are being pursued by developing self-healing glasses with appropriate thermophysical properties, video imaging to demonstrate self-healing, and leak testing to identify/demonstrate self-healing glasses and seals.

2.2 Fabrication of Seals for SOFCs

A generic approach, as described earlier, was used to fabricate seals for SOFCs in which three types of metals were sealed to YSZ electrolyte in a window-frame type of configuration using a glass as a sealing material. The important part of this study has been to select a glass that has a good expansion match with the YSZ but can have a significant difference in the expansion match with some of the metals. The metals used in this study were Ni, SS304, and SS430. These alloys have widely different expansion behavior. The CTEs of these metals, YSZ, and the sealing glass were measured, and the results are plotted in Fig. 3. The glass has a softening point near 700 °C and expansion behavior very close to the YSZ. The SS430 has an expansion coefficient slightly higher than YSZ at temperatures below ~650 °C and slightly lower at temperatures above 650 °C. In contrast, Ni and SS304 have much higher expansion coefficients than the YSZ and glass over the entire range of this measurement up to 1050 °C.

Using this glass, and by engineering the ceramic-metal interlayers, successful seals to each of the metals were made as shown in Fig. 4. In no case was any cracking of the YSZ observed, even when seals between YSZ and metals like Ni or SS304 with much higher expansion mismatch with YSZ were made. Leak tests at both room and elevated temperatures are underway to validate the applicability of the approach for making seals for SOFCs. In addition, research is planned to test these seals under thermal transients of a SOFC to study the durability of the seals.

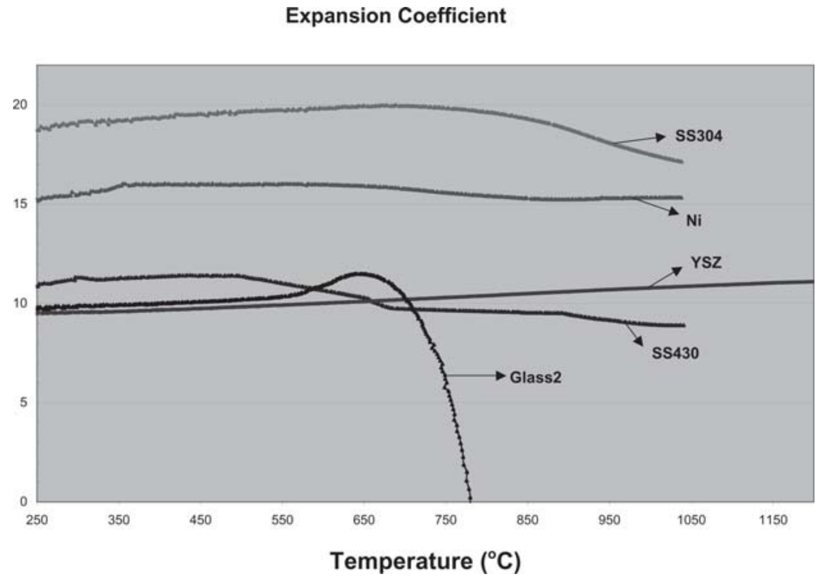

Fig. 3 Coefficient of thermal expansion of Ni, SS304, SS430, YSZ, and a glass used for fabricating seals useful for SOFC

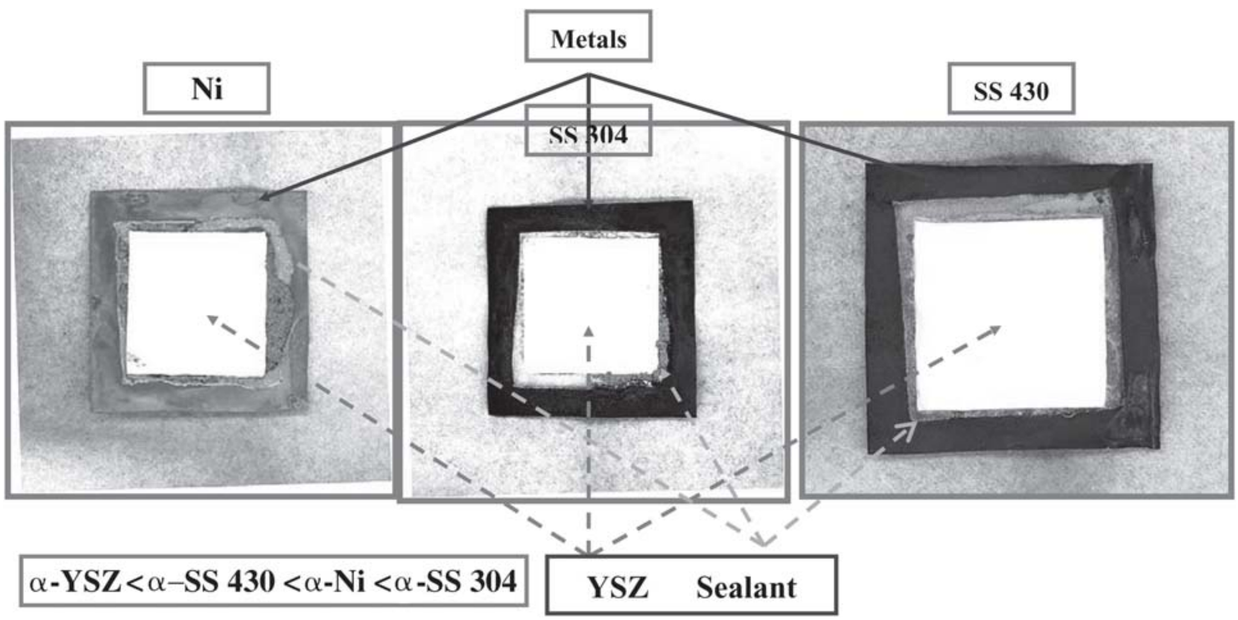

Fig. 4 Metal-YSZ seals for SOFC fabricated using a sealing glass. Note that metals with a significantly different expansion than YSZ were successfully sealed with YSZ.

3. Conclusions

A brief review of the requirements for SOFC seals has been performed. This was followed by a description of the current status of seal development for SOFC. On the basis of this information, an attempt has been made to formulate an approach for successful seal development utilizing materials selection, thermomechanical modeling, property measurement, processing, and seal testing. In addition, a new concept of self-healing seals has been proposed for creating seals for SOFC. The advantage of the self-healing concept lies in its ability to heal cracks at the cell operating temperatures. This concept is expected to create functioning seals among materials with significant expansion mismatch. A few seals have been successfully fabricated using these approaches, and leak testing is underway to further validate the idea.

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