

VII.D.2 Cost-Effective Surface Modification for Metallic Bipolar Plates

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Projected End Date: Project continuation and direction determined annually by DOE

Objective

Develop a low-cost metallic bipolar plate alloy that will form an electrically conductive and corrosion-resistant nitride surface layer during thermal nitriding to enable use in a proton exchange membrane (PEM) fuel cell environment.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- A. Durability
- B. Stack Material and Manufacturing Cost

Technical Targets

This project is directed toward the DOE bipolar plate technical targets of \$6/kW and <1 kg/kW by 2010. Specific DOE bipolar plate property targets have also been set for H₂ permeation rate, corrosion, electrical conductivity, resistivity, flexural strength, and flexibility, some of which are more relevant to graphite and composite bipolar plates than to metallic bipolar plates. Corrosion and fuel cell testing of nitrided Ni-Cr base alloys in the range of \$20–30/lb indicate that these property targets can potentially be met. To meet the cost and weight goals, the allowable alloy cost is estimated at no greater than \$5–10/lb, with plate thickness on the order of 0.1 mm. Preliminary short-term corrosion and contact resistance tests suggest that protective nitride layers can be formed on Fe-Cr base alloys that can potentially be made at the \$5–10/lb range. Long-term durability of these nitrided alloys remains to be demonstrated.

Approach

- Thermally nitride Cr-bearing bipolar plate alloys to form a pinhole-free, protective Cr-nitride surface layer.
- Establish the potential of a Cr-nitride surface to meet durability goals by fuel cell testing of a model thermally nitrided Ni-50Cr alloy.
- Determine the key issues controlling the mechanism of nitridation to form Cr-nitride surface layers on lower-cost Fe, Fe(Ni), and Ni-Cr base alloys; optimize nitride formation; and evaluate the level of protection achieved by corrosion and fuel cell testing.

Accomplishments

- Tested anode plates of nitrided Ni-50Cr for 2,000 h at FuelCell Energy, Inc. (60°C/400 mA/cm²) and for 545 h at General Motors (GM) (80°C/cycled 0.2 A/cm² for 23 h, 1A/cm² for 1 h) with no degradation of

the surface CrN/Cr₂N evident. Isolated local attack was observed at regions traced to significant casting/Cr segregation defects in the initial Ni-50Cr casting, which formed less protective Ni-Cr-N phases at these spots instead of CrN/Cr₂N.

- Successfully nitrided 0.1-mm-thick foil of Hastelloy[®] G-35[™] (commercial Ni-30Cr base alloy) stamped by GenCell Corporation. There was no evidence of significant warpage.
- Delivered nitrided coupons and machined plates of Ni-50Cr, G-35, AL-29-4C[®] (commercial stainless steel), and developmental Fe-Cr base alloys to MTI Microfuel Cells, Inc., for testing
- Made significant gains in understanding and improving the robustness of the nitrided surface formed on Fe-Cr base alloys, with short-term corrosion and contact resistance measurements indicating behavior equal to that of the nitrided Ni-50Cr. Issues remain relative to effects of oxygen impurities on the effectiveness of the nitriding process.

Future Directions

- Complete delivery in FY 2005 of nitrided anode and cathode plates of Hastelloy G35, and G30[®] to FuelCell Energy and GM for fuel cell testing. Post-test analysis of these plates will be completed in FY 2006.
- Complete optimization of nitrided surface on Fe-Cr base alloys and deliver plates for fuel cell testing by industrial and national laboratory collaborators.
- Downselect to an austenitic or ferritic base and complete optimization of the baseline alloy composition range to provide a basis for scale-up activities.

Introduction

The bipolar plate is one of the most expensive components in PEM fuel cells. Thin metallic bipolar plates offer the potential for (1) significantly lower cost than currently-used machined graphite bipolar plates, (2) reduced weight/volume, and (3) better performance than developmental polymer/carbon fiber and graphite composite bipolar plates. However, most metals exhibit inadequate corrosion resistance in PEM fuel cell environments. This leads to high electrical resistance due to the formation of surface oxides and/or contamination of the polymer membrane by metallic ions, both of which can significantly degrade performance. Metal nitrides offer electrical conductivities up to an order of magnitude greater than that of graphite and are highly corrosion resistant. Unfortunately, most conventional deposited coating methods (for metal nitrides) are too expensive for PEM fuel cell stack commercialization or tend to leave pinhole defects, which result in accelerated local corrosion and unacceptable performance.

Approach

The goal of this effort is to develop a bipolar plate alloy that will form an electrically conductive and corrosion-resistant Cr-nitride surface layer during thermal (gas) nitriding. There are three

advantages to this approach. First, because the nitriding is performed at elevated temperatures, pinhole defects are not expected because thermodynamic and kinetic factors favor complete conversion of the metal surface to nitride. Rather, the key issues are nitride layer cracking, adherence, and morphology (discrete internal subsurface precipitates vs. continuous surface layers), which can potentially be controlled through proper selection of alloy composition and nitridation conditions. Second, the alloy can be formed into final shape by inexpensive metal forming techniques, such as stamping, prior to thermal nitridation. Third, thermal nitridation is an inexpensive, well-established industrial technique.

Results

Work in FY 2005 was divided into two areas: (1) completion of studies of nitrided Ni-(30–50)Cr wt % base alloys and (2) identification of alloy composition/nitridation conditions that lead to protective Cr-nitride formation on Fe-(20–30)Cr wt % base alloys. The high level of Cr soluble in Ni(Cr) without risk of embrittling σ phase formation makes Ni-Cr base alloys more readily amenable to external Cr-nitride layer formation by thermal nitridation than Fe-Cr base alloys. Therefore, nitrided Ni-Cr base alloys were used to establish and optimize performance and durability of thermally grown

Cr-nitride surfaces in PEM fuel cell environments. Because of the high cost of Ni, however, Fe-Cr base alloys are needed to meet DOE transportation cost goals. (Ni-Cr base alloys may be cost-viable for stationary or portable applications).

Proof of principle for thermally grown Cr-nitrides was initially established via excellent behavior of a nitrided model Ni-50Cr alloy in a 1,000-h, 0.7V single-cell fuel cell test and a 4,000-h corrosion test at Los Alamos National Laboratory (LANL) [1]. To investigate durability in PEM fuel cell environments for cyclic and/or longer-term operating conditions, nitrided anode plates of Ni-50Cr were manufactured in FY 2004 and tested in FY 2005 at GM and FuelCell Energy. Graphite cathode plates were used to isolate anode-side behavior, which is generally considered the more aggressive environment for metallic plates.

The testing at GM was conducted for 545 h at 80°C and cycled from 0.2 A/cm² for 23 h to 1A/cm² for 1 h. The testing at FuelCell Energy was conducted for 2,000 h at 60°C and 400 mA/cm². Post-test analysis of the membrane electrode assembly in the GM test indicated trace amounts of Ni, in the range of 3×10^{-6} g/cm², and Cr levels $<1 \times 10^{-6}$ g/cm². No visible corrosion was evident. In the Fuel Cell Energy tests, only limited degradation of 5.9 mV/1,000 h was observed over the course of the 2,000 h of operation, although a few isolated corroded spots in the plate were visible. Post-test scanning electron microscope analysis found occasional, isolated sites of local attack in both plates. These were traced to the initial local formation of a few isolated areas of less protective Ni-Cr-N phases on thermal nitridation, instead of CrN/Cr₂N. The Ni-Cr-N phase formation appeared to result from significant chromium segregation defects in the initial Ni-50Cr casting. The Ni-50Cr alloy is difficult to manufacture without significant Cr segregation; commercial Ni-Cr base alloys and Fe-Cr alloys are easier to manufacture and result in higher uniformity than the model Ni-50Cr alloy, and they are not expected to exhibit similar problems. Outside of these few spots, the CrN/Cr₂N surface formed on the plates showed no signs of degradation (Figure 1) and thus excellent potential to meet DOE durability goals. Nitrided Ni-50Cr plates are also currently in long-term single-cell fuel cell evaluation

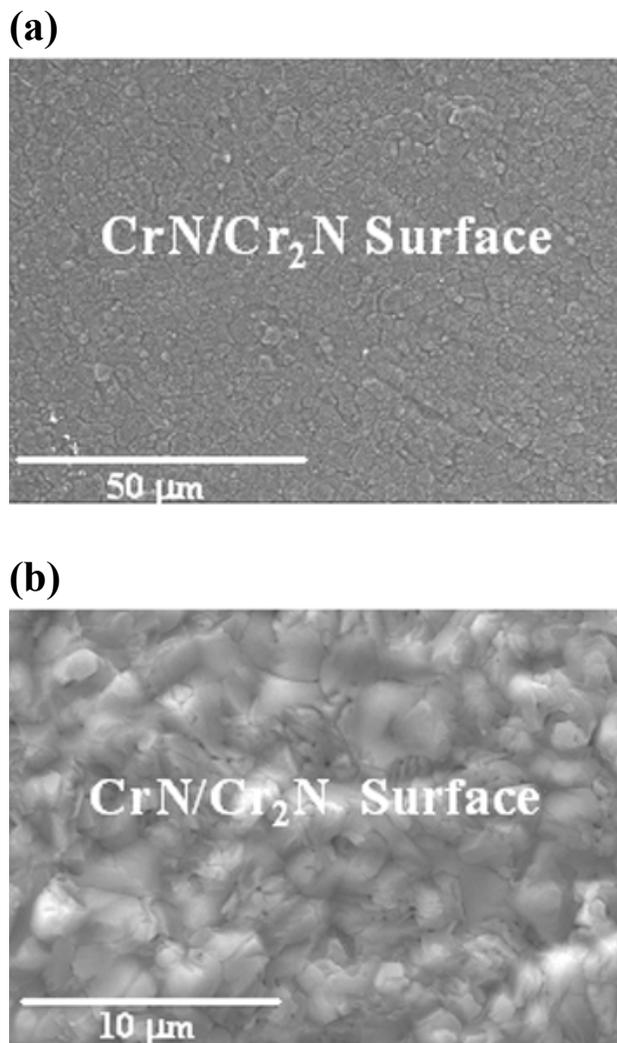


Figure 1. Scanning electron microscope surface images of 1100°C/2 h/N₂-4H₂ nitrided Ni-50Cr anode plates showing dense, intact CrN/Cr₂N surface: (a) after 545 h of cyclic fuel cell testing at GM; (b) after 2000 h of fuel cell testing at FuelCell Energy, Inc. (Note that the GM tested plate is shown at low magnification and the FuelCell Energy tested plate at high magnification)

at LANL; thus far, no degradation of these plates is evident. Bipolar plates of nitrided Ni-50Cr have also been delivered to DANA Corporation for sealing for stack testing with Tennessee Technological University and the University of South Carolina.

To facilitate more widespread evaluation of this technology, nitridation parameters suitable for two commercially available Ni-30Cr base alloys, Hastelloy G35 and G30, were developed. Corrosion

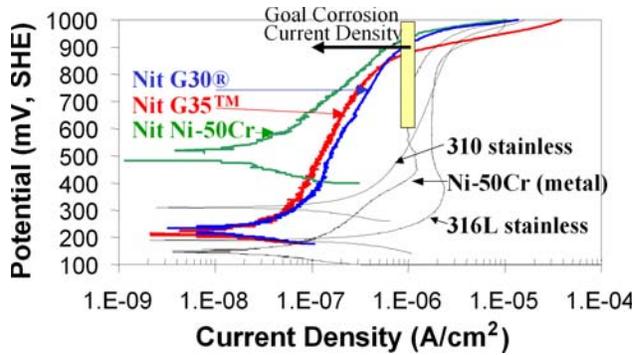


Figure 2. Polarization Curves in Aerated pH 3 Sulfuric Acid at 80°C (0.1mV/s) for Nitrated Ni-50Cr (1,100°C/2 h/N₂) and Nitrated G35™/G30® (1,100°C/8 h/N₂-4H₂) (Data for 310 stainless steel, 316 stainless steel, and Ni-50Cr [not nitrated] are shown for comparison.)

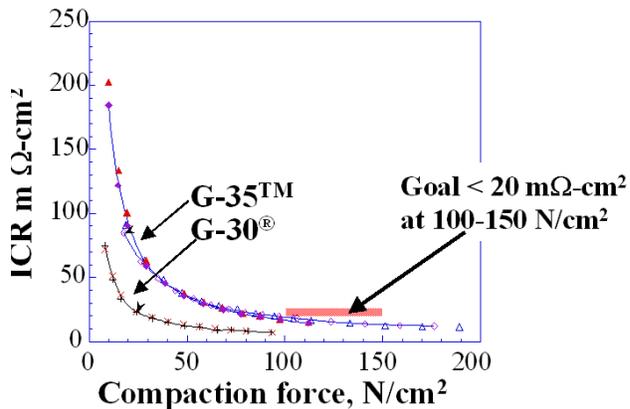


Figure 3. ICR Data for As-Nitrated G35™/G30® (1100°C/8 h/N₂-4H₂) Only very minor increases in ICR were observed after polarization corrosion exposures. The goal ICR level of <math>< 20 \text{ mohm-cm}^2</math> at 100-150 N/cm² was arrived at via input from several industrial sources.

and interfacial contact resistance (ICR) data are shown in Figures 2 and 3. Nitrated anode and cathode plates of these alloys will be delivered in the final quarter of FY 2005 to GM and FuelCell Energy for single-cell testing. In collaboration with GenCell Corp., nitridation of stamped 0.1-mm foil of G30 and G35 was also explored (Figure 4). Significant warpage during nitridation, which has been a potential concern, was not encountered. However, internal nitridation of alloy grain boundaries, which

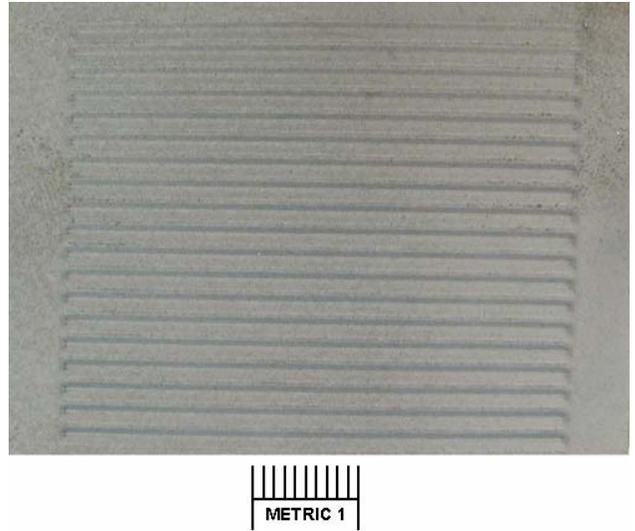


Figure 4. Macrograph of 0.1-mm Foil of G35™ Stamped by GenCell Corp. after Nitridation

can occur during nitridation treatment, in addition to external Cr-nitride layer formation, was observed in stamped G30 foil under the nitriding conditions used, resulting in significant embrittlement. Although the stamped G35 foil remained flexible after nitridation, repeated extensive flexing did ultimately result in fracture, which suggests it was likely partially embrittled by the nitriding treatment. Such embrittlement can be mitigated by nitridation for shorter times and/or at lower temperatures and by the use of lower nitrogen partial pressures to limit the extent of inward nitrogen penetration.

Detailed study of the nitridation of ferritic and austenitic Fe-Cr base alloys in the range of 20–30 wt % chromium, which are capable of meeting DOE cost goals, was also pursued in FY 2005. A key finding was that the presence of oxygen impurities in the nitriding environment, which is unavoidable on an industrial scale, can aid in the establishment of a dense, external Cr-nitride layer. This occurs by the formation of a submicron Cr-rich oxide film at the alloy/scale interface during the initial stages of reaction. The film slows penetration of nitrogen into the alloy, limiting internal nitride precipitation and favoring formation of the external Cr-nitride layer. Alloying additions of molybdenum and/or vanadium in the 1–6 wt % range also appear to be particularly beneficial in favoring dense Cr-nitride surface formation, as does reduction of nitridation

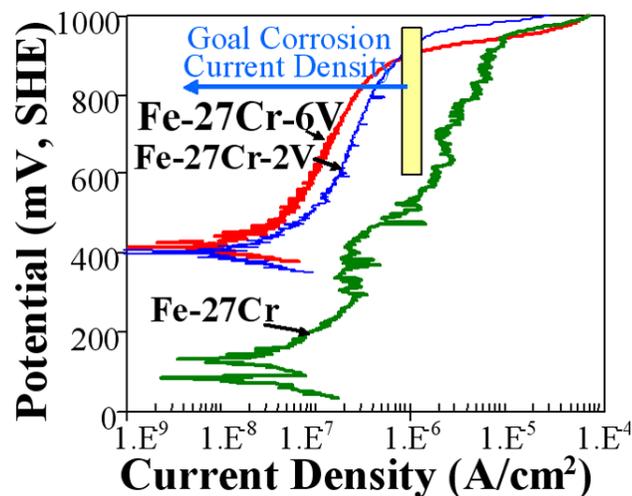


Figure 5. Polarization Curves in Aerated pH 3 Sulfuric Acid at 80°C (0.1mV/s) for Nitrided Fe-27Cr, Fe-27Cr-2V, and Fe-27Cr-6V wt%

temperatures from the 1,100°C range used for the Ni-Cr base alloys to the 800–900°C range. Figures 5 and 6 show corrosion and ICR data for vanadium-modified Fe-27Cr base alloys nitrided at 850°C for 24 h, indicating behavior comparable to that of the nitrided Ni-50Cr. With internal nitridation minimized, these conditions are not expected to embrittle thin, stamped alloy foil. Some repeatability and robustness issues with the nitridation of these alloys have been encountered, as a result of the dependence on initial Cr-rich oxide formation; and efforts to better understand and optimize surface Cr-nitride formation on the Fe-Cr base alloy are under way. Test plates of these and related Fe-Cr base alloys (as well as several Ni-Cr base alloys) will be nitrided in the last quarter of FY 2005 and delivered to MTI MicroFuel Cells for testing.

Conclusions

Thermally grown Cr-nitride surfaces on Ni-(30–50)Cr base alloys show excellent promise to protect metallic bipolar plates and meet DOE durability goals. The nitriding approach also appears viable for stamped alloy foil, which will be needed to meet DOE bipolar plate cost and weight goals. Dense Cr-nitride formation is also possible on Fe-Cr base alloys, which are potentially capable of meeting DOE transportation cost goals. However, further development is needed to improve the robustness

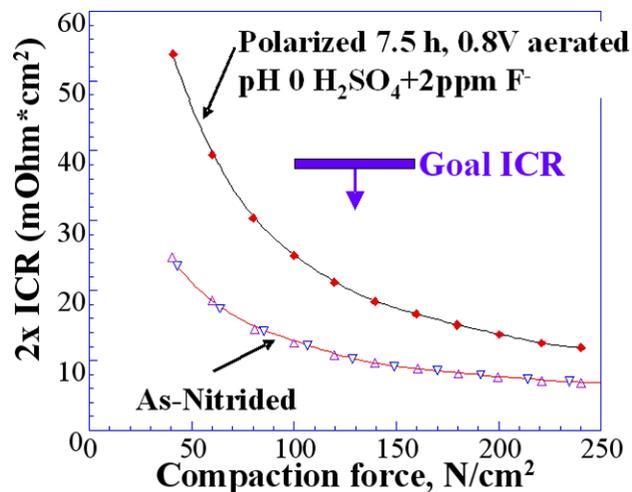


Figure 6. ICR Data for Nitrided Fe-27Cr-6V Before/ After Polarization in Aerated pH 0 Sulfuric Acid + 2 ppm F⁻ at 70°C, Held for 7.5 h at 0.8V vs standard hydrogen electrode [1-3] (The plot is for 2× ICR because both coupon faces were measured [only one face polarized].)

of the nitriding response needed to promote such formation on current Fe-(20–30)Cr base alloys.

Special Recognitions and Awards/Patents Issued

1. M. P. Brady, H. Wang, and J. A. Turner, “Surface Modified Stainless Steels For PEM Fuel Cell Bipolar Plates,” U.S. Patent Disclosure, February 2005.
2. M. P. Brady was named to the International Editorial Advisory Board for the journal *Oxidation of Metals*.
3. M. P. Brady was invited to join the Editorial Advisory Board of the new journal *Trends in Corrosion Research*.

FY 2005 Publications/Presentations

1. I. Paulauskas, M. P. Brady, H. M. Meyer III, R. A. Buchanan, and L. R. Walker, “Corrosion Behavior of CrN, Cr₂N and π Phase Surfaces Formed on Nitrided Ni-50Cr with Application to Proton Exchange Membrane Fuel Cell Bipolar Plates,” *Corrosion Science* (accepted for publication).
2. M. P. Brady, P. F. Tortorelli, K. L. More, E. A. Payzant, B. L. Armstrong, H. T. Lin, M. J. Lance, F. Huang, and M. L. Weaver, “Coating and Surface Modification Design Strategies for Protective and Functional Surfaces,” *Materials and Corrosion* (accepted for publication).

3. M. P. Brady, B. Yang, P. F. Tortorelli, K. L. More, H. Wang, J. A. Turner, "Thermally Nitrided Metallic Bipolar Plates for Proton Exchange Membrane Fuel Cells," invited presentation for the Materials for the Hydrogen Economy Symposium at the MST 2005 TMS Meeting, September 2005, Pittsburgh, PA.
4. M. P. Brady, "Multi-Component/Multi-Phase Alloys as Precursors to Protective/Functional Surfaces via Gas Reactions," invited presentation for the 2005 Gordon Research Conference on High-Temperature Corrosion, July 2005, New London, NH.
5. M. P. Brady, P. F. Tortorelli, H. Wang, B. Yang, M. Wilson, F. Garzon, J. A. Turner, and R. A. Buchanan, "Thermally Nitrided Metallic Bipolar Plates for PEM Fuel Cells," poster presented at the Fuel Cell Seminar, October 2004, San Antonio Texas.

References

1. M. P. Brady, K. Weisbrod, I. Paulauskas, R. A. Buchanan, K. L. More, H. Wang, M. Wilson, F. Garzon, and L. R. Walker, *Scripta Materialia*, **50**(7), 1017–1022 (2004).