IV.A.23 Thermochemically Stable Sealing Materials for Solid Oxide Fuel Cells

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Objectives

- Develop 'invert' glasses with requisite properties and chemical stability for hermetic seals for solid oxide fuel cells (SOFCs).
- Develop processing techniques to fabricate hermetic seals for SOFC components, including understanding the crystallization behavior of sealing glass.
- Demonstrate hermeticity and materials compatibility under SOFC operational conditions.

Accomplishments

- Developed alkaline earth/zinc silicate glasses that form glass-ceramics with requisite thermal properties, including sealing temperatures at or below 900ºC and coefficients of thermal expansion (CTE) in the range $10\text{-}12 \times 10^{-6}$/ºC.
- Demonstrated the effect of B_2O_3 on the volatility of promising sealing materials under SOFC operational conditions at temperatures up to 800ºC, for up to 28 days in wet forming gas; identified new sealing glasses compositions with weight loss in wet forming gas/or air at 800°C over 500 hours in the range 0.01-0.1 g/m^2 (under 0.001-0.0001 wt%).
- Studied the effects of glass composition on the formation of deleterious chromate phases at glass-steel interfaces.

Introduction

SOFCs require seals to prevent the mixing of fuel/oxidant within the stack, prevent leaking of fuel/oxidant from the stack, electrically isolate cells in the stack and also provide mechanical bonding of components. There have been many reports on the development of a variety of compositional systems to form suitable glass and glass-ceramics seals for SOFCs, including silicates, aluminosilicates, borosilicates, and aluminophosphates, i.e. see reference [1]. Many of these sealing materials have property or performance shortcomings. Some fail to remain thermomechanically stable under SOFC operational conditions, and others undergo deleterious interfacial reactions with other SOFC components. One such reaction occurs between BaO-containing sealants and the Cr-oxide scale that forms on interconnect alloys, resulting in the formation of a $BaCrO_4$ interfacial phase that can adversely affect the mechanical integrity of the seal [2,3]. The materials developed in the present project have unusual structural characteristics that contribute to a desirable set of thermal and chemical properties required for SOFC seals.

Approach

The glasses developed at the University of Missouri-Rolla (UMR) are based on alkaline earth silicate compositions modified by ZnO. They possess relatively low silica contents (45 mole%) and rapidly crystallize to form silicate crystals with the desirable thermomechanical properties, including long-term stability of the CTE. The glasses are designed to be thermochemically stable, both against volatilization under SOFC conditions, and against the formation of deleterious interfacial reaction products in seals to SOFC materials.

Results

Figure 1 shows that glasses with greater concentrations of B_2O_3 exhibit greater weight losses under simulated SOFC operational conditions; e.g., wet forming gas at 800°C. Thermochemical calculations have been performed to determine the equilibrium reactions that might contribute to this weight loss, and it was shown that B_2O_3 is the least stable of the oxides that constitute these sealing glasses. Figure 2 shows which B-species will have the greatest partial pressures at 800ºC in a wet, reducing environment.

X-ray diffraction (XRD) analyses (not shown here) reveal no boron-containing crystalline phase in the glass-ceramics, suggesting that the borate components are to be found in residual glassy phases. Borate species in a liquid state (glassy or amorphous phase) are more likely to volatilize than those in solid state (crystal). Increasing the B_2O_3 content of the base composition increases the fraction of residual glass in the glass-ceramic, which in turn leads to greater weight lost under SOFC operational conditions. More detailed

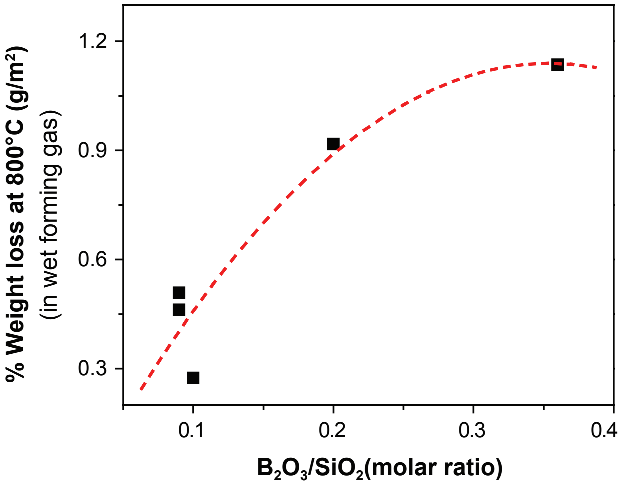

FIGURE 1. The Effect of B_2O_3/SiO_2 Molar Ratio on the Cumulative Weight Lost after 28 Days at 800°C in Wet Forming Gas

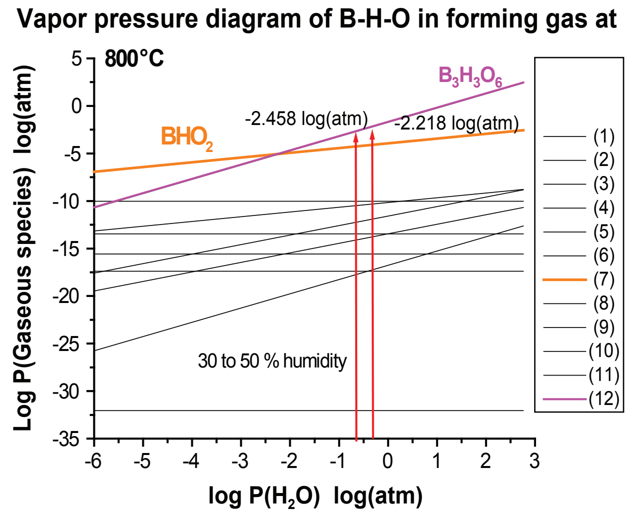

FIGURE 2. Thermochemical Predictions of the Effect of Atmosphere at 800°C on the Stability of B_2O_3

experiments are currently underway to characterize volatilization behavior and its effect on the glass-ceramic sealing materials.

Glass ID	ZnO (mole%)	SrO (mole%)	$SrCrO_4$
27	13.0	18.5	4 wt%
50	5.0	25.5	11 wt%
36	0.0	26.5	14 wt%

A second issue related to thermo-chemical stability involves the reaction in oxidizing environments between alkaline earth oxides in the sealing glass and chromium in the steel interconnects. The reaction leads to the formation of chromates like $SrCrO_4$ and $BaCrO_4$, high expansion phases that could adversely affect the thermo-mechanical integrity of the seal [2]. One simple experiment to test relative stability of a composition against chromate formation is to mix glass powder with 10 wt% Cr_2O_3 in air for 24 hours at 800°C, and then to characterize the resulting reaction products using quantitative x-ray diffraction techniques. Table I summarizes experiments done with glasses with a range of SrO and ZnO contents, and shows that glasses with greater ZnO content produce relatively lower amounts of $SrCrO_4$. The effects of composition on the relative reactivity of glasses is illustrated in Figure 3, which shows an optical micrograph of the surfaces of G#27 (13.0 mol% ZnO, left) and G#50 (5.0 mole% ZnO, right) coatings bonded to a 430SS substrate, then held in air at 800ºC for 60 days. The Glass #27 coating retains the white color of the original glass ceramic, whereas the Glass #50 coating has turned yellow, an indication of the formation of $SrCrO_4$. The mechanism for the reduced reactivity of the ZnO-containing glasses is unknown but is the focus of current research.

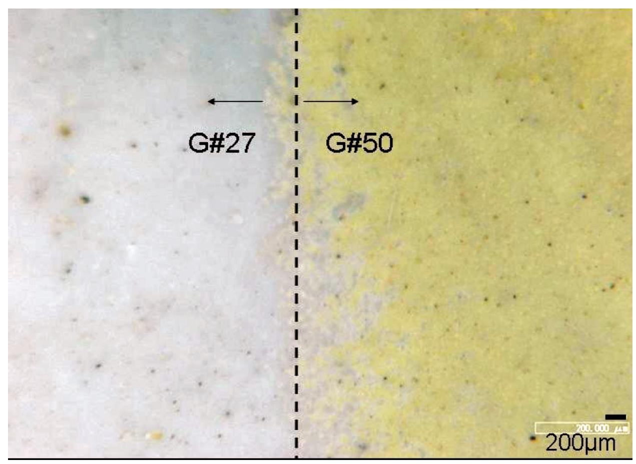

FIGURE 3. Optical micrograph of SOFC glass coatings bonded to 430SS, then held in air for 60 days at 800°C. The G#27 coating (left) retains its original color, whereas the G#50 coating (right) has turned yellow because of the formation of $SrCrO_4$.

Conclusions and Future Directions

- Both B-O and Zn-O species are more volatile in wet conditions than in dry conditions at 800°C.
  - $B_3H_3O_6$ (gas) has the highest vapor pressures in wet conditions at 800°C.
  - Zn (gas) has the highest vapor pressures in dry and wet conditions at 800°C.
- The addition of ZnO appears to impede the formation of $SrCrO_4$ when glasses react with chromium in air.
- There is a size dependence on the crystallization behavior of the 'invert' sealing glasses.

  - For G#50, particle sizes of 45-53µm exhibit desirable thermal stability against crystallization.
- The volatility calculations will be correlated with weight-loss measurements from glasses with different compositions.
  - Volatile species collected from reacted glasses will be analyzed.
- The effect of ZnO on the formation of $SrCrO_4$ will be modeled using thermodynamic calculations like those used to study the volatility conditions.
- The study of the effects of glass particle size on crystallization behavior will be completed and the results will be applied to optimize processing conditions for SOFC seals.

Special Recognitions & Awards/Patents Issued

1. R.K. Brow, S. T. Reis, G. M. Benson, "Glass and glass-ceramics for solid oxide fuel cell hermetic seals," US Patent Application, UM Disclosure No. 04UMR023 entitled "Glass and Glass-Ceramic Sealant Compositions," filed January 2005.

FY 2007 Publications/Presentations

1. C. S. Ray, T. Zhang, S. T. Reis, and R. K. Brow, "Determining Kinetic Parameters for Isothermal Crystallization of Glasses," *Journal of the American Ceramic Society*, **90**[3], 769–773 (2007).

2. S. T. Reis*, Teng Zhang, and R. K. Brow, "Development of thermochemically stable sealing glasses for solid oxide fuel cells" 4th International Symposium on Solid Oxide Fuel Cells: Materials and Technology, Daytona Beach, Florida, January 22–27, 2007.

3. S.T. Reis, R.K. Brow, "Designing Sealing Glasses for Solid Oxide Fuel Cells," Journal of Materials Engineering and Performance, **15** 410–413 (2006).

References

1. J.W. Fergus, *J. Power Sources*, **147** 46-57 (2005).

2. Z. Yang , J. W. Stevenson, and K. D. Meinhardt, *Solid State Ionics*, **160** 213–222, (2003).