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SEALANT RESEARCH FOR SOLID OXIDE FUEL CELLS*

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Sealant Research for SOFC

CONTRACT INFORMATION

Contract Number	49638
Contractor	Argonne National Laboratory 9700 South Cass Avenue Argonne, IL 60439 (708) 252–4516
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OBJECTIVE

The objective of this work is to develop sealing materials for solid oxide fuel cells (SOFCs). A suitable sealant must form strong, dense bonds with SOFC components, be chemically and mechanically compatible with the components, be stable at 1000°C in the operating environment of the SOFC (H_2 and H_2O on the anode side, O_2 on the cathode side), and must be nonconductive.

BACKGROUND INFORMATION

Solid oxide fuel cells are potentially more durable than other types of fuel cells because the electrolyte does not evaporate, corrode, or leak and thus should achieve a long and trouble-free service life. SOFCs have the additional advantage of being able to run directly on hydrocarbon and CO fuels without the need for a fuel reformer. This, in turn, simplifies system design and lowers capital cost. Because state-of-the-art SOFCs operate at the rather high temperature of 1000°C, however, it is difficult to find materials to seal the edges and the manifolds of the fuel cell stack.

To circumvent this problem, researchers have developed cell designs that do not need seals. However, this use of an engineering approach to avoid a materials problem has resulted in a fuel cell that is complicated and expensive. As SOFCs approach commercialization, new and less-expensive designs have been proposed, including the monolithic SOFC and several flat-plate configurations. In these designs, gas-tight seals must be used at the edge of each electrode and between the stack and the manifold.

The objective of this work is to develop suitable sealants for the SOFC. A suitable sealant must form gas-tight seals capable of withstanding an operating temperature of 1000°C. It must be

chemically compatible with SOFC components, i.e., it must react with the components to form bonds, but should not attack the SOFC extensively. The sealant must also be stable when exposed to the fuel cell gases. Ideally, it is desired to have one material that is stable in both fuel and air, but it is possible that two different sealants might be needed, one for the fuel side and one for the air side. In addition, the thermal expansions of the sealant and SOFC components should match to avoid cracking during operational thermal cycling. Finally, a suitable sealant must be an electronic insulator to avoid formation of electrical short circuits at the edges of the stack.

PROJECT DESCRIPTION

The scope of this project includes the evaluation of commercially available cements and of novel sealing materials. In the past, novel materials were classified according to their as–applied state: polycrystalline, glassy, or a composite of the two. Because the nature of a sealing material can change during formation of the seal, e.g., due to devitrification, novel materials are now loosely classified according to the temperature at which they bond to SOFC components. Materials presently being tested form seals at temperatures ranging from room temperature to ≈1350°C, the approximate sintering temperature of the SOFC.

As the first test of a sealant, its ability to bond to SOFC components (anode, electrolyte, and cathode) is determined qualitatively. This aspect of the testing can be complicated, because the bond quality can depend strongly on temperature and composition. Materials that form strong bonds are subsequently examined by microscopy to determine the level of porosity, since the sealant must be dense. Some sealants are tested for chemical stability towards humidified hydrogen at 1000°C. This test approximates the conditions found in the anode compartment of the SOFC.

Finally, assuming that a chemically stable bond is formed, the electrical conductivity of substrate/sealant/substrate composites is measured. These composites include cathode, electrolyte, and anode substrates and are tested under the appropriate gases.

RESULTS

Commercial Cements

Commercially available cements were surveyed to determine their suitability as a SOFC sealant. Many commercial high–temperature cements are available, but most contain high levels of SiO_2 (10–50 wt.%). These cements were considered unacceptable and were not obtained for testing because SiO_2 is volatile under reducing conditions and can contaminate SOFC components. Two commercial cements rich in calcium aluminate and low in SiO_2 (<3 wt.%) were obtained and tested. Both cements were used to bond pairs of anode, cathode, and electrolyte disks. All bonded disk pairs were heated to 1000°C and held for 24 h in air. In both cases, strong bonds were formed. Also, there was no evidence of cracking in either case, despite the fact that the coefficient of thermal expansion (CTE) of one cement (≈4.4 x 10^{-6}) is significantly lower than that of the SOFC components (≈11 x 10^{-6}). The lack of cracks indicates that the materials are strong enough to withstand the mismatch in thermal expansion. Figures 1 and 2 show that the bonds contained regions of high porosity, presumably due to the loss of water during the setting reaction. Such high porosity precludes the use of these cements as sealants by themselves.

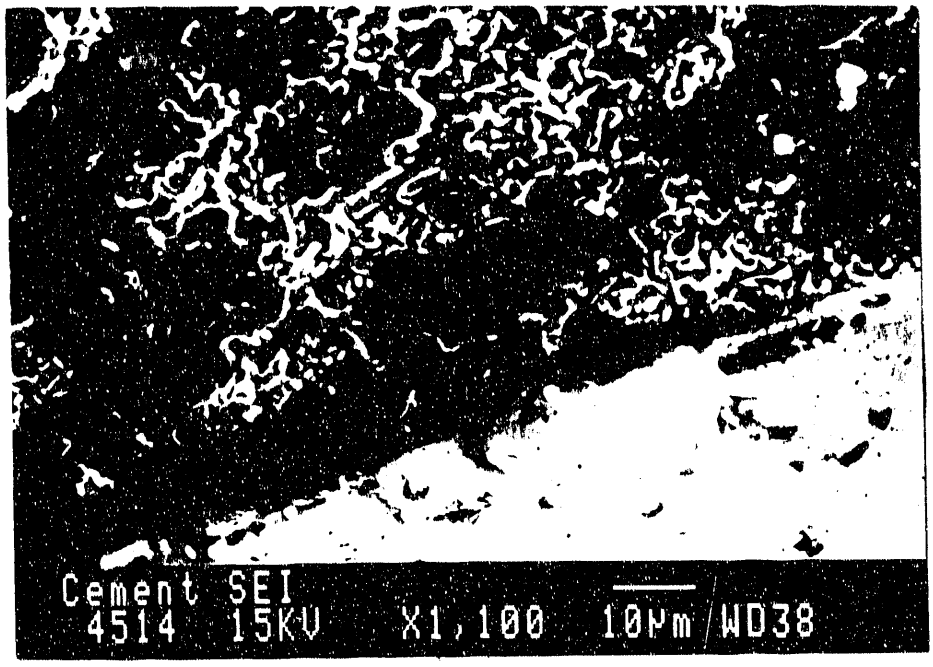

Figure 1. Photomicrograph Showing Bond between Commercial Cement A and Electrolyte; Bond Contains Both Dense and Porous Regions

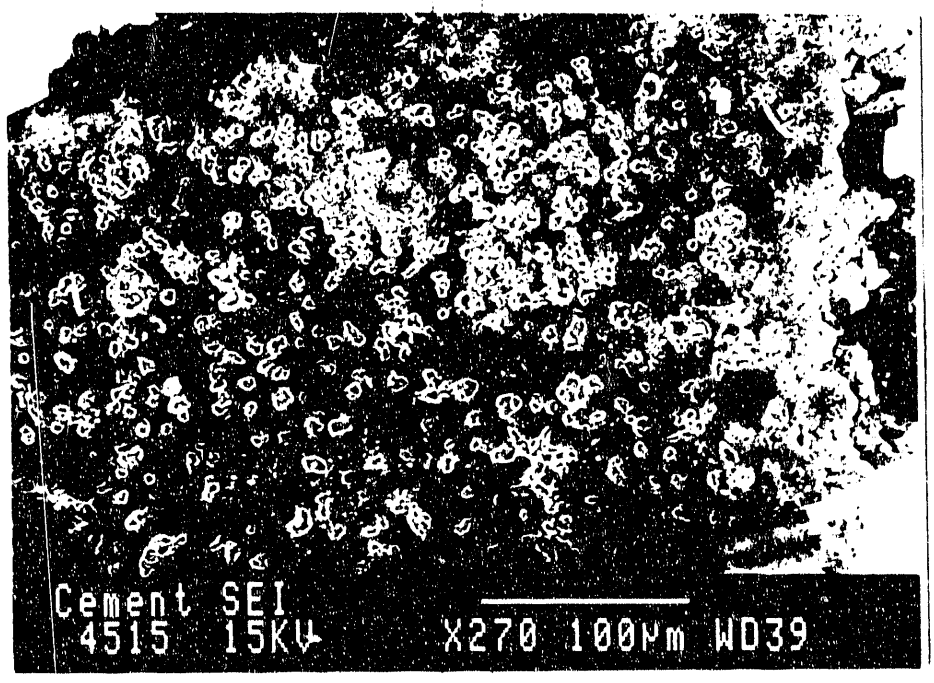

Figure 2. Photomicrograph Showing that Bond between Commercial Cement B and Electrolyte Also Contains Both Dense and Porous Regions

Novel Materials

Novel materials are loosely classified according to the temperature at which they bond to SOFC components. Materials presently being tested have bonding temperatures in the range of ≈25–1350°C. Because low–temperature materials bond without heating, seals can be made and inspected without subjecting the SOFC to thermal stresses during thermal cycling. However, low–temperature materials tend to form porous bonds. High–temperature materials, on the other hand, form strong, dense bonds, but subject the SOFC to additional thermal stresses because they bond to the SOFC only at high temperature. Because each type of material offers its own advantage, and because it is not known at this point which type will ultimately be the most suitable, a wide range of possible sealing materials is being tested. Results from these tests are described below.

Low–temperature (<200°C) bonding occurs by a cementitious reaction in which a material is first hydrated and then forms a long–range network of bonds by losing the water of hydration. Strong bonds can be formed by this method at room temperature, but debonding occurs upon heating to 1000°C, possibly due to the further evolution of gaseous species. Also, the evolution of water (or other species) that accompanies bond formation tends to produce porous bonds. The porosity of one material was ≈20% at room temperature and increased to ≈28% after heating to 1000°C. For present low–temperature materials to serve as suitable sealants, their bonding at high temperature must be improved and their porosity must be reduced.

Intermediate–temperature (200–600°C) bonds form by an inorganic polymerization reaction, i.e., a long–range network of bonds results, as with cementitious materials, but water is not thought to be involved in the reaction. Like low–temperature bonds, these bonds tend to be porous. For these materials to be useful sealants, their porosity must be reduced. One intermediate–temperature material did not attack the anode or electrolyte upon heating to 1000°C in air, but attacked the cathode extensively. During exposure to reducing conditions (15 h at 975°C in 6% H_2), the material slumped slightly and darkened in color, but X–ray analysis showed no signs of reduction. While this shows no immediate problem with reduction, longer term experiments are necessary to determine the stability of the material in reducing conditions. Dilatometry on the material showed that its CTE was 8.9 x $10^{-6}°C^{-1}$, indicating that an adjustment of composition might be necessary to match the CTE of SOFC components.

High–temperature bonds (>600°C) can be formed with glasses or polycrystalline materials. Bonds formed with high–temperature glasses tend to be dense, and they offer the advantage that their thermal expansions can be modified relatively easily and predictably by changing the balance of glass formers, intermediates, and network modifiers within the glass composition. Several glass compositions have been made with CTEs in the range of 7–10.8 x $10^{-6}°C^{-1}$. The interaction of these glasses with SOFC components and the extent of devitrification depends on composition. Strong, dense bonds have been formed with several of the glasses but their stabilities in reducing conditions have not yet been determined.

Several polycrystalline materials also form strong, dense bonds at high temperature if a liquid phase is present to provide intimate contact and enhance reaction between the sealant and SOFC component. The bonds formed with these materials tend to be dense, because the liquid fills in the porosity. Figure 3 shows an example of the bond formed when liquid is present during bonding. When no liquid forms during bonding, the polycrystalline material densifies and becomes strong itself, but forms only weak bonds with the SOFC components.

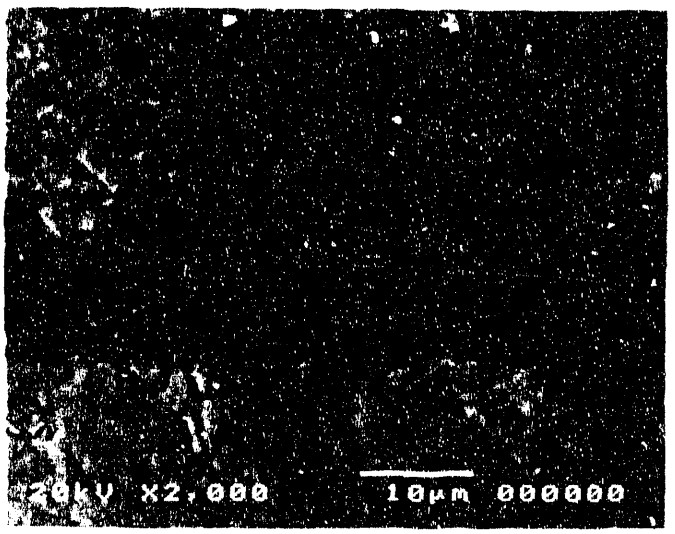

Figure 3. Photomicrograph Showing Dense Bond Formed at 1210°C

To avoid cracking during thermal cycling, the CTE of the bond phase should match that of the SOFC components. However, because reaction kinetics in the presence of a liquid are very fast, polycrystalline materials that form a liquid phase can convert to an altogether different material during bond formation . One high–temperature material has a CTE of $\approx 9 \times 10^{-6}°C^{-1}$ (vs. $\approx 11 \times 10^{-6}°C^{-1}$ for the SOFC components), suggesting that cracking might be a problem. However, the material forms a strong, dense bond (see Figure 3), and cracking is not evident. X–ray analysis of the material after bonding shows that it reacted to form another phase that has yet to be identified. The weight loss of this material after exposure to reducing conditions (60 h at 1000°C in H_2) was ≈1%. Further experiments are needed to determine if this weight loss resulted from decomposition of the bond material or from evaporation of adsorbed species.

FUTURE WORK

Numerous materials have been identified that form strong bonds with SOFC components (anode, electrolyte, and cathode), but several issues remain to be addressed before these materials can be considered suitable sealants. The porosity of low– and intermediate–temperature materials must be reduced and the bonding of low–temperature materials at high temperature must be improved. The long–term stability and electrical properties of these materials must also be characterized. High–temperature materials form strong, dense bonds, and are stable in reducing conditions for relatively short times, but their long–term stabilities must be determined. The electrical properties of these materials must also be measured.

END

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