Evaluation of a Functional Interconnect System for Solid Oxide Fuel Cells

Program #DE-FC26-05NT42513

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July 28, 2010

Presentation Overview

- Overview of ATI and ATI Allegheny Ludlum
- Alloy Design
  - Third-Generation Alloy Development
  - ASR Testing
  - Oxidation Testing
- Post-Processing Surface Modification
  - Sample Preparation
  - ASR Testing
- Additional SECA Activities
  - Processing of Material for Low-Chromium Alloy Research

Conclusions 1

- A cerium-modified manganese cobaltite spinel coating continues to be effective in reducing the rate of ASR increase for nearly all of the potential interconnect alloys tested
- The rate of increase in ASR of ATI 441HP™ alloy coated with PNNL's cerium-modified manganese cobaltite spinel coating was 0.8 $m\Omega \cdot cm^2$/1,000 hr after the test system reached steady-state conditions. In the coated condition, this commercial alloy outperforms other experimental Fe-17Cr type alloys and is expected to meet the 40,000 hr SECA goal for IC performance.

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Conclusions 2

- An experimental Fe-17Cr type alloy with 0.15 wt% Si is less prone to breakaway oxidation than both one with 0.05 wt% Si and commercial ATI 441HP alloy with 0.40 wt% Si, suggesting that there is an optimal silicon content which is not as low as possible.
- Early results indicate that post-processing surface modifications are effective for ATI 441HP alloy.

Allegheny Technologies (ATI) Overview

ATI is one of the largest and most diversified specialty metals producers in the world. We use innovative technologies to offer global markets a wide range of specialty metals solutions.

- 8,500 employees – worldwide
- $899.4 Million in Sales in Q1 2010
- Global presence
- Provides customer focused specialty metals solutions
  - Titanium and Titanium alloys
  - Nickel-based alloys and superalloys
  - Stainless Steels, Grain Oriented Electrical Steel & Duplex Alloys
  - Zirconium, Hafnium and Niobium Alloys
  - Tungsten metals & carbide cutting tools
  - Powder metals

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Flat-Rolled Products

Foil

Plate

Coil

Sheet

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Over 150 different alloys are made by ATI Allegheny Ludlum

Stainless Steels and Specialty Alloys	
Austenitic (Fe-Cr-Ni)	**Ferritic (Fe-Cr)**
ATI 201HP™, ATI 201LHP™ ATI 201LN™, ATI 216Cb™, AL 219™ AL 301, AL 304, AL 316, AL 317, AL 321, AL 347 ATI 309S, ATI 310S, AL 332MO® AL 904L™, AL-6XN®, AL-6XN® Plus, AL 4565™	Types 409, 430, 439, 441HP™, 444, AL 18CrCb™ E-BRITE®, SEACURE®, AL 29-4C® ALFA™ I, II alloys (FeCrAl)
Duplex (Fe-Cr-Ni)	**Precipitation-Hardening (Fe-Cr-Ni)**
ATI 2003®, ATI 2102™, ATI 2205™, ZERON® 100, ATI 255™	ATI 13-8™, ATI 15-5™, ATI 15-7™ ATI 17-4™, ATI 17-7™, AM 350®, ALTEMP® A-286
Specialty	**Titanium**
Martensitic stainless steels (420, 440A) Grain-oriented electrical steels Controlled magnetic property alloys Controlled CTE (AL 36™, AL 42™ alloys) Armor plate (K12®, AL 521™) Tool Steels	CP grades 1-4 Grade 9 (Ti 3–2.5) Grades 5 (6-4) and 23 (6-4 ELI) Grades 7, 11, 16, 18 (Pd-bearing) ATI 64, ATI 325, ATI 425®
Nickel-Based Alloys	
Heat-Resistant Grades	**Corrosion-Resistant Grades**
AL 800™/AL 800H™, AL 600™, AL 601™ ALTEMP® 625, ALTEMP® 718, ALTEMP® HX, ALTEMP® 263, ALTEMP® X-750	AL 20™, AL 22™, AL 276™, AL 825™, ALLCORR®, AL Ni 200™, AL Ni 201™, AL 400™, AL 625™

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Project History and Major Milestones

Phase I ALC prime contractor, CMU and WVU subcontractors 2005-2006

- ALC – Alloy development, surface modifications, and oxidation testing of ferritic stainless steels
- CMU – Indentation techniques for studying coating/oxide adhesion
- WVU – Performance and characterization of pure and sterling silver contact pastes

Subcontract from U. Pittsburgh

- Melted and processed several FeCrTi heats for proof of concept of formation of external TiO_2 layer
- Attempted to reduce evaporation tendency

Phase II ALC sole contractor 2007-2008

- Alloy development and processing of two sets of Fe-Cr stainless steel compositions (high-Cr and lower-Cr)
- Refinements to surface modifications; proof of concept solid-state silicon removal
- Built and commissioned ASR test facility (2008); short and long-term ASR testing
- Long-term SCG and SAG oxidation testing
- Production and testing of clad IC structures
- Mill-scale materials supply of Type 441

2005 2006 2007 2008 2009 2010

Phase II revised for 2009-2010

- 3rd-Gen alloy compositional refinement, melting, and processing
- Novel post-process modifications to standard Type 441 alloy to reduce scale growth rate
- Long-term ASR testing and evaluation
- Multi-sample testing and analysis of breakaway oxidation for Fe-17Cr type alloys
- Processing and materials supply of four experimental low-chromium ferritic alloys

Previous Results from Phase II

- Reducing silicon to low levels with lower-Cr alloys tended to reduce the rate of ASR increase but also tended to add instability, similar to the effect seen in oxidation behavior
- Higher-Cr alloys exhibited relatively low rates of ASR evolution, with a trend towards decreased rates as a function of Cr content
- The addition of Mn was beneficial for higher-Cr alloys
- An extension to Phase II was agreed upon to further explore these alloys

Alloy	Cr	Nb	Si	Others
ATI 441HP™ alloy	17.5	0.3	0.4	0.3 Mn, 0.2 Ti
EXP. 580-6	17	0.3	0.15	0.3 Mn, 0.2 Ti
EXP. 580-7	17	0.3	0.05	0.3 Mn, 0.2 Ti
E-BRITE® alloy	26	0.2	0.3	1 Mo
EXP. 580-5	26	0.2	0.3	1 Mo, 0.3 Mn

Further characterization of breakaway oxidation (ATI 441HP™ alloy, EXP. 580-6, EXP. 580-7)

Basis for 3rd-gen alloys (EXP. 580-6, EXP. 580-5)

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Current Focus – Revised Phase II

- Third generation alloy development
  - Primary focus on ATI 441HP™ alloy variants
  - Secondary focus on E-BRITE® alloy variants
- Statistical analysis to relate breakaway oxidation to Si content and other parameters
- Post-processing techniques to reduce ASR increase
  - Primary focus on surface/bulk deformation
  - Secondary focus on metal surface chemistry modification
- Processing four heats of experimental material for Auburn Univ. test program to characterize Cr-content variation

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Alloy Matrix – Third Generation

Alloy	Cr	Nb	Si	Others	Comments
ATI 441HP™ alloy	17.5	0.3	0.4	0.3 Mn, 0.2 Ti	Commercial material
EXP. 580-6	17	0.3	0.15	0.3 Mn, 0.1 Ti	Moderate Si
EXP. 580-6 MOD1	17.3	0.5	0.15	0.3 Mn, 0.2 Ti	Increased Nb, mid Si
EXP. 580-6 MOD2	17.3	0.7	0.15	0.3 Mn, 0.2 Ti	Increased Nb (max), mid Si
EXP. 580-6 MOD3	17.3	0.7	0.35	0.3 Mn, 0.2 Ti	Increased Nb (max)
EXP. 580-6 MOD4	17.3	0.3	0.35	0.3 Mn, 0.0 Ti	Modified stabilization
EXP. 580-6 MOD5	17.3	0.3	0.35	0.8 Mn, 0.2 Ti	Increased Mn
E-BRITE® alloy	26	0.2	0.3	1 Mo	Commercial material
EXP. 580-5	26	0.2	0.3	1 Mo, 0.3 Mn, 0.1Ti	Commercial E-BRITE® comp. + 0.3 wt.% Mn
EXP. 580-5 MOD1	26	0.5	0.35	1 Mo, 0.3 Mn, 0.2 Ti	Increased Nb
EXP. 580-5 MOD2	24	0.3	0.35	1 Mo, 0.3 Mn, 0.2 Ti	Reduced Cr

- 2nd-Generation experimental alloys EXP. 580-6 and EXP. 580-5 performed well in earlier experimentation
- Further characterization of the effect of Cr, Nb, Si, Mn, and Ti

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Overview of ASR Test Results

Sample ID	ASR Evolution Rate ($m\Omega \cdot cm^2$/1,000h)		Comments
	Uncoated	Coated	
ATI 441HP™ alloy	35.4	0.8	Commercial material (0.4 wt.% Si)
EXP. 580-6	25.1	6.9	Moderate Si (0.15 wt.%)
580-6 MOD1	no test	4.6	Increased Nb (0.5 wt.%), Moderate Si (0.15 wt.%)
580-6 MOD2	no test	1.6	High Nb (0.7 wt.%), Moderate Si (0.15 wt.%)
580-6 MOD3	no test	0.8	High Nb (0.7 wt.%)
580-6 MOD4	no test	77.1	Modified stabilization with no Ti
580-6 MOD5	no test	118.6	Increased Mn (0.8 wt.%)
E-BRITE® alloy	936.5	21.1	Commercial material (0.3 wt.% Si)
EXP. 580-5	38.1	1.4	Standard E-BRITE® + 0.3 wt.% Mn
580-5 MOD1	no test	4.4	Fe-26Cr-1Mo-0.3Mn, Increased Nb (0.5 wt.%)
580-5 MOD2	no test	2.4	Fe-24Cr-1Mo-0.3Mn, Reduced Cr

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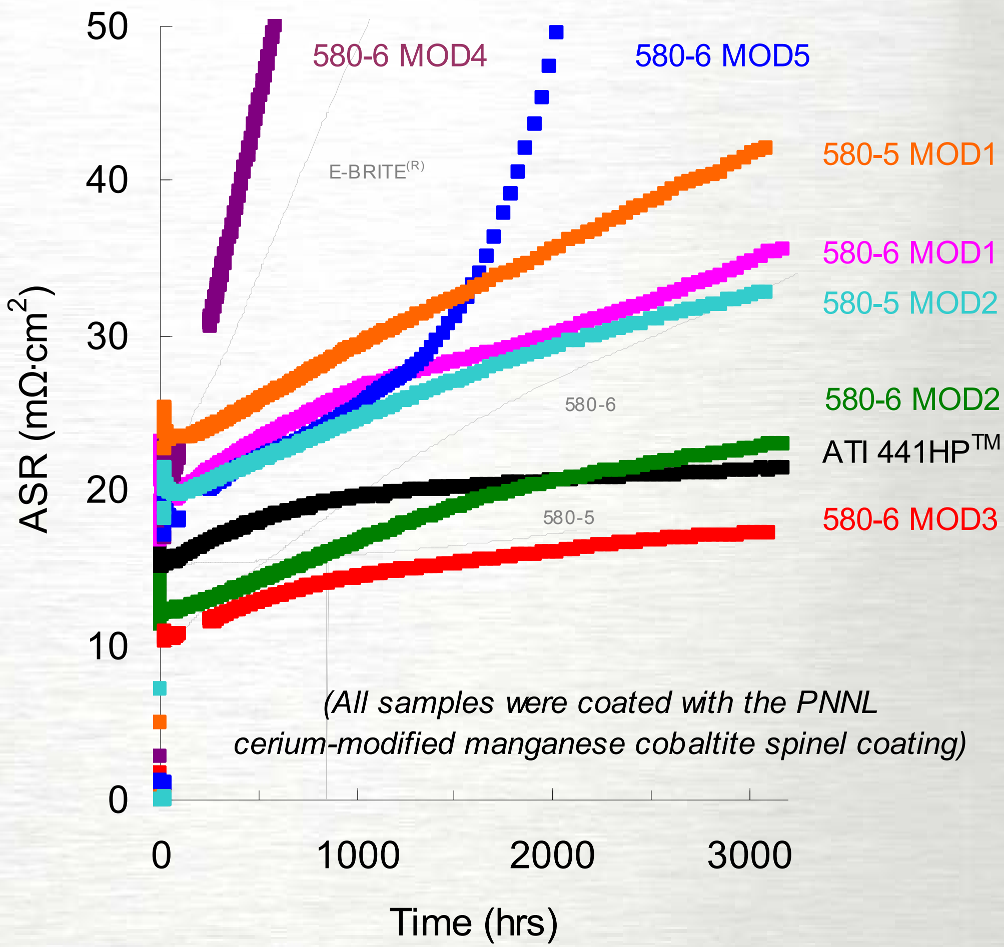
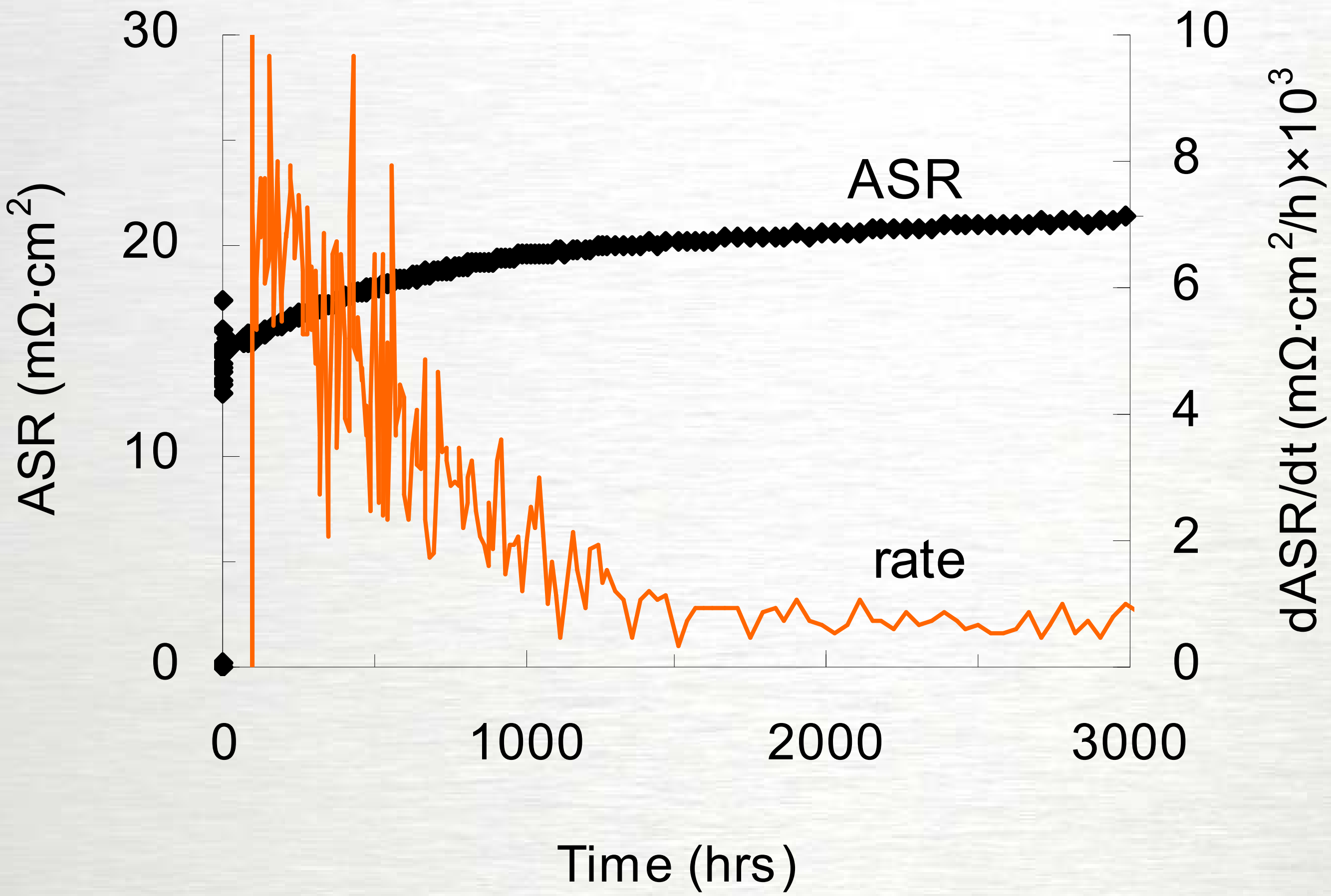
ASR Test Results

- 800°C test temperature
- LSM ceramic contact layer
- Constant current density of 0.5 A/cm² of contact area
- All coupons tested in coated condition as previous testing established its advantage
- Test setup simulating cathode side of cell
- ASR rate of change more important parameter than relative position of ASR curves



ASR Test Results – Coated ATI 441HP™ Alloy



Test coupon coated with the PNNL cerium-modified manganese cobaltite spinel coating

ASR Test Results – Summary

- The cerium-modified manganese cobaltite spinel coatings continue to be effective in reducing the rate of ASR increase for nearly all of the alloys tested
- The combined effect of the base alloy and coating may obscure the differences between performances of the base experimental alloys to some extent
- The coated commercial ATI 441HP™ alloy yielded the best long-term performance in the test matrix

ASR Test Results – Summary

Observations for the coated, modified ATI 441HP samples:

- The addition of Nb (EXP. 580-6 MOD3) did not show an improvement beyond the commercial alloy composition
- The elimination of Ti (EXP. 580-6 MOD4) was detrimental to alloy performance
- The addition of a higher amount of Mn (EXP. 580-6 MOD5) was detrimental to alloy performance after 1,500 hours of testing

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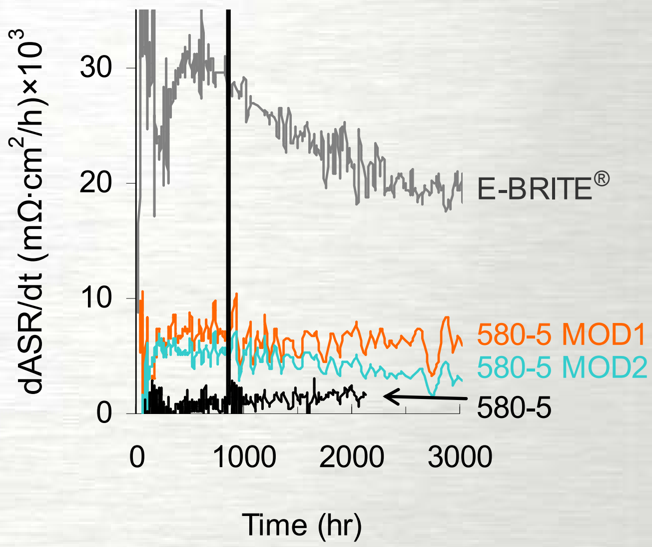
ASR Test Results – Summary

Observations for the coated, modified E-BRITE® samples:

Coated Alloy	Cr	Nb	Si	Others	ASR Evolution Rate ($m\Omega \cdot cm^2$/1,000h)
E-BRITE® alloy	26	0.2	0.3	1 Mo	21.1
EXP. 580-5	26	0.2	0.3	1 Mo, 0.3 Mn, 0.1Ti	1.4
EXP. 580-5 MOD1	26	0.5	0.35	1 Mo, 0.3 Mn, 0.2 Ti	4.4
EXP. 580-5 MOD2	24	0.3	0.35	1 Mo, 0.3 Mn, 0.2 Ti	2.4

- The modification of a 0.3 wt.% Mn addition to a base E-BRITE® alloy composition (EXP. 580-5) continued to yield the best long-term performance of higher-chromium alloys
- An increased Nb content does not appear to be beneficial (EXP. 580-5 MOD1)
- A slight drop in IC performance is associated with a reduction in Cr content (EXP. 580-5 MOD2)



Post-Processing Techniques

- All starting material sourced from production lots of ATI 441HP™ stainless steel
- Localized surface deformation
  - Mill surface (acid pickled) will serve as a control
  - Rough surface grinding
  - Grit blasting
- Delocalized through-thickness deformation by temper rolling
  - 1.00 mm thick material lab rolled to 50% reduction (0.50 mm)
  - Mill-annealed 0.50 mm thick material serves as a control
- Desiliconization
  - Testing treated and untreated material side-by-side
  - Examining two gauges (thickness effect on a diffusional process)

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Testing Surface-Modified ATI 441HP™ Alloy

- ASR testing on coated, surface-modified ATI 441HP™ stainless steel was recently started
- Long-term (> 5,000 hrs) oxidation testing is being performed
  - Detailed characterization of the oxide and oxide-coating interaction will be completed at the end of the aging treatment

Oxidation Study of Fe-17Cr Alloys

- Reduction of Si to low levels …
  - Reduced the rate of ASR increase
  - Tended to add instability in overall resistance to accelerated oxidation (noted in weight gain and ASR curves)
- Oxidation test program to quantify risk associated with low Si
  - Varying Si content
  - Temperatures from 800-900°C
  - Humidified air (SCG)
  - Test numerous small samples to gain statistical significance

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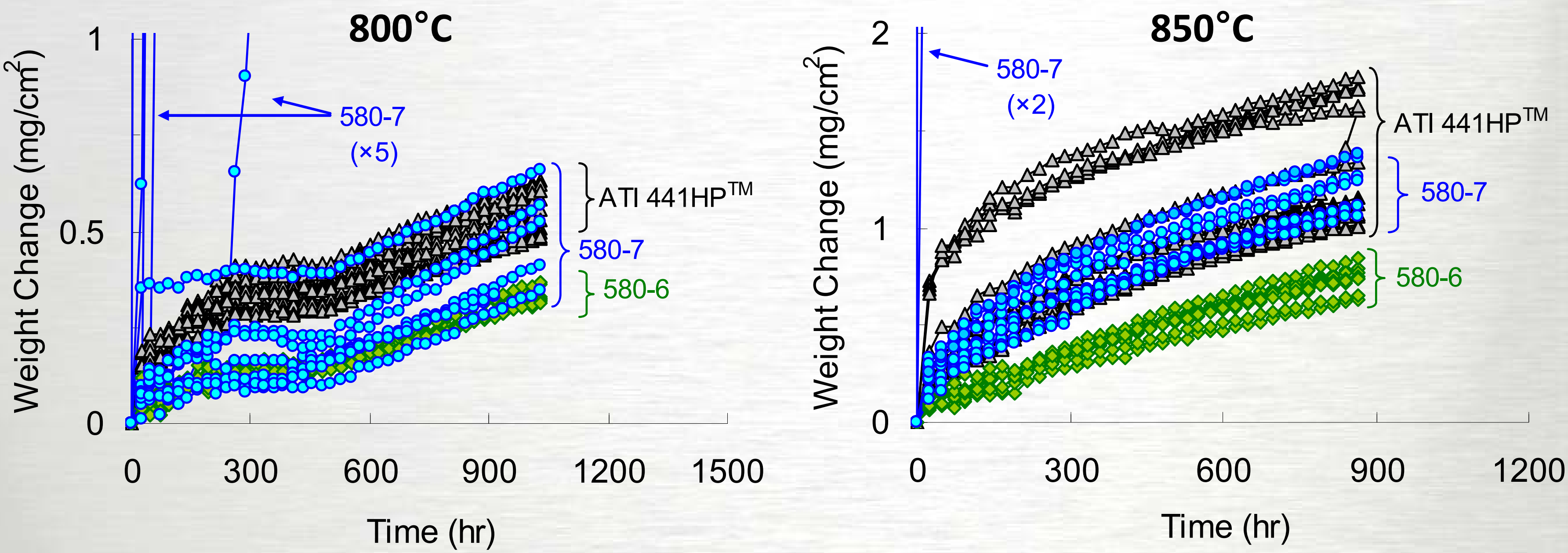
Oxidation Study of Fe-17Cr Alloys



Alloy	Si
ATI 441HP™ alloy	0.40 (high)
EXP. 580-6	0.15 (mid)
EXP. 580-7	0.05 (low)

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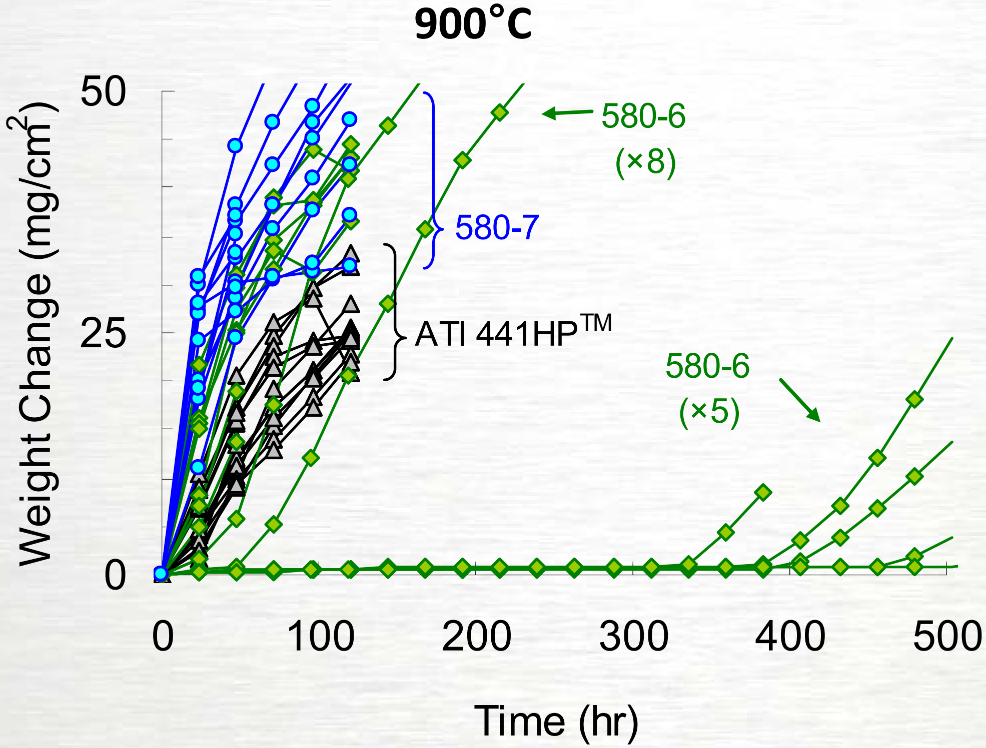
Oxidation Study of Fe-17Cr Alloys



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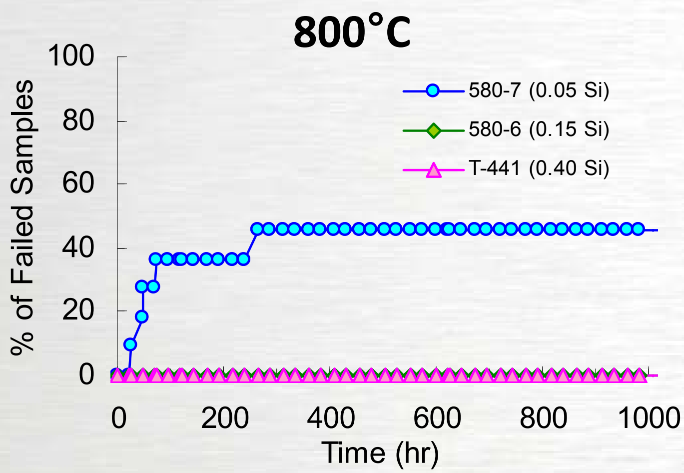
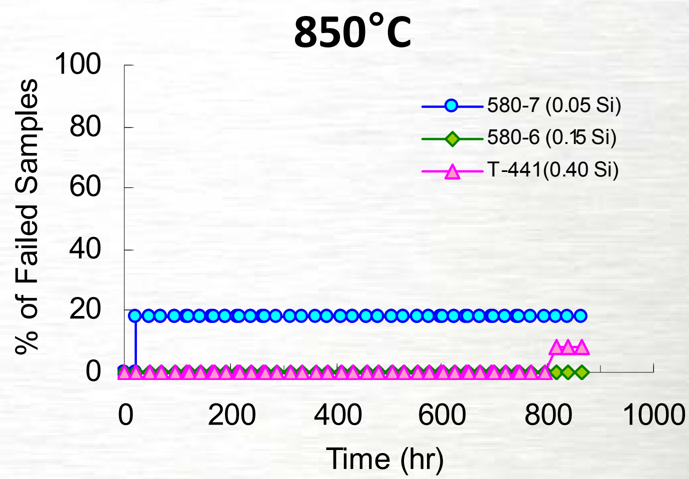
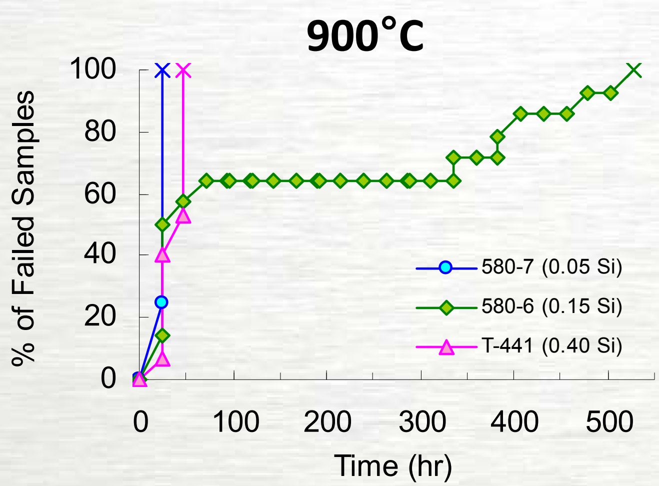
Oxidation Study of Fe-17Cr Alloys







Investigation of Chromium Content Variation

Alloy	ID	Cr	Nb	Si	Others
Alloy 1	983-1	13	0.3	0.35	0.3 Mn, 0.2 Ti
Alloy 2	983-2	15	0.3	0.35	0.3 Mn, 0.2 Ti
Alloy 3	983-3	17	0.3	0.35	0.3 Mn, 0.2 Ti
Alloy 4	983-4	18	0.3	0.35	0.3 Mn, 0.2 Ti

- Melted and processed four 50-lb. ingots to 0.040" and 0.020"
- Studying the interaction of the coating with the oxide formed on ferritic stainless steels containing lower levels of Cr content

Summary 1

- Promising commercial compositions were identified and minor chemistry modifications were explored to study their effect on electrical properties of the IC surface
- *Phase II – Revised* initiated on 01 April 2009
  - 3rd-gen compositions studied with ASR and oxidation testing
  - Post-processing performed on ATI 441HP™ alloy; ASR and oxidation testing initiated
  - Lifetime definition and prediction as function of Si content

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Summary 2

- Material supplied
  - Full-size production coil of ATI 441HP™ stainless produced and distributed to Core Technology and Industrial Teams
  - Four ferritic stainless steel alloys with lower Cr contents melted, processed, and supplied

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Acknowledgements

- Robin Ames, Travis Shultz, Wayne Surdoval, and NETL program management for their support of this program
- Dr. Jeffry Stevenson and PNNL for coating test specimens, for input on the operation of the ASR test facilities, and for general guidance
- Dr. Jeff Fergus for continued collaboration
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- Mark Miecznikowski for laboratory assistance

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Thank you for your attention.

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