Cost-Effective Surface Modification For Metallic Bipolar Plates

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Objective: Develop a Surface Treatment to Protect Metallic Bipolar Plates

Thermal (Gas) Nitridation of Cr-Bearing Alloys to Form a Pin-Hole Free Cr-Nitride Surface

For 2004:

- Nitrided Ni-50Cr plates to collaborators for fuel cell testing
  - More aggressive testing than initial 0.7V/1000 h test
  - Optimize Cr-nitride surface and establish limits

- Form protective nitrides on cheaper alloys
  - Commercial Ni-Cr base alloys
  - Fe-base stainless steels

- Scale up efforts/broaden and deepen industrial collaborations

Budget

99	2000	2001	2002	2003	2004
↓	↓	↓	↓	↓	↓
50 k	100 k	200 k	200 k	200 k	300 k

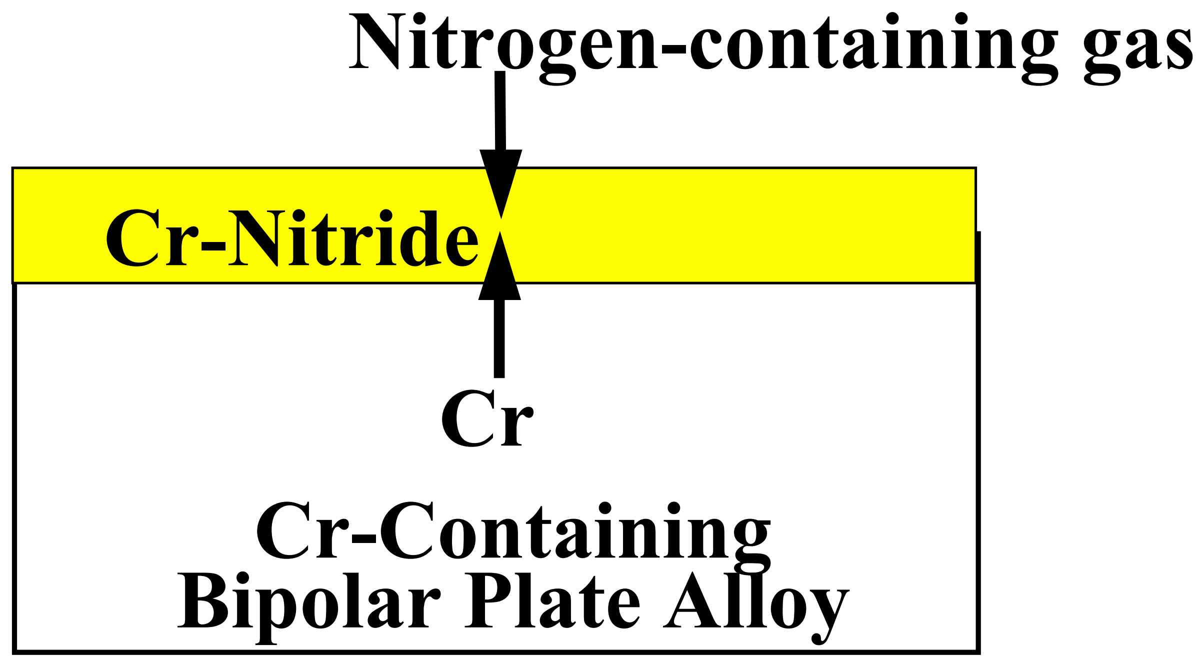
- Started as small proof of principle exploration (FY 99/2000)
- Budget increase in FY 04 for initiation of scale up and manufacture of plates for fuel cell testing with collaborators

Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components
  - O. Stack Material and Manufacturing Cost
  - P. Durability

- DOE 2010 Technical Targets for Fuel Cell Stacks
  - Cost $35/kW
  - Durability 5000 hours

Approach: Thermally Grown Nitride for Corrosion Protection



- Surface conversion not deposited coating: High temperature favors reaction of all exposed metal surfaces
  - No pin-hole defects (other issues to overcome)
  - Amenable to complex geometries (flow field grooves)
- Stamp to final form then nitride: Industrially established and cheap

Safety

- High-temperature furnaces, vacuum systems, gas mixtures containing up to 4%H_2 at $\leq$ 1 atm, small volumes of acids and simple solvents, low-voltage instrumentation
- Project activities are covered by a formal, integrated work control process for each practice/facility
  - Definition of task
  - Identification of hazards
  - Design of work controls
  - Conduct of work
  - Feedback
- Each work process is authorized on the basis of a Research Safety Summary (RSS) reviewed by ESH subject matter experts and approved by PI's and cognizant managers
- RSS is reviewed/revised yearly, or sooner if a change in the work is needed
- Staff with approved training and experience are authorized through the RSS

Timeline

1999 - 2000	2001 - 2003	2004 - 2006
Phase 1	Phase 2	Phase 3
1 2	3 4	5 6 7

Phase 1- Proof of Principle

1: Nitrided model Nb-Ti base alloy resists corrosion

2: TiN formed on developmental Ni-Ti and Fe-Ti base alloys

Phase 2- Development, Testing, and Evaluation

3: Lack of robustness in nitrided Ni/Fe-Ti (**No go**)

New family of Cr-nitride/Ni-Cr alloys identified

4: Successful fuel cell test with model nitrided Ni-50Cr (**Go**)

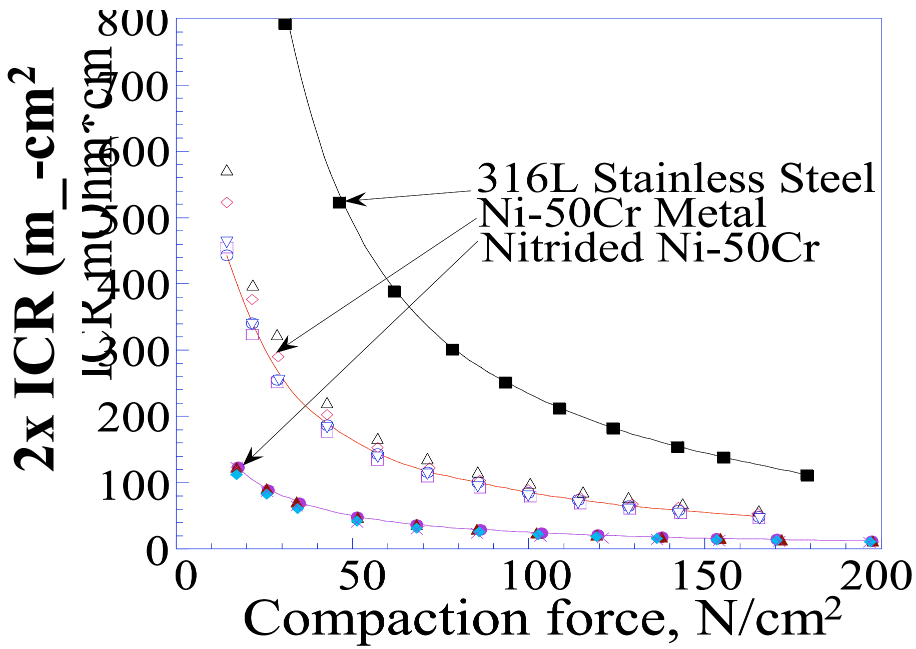
Phase 3 – Optimization, Scale-Up, and Tech Transfer

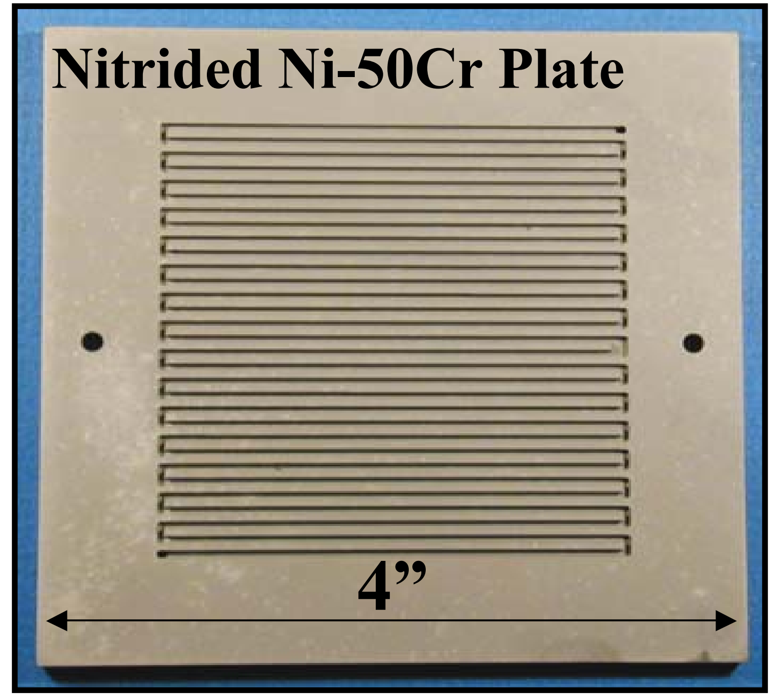
5: Establish capability of Cr-nitrides to meet durability goals

6: Form protective Cr-nitrides on alloys that can meet cost goals

7: Complete scale up and transition to industry

Where Did We Leave Off Last Year?



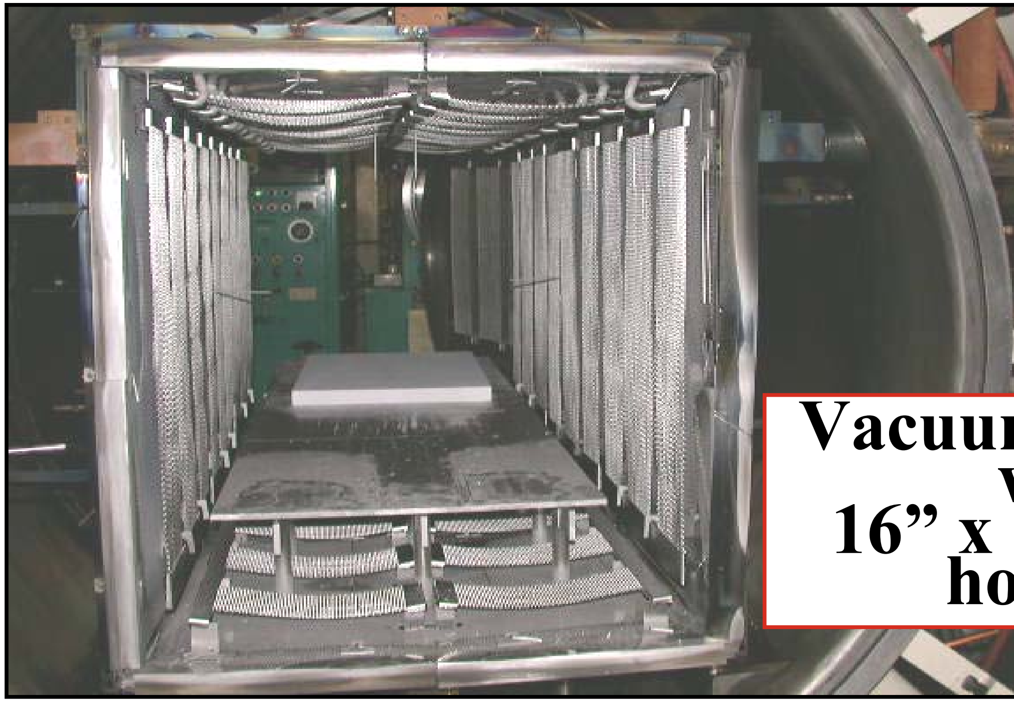


- 4000 h corrosion test* under anodic and cathodic conditions showed no increase in contact resistance/little dissolution (~ 3 ppm Ni)

- Successful 1000 h of fuel cell testing at Los Alamos with nitrided model Ni-50Cr plates (M. Wilson and F. Garzon)
  - Negligible membrane contamination (as "clean" as graphite plates)
  - No increase in cell resistance

* Los Alamos Corrosion Test Cell, K. Weisbrod

This Year: Scale-Up of Nitriding and Delivery of Model Nitrided Ni-50Cr Plates



- Nitrided Ni-50Cr plates for fuel cell testing to establish durability limits and optimize Cr-nitride surface

  General Motors, Los Alamos, DANA Corp, FuelCell Energy

- Complications with gas impurities, heating/cooling rates
  - Knowledge gained will make transition to industry easier
  - Capability now established to nitride large/many plates

Move to Cheaper, Commercially Viable Alloys and Processes

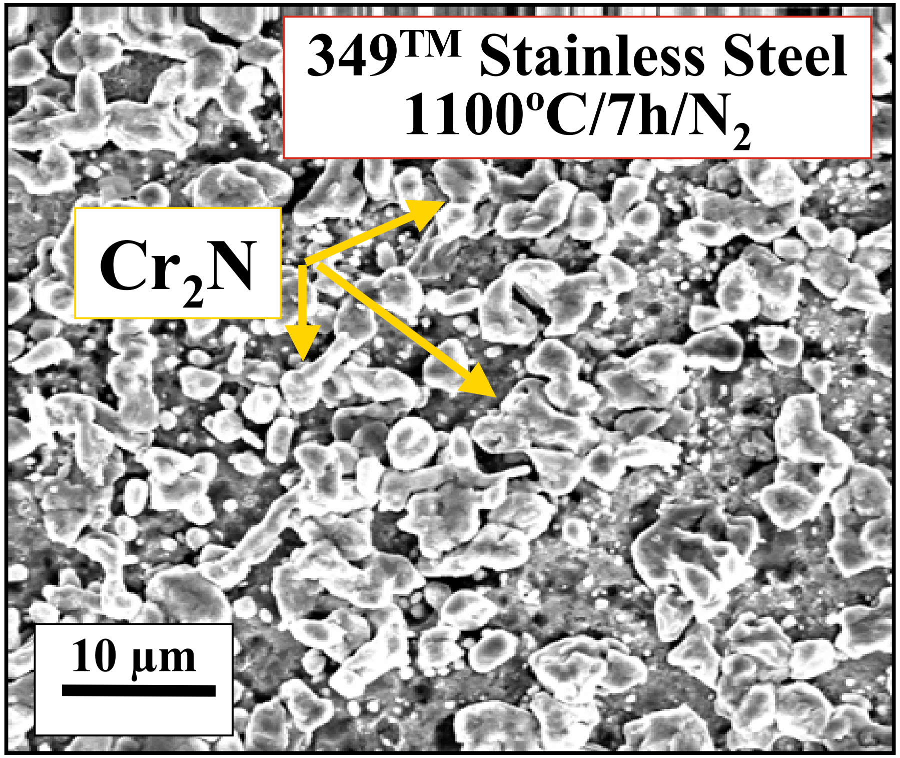
- **Ni-(30-35) Cr wt.% Base**
  - HASTELLOY® G-30®, HASTELLOY® G-35™, ALLCORR®
  - Cost High: intermediate step toward DOE goals (cost may be viable for portable/stationary/specialty apps)
  - Optimization of Cr-nitride surface in progress

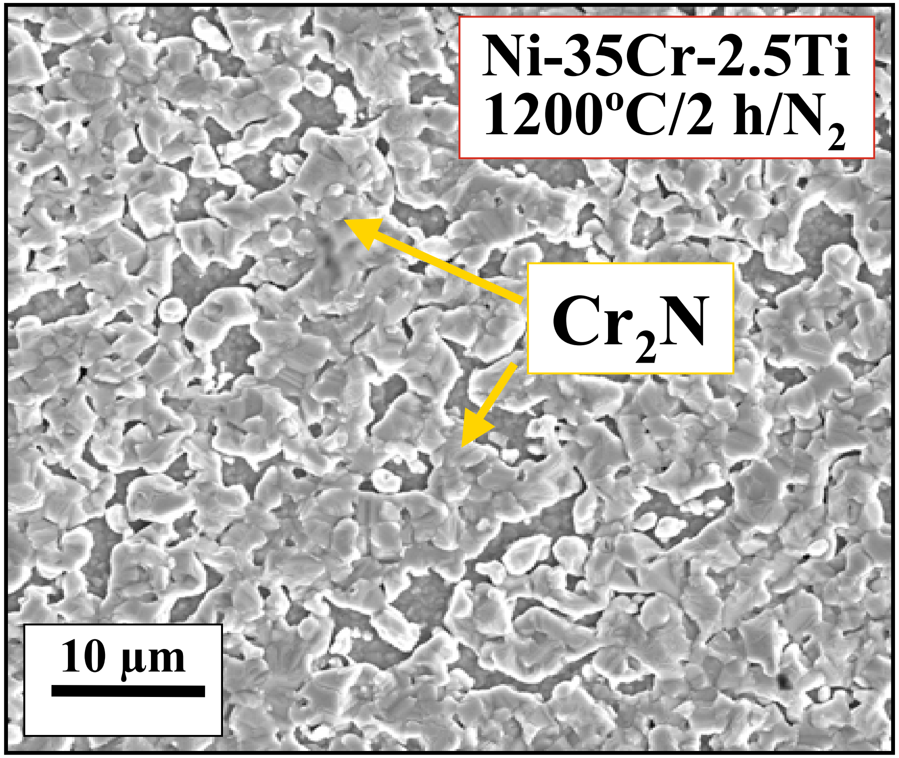
- **Fe-Cr and Fe(Ni)-Cr Base**
  - Potential to meet DOE transportation cost goals
  - More difficult to get continuous Cr-nitride surface
  - New finding: N_2-modified passive layer (w/NREL)

Collaboration initiated with GenCell Corp for stamping, and nitriding of commercial alloys (0.1-0.2 mm thick)

Key Issue is Getting Dense, Continuous Cr-Nitride to Form at Surface

Typical Surfaces (SEM) of Nitrided Fe-Cr and Ni-Cr Base Alloys (Cr < 35 wt.%)

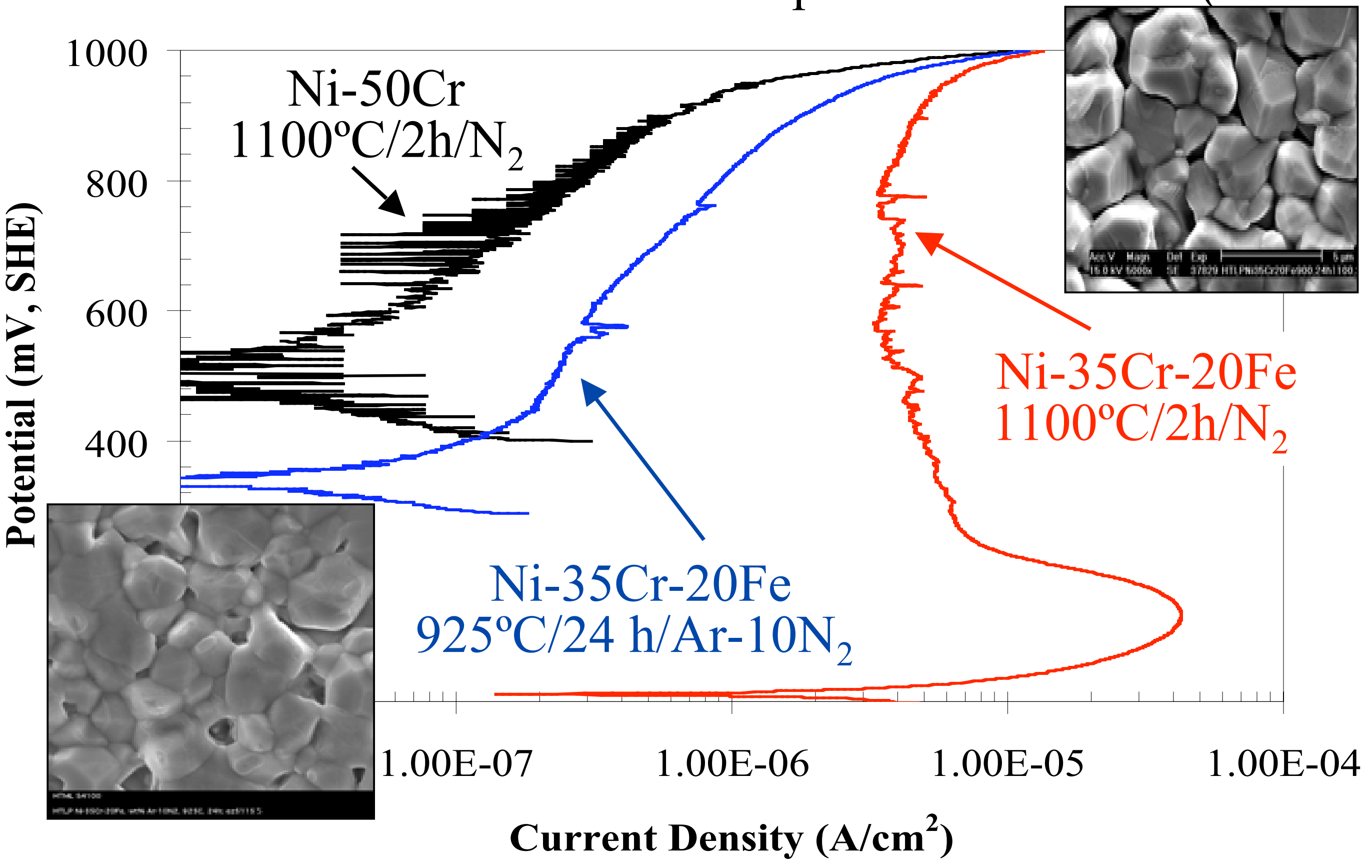




- External Cr-nitride formation readily achievable/control of morphology and continuity is the key
- Gaps expose internally nitrided metal/mixed nitrides

Modification of Nitridation Conditions Yields Dense Cr-Nitride Surface

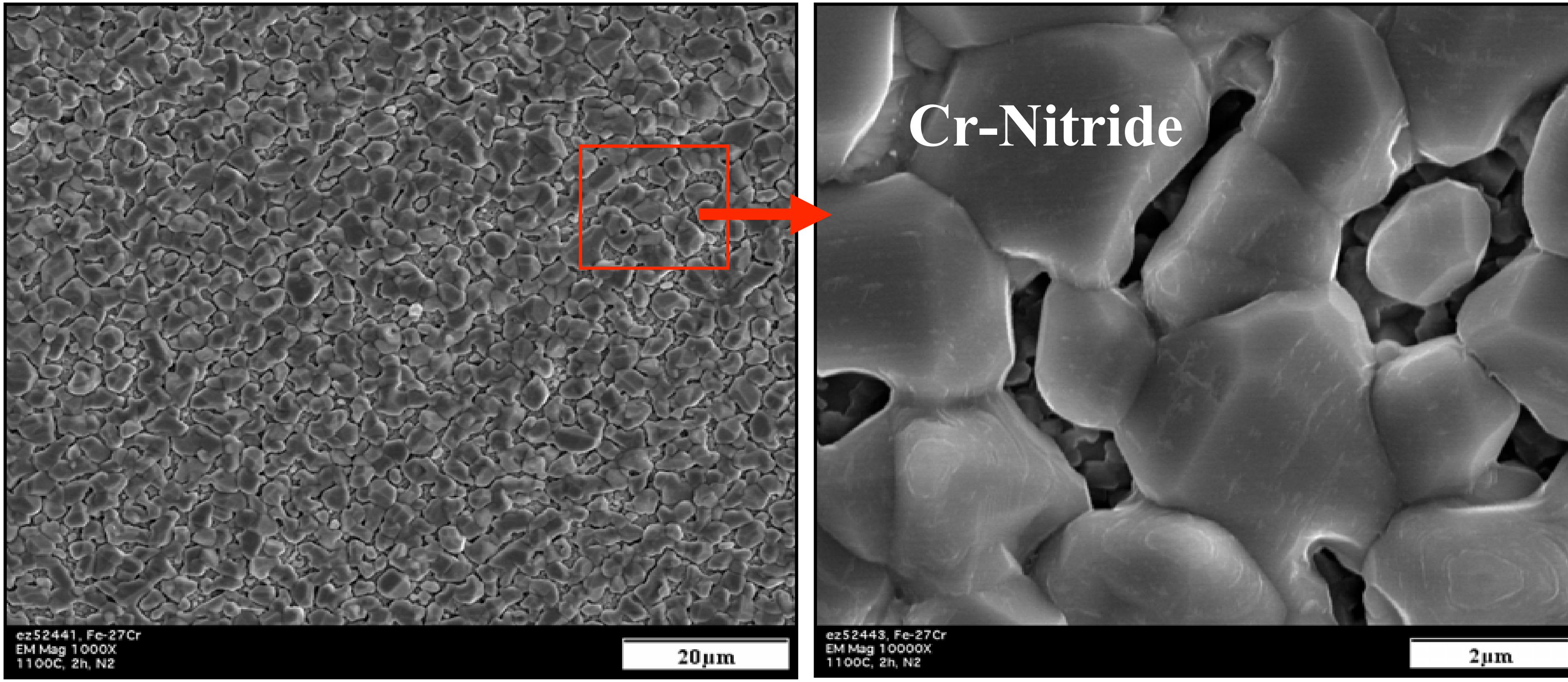
Anodic Polarization in Aerated 80°C pH3 Sulfuric Acid (0.1 mV/s)



- Control of temperature and nitrogen activity can result in dense, continuous Cr-nitride surface
- Ni(Fe) base in many commercial alloys (Fe lowers cost)

Initial Efforts on Binary Fe-27Cr Close to Achieving Dense Cr-Nitride Surface

SEM Surface of 1100°C, 2 h Nitrided Fe-27Cr wt.%



Some gaps: need to modify growth characteristics

– want more inward growing product

– surface energy/nucleation effects

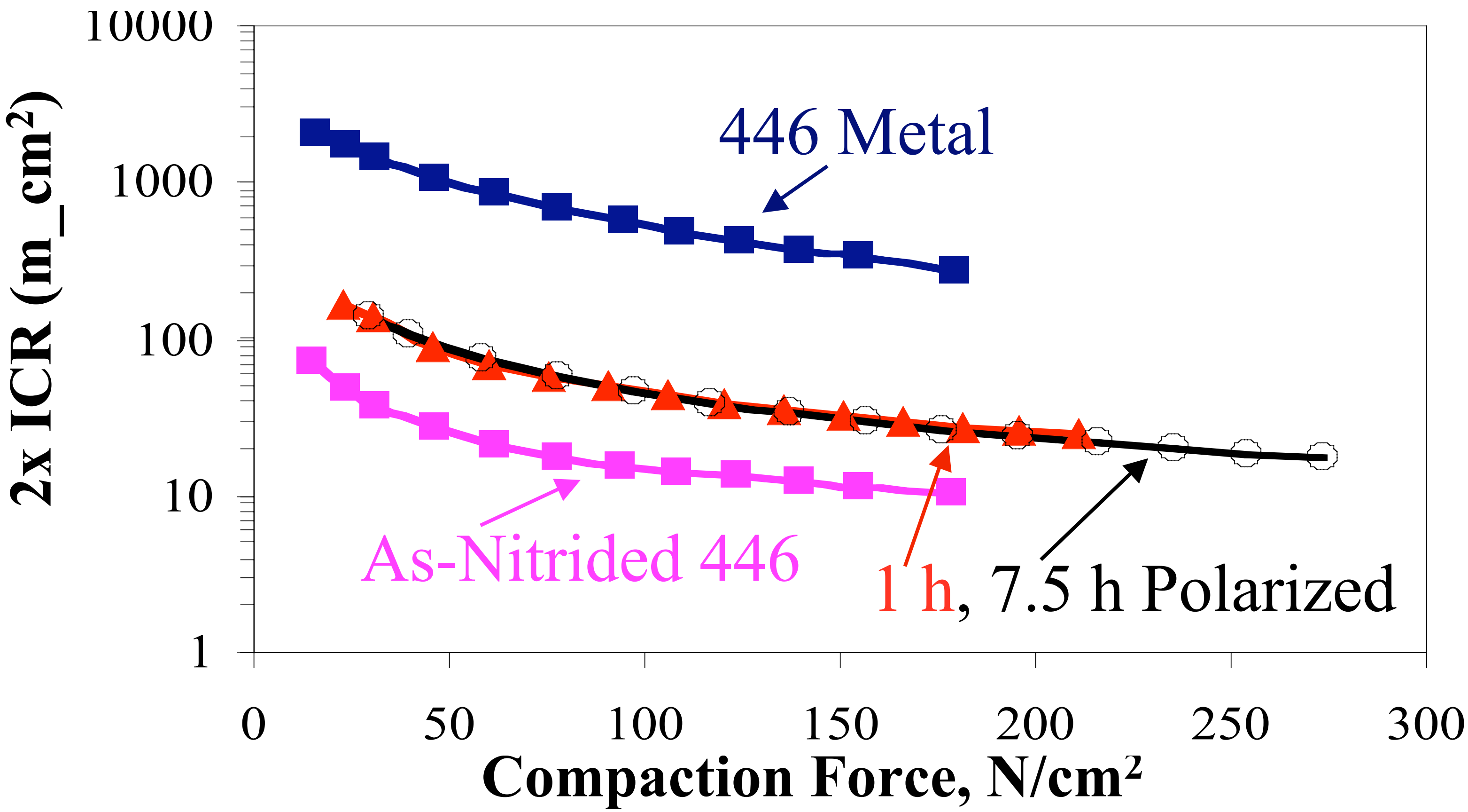
New N_2-Modifed Surface Effect (Joint ORNL/NREL Finding)

- ORNL focus has been on formation of a dense, continuous Cr-nitride surface for protection

- New finding with NREL shows promising behavior by a nitrogen-modified passive layer/not a dense, thick Cr-nitride

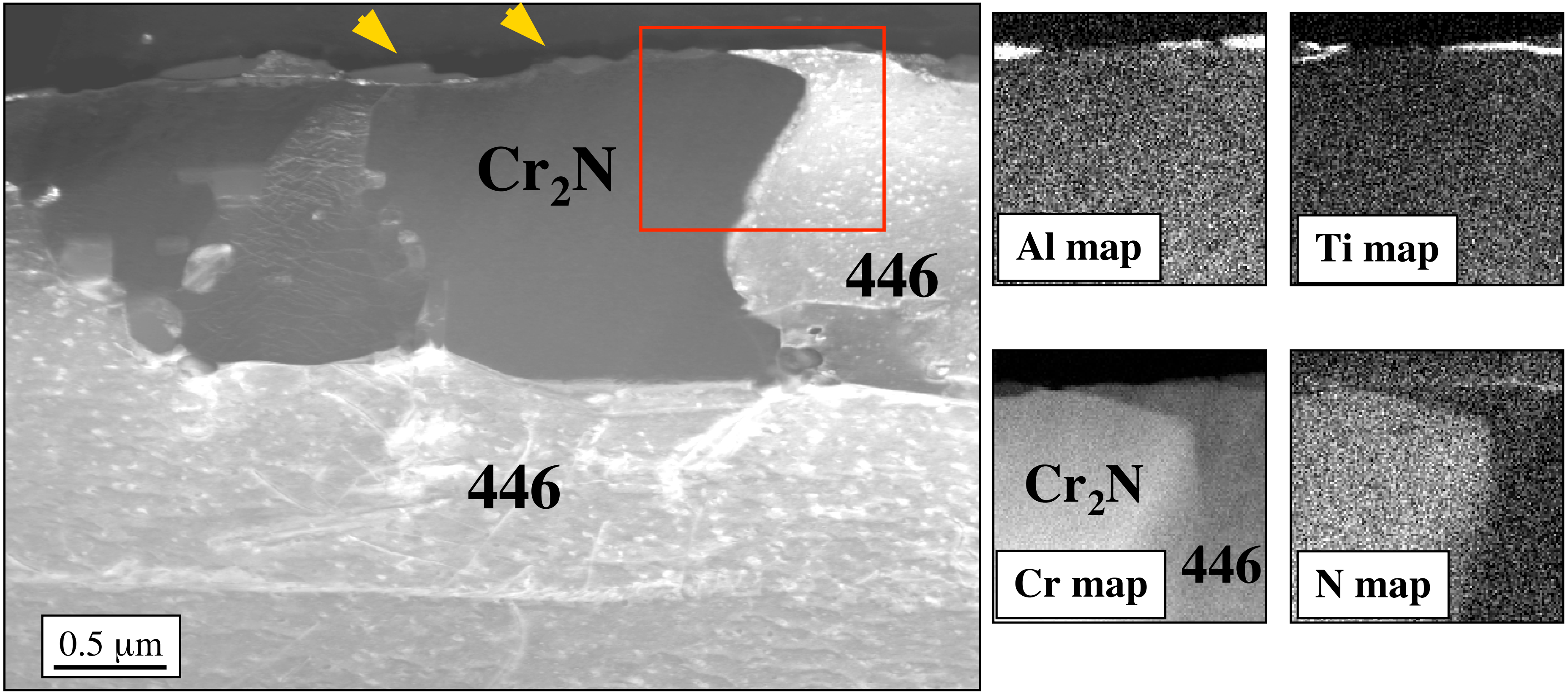
- Nitridation of a commercial ferritic alloy, 446-MOD 1 (Fe-27Cr-(4-8)(Mo+Ni)-0.5Ti base) - *Relatively Cheap*
  - Order of magnitude decrease in contact resistance
  - Moderate improvement over already good corrosion resistance of these alloys (studied by NREL)
  - Preliminary studies suggest effect possible in a number of existing stainless steel alloys (AL 29-4C®)

Nitridation Treatment Significantly Decreased Contact Resistance of 446 Steel



- Polarized (0.85 V vs SHE, pH 0 Sulfuric/2 ppm F^-/70°C/Air) - *slight increase in contact resistance, still meets 20 m_-cm^2 goal*
- 7.5 h hold at +0.1 V vs SHE (H_2 purge) - *~20x less metal ion dissolution compared to 316L* (preliminary result)

Cross-Section TEM Shows Nitrided 446 Did Not Form Continuous Cr-Nitride



- Surface tint after nitridation: surface O-rich, minor N
- Isolated Cr_2N grains and 10-100 nm thick Al-oxide/Ti-nitride surface (not yet clear what yields good properties)
- After polarization, continuous Cr-nitride shows oxygen uptake but retains low contact resistance: Related to this new effect?

Interactions and Collaborations

- Fuel Cell Testing of Nitrided Ni-50Cr (Delivery Spring 04)
  - Single-Cell: *General Motors, Los Alamos, FuelCell Energy*
  - Stack: *DANA Corp/TN Tech/USC* (State program $)
    side-by-side test with polymer composite plates
  - Plan to follow-up with tests of nitrided lower Cr alloys
- Thin Stamped Plates: *GenCell Corp*. (Ni and Fe base planned)
- Chemically Machined Plates: *H_2 Solutions Inc*. (low cost Fe-base)
- Nitrided coupons for evaluation delivered to several other fuel cell manufacturers – prelude to collaboration
- Technical Assistance on Commercial Alloys:
  Haynes International and ATI Allegheny Ludlum
- 3 papers and 1 disclosure submitted thus far in FY 2004

Response to Reviewer Comments

- *Negative comments on thick plates, cost of process, ...*
  - Standard Los Alamos graphite plate design for test hardware compatibility and to benchmark results
  - Nitridation ~ 10 cents - $1/part possible (depends on part size/shape, cycle time, nitridation method)

- *More extensive/real world test conditions/industry teaming*
  - Plates being manufactured for testing with GM, FuelCell Energy, DANA Corp
  - Los Alamos testing will include transient voltage spikes

- *Need focus on cheaper substrate alloys* - FY 04 efforts on nitridation of lower-Cr and Fe-base alloys

- *Need to demonstrate for sheet metal* - GenCell Corp collaboration on stamped 0.1-0.2 mm sheet

Future work

- Remainder of FY2004
  - Complete manufacture of nitrided Ni-50Cr plates for testing
  - Ramp-up GenCell collaboration/Nitriding of stamped sheet
  - Continue nitridation optimization/corrosion studies of available commercial Ni-Cr and Fe-Cr base alloys (down select for fuel cell testing)
  - New N_2-modified surface effect in fuel cell test - Are the improvements enough? Does it have potential?

- Major Goals for FY 2005
  - Complete analyses of Ni-50Cr plates from fuel cell tests at Los Alamos and GM
  - Successful fuel cell tests of "cheaper" substrate alloys
  - Viability of approach for thin sheets fully demonstrated
  - License technology and/or other forms of significant tech transfer