SURFACE MODIFIED METALLIC BIPOLAR PLATES

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Objective

Develop a bipolar plate alloy which will form an electrically conductive and corrosion resistant TiN surface layer during thermal nitriding

Newer Effort

Timeline and History of Project

- 1999-2000: Small, Proof of Principle Effort

- September, 2000: Project Approved
  Funded at $^{4}/_{5}$ person-year for FY 2001

- Sept. 30, 2001 Milestone: Demonstration of Single-Cell Performance Equivalent to Graphite with Alloy That Can Meet DOE Cost Goals

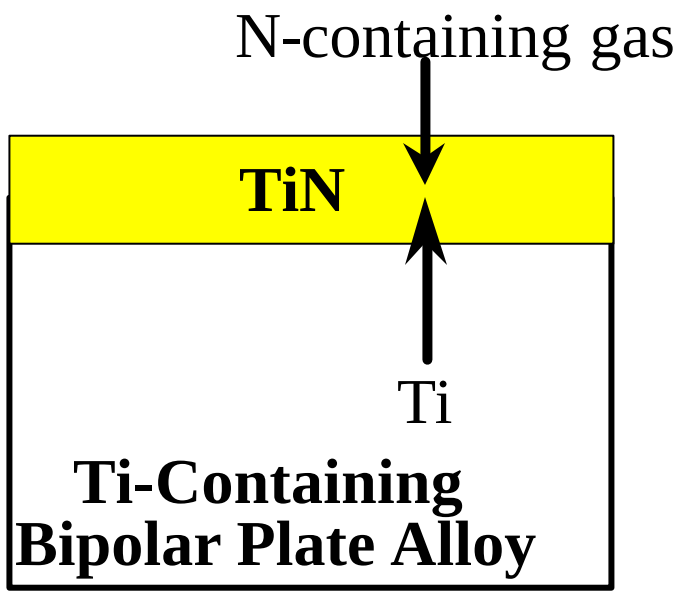
Key Targets for Nitrided Metal Bipolar Plates

- Corrosion < 1.6 X 10^{-6} A/cm^2 (pH3 Sulfuric, 80°C)

- Cost < $1-2 for a 0.1- 0.25 mm (≈ 5-10 mil) thick, 500 cm^2 (80 square inch) plate (input garnered at 2000 DOE review)

- Amenable to high-volume, low cost manufacturing (e.g. rolling, stamping, etc.)

Approach: Thermally Grown TiN for Protection



- Surface Modification- Not a Deposited Coating (Edges and Corners Can be Better Handled)
- Thermodynamic/Kinetic Factors Strongly Favor Complete Conversion of Surface Metal to Nitride-No Pin Hole Gaps (Issues Relate to Nitride Continuity/Adherence/Cracking)
- Stamp to Final Form/Nitride (Industrially Established, Cheap)

What's Unique About Our Effort?

- **Alloy Design** to Form Dense, Corrosion-Resistant TiN Surface Layers During Gas Nitridation
  - -Existing alloys typically do not form corrosion resistant nitride layers (designed to form protective oxides)

- High Density Infra-Red Processing (Exploratory)
  (Craig Blue and Vinod Sikka)
  - -Surface conversion to nitride in seconds

Alloy Composition Influences Corrosion Resistance of Resultant Nitrided Surface

All Ti-Nitride Layers Are Not the Same!

Nitrided Ti Alloys after 20 h immersion in 5% HF

Ti Ti-10Zr Ti-10V-5Zr

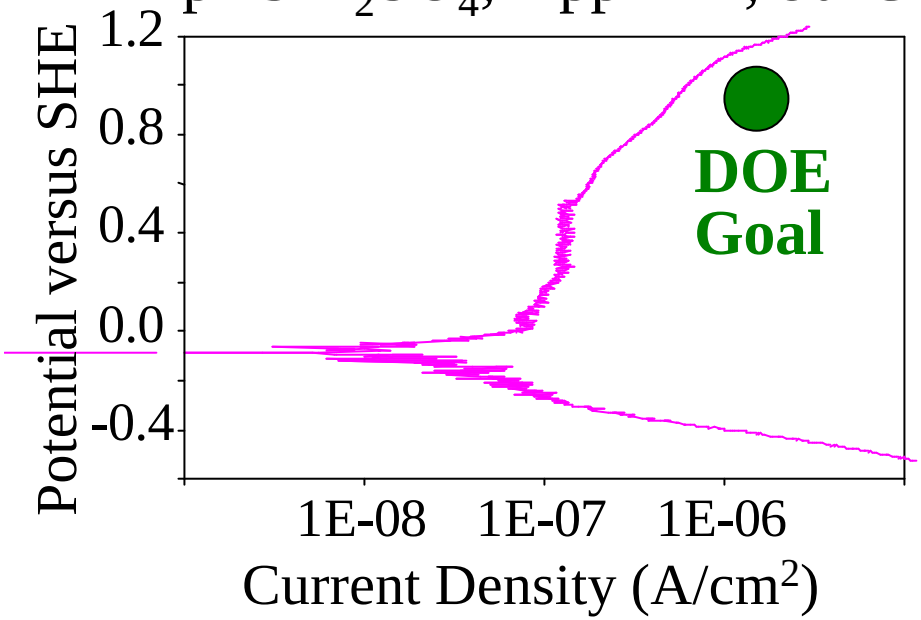
- Proper alloy design yields corrosion resistant nitride surface
- Nitrided pure Ti inadequate performance for PEM service

Thermally Grown TiN-Base Layer Can Behave Well in PEM Environment

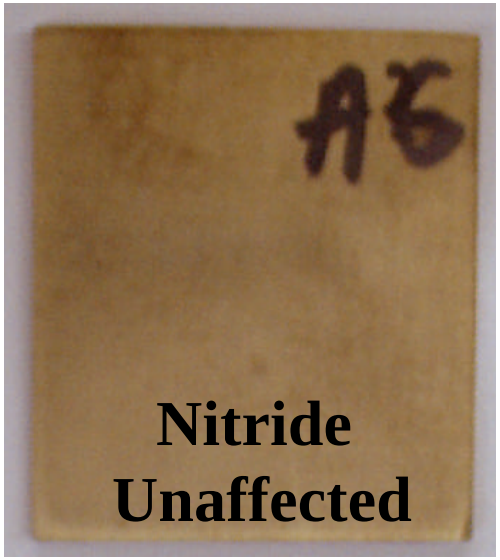
Model Alloy: Nitrided Tribocor (Nb-30Ti-20W)

(Data of K. Weisbrod/C. Zawodzinski)

Corrosion Test Cell
pH3 H_2SO_4, 2 ppm F-, 80°C



300 h pH2/pH6
H_2SO_4 (Air/H_2)

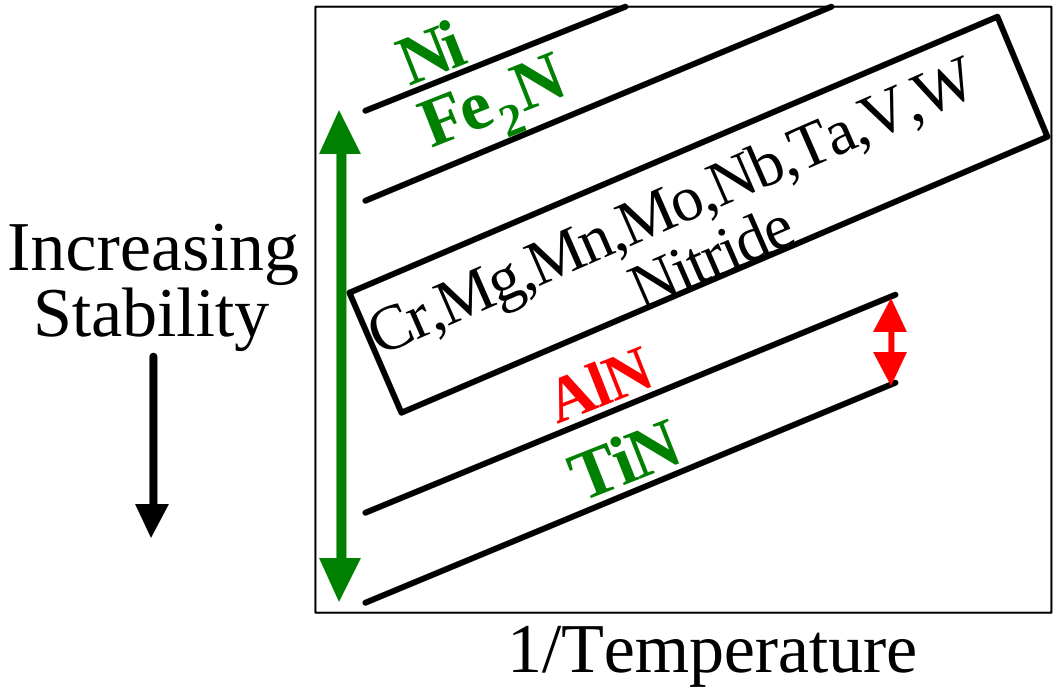


- Stable behavior for 700 h in Corrosion Test Cell
- <1% Active site blockage in Nafion membrane after 300 h Immersion screening in H_2SO_4

Can a Sufficiently Inexpensive Alloy be Developed Which Forms a Corrosion Resistant Nitride Surface?

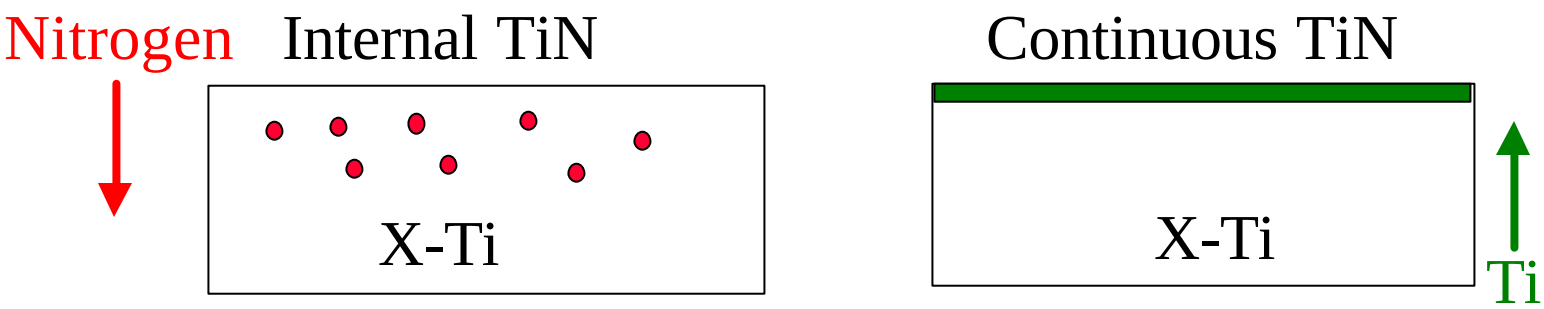
Effort Focused on Inexpensive Ni-Ti And Fe-Ti Base Alloys

Schematic Ellingham Stability Chart for Nitridation



- Large stability difference makes easier to establish protective surface layer: **Ni-Ti, Fe-Ti ideal**, **Al-Ti not**
- Estimate $6-10/lb for Ni-Base and <$5 for Fe-Base (Can meet DOE cost goal)

Alloy Design Based on Flux Criteria (Classical Wagner Oxidation Theory)

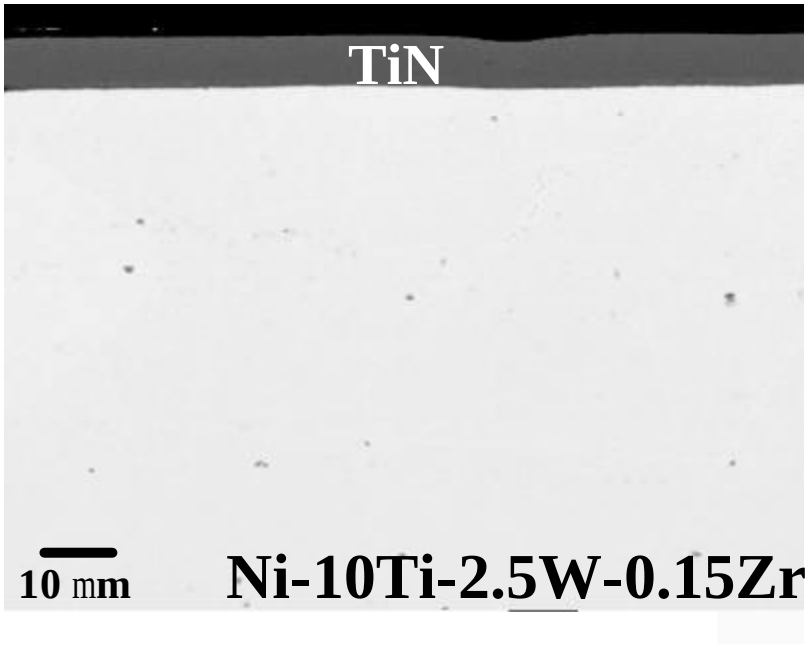


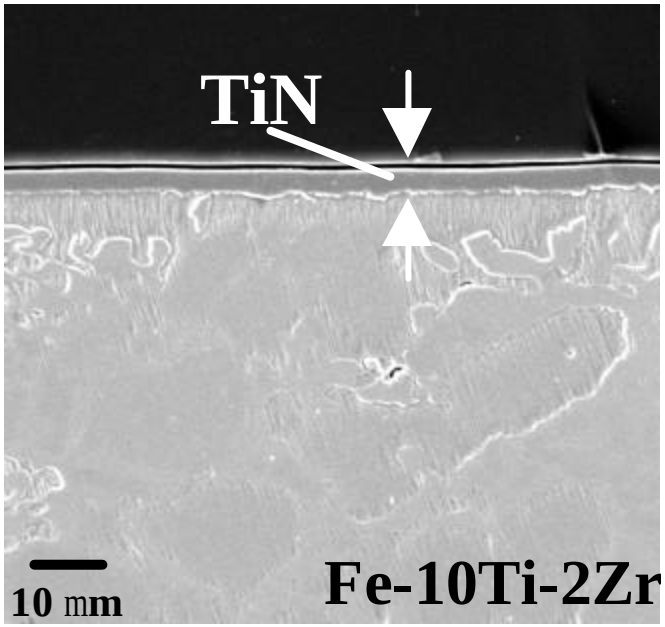
Minimum Ti for Continuous TiN $\mu \left[N_{solubility} * \frac{N_{diffusivity}}{Ti_{diffusivity}} \right]^{1/2}$

- Continuous TiN favored by alloy additions/reaction conditions that <u>decrease</u> nitrogen permeability or <u>increase</u> Ti diffusivity

TiN Surface Layer Demonstrated For Ni-10Ti and Fe-10Ti wt.% Base Alloys

SEM X-Section: 1100°C, 1-3 days, Nitrogen



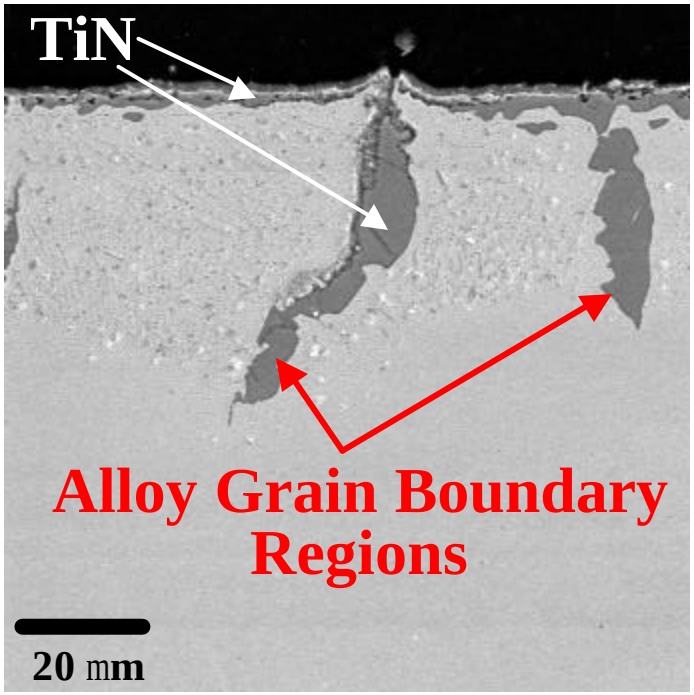


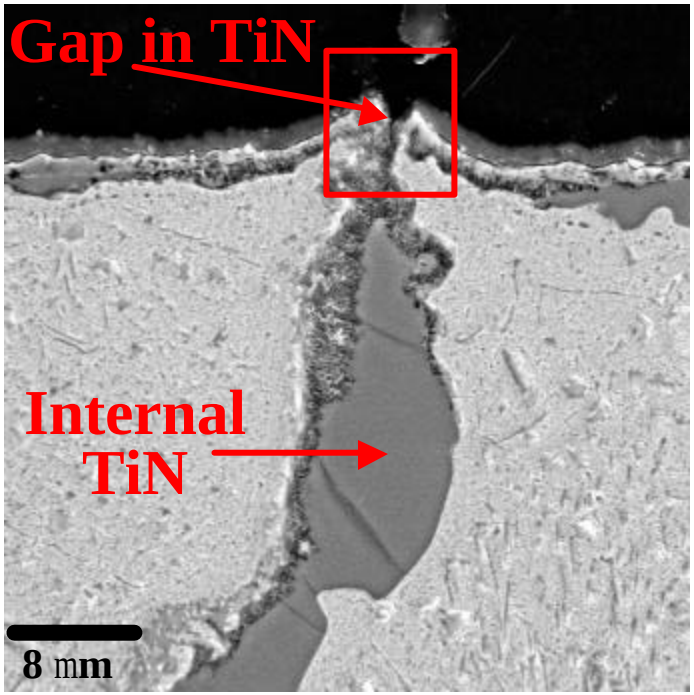
- Electrical conductivity of 1.5 X 10^4 $\Omega^{-1}cm^{-1}$ (Exceeds Goal)
- Unacceptably high corrosion rates in pH2-pH6 H_2SO_4-Nafion membrane contamination detected

Corrosion Susceptibility Traced to Alloy Grain Boundary Regions

Cross-Section SEM View of Nitrided Fe-35Ni-8Ti

(Worst Case Example Shown to Highlight Issue)

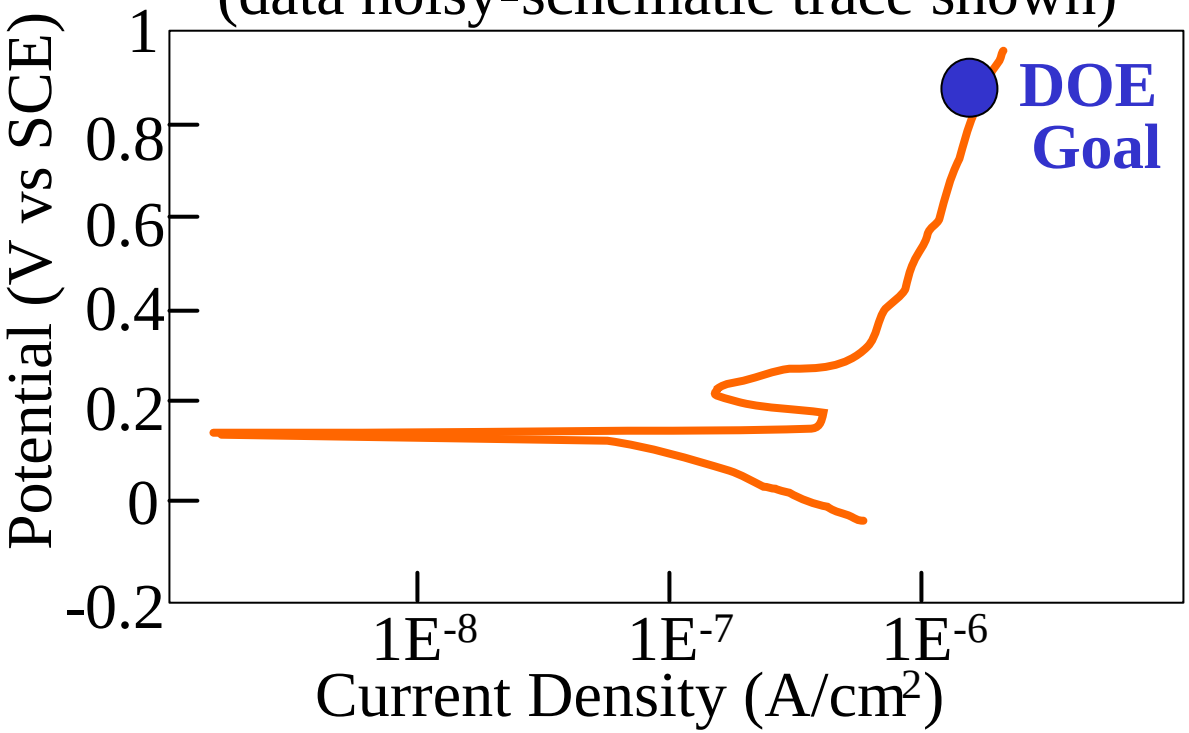




- Local internal nitridation at alloy grain boundaries
- Exacerbated by alloy grain growth during nitridation

Preliminary Data Suggests Prior Heat Treatment to Limit Alloy Grain Growth Improves Nitride Protectiveness

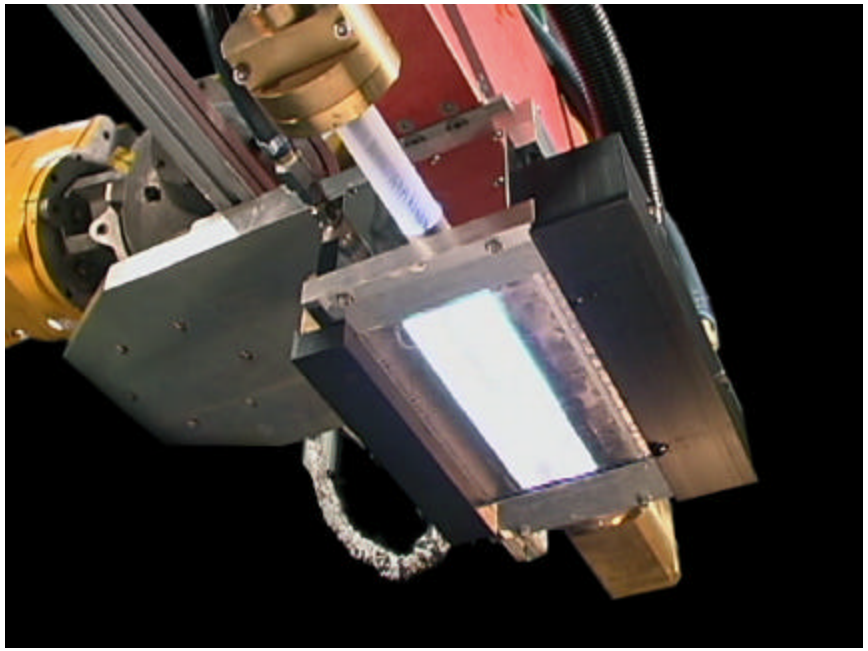
Heat Treated and Nitrided Ni-10Ti-0.15Zr
H_2SO_4 / pH3 / Room-Temperature
(data noisy-schematic trace shown)



- Alloying to eliminate preferential nitridation at alloy grain boundaries underway (small additions of V promising)

High Density Infra-Red Processing Converts Surface To Nitride in SECONDS

(C. Blue and V. Sikka, ORNL)



•High-Power Density Plasma Arc Lamp Yields a Heating Rate of 50-400^{+}°C/sec (**Rapid and Inexpensive**)

•Preliminary Efforts Suggest Very Amenable to Gas Nitriding (Model Ti and Fe-(5-10)Ti Base Alloys Successfully Nitrided)

Collaborations Significant Part of Effort

- Special Metals Corporation and Allegheny Ludlum

  (M. Harper/J. Rakowski)

  -Alloy Design/Scale Up Issues

  -Rapid Transfer to Commercial Alloy Producers If Successful

- Los Alamos National Laboratory

  -Corrosion testing in simulated fuel cell environments

  (C. Zawodzinski, K. Weisbrod)

- Honeywell

  -Input on Bipolar Plate Issues, Corrosion Screenings

  (T. Rehg, *H. Dai)

- Plug Power

  -Delivered Coupons for Corrosion Screenings

* No longer with Honeywell (Allied Signal)

Response to Reviewer Comments

•*Bipolar plate issue resolved by graphite/carbon fiber composites:* Excellent progress made with these approaches but scale-up/performance issues remain.

•*Too much focus on refractory and Ti alloys*: Studied for model reasons for proof of principle/science basis for development; effort now fully focused on inexpensive Ni- and Fe- base alloys.

•*More evaluation needed in fuel cell environments*: Excellent point, teamed with Los Alamos this past year to do this, will continue to emphasize and pursue with industry as well.

Plans

•**Remainder FY 2001**: Complete alloy optimization to eliminate grain boundary nitridation issue-Must demonstrate acceptable corrosion resistance! (Close/On the Right Track)

Go/No Go Decision Point

•**FY 2002**:

- Formalize Teaming with Los Alamos to Pursue In-Cell Testing
- Explore Scale-Up Issues with Alloy Producers and ORNL Metals Processing Group (down-select to final alloy compositions)
- Deliver Plates to Fuel Cell Manufacturers for Evaluation