



Development of Low-Cost, Clad Metal Bipolar Plates for PEM Fuel Cells

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Project ID FCP13

**Pacific Northwest
National Laboratory**
Operated by Battelle for the
U.S. Department of Energy

Timeline

- **Project start date: 3/1/05**
- **Project end date: 9/1/05**
- **Percent complete: 10%**

Barriers

- **This project addresses the following key technical barriers identified in the HFCIT Program Multi-Year Program Plan :**
 - ▶ **Fuel cell stack (bipolar plate) durability - e.g. corrosion/MEA poisoning effects**
 - ▶ **Fuel cell stack (bipolar plate) cost**

Budget

- **Total project funding: \$120K**
- **Funding received in FY04: \$0**
- **Funding received in FY05: \$120K**

Partners

- **Engineered Materials Solutions Inc. (EMS, Inc.), Attleboro, MA**

To assist the DOE in lowering the cost and improving the durability of PEM fuel cell stacks by reducing the material and manufacturing costs of bipolar plates, while substantially increasing their resistance to corrosion and mitigating the release of poisoning metallic ions into the MEA

- **Feasibility study to determine the potential efficacy of a clad metal approach in developing a low-cost/low-mass/low-volume PEM bipolar plate**
 - ▶ Design and analysis of potential clad material options
 - ▶ Fabrication of demonstration pieces
 - ▶ Protective coating (passivation layer) development
 - ▶ Short-term and electrical and corrosion testing
- **Identify potential opportunities for further cost reduction using this material processing approach**
- **If feasible, initiate prototype bipolar plate development for longer-term testing under typical PEM operating conditions**



- **Development of a clad metal material (a sandwich metal composite) that can be readily heat treated (e.g. nitrided or carburized) to form an outer layer that is both electrically conductive and corrosion resistant. Roll cladding is a low-cost process that affords great flexibility in fabricating metal materials that are difficult to manufacture by other traditional metallurgical processes.**
 - ▶ **The core metal would offer:**
 - ◆ **Low base cost (i.e. an inexpensive material)**
 - ◆ **Mechanical robustness**
 - ◆ **Moderate to low density**
 - ◆ **High thermal conductivity (for better thermal management)**
 - ◆ **Low hydrogen permeability**
 - ▶ **The cladding metal would offer:**
 - ◆ **A thin, low-cost outer surface that could be thermally heat treated to form a conductive passivation layer on the electrolyte exposed surface; for example a transition metal nitride or carbide**
 - ◆ **A thin brazing layer that would be useful in forming internal cooling water channels when mated with a second plate**
 - ▶ **The overall clad material combination provides:**
 - ◆ **Reduced bipolar plate thicknesses (to 200 – 300 μ m or less) and therefore reduced stack volume, stack weight, lower thermal mass, and lower raw material costs**
 - ◆ **Excellent geometrical tolerance, material stiffness, and strength; providing mechanical robustness**
 - ◆ **Good formability – i.e. flow field channels can be readily stamped into the plates**



Key Accomplishments to Date

- **FY05 Project Milestones:**

- ▶ **Identify candidate filler and cladding alloys for the metal clad bipolar plate design April 05**
- ▶ **Present initial findings at the DOE Hydrogen Program Review . . . May 05**
- ▶ **Establish concept feasibility via electrical resistance and corrosion testing August 05**

- **Results to date:**

- ▶ **A list of material combinations have been identified that can be cost-effectively manufactured via roll cladding, followed by thermal treatment to form a potentially corrosion resistant bipolar plate. Over the next two months, a proprietary cost-analysis formula/vendor database (EMS, Inc.) will be employed to refine the list with the DOE technology targets in mind (cost/KW, power density, specific power, and durability as they relate to the bipolar plate).**
- ▶ **For the purposes of technology demonstration, several of these combinations have been or are currently in process development – i.e. the appropriate roll cladding conditions are being established: for example, starting material thicknesses; surface treatments; rolling pressure, temperature, and rate; and post-roll annealing time, temperature, and atmosphere.**
- ▶ **In parallel with preparing the clad materials, a series of heat treatment experiments has been initiated on samples of the outer cladding metal to identify the appropriate conditions that will ultimately yield a conductive, corrosion-resistant layer that forms over the clad material. Key parameters include: temperature, time, and heat treatment atmosphere.**

Functional Requirements for Bipolar Plates

- **Low Cost**
- **High Corrosion Resistance**
- **High Electrical Conductance**
- **Acceptable Mechanical Strength/Toughness**
- **Lightweight**
- **Low Volume/Thickness**
- **Minimal Interaction(s) with the Electrolyte and/or Membrane Materials – either via direct contact or dissolution**
- **High Thermal Conductivity**
- **Low H₂ Permeability**
- **High Degree of Processability/Manufacturability**



Bipolar Plate Materials

Benefits and Development Needs of Potential Bipolar Plate Materials

	Carbon Composite	300-Series SS	Nitrated High Cr Ni-Based Alloy	Clad Metal Concept (Ti/SS/Ti)
Benefits¹	<ul style="list-style-type: none"> • Electrochemical Stability • Low density • Low contact resistance • Corrosion resistant 	<ul style="list-style-type: none"> • Recyclable • High manufacturing reliability • Can be rolled very thin • Mechanically robust 	<ul style="list-style-type: none"> • High thermal conductivity • Recyclable • High manufacturing reliability • Low contact resistance • Corrosion resistant • Mechanically robust 	<ul style="list-style-type: none"> • High thermal conductivity • Recyclable • High manufacturing reliability • Can be rolled very thin • Low contact resistance • Corrosion resistant • Mechanically robust
Estimated Relative Cost [~\$/plate]^{1,2}	<ul style="list-style-type: none"> • 2.80 + processing cost to ensure hermeticity • Assumed thickness of 3mm 	<ul style="list-style-type: none"> • 7.00 (thickness = 1mm) • 4.70 (thickness = 0.1mm) (Primary cost is in coating) 	<ul style="list-style-type: none"> • 27.25 (thickness = 1mm) • 6.22 (thickness = 0.1mm) 	<ul style="list-style-type: none"> • 1.85 (thickness = 0.15mm)
Development Needs	<ul style="list-style-type: none"> • Reduce thickness (to improve volumetric power density)³ • Improve mechanical properties • Low cost manufacturing processes needed - both for the bulk plate and the hermetic surface seal coating 	<ul style="list-style-type: none"> • Requires lower cost protective coating to mitigate corrosion, eliminate membrane poisoning, and improve surface conductivity 	<ul style="list-style-type: none"> • Longer-term corrosion/ conductivity testing under prototypical PEM operating conditions • Material/ manufacturing costs need to be reduced – i.e. a lower cost, more formable alloy needs to be identified/developed 	<ul style="list-style-type: none"> • Requires materials/manufacturing development • Concept must be verified through corrosion and electrical testing under prototypic PEM operating conditions

¹ E. J. Carlson, FY03 Progress Report (EERE – Hydrogen, Fuel Cells, and Infrastructure Technologies)

² Based on London Metal Exchange relative raw material costs and manufacturing costs assumed in reference 1.

³ Based on General Motors review of PEM materials needs (DOE-BES Workshop on Transportation Needs, October 2002).

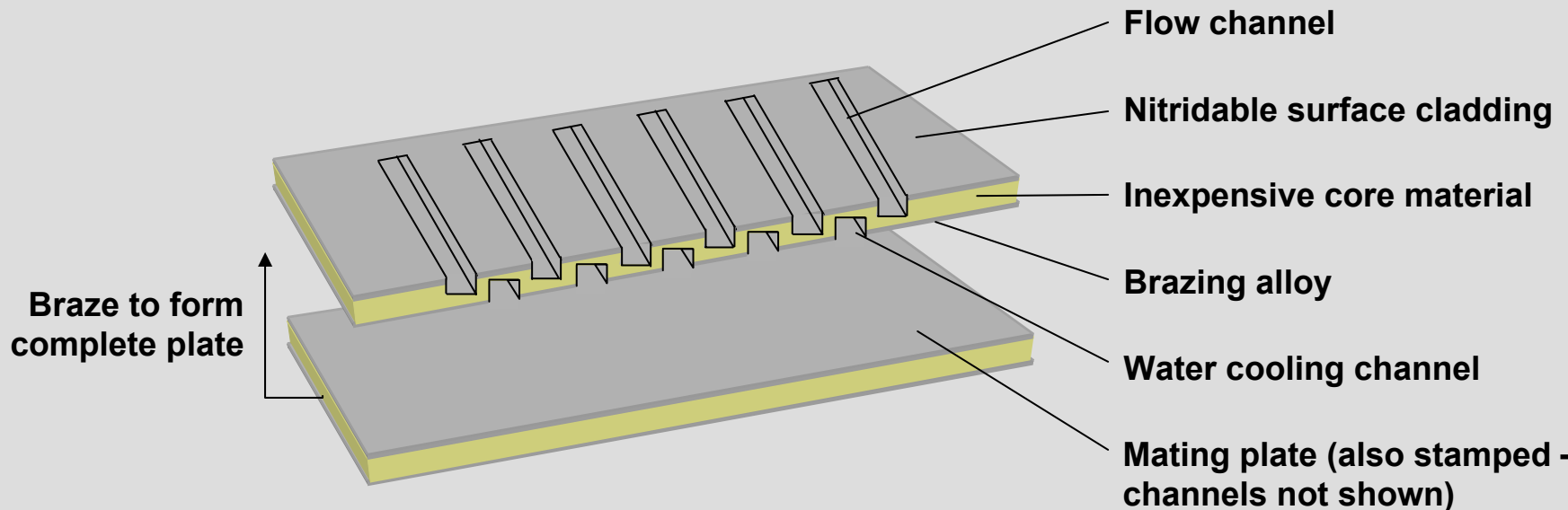
Recent Developments in Metal Bipolar Plates

- **Thermal nitridation of Ni-50Cr yields:**
 - ▶ **A dense, protective CrN/Cr₂N layer on the surface of the alloy**
 - ▶ **Low contact resistance**
 - ▶ **Low corrosion current densities in simulated PEMFC conditions**
(M. P. Brady et al., *Electrochem. Sol. St. Lett.*, 5 [2002] 245)
- **Thermal nitridation of ferritic AISI446 stainless steel yields:**
 - ▶ **The formation of an apparent nitrogen-doped passive oxide surface layer**
 - ▶ **Improved contact resistance vis-à-vis the untreated alloy**
 - ▶ **Improved corrosion resistance in simulated PEMFC conditions**
(H. Wang et al., *J. Power Sources*, 138 [2004] 86)
- **Thermal pyrolysis of a polymeric coating over austenitic 316L stainless steel yields:**
 - ▶ **The formation of a passive pyrolytic carbon layer**
 - ▶ **Improved contact resistance vis-à-vis the untreated alloy**
 - ▶ **Improved corrosion resistance in simulated PEMFC conditions**
(N. Cunningham et al., *J. Electrochem. Soc.*, 149 [2002] A905)
- **The above examples indicate that thermal nitridation/carburization/pyrolysis treatments are promising**
 - ▶ **Key: proper selection/design of the metal bipolar plate material with particular attention to cost and fabricability**



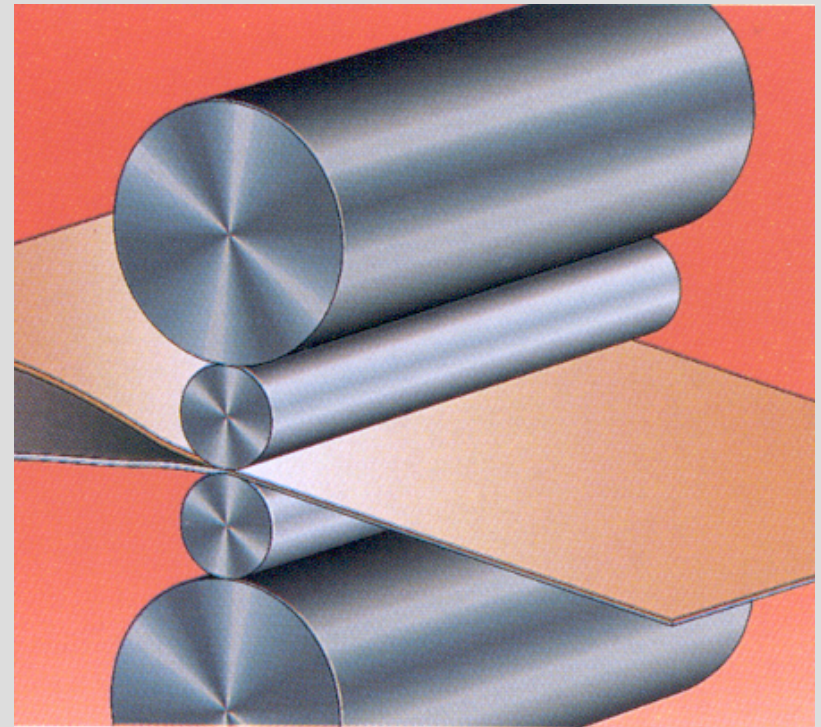
Concerns with Thermal Treatments

- At issue are:
 - ▶ The cost of the alloy and/or cost of subsequent stamping/forming processes to manufacture bipolar plates with complex flow field channels
 - ▶ The cost of the coating technique (in the case of pyrolytic carbon)
 - ▶ The reliability of the thermally formed passivation layer
- One means of fabricating a low-cost, thin metal component that can be readily thermally treated (e.g. nitriding) to form a corrosion resistant layer is by cladding a nitridable metal layer to an underlying inexpensive core material



The Cladding Process

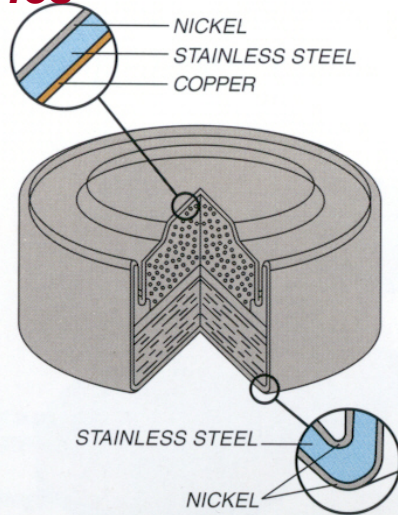
- **Two or more layers of thin sheet metal are simultaneously deformed under high pressure in a compound roll mill**
- **Causes the solid state bonding of the dissimilar alloys to form a single, multilayer sheet**
- **Can fabricate a single composite material containing as many as fourteen distinct metal layers**
- **By employing a post-roll sintering anneal, it is possible to homogenize the material and thereby form a unique monolithic alloy**
- **With a partial anneal, a gradient material can be formed**



Common Cladding Applications



Batteries



HEAT EXCHANGER MATERIAL

COPPER
STAINLESS STEEL
COPPER

TEXAS INSTRUMENTS

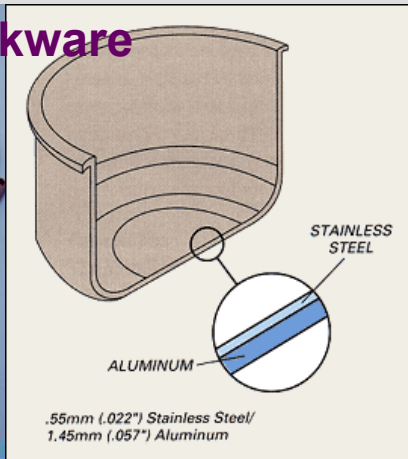
- JOINABILITY
- STRENGTH
- MANUFACTURING COST REDUCTION



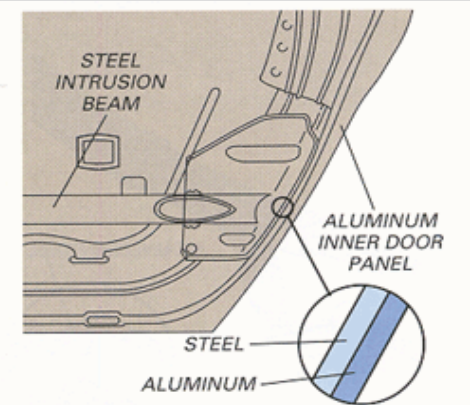
Bumpers



Cookware



Coinage

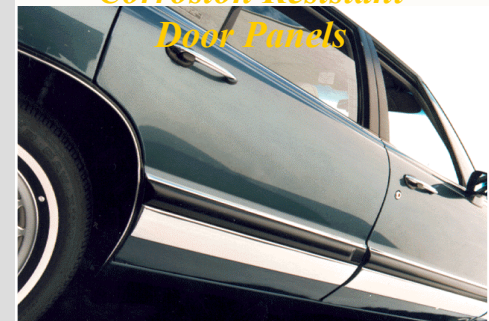


40% Aluminum: 60% Steel

Corrosion Resistant Door Panels



Fuses

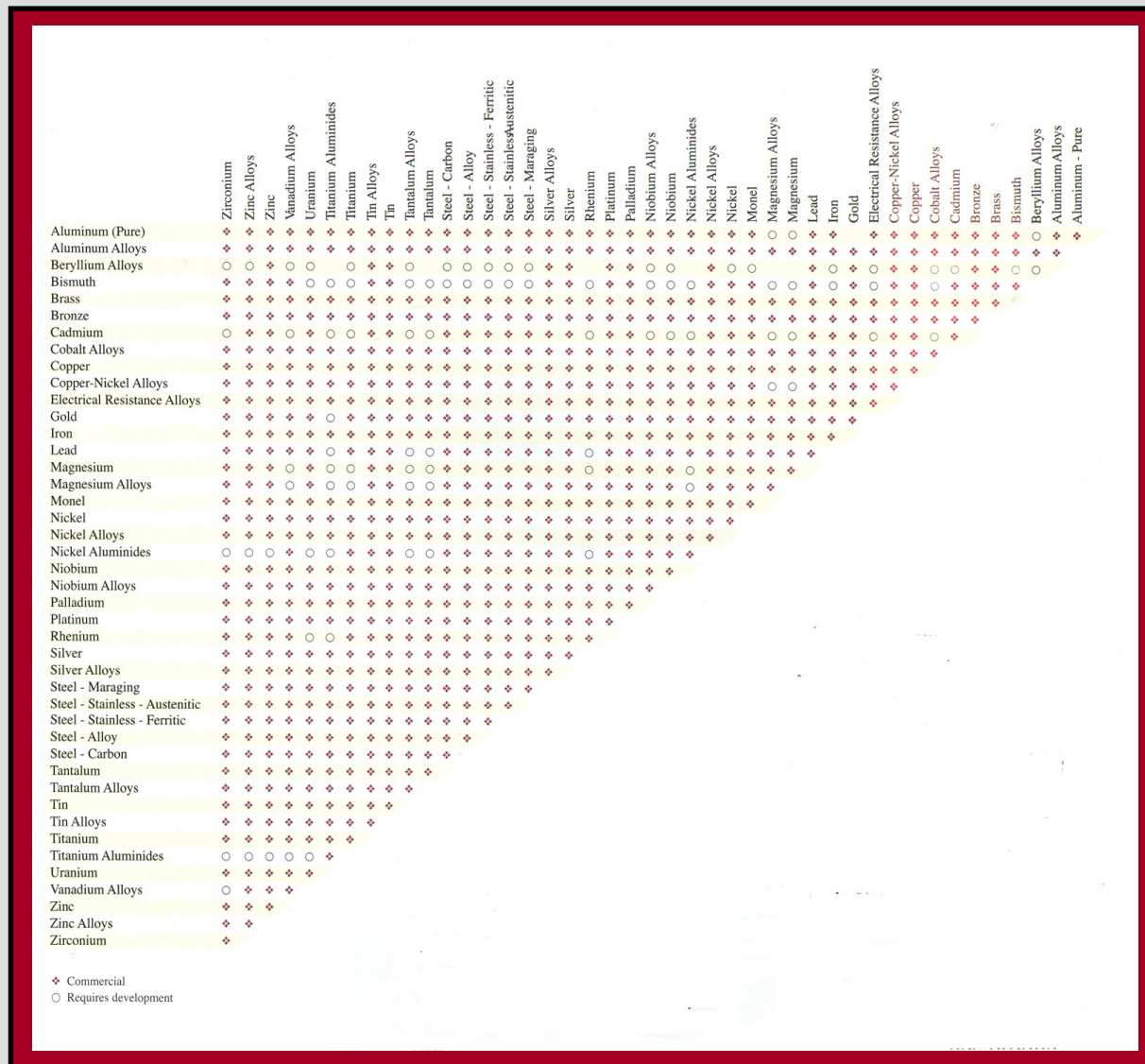


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Possible Material Combinations

A wide variety of metal combinations have been produced over the past 40+ yrs



Initial Results of Materials Selection

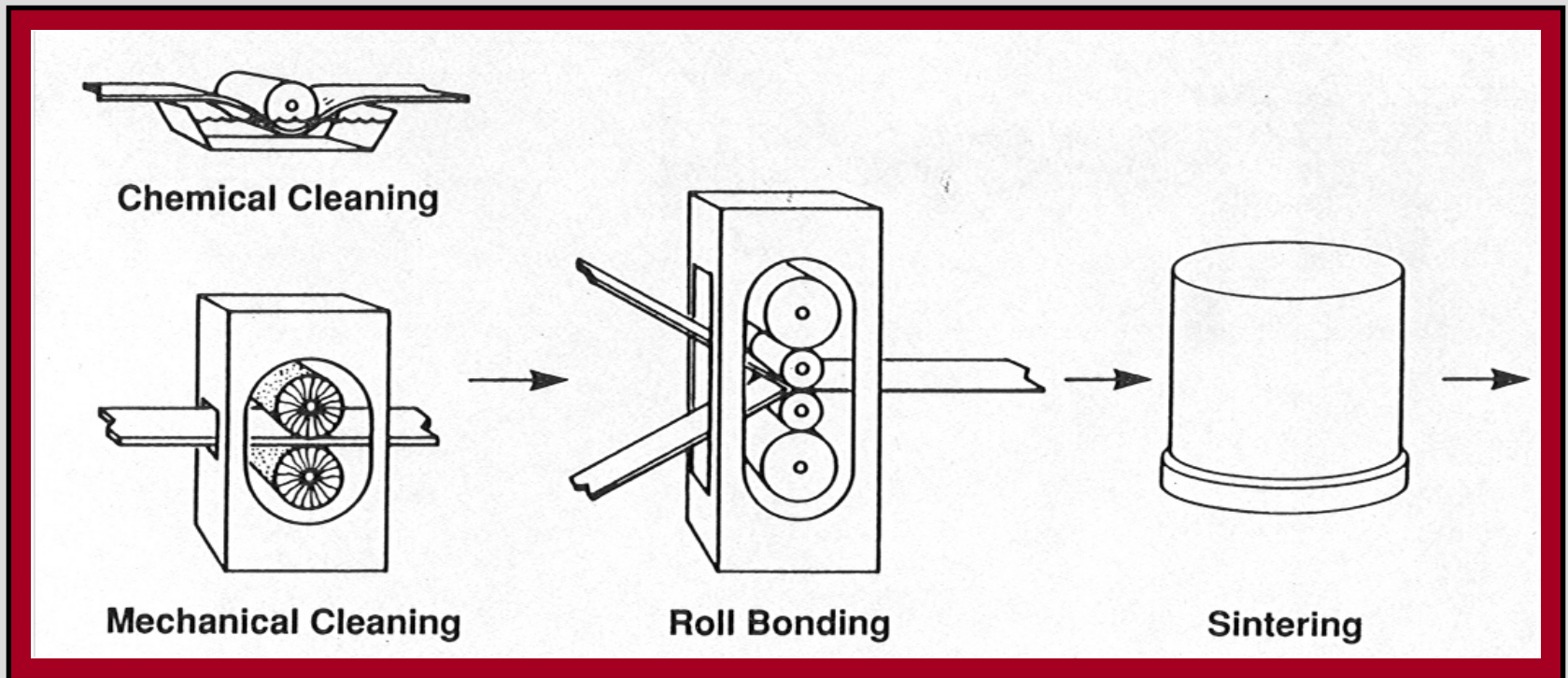
- The initial materials selection was based on the following parameters:
 - ▶ Raw material cost of the candidate core and cladding metals
 - ▶ Ease of thermally treating the cladding metal to form the passivation layer
 - ▶ Expected contact resistance and corrosion properties of the passivation layer
 - ▶ Commercial availability of the candidate core and cladding metals in the appropriate thicknesses
 - ▶ Relative forming properties of the candidate core and cladding metals
 - ▶ Desired final thickness/formability of the as-clad product (i.e. amount of reduction required and the degree of work hardening or residual stress in the final material)
- A partial list of viable clad material candidates that will be investigated in the feasibility study include:

<u>Core</u>	<u>MEA side cladding</u>	<u>Water channel side cladding</u>
430 stainless steel	CP titanium	Copper braze alloy
430 stainless steel	CP niobium	Copper braze alloy
453 stainless steel	Nickel 201	Copper braze alloy

- A full list is still in the process of being established. Once completed, it will be refined based on material vendor pricing information and cost analysis spreadsheet program, an in-house clad processing parameter database, and the initial results of the feasibility study.

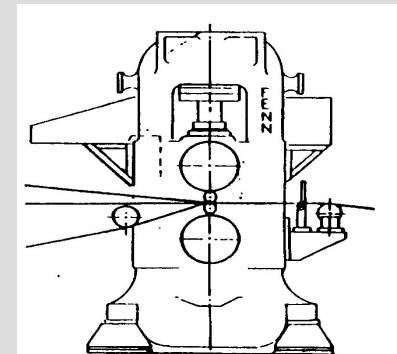
Cladding Processing Steps

Three basic steps:



- **A clean surface is critical for achieving a high quality metallurgical bond**
 - ▶ **Must be free of organic contaminants and metal oxides**
- **Two processes are employed**
 - ▶ **Chemical cleaning**
 - ◆ **Alkaline detergent to remove organic/oils**
 - ◆ **Acid pickle to remove surface oxide**
 - ▶ **Mechanical cleaning**
 - ◆ **Dry grinding using abrasive belts**
 - ◆ **Steel brush with hard bristles**
 - ◆ **Used on metals with tenacious oxide which otherwise can not be removed chemically**
 - ◆ **Creates a thin hardened surface layer for mechanical locking**
 - ◆ **Over-grinding or -brushing may result in surface oxidation**

- **Very high plastic deformation**
 - ▶ > 40% cold reduction in one pass (e.g. 0.200" → 0.070")
- **Generates high pressure (600+ ksi) and heat**
- **Virgin metal surfaces are created**
 - ▶ Due to very high reduction in thickness
- **Metal is bonded**
 - ▶ Within interatomic distances at the roll bite, forming a metallurgical bond
 - ▶ Mechanical locking/electron sharing between bonded components
- **The final material ends up heavily cold worked and in state of high residual stress – typically requires a post-roll sintering anneal**



4-High
Roll Bonding Mill



Sintering Anneal – A Post-Roll Heat Treatment

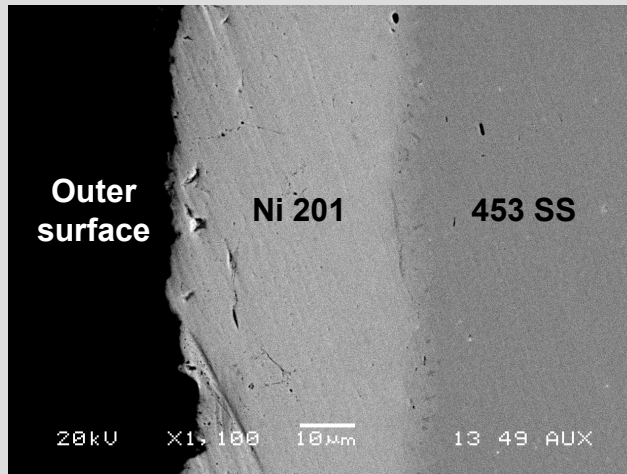
- **Recovery and recrystallization**
 - ▶ Provides stress relief of the worked material
 - ▶ Cold working causes the formation of elongated grains and recrystallization leads to a more uniform microstructure
 - ▶ The recrystallized metal becomes soft again, a metallurgical state that is often necessary for further forming operations (e.g. stamping)
- **Post-roll heat treatment often facilitates the bonding of the clad metals at an atomic level**
 - ▶ Atoms diffuse across the bond interface
 - ▶ A common or transitional lattice structure is attained at the bond interface
 - ▶ Can be employed to fully homogenize the material
 - ▶ Potential concerns include: the formation of undesired intermetallic compounds and/or Kirkendall voids
- **Annealing temperature and time depends on the composition and cold worked state of each component in the clad material system**
 - ▶ Recrystallization temperature of each component
 - ▶ Intermetallic compound and other brittle phase formation issues
 - ▶ Diffusion of the elemental species in each alloy layer
 - ▶ Note: self annealing can occur in some alloy systems during the bonding process



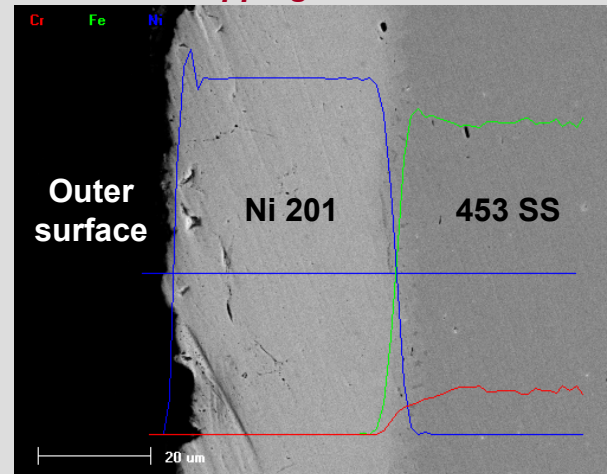
Roll Cladding Experiments

- Current focus is on the core and MEA side clad metal layers
- To date, two symmetric sandwich materials have been prepared
 - ▶ Ti/430 SS/Ti: target as-clad thickness of $<250\mu\text{m}$ (clad/core thickness ratio is currently proprietary)
 - ▶ Ni/453 SS/Ni: target as-clad thickness of $280\mu\text{m}$; $\sim 40\mu\text{m}$ of Ni 201 over $200\mu\text{m}$ 453 SS
 - ▶ Both clad materials are post-roll heat treated under modest sintering-anneal conditions, primarily for stress relief
 - ▶ Both the roll-cladding and sinter-annealing processing steps will be optimized in the second phase of the project (FY06)
 - ▶ Cross-sectional analysis of the Ti/430 SS material is currently in process. Typical as-clad microstructure of the Ni/453 SS material:

As-clad Ni 201/453 SS/Ni 201:



Elemental mapping of Ni 201/453 SS/Ni 201:



Effect of Partial vs. Full Sintering Anneal

- One of the key features that cladding affords is the potential to control the amount of diffusion that takes place between the core and clad metal layers. As shown in the example of a catalytic converter material below, the clad layer (Al in this case) can be left in the as-rolled condition, partially diffused into the underlying stainless steel, or fully homogenized to form a new FeCrAl alloy. This project will examine whether this phenomenon can be exploited in forming a PEMFC bipolar plate material.

As-clad condition



Al clad layer

Stainless steel core layer

Partial diffusion



Moderate, short-term sintering anneal

Homogenized Fe-Cr-Al alloy



Higher temperature/longer-term sintering anneal



Thermal Formation of the Passivation Layer

- Open questions regarding the formation of the passivation layer include:
 - ▶ How thick must the passivation layer be to provide both initial and long-term corrosion resistance?
 - ▶ What are the optimal heat treatment conditions (time and temperature) to grow this layer?
 - ▶ What is the effect of atmosphere (e.g. N_2 vs. NH_3 for nitridation) on the mechanism(s) and rate of layer growth?
 - ▶ Does the surface condition of metal cladding significantly affect the growth of the passivation layer?
- To answer these questions, the following experimental matrix (3x3x2x2) has been used as a guide in investigating the thermal nitridation of Ti/430 SS/Ti (a separate thermal treatment is being investigated for Ni/453 SS/Ni):

		Temperature		
		600°C	700°C	800°C
Time	2hrs	x	x	x
	4hrs	x	x	x
	8hrs	x	x	x

x – each condition employed separately in a series of UHP N_2 and CP NH_3 heat treatments. The effect of surface pickling of the Ti cladding is also being examined.



Subsequent Characterization/Analysis

- The thirty-six samples are currently in process for microstructural analysis by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and X-ray diffraction (XRD) to determine:
 - ▶ The compositions and thicknesses of the nitride layer and the underlying titanium substrate
 - ▶ The morphologies of the core and clad metal layers and the thermally grown nitride
- Based on this analysis, the most promising thermal treatment conditions will be used to prepare specimens for contact resistance and corrosion testing
 - ▶ Resistance testing will be conducted using the methodology established by NREL researchers (H. Wang et al., *J. Power Sources*, 115 [2003] 243)
 - ▶ Corrosion testing will be conducted under simulated PEMFC operating conditions in a series of potentiostatic polarization experiments
 - ▶ The specimens will be re-examined via SEM and EDX analysis to determine the resulting effect of the corrosive environment on the thermally nitrated clad material



- **Have conducted an initial analysis of compatible alloys for use in a clad PEMFC bipolar plate concept. A partial list includes:**
 - ▶ 430 or 453 ferritic stainless steel as the core metal
 - ▶ A copper-based braze alloy as the water channel side cladding metal
 - ▶ Either CP Ti, CP Nb, or 201 Ni as the MEA side cladding metal
- **Symmetric sandwich samples of the Ti/430 SS and Ni/453 SS clad materials have been prepared**
 - ▶ The as-clad sheets of each material combination are <math><300\mu\text{m}</math> thick
 - ▶ The materials are currently being employed in a stress relieved, annealed condition
 - ▶ Optimization of the roll-cladding and sinter annealing processes will be the focus of a later study
- **Investigating the thermal nitridation conditions of the Ti/430 SS clad material**
 - ▶ Examining the effects of heat treatment atmosphere, temperature, and time at temperature on the formation of the nitride layer
 - ▶ Investigating titanium surface preparation conditions on nitride growth
 - ▶ Currently conducting microstructural analysis of the nitrified as-clad material

- **Remainder of FY 2005:**
 - ▶ **Choose several promising nitriding conditions for the Ti/430 SS/Ti material, prepare heat treated samples for electrochemical characterization, and conduct the characterization tests**
 - ▶ **Prepare Nb/430 SS/Nb clad specimens and carry out nitridation experiments and subsequent electrochemical characterization in the same manner as for the Ti-clad materials**
 - ▶ **Conduct passivation experiments on the Ni/453 SS/Ni clad materials using a proprietary thermal treatment and carry out follow-up electrochemical characterization studies**
 - ▶ **Complete the feasibility study based on a refined cost analysis of the candidate clad materials**

- **FY 2006:**
 - ▶ **Optimize the design and processing parameters of the most viable clad material established in FY 2005 in conjunction with the DOE cost targets (i.e. paying attention to raw material and processing costs):**
 - ◆ **A key focus will be to demonstrate that the clad material can be stamped without dramatically thinning or forming defects in the cladding layer**
 - ◆ **A second key element to be demonstrated is the protection/passivation of through-holes (i.e. gas manifold holes) in the clad material – optimization of the sintering anneal step is likely to be the focal point of this work**
 - ▶ **Optimize the formation of the passivation layer**
 - ▶ **Initiate long-term electrochemical characterization of the optimized material**
 - ▶ **Conduct initial electrochemical testing of a demonstration stamped clad component**

- The most significant hydrogen hazard associated with this project is:
 - ▶ *At present, we do not use hydrogen in our work. However, in the next two months we will carry out electrochemical testing of the bipolar plate materials that we are investigating and will need to bubble H_2 through an H_2SO_4 electrolyte to simulate a PEMFC operating environment for the component test. The most significant hazard associated with this work will likely be changing the high pressure hydrogen gas bottles used to provide the low flow of hydrogen in the experiments.*



- **Our approach to deal with this hazard is:**
 - ▶ ***The flow rate of H_2 in the above experiments will be quite low and the amount of H_2 employed will be small. The electrochemical testing studies will be conducted in a well-ventilated hood to mitigate the potential build-up of hydrogen and to avoid exposure of the test researcher to the acid electrolyte environment.***
 - ▶ ***In our laboratory, hydrogen gas bottles are kept in a safety cabinet (designed specifically for flammable/explosive gases) during the entire use. The hydrogen line is hard plumbed from the gas cabinet to the point of use.***
 - ▶ ***Only trained personnel are allowed to change out hydrogen gas bottles. They employ non-sparking tools and use appropriate electrical grounding during the operation.***
 - ▶ ***All of the experimental researchers working on this program have taken and passed a hydrogen safety class.***
 - ▶ ***Prior to conducting the above electrochemical experiments, we will review our test procedure with our safety staff at PNNL to determine if additional measures are required before testing begins.***

