FABRICATION METHODS OF A LEAKY SOFC DESIGN

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ABSTRACT

Fabrication methods are discussed for the separate components comprising the INEEL designed Solid Oxide Fuel Cell. Primarily using plasma spray techniques, the ceramic electrode, electrolyte, and interconnect layers are deposited on a planar intermetallic bipolar plate. Combinations of dry powder, slurry suspension, and liquid injection plasma deposition techniques are used to deposit graded porosity electrode layers. A brief discussion about creating the necessary air channels, dense edge seals surrounding the electrode layers, and braze joints between completed cells is presented. All process parameters and methodologies used to deposit the graded porosity electrode layers, removable filler materials in the air channels, and fully dense seal coats on the bipolar plate are discussed.

INTRODUCTION

Minimizing the mismatch in material properties between component materials remains a primary objective in solid oxide fuel cell (SOFC) fabrication (1-3). A variety of methods have been employed to achieve a lower mismatch in thermal expansion of the interface joints between the interconnect, electrode, and electrolyte materials. It is important to keep in mind that the electrode materials need maximum porosity for gas transportation (2) while the electrolyte and interconnect materials should be fully dense for hermetic sealing. Creating microstructural spatial variations within each distinct material layer has succeeded in reducing material mismatch issues while satisfying the porosity, structural strength, and electrochemical efficiency requirements (3).

A graded, or gradient, approach to fabricating the ceramic layers can produce these microstructural variations by inducing a gradual material transition through the material interfaces or graded porosity in the microstructures. This methodology has been used successfully in both fuel cell fabrication (4, 5) and a variety of other graded applications (6, 7). By producing material gradients through the interfaces and porosity gradients through the electrode microstructures both the structural strength and the overall gas transport efficiency of the cell will be improved.

For our planar SOFC design, plasma deposition allows the greatest flexibility in fabricating graded layers. A variety of plasma spray processes in association with a dual material injection system are used to achieve both the material and porosity gradients for all the deposited layers.

An additional help to fabricating a stable SOFC structure is the design considerations for this planar cell configuration. While fully dense metallic coatings can be achieved it has
proved problematic to consistently deposit a hermetic coating with ceramic materials. This can be a problem for the edge seals where it is not desirable for the gases to escape from the electrode layers. This factor is accounted for in our design, which allows for controlled leakage of the fuel and oxygen from the cells (8). Thus, the design of the cell eliminates the stringent requirement of perfect hermetic edge seals, allowing the use of plasma deposited material.

However, even when depositing less than perfectly hermetic edge seals the spray parameters are very aggressive which can lead to thermal damage of the underlying layers. This is especially important when the underlying material is a removable filler such as used in the air channels to assist in bridging the air channels with cathode material. This paper outlines the methods used to successfully fabricate a planar SOFC design incorporating graded porosity electrodes, a low CTE bipolar plate, and high temperature ceramic materials while taking advantage of our controlled leakage design for the cells.

**EXPERIMENTAL**

Figure 1 shows a schematic of all layers that are formed for the INEEL fuel cell design. The lanthanum strontium chromite (LSC) layer in combination with the thick, porous nickel-aluminide (NiAl) structural plate forms a bipolar plate, which acts as a stable substrate for all other subsequent deposited layers. Air is input on the cathode

![Figure 1. Exploded schematic view showing layers for a single cell.](image)

(lanthanum strontium manganite, LSM) side of the electrolyte (stabilized-zirconia) with fuel gases input from the anode (nickel-YSZ) layer.

A single cell is constructed from a NiAl structural plate coated with a dense LSC layer on the air side creating a bipolar plate. After filling the air channels with a removable filler material a graded, porous LSM coating is sprayed directly onto the LSC layer and filled air channels. A 2 mm wide zirconia seal coat is deposited on top of the LSM coating along the outer edges of the cell. The seal coat is a dense, thick strip of zirconia that provides a hermetic frame to bond to the thin zirconia electrolyte. This creates a sealed pocket to minimize oxygen leakage to the fuel side of the cell. A graded porous anode layer is deposited on top of the fully dense electrolyte permitting maximum transport of the fuel into the cell.
Three different material transport techniques were used to produce the graded porosity in the electrode layers and the material gradients for each layer interface. A pneumatic powder feed system (Metco Type 4MP) was used to deposit large (~ 35 - 50 μm) particles creating a coarse microstructure. Small particles (~ 0.5 - 1.7 μm) suspended in a liquid solution were used to produce a finer porosity within the microstructure (9). An extremely fine microstructure (particle diameters ~ 100 - 250 nm) in the interface areas directly adjacent to the electrolyte was produced by Liquid Plasma Injection Deposition (LIPD) using chemical solutions. The chemical solutions of LSM, YSZ, and nickel nitrate were injected into the plasma using a dual action, internal mix airbrush. Optimal plasma spray parameters for each deposited layer are shown in Table I.

Table I. Optimal Plasma Spray Parameters for All Coatings/Layers.

| Parameters       | LSC (bipolar) | LSM (cathode) | Zirconia (electrolyte) | YSZ (seal coat) | Ni-YSZ (anode) |
|------------------|---------------|---------------|------------------------|----------------|---------------|
| Total energy, kW | 35            | 16            | 35                     | 35             | 16            |
| Dry powder feed, g/min | 30            | 25            | -                      | 30             | 25            |
| Slurry feed, ml/min | -             | 40            | -                      | -              | 40            |
| LIPD feed, ml/min | -             | 10            | 20                     | -              | 20            |
| Travel rate, cm/min | 100           | 400           | 100                    | 100            | 100           |
| Thickness, um    | 250           | 200           | 15-25                  | 250            | 200           |

A stack is formed by brazing single cells together with a low CTE, high-temperature brazing compound. Initial braze tests did not use completed cell structures. Instead 25-mm diameter NiAl substrate discs were used to test the viability of specific braze compounds. The discs were cut in half, with the faces polished and cleaned with an ultrasonic bath of ethanol. The samples were held in place with weights made of alumina or silicon carbide and heated in a muffle tube furnace to the brazing temperature. The furnace atmosphere is argon (welding grade or UHP grade) with some tests adding 4-vol% hydrogen in argon.

Microstructural characteristics (thickness, porosity, connectivity, particle size, and interface bonding) for the NiAl substrate, each ceramic layer, and the braze joints were analyzed using an optical (Nikon Epiphot 300) and SEM (Phillips XL 30 SEM) microscope.

RESULTS AND DISCUSSION

LSC (Protective NiAl Coating)

The protective LSC layer deposited upon the low CTE NiAl structural plate is designed to be dense and hermetic to both fuel and oxygen-rich gases. This relatively thin, ceramic layer actually performs the function of a bipolar plate for our planar SOFC design. Nominal deposition thicknesses of 200-300 μm are deposited directly onto the NiAl plate.
forming the foundation for all future ceramic layer depositions (Figure 2). The LSC deposit is clearly much denser than the adjacent NiAl microstructure, as seen in the magnified view of Figure 2.

Figure 2. Micrograph of NiAl/LSC interface.

The porosity and extensive surface roughness of the NiAl plate provide significant bonding between the LSC ceramic and NiAl intermetallic through mechanical interlocking. This strong bond is necessary for the structural stability during subsequent deposition of the electrolyte and electrode layers. In addition, the bonds provide electrical contact between the layers producing an electrical interconnect between each individual cell. The LSC coating has only moderate conductivity (Figure 3). This requires a relatively thin coating to help keep the resistivity of the interconnect low enough to provide adequate conductivity through the entire cell stack.

Electrodes (Cathode and Anode Layers)

For the porous electrode coatings all three deposition techniques were employed to create a fully graded structure. To create the initial coarse microstructure adjacent to the incoming gases a dry particle & LIPD solution were simultaneously injected into the plasma flame. This was immediately followed by a thinner layer using only a fine particle slurry transitioning to a final top coat using LIPD with chemical solutions to produce a coating with extremely fine microstructure at the interface between the electrodes and the electrolyte.
Representative micrographs for each stage of the porous microstructure are shown in Figure 4. The large dry powder is shown as large particles that are "glued" in place by small particles formed during the LIPD spray. The large particles are not completely melted during deposition providing the desired large porosity (~20 μm) for maximum gas transport through this structure. In addition, this coarse deposit results in a very rough surface that assists in the adherence of the adjacent layer. The effect is to produce a very porous, light, and thermally shock resistant microstructure that can be sprayed over previous coatings without damage to them.

The slurry deposit in the middle micrograph shows a very porous structure with pore sizes ranging from 1 to 3 μm, a factor of about 10 less than the coarse microstructure. The final LIPD coating has a very fine microstructure with pore and particle sizes ranging from 250 –500 nm. The nanosized microstructure provides a maximum number of catalytic sites possible at the electrode/electrolyte interface.

The plasma flame was run at very low energy levels (16 kW) to reduce the thermal load on the previously deposited coatings. This helps protect these materials from excessive heating during deposition of the electrode materials. Even at this relatively low deposition energy partial melting occurs in the small size of the LIPD particles. The partially melted particles assist in "gluing" the larger dry spray particles to the substrate and providing a strong bond throughout the microstructure.

The process of plasma depositing the anode coating varies somewhat from the cathode in that two constituents are being injected into the plasma simultaneously. Nickel and Yttria Stabilized Zirconia (YSZ) are deposited in an optimal ratio for all three the deposition techniques. To this effect the two injection systems, one with nickel bearing solution and one with a stabilized zirconia solution, were used to deposit the fine structured LIPD layer on top of the electrolyte. Next, a slurry suspension of small particles (d50 < 0.5 μm) for both nickel and YSZ were used to produce the adjacent microstructure. Various additives to the aqueous suspension were used to keep the nickel particles suspended in the slurry during deposition (10). Finally, a 50/50 volume mixture of larger (d50 = 30 μm) nickel and YSZ particles were used to deposit a more porous layer adjacent to the fuel gas channels. The resulting microstructures are similar to the LSM depositions seen in Figure 4.
Resistivity measurements of the LSM and Ni/YSZ electrode materials show relatively low resistivity for each layer (Figure 3). Thus, plasma deposition of electrically conductive, thermally and mechanically stable, porous electrodes is made possible taking a graded approach to deposition of the materials.

**Electrolyte (YSZ Interfaces)**

A graded transition from electrode to electrolyte enhances the transport of ions across the electrolyte and thus increases the efficiency of the cell (11). This graded transition is performed using the dual material inject system and decreasing the feed rate of one material while the second material is increased during deposition. This creates a graded composition profile through the interface. Increasing or reducing the feed rate of either material allows the graded profile to be tailored for each specific interface if desired (i.e. linear, exponential, or logarithmic composition profile).

Optimal porosity and particle sizes at the electrode/electrolyte interface are generally in the nanometer size range dictating the use of chemical solution LIPD, Figure 5. This simplifies construction of the graded interface by simply using two liquid injection systems simultaneously. A linear material gradient is used for both electrode/electrolyte interfaces in our current SOFC design (Figure 5).

![Material gradient in porous anode layer showing a) porous microstructure, b) elemental map of nickel, and c) zirconium. Dark areas depict low signal counts from indentations or pores in the structure.](image)

The elemental maps in Figure 5 illustrate the linear composition gradient achieved through the dual material injection process. A high concentration of zirconia (Zr signal) is seen on the bottom of the anode layer while an even mixture of nickel and zirconia is seen in the top half of the structure. Porosity is generated by diluting the chemical precursor solutions and using a lower deposition temperature.

A dense electrolyte of stabilized zirconia is deposited through a special chemical vapor deposition (CVD) technique. An extremely thin (10 - 20 µm), hermetic layer allows easy transport of oxygen ions through the electrolyte for maximum efficiency.

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YSZ Seal Coat

The edge seal serves two functions in our SOFC design. First, it is a dense, non-conductive, hermetic frame that is bonded to the outer edges of the electrolyte layer creating an impervious boundary between the fuel and air gases. Second, it provides a solid platform for joining adjacent cells without damaging the electrolyte and electrode materials. A high temperature braze material is applied to the top surface of the edge seal ring and to corresponding locations on the bottom surface of the next NiAl bipolar plate to provide a strong bond between individual cells, as described below.

The edge seal is composed of yttria stabilized zirconia (YSZ). Deposition parameters given in Table I yield a fairly dense, thick deposit which provides the necessary density to minimize gas transport and structural strength for the braze joint. The relatively thick deposit (≈300 μm) requires the use of dry powder deposition (d50 particle size = 30 μm) and a fairly high thermal energy load (35 kW) to melt the particles and create the solid structure (Figure 6). Although the coating is not deposited as a fully dense microstructure the leakage of gasses through the edge coat is minimal and is accounted for within our controlled leakage design.

![Figure 6. Micrograph of fractured YSZ seal coat a) directly adjacent to LSC coating and b) at 2000X magnification showing microstructure.](image)

Air Channels (Removable Filler Material)

A temporary filler material is used to fill the air channels before depositing the ceramic layers to keep the air channels clear and open. A number of filler materials were suggested, assessed, and rejected before finally arriving at the current filler material used in the INEEL design, Table II. The problem was, and remains, one of thermal stability to temperatures as high as 700 - 800°C but requires eventual removal from the channels without disrupting the ceramic layers deposited on top of the channels.

| Compound     | Melting Point, °C | Method of Removal     |
|--------------|-------------------|-----------------------|
| NaCl         | 801               | H2O soluble           |
| K2MoO4       | 919               | H2O soluble           |
| NaAlO2       | 1800              | H2O soluble           |
| Graphite     | 1000              | CO/CO2 oxidation      |
| Furfural alcohol | 600           | CO/CO2 oxidation      |

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Thermally stable water-soluble compounds were a logical first choice but were found to contaminate the top coatings during dissolution in water. Graphite and the carbon-based furfural alcohol were found to be thermally stable at the deposition temperatures and did not contaminate the top layers during oxidation/decomposition into CO or CO$_2$ gas. However, the graphite was difficult to keep in the channels during deposition while the furfural material shrank after curing/drying.

A composite material was developed using both graphite and furfural alcohol. A slurry of graphite particles ($d_{50}$ particle size = 150 µm) and furfural alcohol (66:33 vol%, respectively) is injected into the channels, dried at 40°C for 8 hours, and carbonized at 500°C in ultra high purity (UHP) argon for 4 hours. The high graphite content in the slurry filler minimizes shrinkage during the drying and carbonization steps. Once carbonized, the material forms a very hard and thermally stable filler that can withstand the plasma spray deposition process.

The deposition temperature for the cathode (LSM) layer directly adjacent to the air channels is fairly low. This serves a dual purpose; first, the LSM material is not thoroughly melted, thereby creating a very porous microstructure (Figure 4) and second, the low deposition temperature reduces degradation of the carbonaceous filler material while deposition takes place over the air channels. Once deposited, the porous LSM coating provides significant protection to the underlying filler material during subsequent plasma depositions (i.e. edge seal, electrolyte, and anode depositions). Visual observations after each deposition indicate no notable degradation of the filler material or ceramic layers.

Figure 7. Backscatter image of completed cell structure showing all layers. Cracks and uneven surfaces result from fracturing the sample for analysis.
The filler material is removed from the air channels after all layers have been deposited (Figure 7). The filler material is exposed to an oxygen-rich environment at normal operating temperature (900 – 1000°C) for 4 hours to eliminate all carbon-based material from the channels. This allows free transport of air into the porous cathode (LSM) layer.

**High Temperature Brazing – Formation of Stack**

Brazing single cells together with a low CTE brazing compound forms a stack. Brazes used in this study are cobalt-, nickel-, and precious metal-based compounds with very high brazing temperatures, Table III. The braze is applied between the first cell’s zirconia edge seal ring and the underside of the adjacent cell. Thus, a joint between zirconia and the NiAl intermetallic substrate is required. Successful braze joints have been fabricated using the precious metal braze compound but to keep future costs of fabrication low the cobalt-based brazes have also been tested with some success.

**Table III. Braze compounds.**

| Braze Compound      | Size (mesh) | Composition, wt%           | Braze Temp, °C |
|---------------------|-------------|----------------------------|----------------|
| Union Carbide CO-285| 325         | 66Co-25.5Cr.-10.5 Ni-7.5W-0.5 C | 1455-1900      |
| Union Carbide CO-216| 325         | 50.8 Co-19 Cr.-17 Ni-8 Si-4 W-0.8 B-0.4 C | 1150-1232      |
| Wall Colmonoy Nicrobraz 210 | 140  | 49 Co-20 Cr-17.5Ni-3.5 W-10 Si | 1107-1149      |
| Wall Colmonoy Nicrobraz X-1 | 40+140 | 41.5 Ni-40 Co-15 Cr-3.5B | 1177-1232      |
| Westgo PALNI        | 325         | 60 Pd-40 Ni                | 1200-1238      |

Ramp rates no faster than 400°C/hour were used to insure braze sample temperature and furnace temperatures were in equilibrium. This is balanced against time at high temperature (using an argon atmosphere) which can reduce the deposited ceramic oxide layers and/or cause interdiffusion. Often the desired powder braze has been applied on top of substrates covered with Wall Colmonoy Nicrobraz Cement #650 and the two halves stacked on each other.

Besides substrate to substrate joining, tests designed to braze the fuel and air supply line tubing to stack end plates have been conducted. High temperature Haynes 230 tubing was joined to thick (18 mm) NiAl test samples using the cobalt-based and PALNI brazes. Successful joints were achieved for all braze compounds. All brazes remained joined after exposing the brazed joints to air at 1000°C and up to 113 hours (Figure 8).

**Figure 8. Optical micrograph (100X) of braze joints after exposure to air at 1000°C for 113 hrs.**

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CONCLUSIONS

A complete cell consists of a 6 mm thick NiAl intermetallic plate, a dense LSC protective coating, hollow air channels, a porous LSM cathode, a dense, thick zirconia edge seal, a thin, dense zirconia electrolyte, and a porous nickel-zirconia anode, Figure 7. The nominal thickness for each layer in a completed cell is given in Table I with a total approximate thickness of 750 μm for all deposited layers. Each layer/component within the completed cell has distinct characteristics tailored for its specific function (i.e., porosity, density, material profile, microstructure size, thickness, etc.). By using a graded approach the fabrication residual stresses are minimized, the catalytic reaction is improved, and the transport efficiency of ions through the electrolyte is increased. This should lead to an overall efficiency increase in the individual cell performance. Individual cells are bonded together to form a stack using a high-temperature, Co-, Ni-, or Pd-based braze compound. The braze compound is applied between the first cell’s zirconia edge seal ring and the underside of the adjacent cell.

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