A LOW CTE INTERMETALLIC BIPOLAR PLATE

W. E. Windes, L. D. Zuck, E. L. Shaber, A. E. Erickson and P. A. Lessing
Idaho National Engineering & Environmental Laboratory (INEEL)
P.O. Box 1625
Idaho Falls, ID 83415, USA

ABSTRACT

A low CTE bipolar plate is fabricated from a NiAl intermetallic and a ceramic filler material. By using inert, ceramic filler materials the intermetallic reaction of the NiAl system is controlled resulting in net-shape formed plates with CTE comparable to the electrolyte and electrode ceramic layers. In addition, the combustion synthesis reaction moderated by the ceramic filler material creates significant porosity in the NiAl microstructure yielding a highly thermal shock resistant substrate material for the subsequent plasma deposited electrode and electrolyte layers. This paper outlines the powder metallurgy process parameters necessary to form these low CTE intermetallic plates.

INTRODUCTION

The fabrication of structurally stable high temperature solid oxide fuel cells is hindered by the mismatch in material properties between component materials (1,2,3). Specifically, the mismatch in thermal expansion between the interface joints of a bipolar plate, electrodes, and electrolyte material has proven to be a difficult fabrication issue problem. Contributing to this fabrication conundrum has been the development of a conductive substrate that has similar thermal expansion as the ceramic components and yet can withstand the very high operating temperatures. These seemingly insurmountable fabrication problems have led the SOFC research community to look toward lower temperature materials to circumvent these problems (3,4,5).

Rather than abandoning the obvious benefits of a fuel cell operating at high temperature a solution to these problems is the development of a lightweight, low coefficient of thermal expansion (CTE) bipolar plate that serves as the structural substrate and electrical interconnect to the relatively thin ceramic SOFC coatings. Intermetallic materials satisfy the electrical, structural and thermal stability requirements for operating temperatures in the 900 – 1000°C range. However, the CTE of these materials remains high, which can cause significant damage to the thin ceramic layers of the cell materials. In addition, if the part is fabricated using solid state combustion synthesis the extremely high thermal temperatures resulting from the intermetallic reaction can result in significant warping and distortions.

The Idaho National Engineering and Environmental Laboratory (INEEL) has been working with a nickel-aluminide (NiAl) intermetallic system as a bipolar plate. By using
inert, ceramic filler materials the intermetallic reaction of the NiAl system is controlled resulting in net-shape formed plates (final dimensions are the same as the original green-formed piece). The ceramic additive lowers the composite CTE making it comparable to the deposited ceramic layers. A ceramic oxide (with a similar CTE value to the composite) is plasma deposited on the cathode side of the plate to protect the NiAl intermetallic from oxidation during operation of the cell. This paper outlines the powder metallurgy process parameters necessary to form these low CTE intermetallic plates.

EXPERIMENTAL

Figure 1 is a schematic of the INEEL fuel cell design showing the NiAl plate and all subsequently deposited layers. The lanthanum strontium chromite (LSC) layer with the

[Diagram of the INEEL fuel cell design]

thick nickel-aluminide (NiAl) structural plate forms a bipolar plate where air is input on the LSC protected side and the fuel (a reducing environment) is input on the NiAl side. This allows the LSC coating to protect the intermetallic plate from oxidizing at the high operating temperature (900 - 1000°C). All subsequent layers are plasma sprayed onto the intermetallic NiAl structural plate to avoid the problems (shrinkage, interdiffusion, etc.) associated with sintering disparate materials simultaneously. Special edge seals formed during the plasma spraying sequences are not shown.

A 50/50 atomic ratio mixture of nickel powder and aluminum powder is thoroughly mixed together. An inert ceramic powder with a low CTE value is then added to the NiAl powder mixture in volumetric ratios of 10 - 50%. The volume ratio of ceramic to metallic powder varies depending upon the desired CTE value, powder morphology, and density of the ceramic. A list of ceramic powders used in this study is presented in Table I.

| Ceramic Powder      | CTE, $10^{-6}$ °C | Filler, vol% |
|---------------------|-------------------|--------------|
| Zirconia (ZrO$_2$)  | 10                | 50           |
| Zircon (ZrO$_2$ - SiO$_2$) | 3.1           | 30           |
| Al$_2$TiO$_5$       | 3.8               | 25           |
| Alumina (Al$_2$O$_3$) | 8               | 50           |
| Current oxide (XO$_2$) | 5.8             | 35           |
An important factor for producing a stable NiAl plate is to assure complete mixing of the nickel, aluminum, and ceramic powders before pressing and firing. To assure thorough mixing approximately 50 vol% ethanol is added to the powder as a lubricant and dust control. The entire mixture is blended, and then ultrasonically mixed (Vibrasonic™ ultrasonic probe) for 2 minutes. The alcohol is evaporated leaving the mixture dry before cold pressing the parts. The cold press dies are lightly lubricated with a colloidal graphite-alcohol mixture before loading the dry powder mixture. A powder weight corresponding to a 6 mm thick bipolar plate is loaded into the die cavity and a pressure of 123 MPa applied to the powder for 1 minute. The ductile aluminum (and to some extent the nickel) powder acts as an excellent binder during cold pressing. No additional binders are required even for the higher ceramic filler volumes.

The pressed plate is inserted in a graphite support fixture, heated to 800°C for 2 hours in argon (where the intermetallic reaction takes place), and furnace cooled to room temperature. After the intermetallic reaction has taken place, the plate is removed from the graphite holder, lightly grit blasted, and coated with the lanthanum-strontium-chromate (LSC) coating (see plasma spray parameters for LSC coating in “Fabrication Methods for a Leaky SOFC Design,” in these Proceedings).

CTE values for composites with varying amounts of filler material were measured (Theta dilatometer) up to a temperature of 1000°C. Microstructural characterization using an optical (Nikon Epiphot 300) and SEM (Phillips XL 30 SEM) microscope were performed on the reacted plates. With our unique cell design requirements porosity within the NiAl plate is desirable. Therefore, to quantify the porosity within this intermetallic microstructure permeability tests were conducted on 1" diameter samples fabricated using the same powder and process used for the bipolar plates. A schematic of the permeability test apparatus is shown in Figure 2.

![Permeability Test Apparatus](image)

**Figure 2. Schematic of the permeability test apparatus.**

**FABRICATION RESULTS & DISCUSSION**

**NiAl Structural Plate**

Residual stresses in the ceramic electrolyte and electrodes were minimized through careful matching of thermal expansion coefficients (CTE) for each layer (6). The use of strontium doping in the lanthanum chromate and lanthanum Manganate brings the CTE...
to levels compatible with the fully stabilized zirconia electrolyte (7). As a consequence, the deposited layers are quite compatible with each other showing no indications of cracking, delamination, or other thermal expansion problems.

Matching the CTE of the intermetallic bipolar plate to these ceramic layers while still maintaining structural, thermal, and electrical stability was determined to be a function of the selected ceramic filler powder. The ceramic’s density, CTE, and the powder’s particle morphology dictated the total volume of material needed to lower the overall plate CTE. The volume of ceramic powder added to the nickel/aluminum mixture directly affected the reaction efficiency between the nickel and aluminum particles (i.e. by physically separating the two reaction constituents and by adsorbing a portion of the exothermic reaction heat). This dictated the strength, conductivity, and porosity of the composite microstructure. A higher volume of ceramic filler added to the powder mixture corresponded to lower strength, density, and electrical conductivity in the formed plate.

From Table I a variety of ceramic filler materials were used with varying success. The relatively high CTE values for zirconia and alumina required filler volumes of 50 vol% or more to achieve an overall CTE that matched the ceramic coatings. While using this amount of filler material was successful in lowering the plate CTE to acceptable levels the strength was severely compromised. Numerous cracks, extensive surface spallation, and problems with thermal shock during plasma deposition of the LSC coating precluded the use of these filler materials.

The CTE value for Zircon and aluminum-titanate (Al₂TiO₅) was low enough (3.1 and 3.8 x 10⁻⁶/°C, respectively) such that considerably less filler was needed to achieve an adequate overall plate CTE. As a consequence the composite NiAl plate was very strong.

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Figure 3. Plot of CTE changes in NiAl intermetallic plate as a function of inert ceramic filler content.

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and dense. However, at high temperatures (> 800°C) some of the SiC constituent in the Zircon filler was shown to exhibit vapor transport while the Al₂TiO₅ filler was seen to decompose. It was assumed that SiO (g) was the silicon species being transported via a vapor phase. However it’s exact nature is unknown. This vapor transport resulted in considerable silicate formations on the exposed surfaces of the NiAl plate which interrupted the wetting ability of the braze compounds used to bond the cells into a usable stack configuration. This leads to weak bonds forming between the cells. As a result, experiments using both the Zircon and Al₂TiO₅ filler materials were discontinued.

A successful low CTE NiAl plate was fabricated using a thermally and chemically stable ceramic filler, XO₂. Though not the lowest CTE filler material it proved to be adequate for lowering the CTE of the intermetallic plate sufficiently close to the levels of the deposited ceramic layers. More importantly, the ceramic material exhibited high thermal stability and the added XO₂ volume was low enough to allow the intermetallic constituents to form a strong, conductive, net-shape plate. A final volume of 35 - 40 vol% ceramic filler powders was adequate for lowering the plate CTE to ~ 12 x 10⁻⁶ cm/cm·°C at planned cell operating temperature (Figure 3).

One of the main benefits of the relatively high filler volume was that the XO₂ powder physically diluted the nickel-aluminide combustion synthesis reaction. By preventing development of a high speed reaction front, the incipient melting of the Ni during the reaction does not occur and dimensional stability of the part is maintained. In addition, the volume reduction involved in the reaction Al + Ni → NiAl causes the formation of voids resulting in an extremely porous microstructure, as seen in Figure 4. Dilution has the effect of slowing the reaction front as it sweeps through the powders and reducing the overall temperature of the component resulting in significantly less warping and physical contraction of the intermetallic material. This produces a net-shaped component with overall dimensional changes less than 0.10 mm after reaction. Components with complex geometry, tight tolerances, and no warping are easily produced.

Figure 4. Micrograph of NiAl microstructure showing large pores in microstructure.
The porous microstructure makes the plate extremely stable to thermal shock. Previous experience with NiAl bipolar plates formed without high volumes of ceramic filler showed cracking when exposed to plasma spray conditions. Since the ceramic electrolyte and electrode coatings are deposited by plasma techniques, the ability of the NiAl substrate to withstand extreme thermal shock is critical for producing a stable cell. This is very apparent when coating the NiAl plate with the Lathanum-Stronium-Chromate (LSC) protective coating which has the most energetic, or aggressive, deposition parameters (35 kW at a deposition rate of 35 g/min).

**LSC Protective Coating**

To protect the NiAl intermetallic from oxidation at the high operating temperature a protective ceramic oxide coating is plasma deposited on the cathode side of the cell. The LSC coating is deposited as a dense, relatively thick coating (~ 200 – 300 μm) which provides the NiAl protection from oxygen in the cathode. The NiAl structural plate has demonstrated that it is capable of withstanding the extremely high temperatures reached during deposition of LSC (~ 1200°C) without cracking, breaking apart, or any apparent damage to the coating (Figure 5).

![Figure 5. Micrograph of LSC/NiAl interface showing porosity of NiAl and dense structure of LSC deposit.](image)

LSC is reported (7) to be fairly conductive (14 Ω⁻¹ cm⁻¹) at the normal operating temperatures which is only a 30% reduction from the measured conductivity in the ceramic filled NiAl plates. Thus, no serious reduction of the electrical conductivity in a cell is anticipated by depositing a thin, protective, coating of LSC on the NiAl plate.

The relatively coarse, porous microstructure of the NiAl provides an extremely rough interface for deposition. This results in significant mechanical interlocking between the two disparate materials creating a very strong bond (Figure 5). This strong bond between the LSC layer and NiAl plate provides a solid substrate foundation for the subsequent deposition of the electrolyte and electrode materials (on top of the LSC).
The composite structure of the LSC coated NiAl plate forms the complete bipolar plate used in the SOFC design fabricated at the INEEL. By minimizing induced stresses resulting from thermal shock or thermal expansion mismatches the LSC coating is kept crack free, allowing full protection of the intermetallic NiAl microstructure from oxidation.

**Porosity in the NiAl Microstructure**

Porosity within the NiAl plate on the anode side is actually desired for our cell since we have shown the nickel in the NiAl microstructure is catalytic to the internal reforming of hydrocarbons (8). As a consequence, the porous nickel-bearing NiAl structure adjacent to the anode significantly assists the autocatalytic reaction efficiency of the individual cells when using hydrocarbon fuels. A high permeability value in the NiAl microstructure corresponds to higher efficiencies within the cell.

Permeability was measured using ASTM Method D 4525 “Standard Test Method for Permeability of Rocks by Flowing Air” for 25 mm diameter NiAl disks with similar process history. The sampling apparatus was modified to hold a 25-mm diameter disk by converting a Millipore filtration system with a double O-Ring. The flow rate was measured through the disks at pressures of 48.3, 34.5, 20.7, and 6.9 x 103 Pa of absolute pressure. The coefficient of permeability, $K_i$ ($m^2$), was calculated and then converted to Darcy ($10^{12}$ Darcy = 1 $m^2$) as follows:

$$K_i = \frac{2Q_{out}P_{out}\mu}{(P_{in}^2 + P_{out}^2)\lambda}$$

where:

- $K_i$ = coefficient of permeability, $m^2$ (=10^{12} Darcy),
- $Q_{out}$ = exit flow rate of air, $m^3/s$,
- $P_{out}$ = exit pressure of air, Pa,
- $L$ = length (thickness) of sample, $m$,
- $A$ = cross-section area of specimen, $m^2$,
- $P_{in}$ = entrance pressure of air, Pa, and
- $\mu$ = viscosity of air at temperature of each test, Pa-s.

ASTM Method D425 requires the sample be 1.3 to 1.7 times the diameter. Our samples were 25 mm diameter x 6 mm thick, which did not meet this requirement. However, the permeability is a function of the sample thickness and should be valid for our thinner samples. In addition, three samples were tested together creating a sample thickness ~18 mm which is closer to the requirement. By extrapolating to a zero intersect at the ordinate gives the permeability of each sample (Figure 6). A mean $K_i$ value of ~ 5.6 Darcy was then calculated from the three test samples. The results are in the realm of known permeability results of similar material structures such as clays, sand and compacted gravel.

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CONCLUSIONS

Inert, ceramic filler materials were added to a nickel-aluminum powder mixture. The ceramic powder diluted the NiAl solid-state intermetallic reaction. This resulted in the production of porous, net-shape formed plates with a CTE comparable to the deposited ceramic layers. The NiAl microstructure provided a highly thermal shock resistant substrate material capable of withstanding high temperatures (>1200°C) with no significant damage. A dense, relatively thin, protective ceramic oxide coating (LSC) was plasma deposited on the cathode side of the cell to protect the NiAl intermetallic from high temperature oxidation. The composite structure of the LSC coated NiAl plate forms the complete bipolar plate. The low CTE and high porosity of the NiAl structural plate allows the subsequent deposition of a ceramic protective coating, electrolyte, and electrodes to be deposited on a thermally stable substrate and ensures high temperature operation without cracking, spallation, or any apparent damage to the added layers.

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