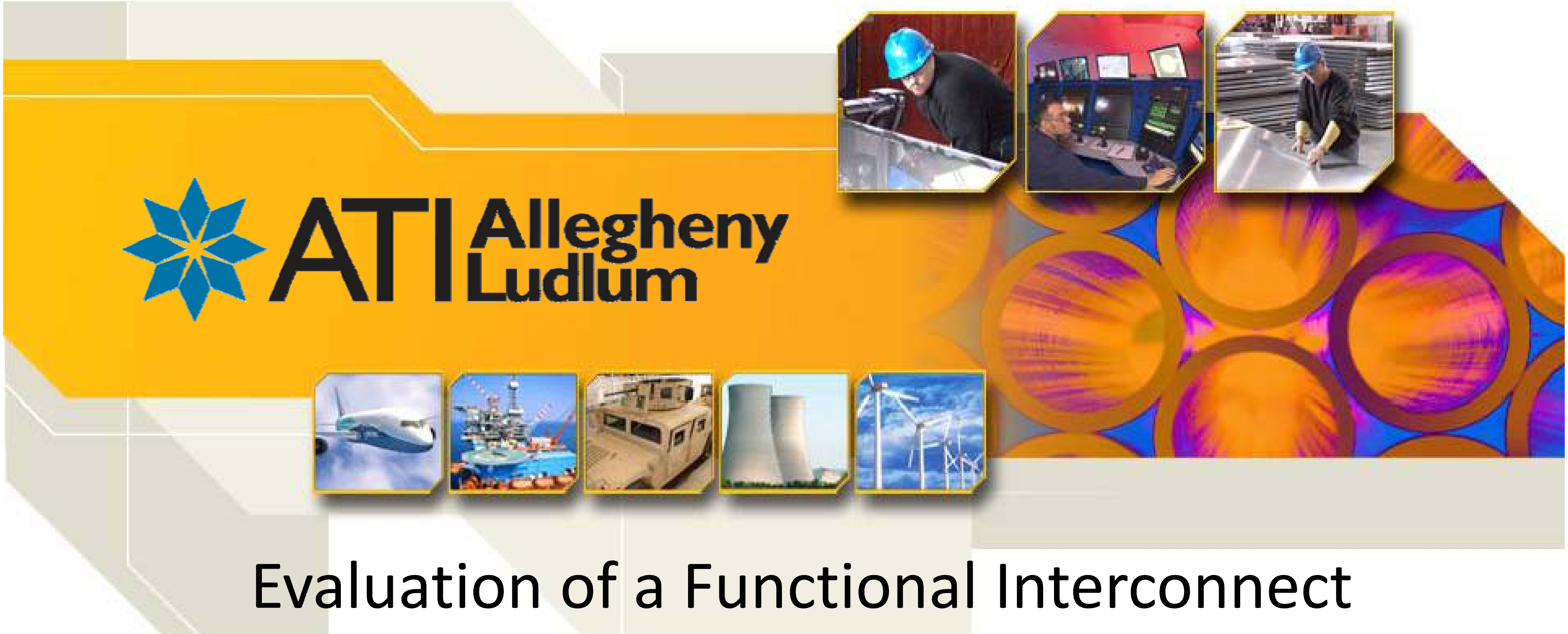

Evaluation of a Functional Interconnect System for Solid Oxide Fuel Cells

Program #DE-FC26-05NT42513

Dr. Matthew Bender – ATI Allegheny Ludlum

SECA Annual Meeting, July 13-15, 2009

Presentation Overview

- Introduction to Allegheny Technologies and ATI Allegheny Ludlum
- Program history
- Recent results
- Current focus

ATI Allegheny Ludlum

Allegheny Technologies (ATI) Overview

We are a leading international metals manufacturer with primary and finishing facilities for semi-finished and engineered products, with headquarters in Pittsburgh, Pennsylvania USA.

- 9,600 employees worldwide
- $5.3 billion in revenue for 2008
- Global presence – operations in 17 countries
- 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

ATI

ATI Allegheny Ludlum Products

- Stainless steel sheet, strip, plate
- Nickel-based alloys and superalloys
- Titanium and titanium alloys
- Grain-oriented electrical steels
- Armor plate

hot-rolled and cold-rolled coils

plate mill plate

Precision Rolled Strip®, standard strip

ATI Allegheny Ludlum

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ATI Allegheny Ludlum

Project History and Major Milestones

multi-sample testing and statistical analysis of breakaway oxidation for Fe-17Cr type alloys
novel post-process modifications to standard Type 441 alloy to reduce scale growth rate
long-term ASR testing and evaluation

2010

identified 3rd generation alloy compositional refinements and initiated melting

mill-scale materials supply of Type 441

Phase II revised for 2009-2010

- Alloy compositional refinement
- Additional surface modifications
- Statistical analysis of breakaway oxidation
- Short and long-term ASR testing

2009

completed long-term ASR testing

completed long-term SCG and SAG oxidation testing

2008

trial materials supply

proof of concept – formation of external TiO_2 layer
melting and processing of several heats of FeCrTi alloys

built and commissioned ASR test facility

melted and rolled high-Cr and low-Cr IC alloys

FeCrTi alloys

- Subcontract from U. Pittsburgh
- Attempt to reduce evaporation tendency

University of Pittsburgh

2007

Phase II ALC sole contractor 2007-2008

- Alloy development, processing
- Refinements to surface modifications
- Long-term oxidation testing
- Short and long-term ASR testing

testing of Type 441 alloy
production and testing of clad IC structures
proof of concept solid-state silicon removal
melted and rolled two sets of Fe-Cr stainless steel compositions

2006

WVU – characterization of pure and sterling silver cermet contact pastes

CMU – proof of concept, indentation techniques for determining coating/oxide adhesion

2005

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

- ALC – alloy development, surface modifications, and oxidation testing of ferritic stainless steels
- CMU – adhesion of scales and coatings,
- WVU – performance of contact layers

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Carnegie Mellon

West Virginia University

ATI Allegheny Ludlum

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Recent Results from Phase II

- Second generation alloy development
- Oxidation testing
- Long-term ASR evaluation

Alloy Matrix – Second Generation

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
EXP. 580-7	17	0.3	0.05	0.3 Mn
EXP. 580-2	17	0.3	0.05	0.1 Ce + La
E-BRITE® alloy	26	0.2	0.3	1 Mo
EXP. 580-5	26	0.2	0.3	1 Mo, 0.3 Mn
EXP. 580-8	23	0.3	0.15	1 Mo, 0.3 Mn
EXP. 580-9	24	0.3	0.05	1 Mo, 0.3 Mn

Oxidation Test Results

- Oxidation testing carried out in controlled atmospheres at 750-850°C
  - Ambient air (baseline)
  - Humidified air (simulated cathode environment)
  - Ar-H_2-H_2O (simulated anode gas)
  - Ar-CH_4-H_2O (carbon-bearing SAG)
- Ambient air and SAG results uniform and predictable
- Humidified air testing provides differentiation between silicon and chromium levels

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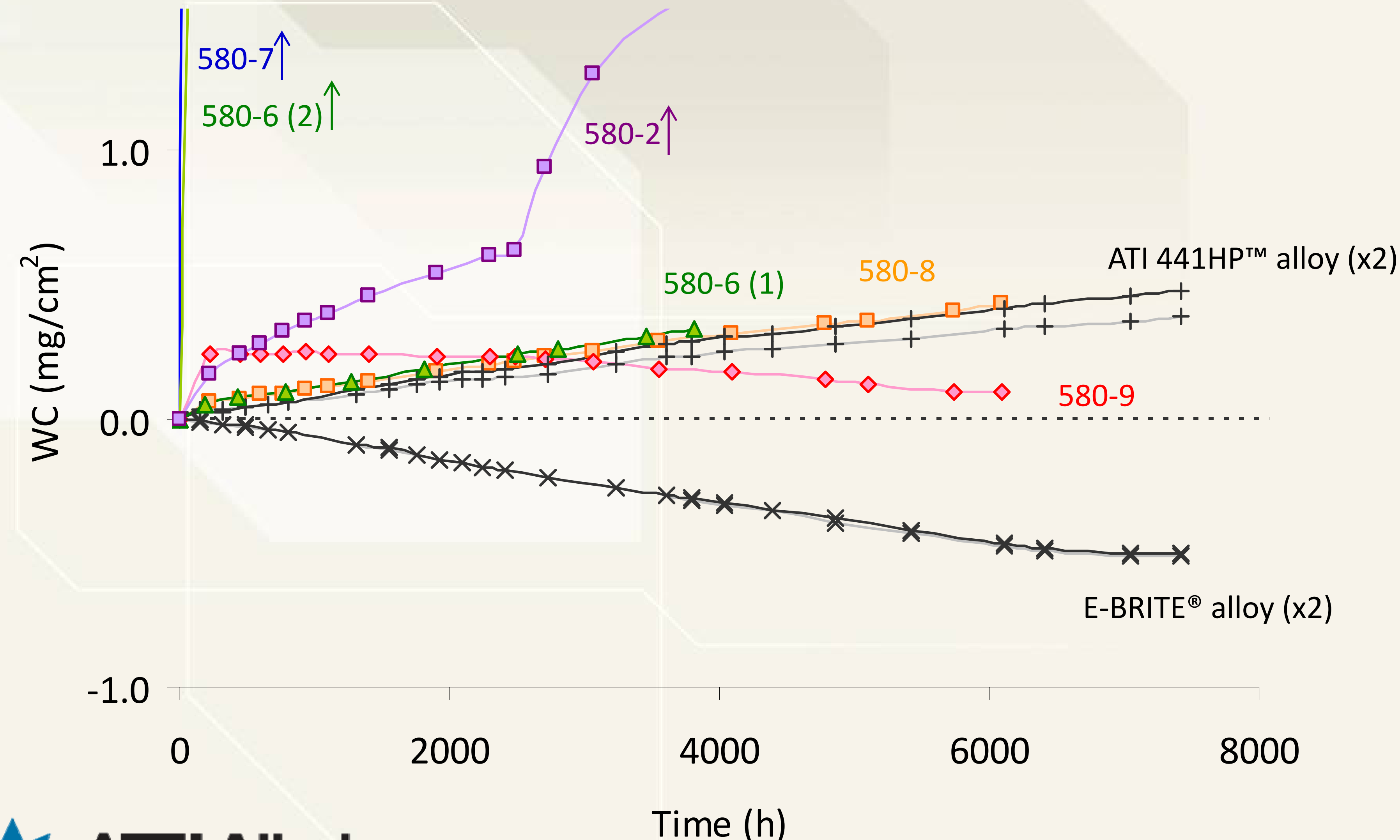
Oxidation Test Results



Oxidation test results at 750°C in air + 10% water vapor

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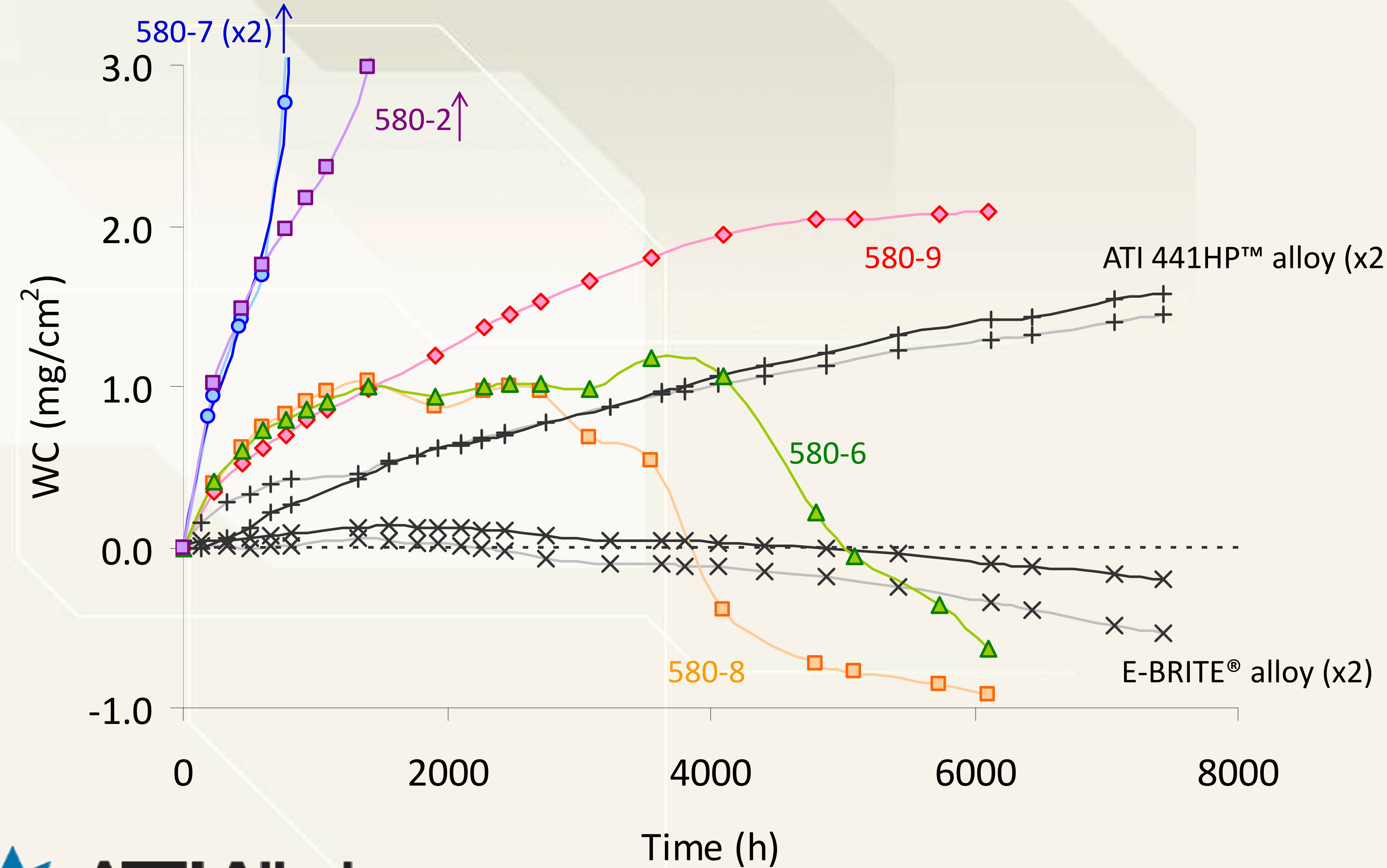
Oxidation Test Results



Oxidation test results at 850°C in air + 10% water vapor

Oxidation Test Results – Summary

- Fe-17%Cr alloys
  - Experimental heat with low silicon level tended to experience rapid transition to breakaway oxidation
  - Addition of reactive element postponed but did not prevent transition to breakaway oxidation in low-silicon chemistry
  - Experimental heat with moderate silicon level more likely to exhibit transition to breakaway oxidation
  - Commercial Type 441 with typical silicon level did not exhibit breakaway oxidation
- Higher-chromium (23-26%) alloys
  - Mn addition critical
  - Irregular weight loss behavior

ASR Testing

- Designed for long-term evaluation
- Three sets of test samples (stacks) are exposed simultaneously
- Each stack consists of…
  - Two **identical** test sample coupons (the interconnect)
  - Intermediary layer of LSM ink (contact paste)
  - A rectangular LSM pellet (cathode)
- Coated samples were prepared by PNNL and used a manganese cobaltite spinel modified with cerium
- Stack compressive load is approximately 0.2 psi (dead weight)
- Data visualized as ASR as a function of time and rate of ASR change (tangential slope) as a function of time

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ASR Test Results – Summary

Sample ID	ASR Evolution Rate ($m\Omega \cdot cm^2$/1,000h)		Comments
	Uncoated	Coated	
ATI 441HP™ alloy	35.4		Commercial material (0.4 wt. % Si)
580-7	33.7 run 1	2.2	Very low Si (0.05 wt. %), divergent test results from two identical uncoated samples
	550.9 run 2		
580-2	47.2		Very low Si (0.05 wt. %)+ Ce addition
580-6	25.1	6.9	Moderate Si (0.15 wt. %)
E-BRITE® alloy	936.5	21.1	Commercial material (0.3 wt. % Si)
580-5	38.1	1.4	Commercial E-BRITE comp. + 0.3 wt. % Mn
580-8	17.2	7.5	Fe-23Cr-1Mo-0.3Mn, moderate Si (0.15 wt. %), divergent results from identical coated samples
		223.7	
580-9	7.9	2.5	Fe-24Cr-1Mo-0.3Mn, very low Si (0.05 wt. %)

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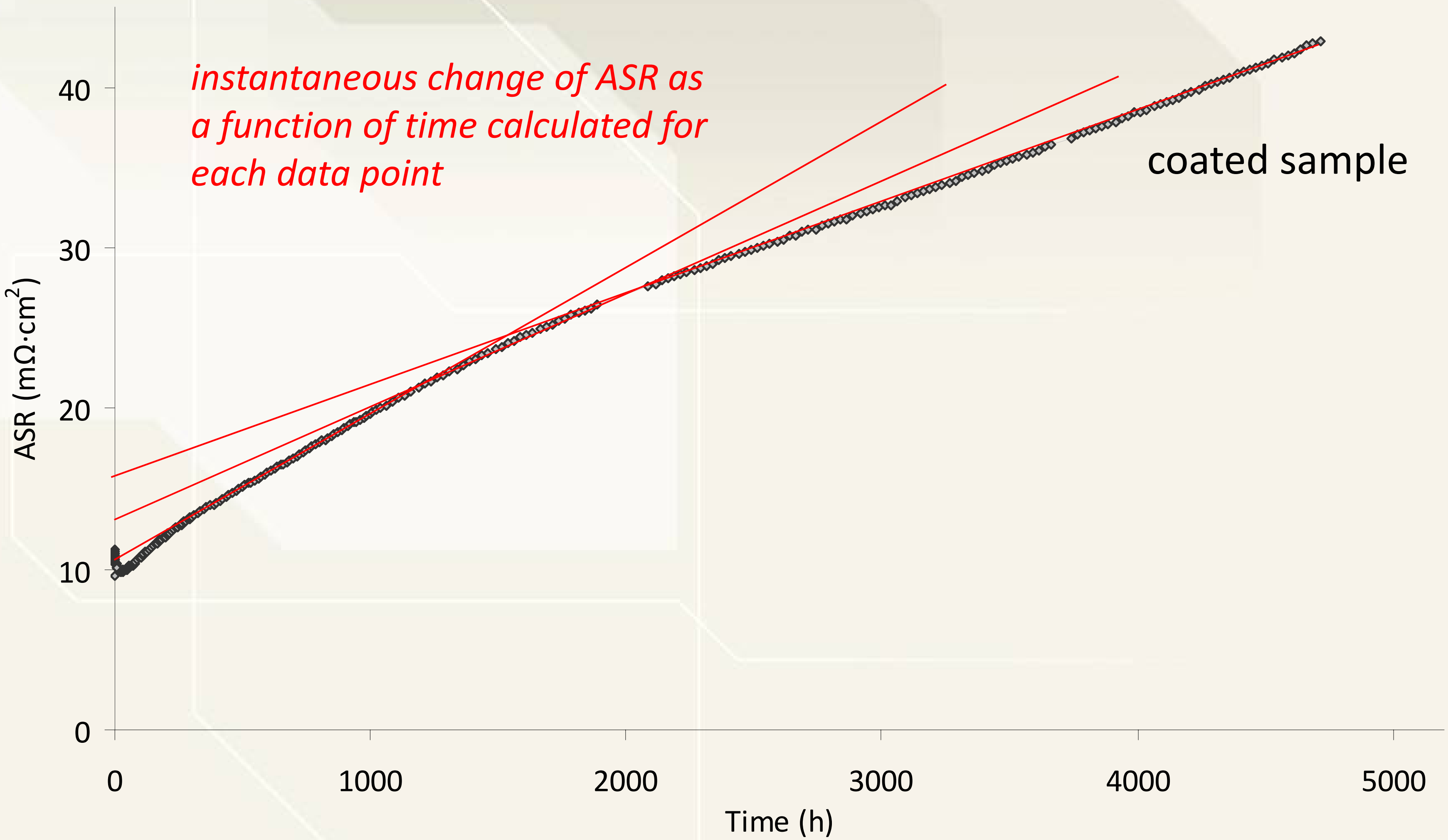
ASR Test Results – Experimental Alloy 580-6



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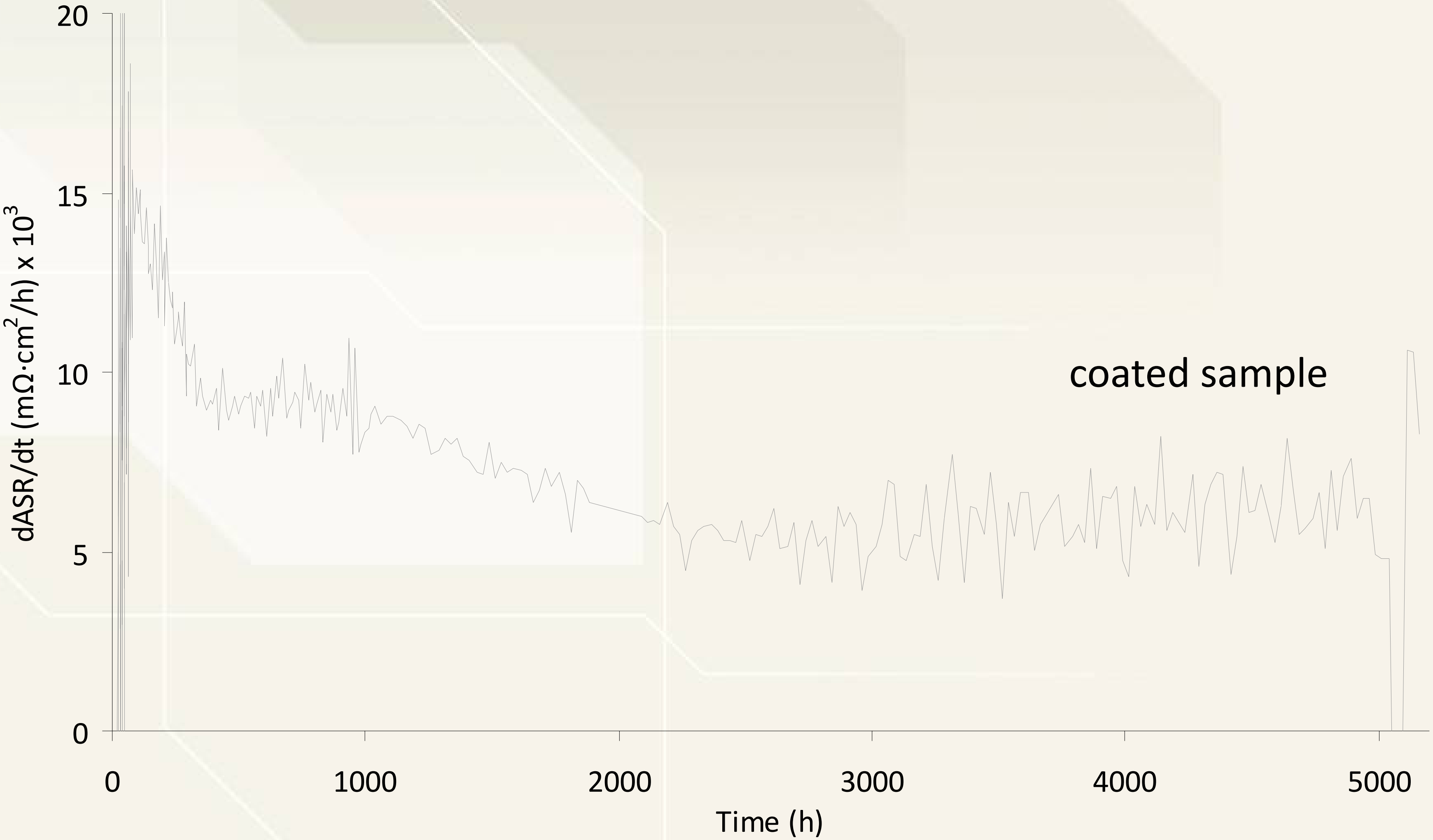
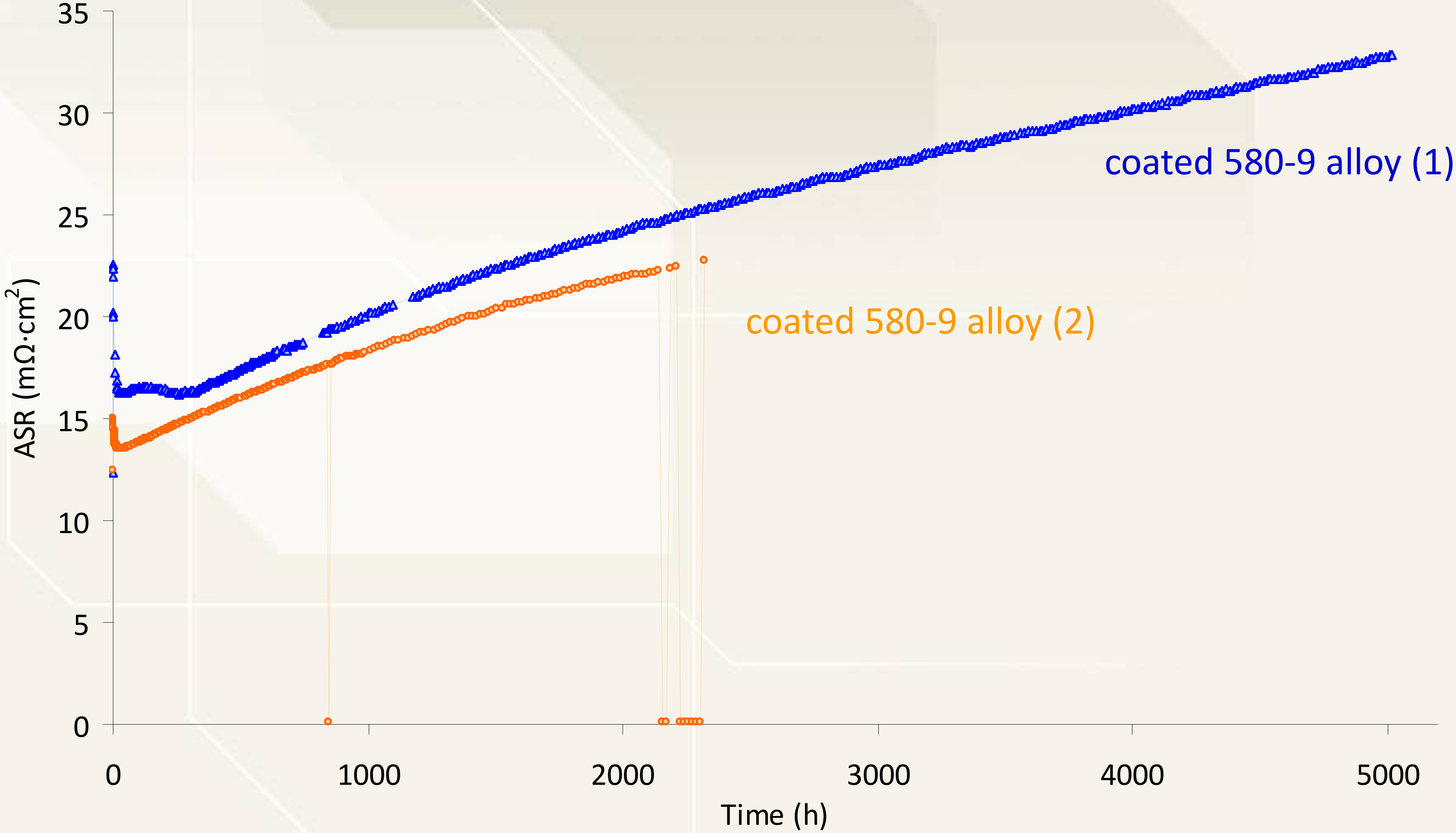
ASR Test Results – Experimental Alloy 580-6



ASR Test Results – Experimental Alloy 580-9



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ASR Test Results – Experimental Alloy 580-9

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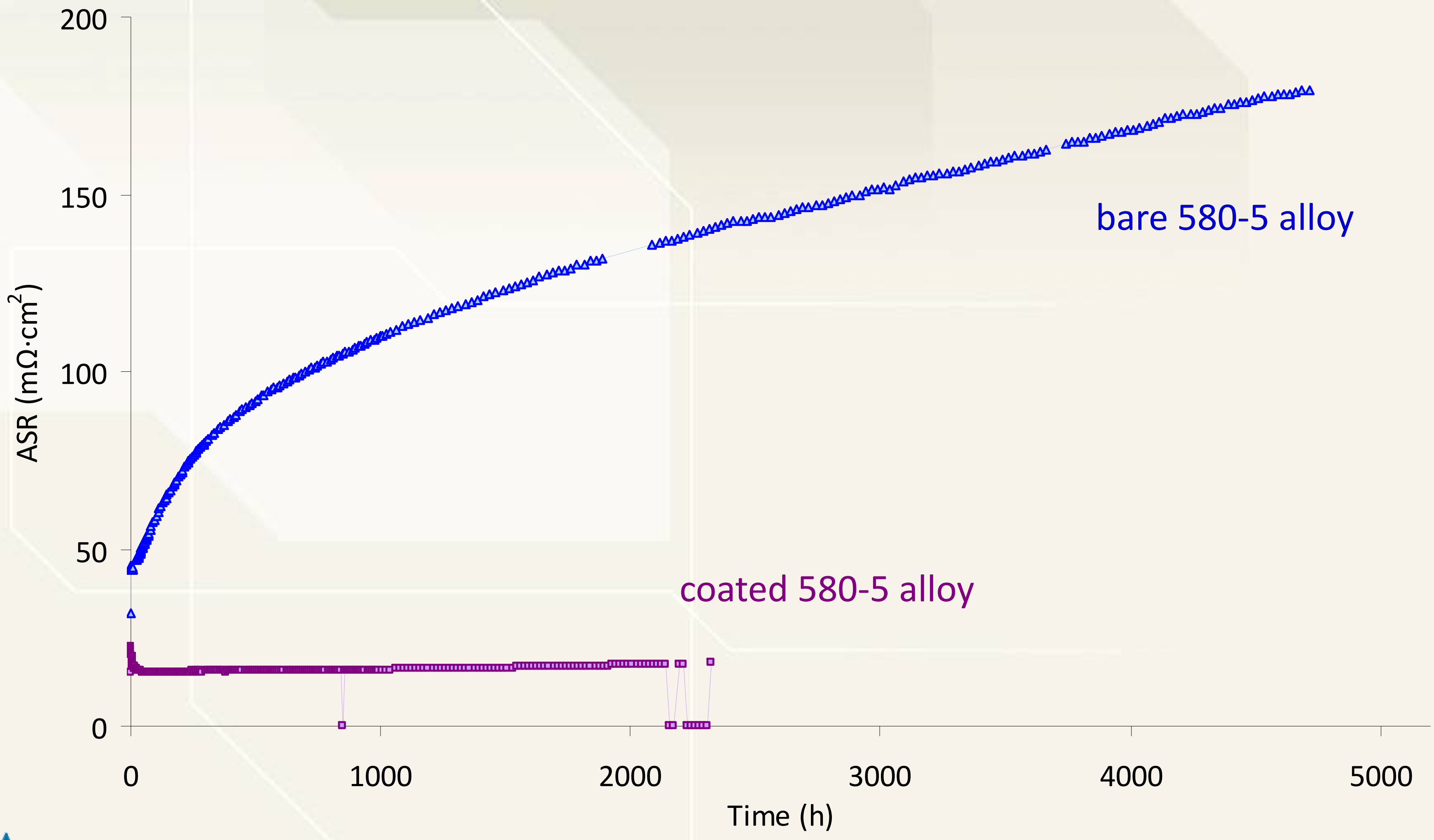
ASR Test Results – Experimental Alloy 580-5



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ASR Test Results – Experimental Alloy 580-5

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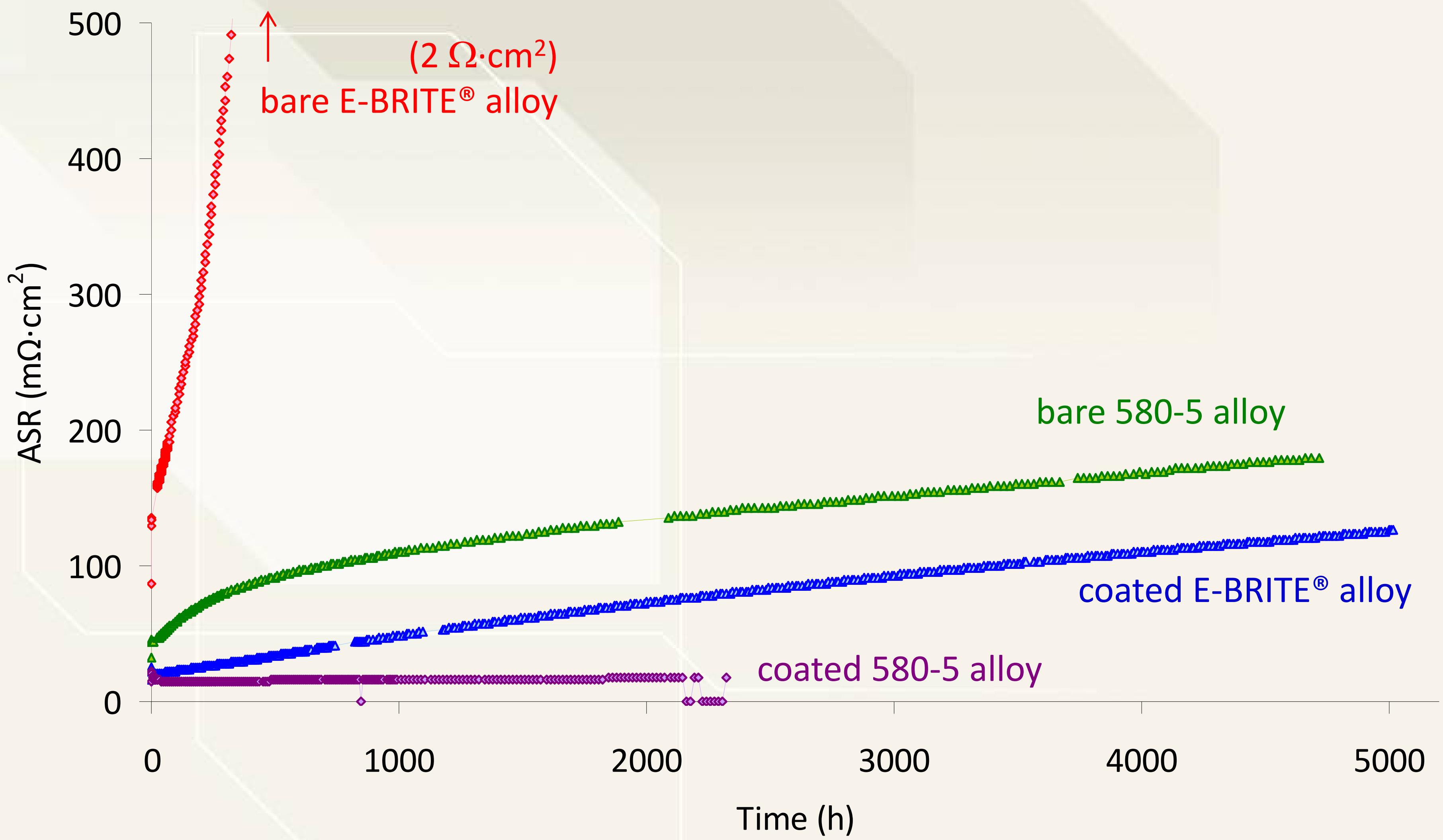
High-Cr Alloy ASR Test Results



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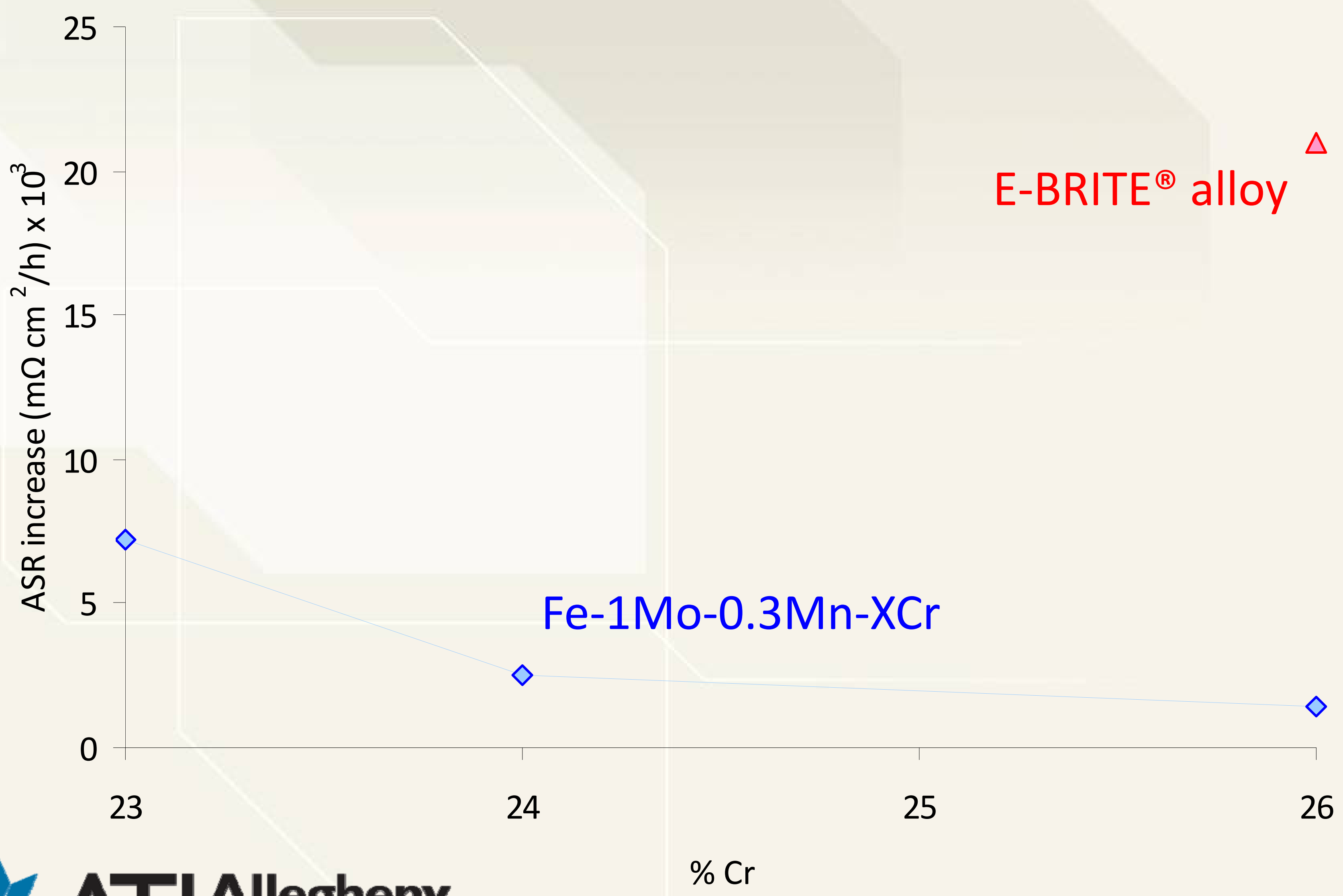
Effect of Manganese on High-Chromium Alloys



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ASR Test Results – Summary

- Reducing silicon to low levels with lower-Cr alloys tends to reduce the rate of ASR increase but also tends 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

Presentation Overview

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Current Focus – Revised Phase II

- Third generation alloy development
  - Primary focus on ATI 441HP™ variants
  - Secondary focus on E-BRITE® alloy variants
- Post-processing techniques to reduce ASR increase
  - Primary focus on surface/bulk deformation
  - Secondary focus on metal surface chemistry modification
- Statistical analysis of breakaway oxidation
- Delivery of ATI 441HP material to Industrial Teams and PNNL / NETL

ATI Allegheny Ludlum

Alloy Development – 3rd Generation Compositions

Alloy	Rate of ASR Increase ($m\Omega \cdot cm^2$/1,000 h)
EXP. 580-6	6.9 (coated)
580-6 MOD 1	*increase Nb*
580-6 MOD 2	*increase Nb (max)*
580-6 MOD 3	*increase Nb and Si*
580-6 MOD 4	*modified stabilization*
580-6 MOD 5	*increase Mn*
EXP. 580-5	1.4 (coated)
580-5 MOD 1	*reduce Cr*
580-5 MOD 2	*increase Nb*

Post-Processing Techniques

- All starting material to be sourced from production lots of ATI 441HP™ stainless steel
- Localized surface deformation
  - Grit blasting
  - Rough surface grinding
  - Mill surface (acid pickled) will serve as a control
- Delocalized through-thickness deformation by temper rolling
  - 0.50 mm thick material lab rolled to 50% reduction (0.25 mm thick)
  - Mill-annealed 0.25 mm thick material will serve as a control
- Desiliconization
  - Treated and untreated material tested side-by-side
  - Examine two different gauges (thickness effect on a diffusional process)

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Oxidation Study

- Reduction of silicon to low levels reduces the rate of ASR increase
- Tends 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 silicon
  - Varying silicon content
  - Test numerous small samples
    - Low requirements for precision measurements
    - Rigorous requirements for sample numbers to gain statistical significance
  - Temperatures ranging from 800-900°C
  - Humidified air (SCG)
  - Statistical analysis of data and generation of breakaway oxidation prediction map

ATI Allegheny Ludlum

Production ATI 441HP™ Material

- Material for testing and for fabrication of prototypes and full scale SOFC stacks
- Material produced from two master coils
- Chemistry consistent between the coils
- Over 18,000# of cut sheets and coils have been shipped to Industrial Teams and PNNL/NETL
- Samples are available

ALC Coil Numbers >>	04228C143	08448C714
C	0.015	0.013
Mn	0.3	0.3
Si	0.38	0.38
Cr	17.7	17.8
Ni	0.3	0.3
Al	0.04	0.03
Cu	0.1	0.13
Nb	0.4	0.5
Ti	0.20	0.22
N	0.12	0.14
YS	67.5 ksi	52.3 ksi
UTS	85 ksi	75 ksi
% El	22%	30%
Grain Size	-	ASTM 9.5
Hardness	84 HRBW	189 HV_{500}
Test gauge	3.4 mm (0.133")	0.25 mm (0.010")

ATI Allegheny Ludlum

Summary

- Promising commercial compositions identified
- Minor chemistry modifications yielded significant improvement in electrical properties of surface
- *Phase II – Revised* initiated on 01 April 2009
  - Third generation compositions
  - Post-processing
  - Lifetime definition and prediction
- Full-size coil of ATI 441HP™ stainless produced and distributed to Core Technology and Industrial Teams

ATI Allegheny Ludlum

Acknowledgements

- Wayne Surdoval and program management at NETL for their support of this program
- Dr. Jeffry Stevenson and Dr. Z. Gary Yang at PNNL for providing coated specimens and for input on the construction and operation of the ASR test facilities
- Industrial teams for various collaborative efforts

ATI Allegheny Ludlum

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