DE-FE0027947

MINIMIZING CR-EVAPORATION FROM BALANCE OF PLANT COMPONENTS BY UTILIZING COST-EFFECTIVE ALUMINA-FORMING AUSTENITIC STEELS

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Outline

- Project Team Information
- Background
- Technical Approach
- Project Objective
- Project Structure
- Project Schedule
- Project Budget
- Risk Management
- Technology Readiness Level (TRL)/commercialization goals

Project Team Information

PI - Xingbo Liu

- Program Management
- Cr-release Measurement
- On-Cell Testing
- TEA
- Phase II Preparation

FuelCell Energy

Ultra-Clean, Efficient, Reliable Power

Co-PI - Hossein Ghezel-Ayagh
Alireza Torabi

- Cr-release Measurement
- TEA
- Phase II Preparation

OAK RIDGE
National Laboratory

Co-PI - Mike Brady

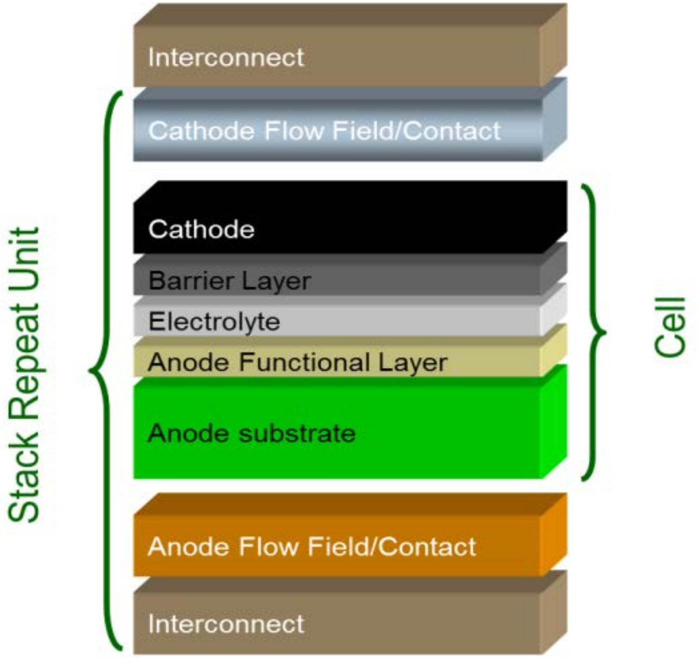
- AFA Development
- Oxidation Measurement

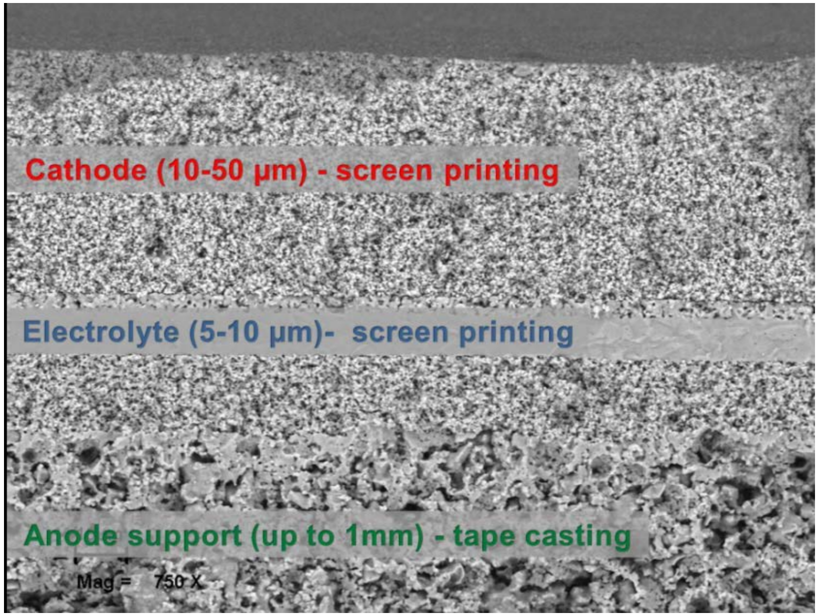
CARPENTER

Industrial Partner – Samuel Kernion

- AFA Manufacturing

Background - SOFC Stacks

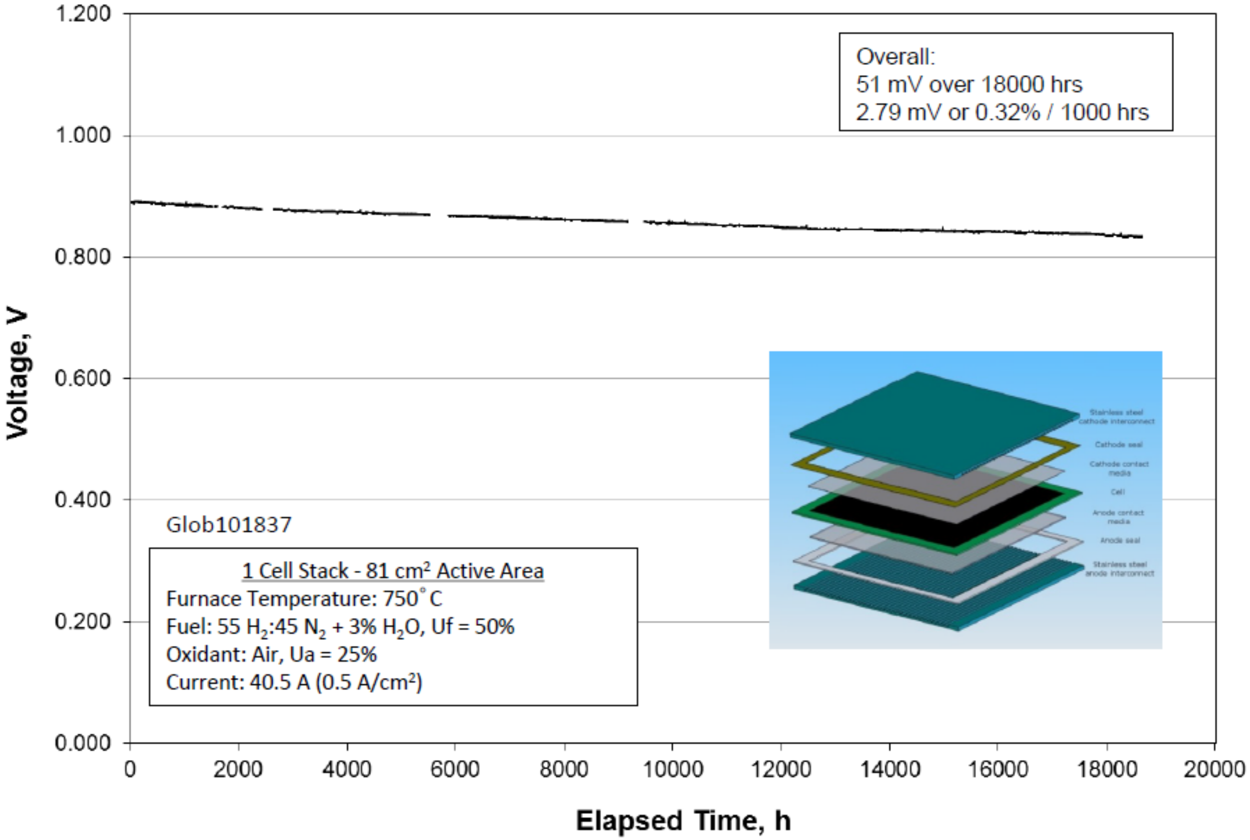




Component	Materials	Thickness	Porosity	Process
Anode	Ni/YSZ	0.3 - 1 mm	~ 40%	Tape casting
Electrolyte	YSZ	5 - 10 μm	< 5%	Screen printing
Cathode	Conducting ceramic	10 - 50 μm	~ 30%	Screen printing

* NETL 2015 SOFC Workshop – FCE Presentation

SOFC Long-term Degradation



Overall:
51 mV over 18000 hrs
2.79 mV or 0.32% / 1000 hrs

Glob101837

1 Cell Stack - 81 cm² Active Area
Furnace Temperature: 750˚C
Fuel: 55 H_2:45 N_2 + 3% H_2O, Uf = 50%
Oxidant: Air, Ua = 25%
Current: 40.5 A (0.5 A/cm²)

➡ Long-term cell endurance was verified in >2 years of operation with a 0.32%/1000h performance degradation

* NETL 2015 SOFC Workshop – FCE Presentation

SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Chemical reaction with YSZ electrolyte.

$$La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \qquad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s)$$

- Strontium segregation related issues

$$2Sr_{La}^{'} + V_{O,LSCF}^{\bullet\bullet} + 2O_O^x \leftrightarrow 2SrO(s)$$

- Poisoning of the cathode (e.g. by CO_2, chromium species etc.)

$$SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \qquad SrO(s) + CO_2(g) \rightarrow SrCO_3(s)$$

$$2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g)$$

Cr_2O_3 Related Degradations

- Cr poisoning of SOFC Cathode

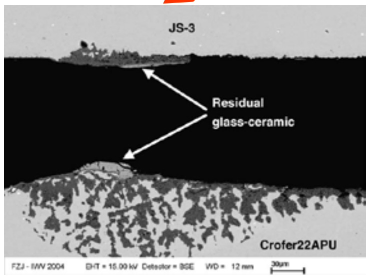
$$Cr_2O_3(s) + 1.5O_2(g) = 2CrO_3(g)$$

$$Cr_2O_3(s) + 1.5O_2(g) + 2H_2O(g) = 2CrO_2(OH)_2(g)$$

- Reactions with other components

$$2Cr_2O_3(s) + 4BaO(s) + 3O_2(g) = 4BaCrO_4(s)$$

$$CrO_2(OH)_2(g) + BaO(s) = BaCrO_4(s) + H_2O(g)$$



J. Power Sources 152 (2005) 156–167

- Cr_2O_3 Sources: Interconnect and BOP

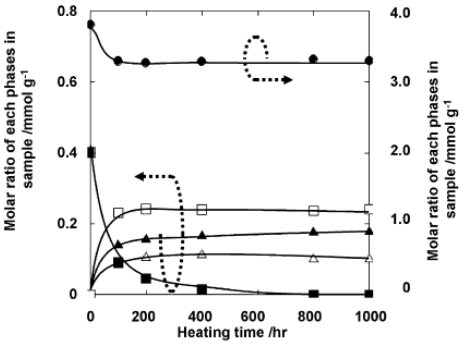
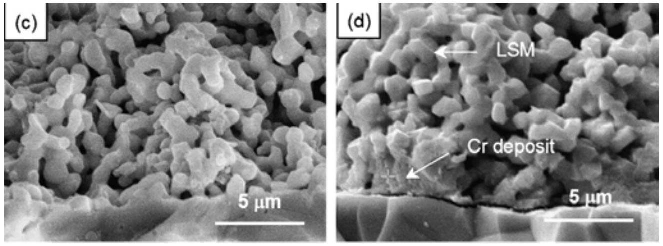
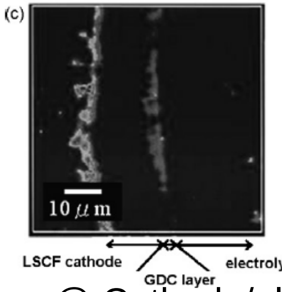


Fig. 4. Molar ratio of phases in LSCF–Cr_2O_3 mixture during heating at 1073 K for 0–1000 h: (●) LSCF, (■) Cr_2O_3, (□) $SrCrO_4$, (▲) $CoCr_2O_4$ spinel, (△) $(Fe,Cr)_2O_3$.



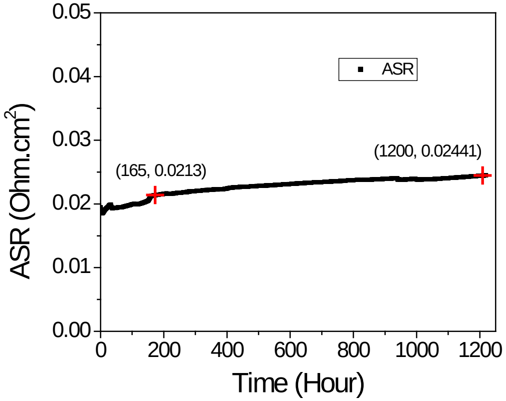
J. Power Sources 162 (2006) 1043–1052

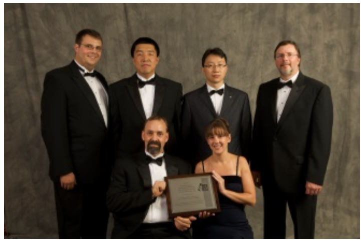


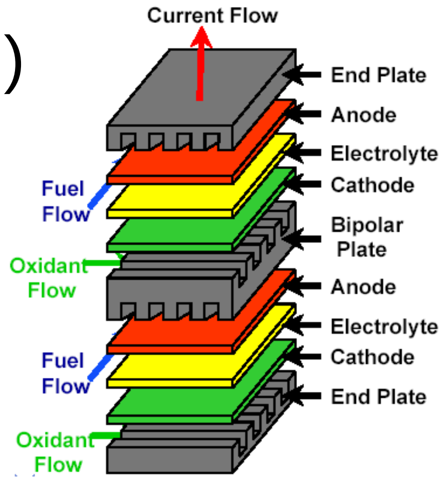
Cr-distribution @ Cathode/electrolyte Interface

SOFC Interconnect Coatings

- Various Spinel Coatings (Mn-Co, Mn-Cu, etc.)
- PVD, CVD, Spray, Electroplating, EPD







Coating impedes degradation of SOFCs

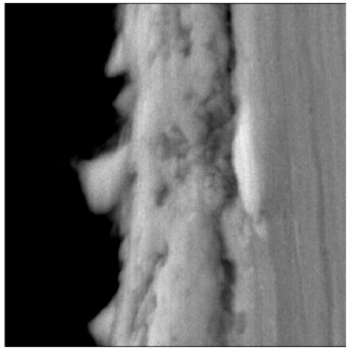
Researchers at West Virginia University have put their heads together with scientists from the Department of Energy's National Energy Technology Laboratory. The result of this collaboration has been the development of a new manganese-cobalt coating for solid oxide fuel cell interconnects.

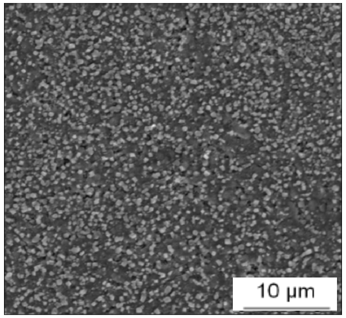
The new process uses an electroplating technique that reportedly does not harm the environment, and offers significant advantages in terms of cost and ease of operations over other coating methods, the researchers say. Extensive on-cell testing has demonstrated considerable improvement of SOFC degradation compared to uncoated interconnects, the researchers contend.

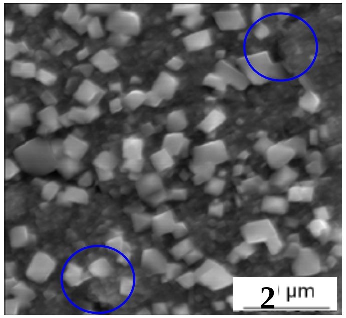
The team has published its research findings in two peer-reviewed journals, and a patent disclosure of the process also has been filed. In addition, team members report exceptionally positive feedback from the report on the coating presented at the 2008 MS&T Conference last October.

Recent results during on-cell testing showed considerable improvement of SOFC degradation with this coating method as compared with uncoated interconnects. Further improvements are anticipated as optimized plating variables are identified. (Visit: http://netl.doe.gov) ■

Junwei Wu, a Ph.D. student at West Virginia University, demonstrates environmentally friendly electroplating for SOFC interconnects.

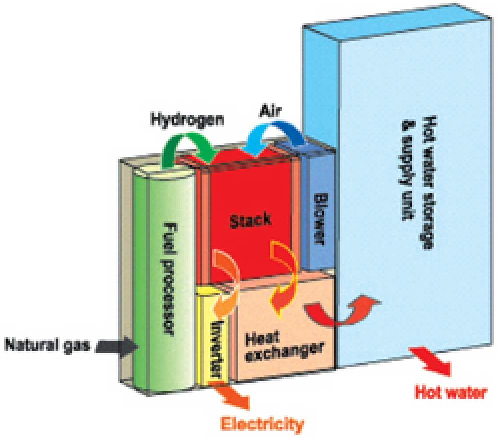






Project Technical Approaches

Developing Cost-Effective Alumina Forming Austenitic Stainless Steels (AFA), to replace Austenitic Stainless Steel 316L and Ni-base Superalloy Inconel 625, for Key **Balance of Plant (BOP) components**, to minimize Cr-Poisoning of SOFC Cathode



Compression Plate in BOP

Stainless Steels with Higher-Temperature Capability Needed

- Driver: Increased efficiencies with higher operating temperatures in power generation and chemical process systems.

- Key issues are creep and oxidation resistance.

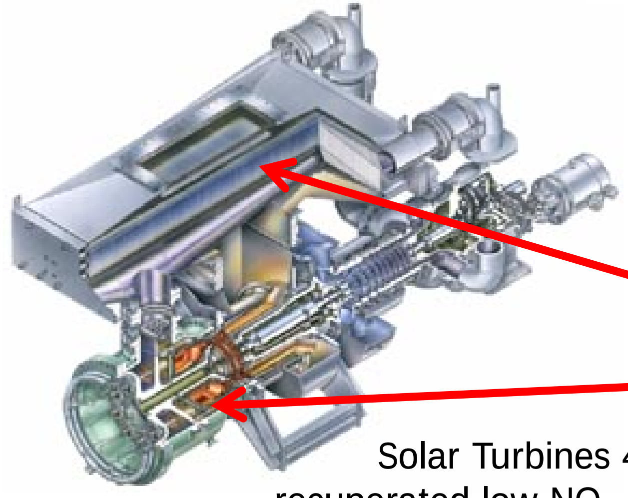
  - Significant gains have been made in recent years for improved creep resistance via nano MX precipitate control (M = Nb, Ti, V; X = C, N).

  - Stainless steels rely on Cr_2O_3 scales for protection from high-temperature oxidation.
    -Limited in many industrial environments (water vapor, C, S)
    -Most frequent solution is coating: costly, not always feasible

Development Effort for Low Cost, Creep and Oxidation-Resistant Structural Alloy for Use from ~600-900°C

- **Approach: Al_2O_3-forming austenitic stainless steels**
  - -background and potential advantages
- **Current alloy status for microstructure, mechanical properties, and oxidation resistance**

Initial target(s)



Solar Turbines 4.6 MW Mercury 50 recuperated low NO_x gas turbine engine

Fossil Power Steam Turbine, Boiler Tubing

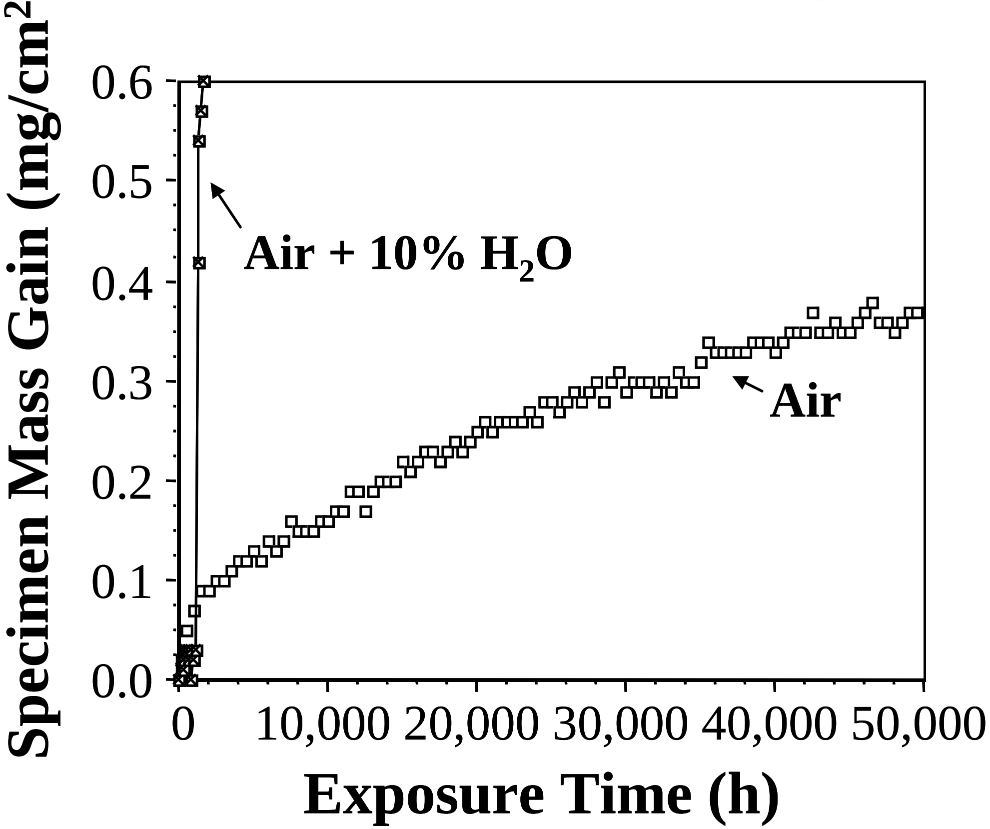
Recuperator, Casing

HMN-Series (High-, Intermediate- and Low-Pressure) Steam Turbine for Combined-Cycle and Steam Power Plants

➢ Tubing in chemical/process industry, etc. also targeted.

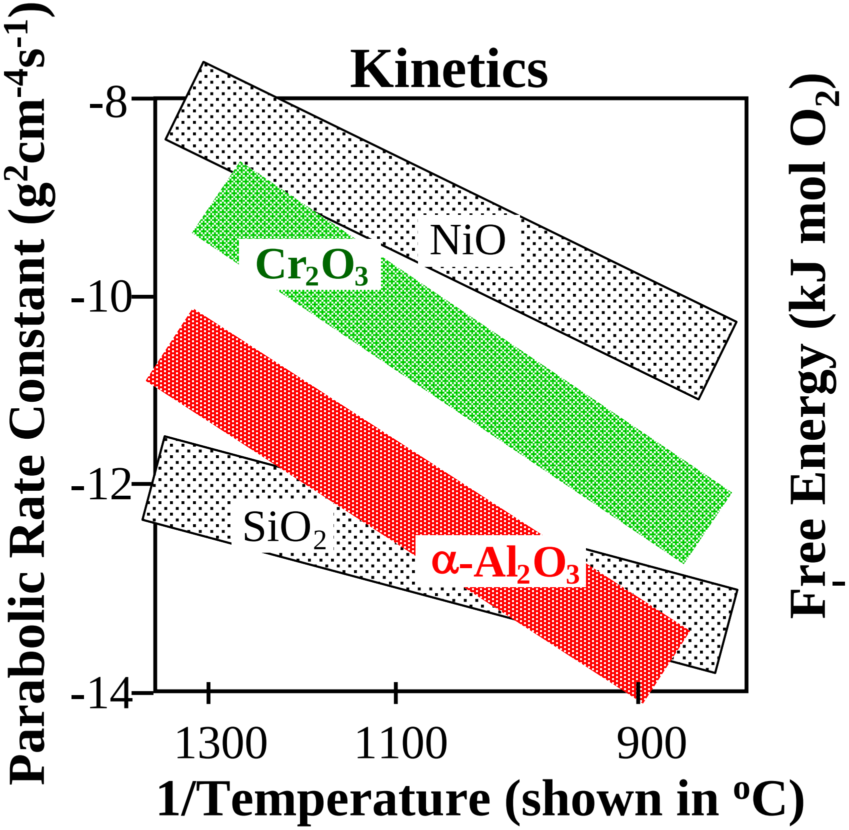
Cr_2O_3-Formers Suffer Accelerated Attack in Water-Vapor Environments

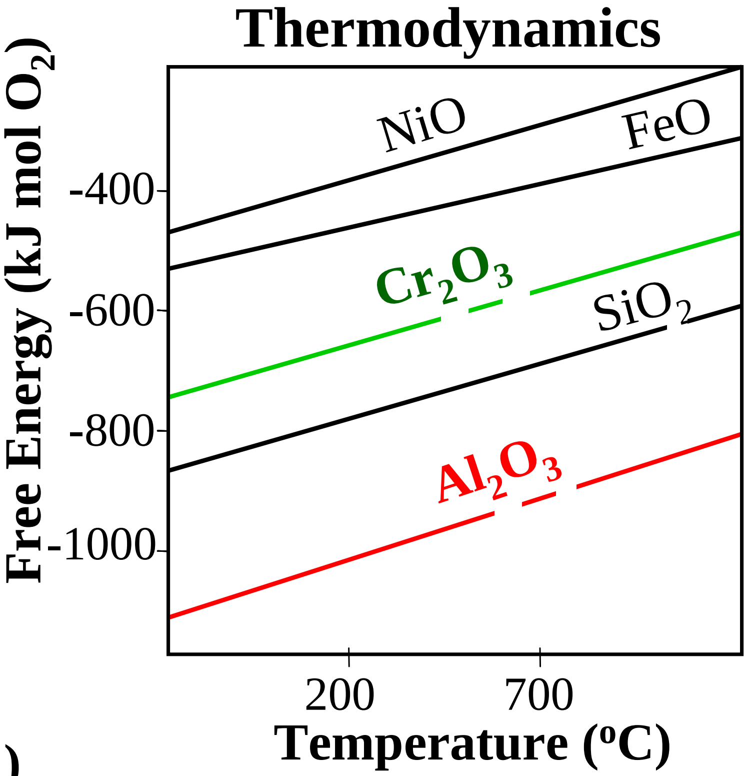
Oxidation Data for 347 Stainless Steel Foil (Fe-18Cr-11Ni base) at 650°C in Air and Air + 10% Water Vapor (Pint et al.)



- Susceptibility from Cr-oxide volatility in H_2O and enhanced internal oxidation
- Particularly important for thin components such as heat exchangers

Al_2O_3 Scales Offer Superior Protection in Many Industrially-Relevant Environments





- Al_2O_3 has lower growth rate/more thermo. Stability in oxygen than Cr_2O_3
- Al_2O_3 highly stable in water vapor
- Al_2O_3 generally (not always) better resistance to carburization and sulfidation

Few Available Options for Al_2O_3-Forming Alloys

- FeCrAl Alloys: Open body-centered cubic structure is weak
  - -Not suitable for most structural uses above ~500°C

- Ni-Base Alloys/Superalloys: too costly
  - -5 to 10 times greater cost than stainless steels
  - -limited to niche applications with ultrahigh performance needs

- Typically use Al_2O_3-forming coatings or surface treatments
  - -increases cost
  - -not feasible for many components/applications

Challenge of Alumina-forming Austenitic (AFA) Stainless Steel Alloys

- Numerous attempts over the past ~30 years (e.g. McGurty et al. alloys from the 1970-80’s, also Japanese, European, and Russian efforts)

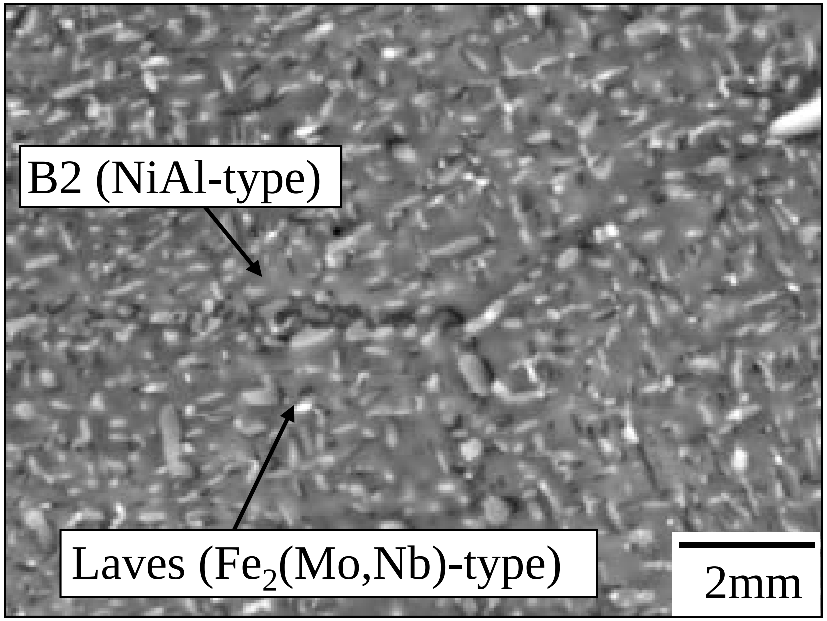
- Problem: Al additions are a major complication for strengthening
  - strong BCC stabilizer/delta-ferrite formation (weak)
  - interferes with N additions for strengthening

- Want to use as little Al as possible to gain oxidation benefit
  - keep austenitic matrix for high-temperature strength
  - introduce second-phase (intermetallics/carbides) for precipitate strengthening

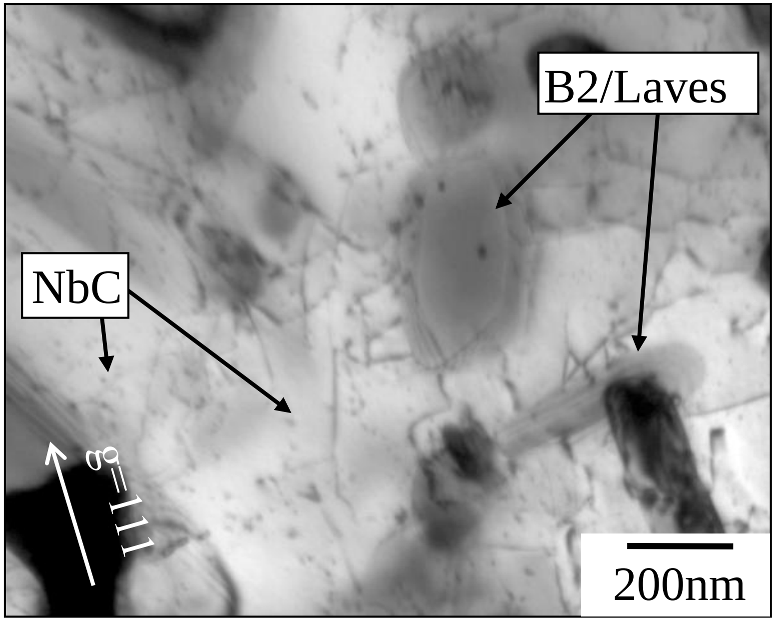
Composition and Microstructure Considerations for AFA Stainless Steels

Typical Fe-(20-30)Ni-(12-15)Cr-(2.5-4)Al-(1-3)Nb-0.1C wt.% Base AFA Alloy Microstructure After Creep

SEM



TEM

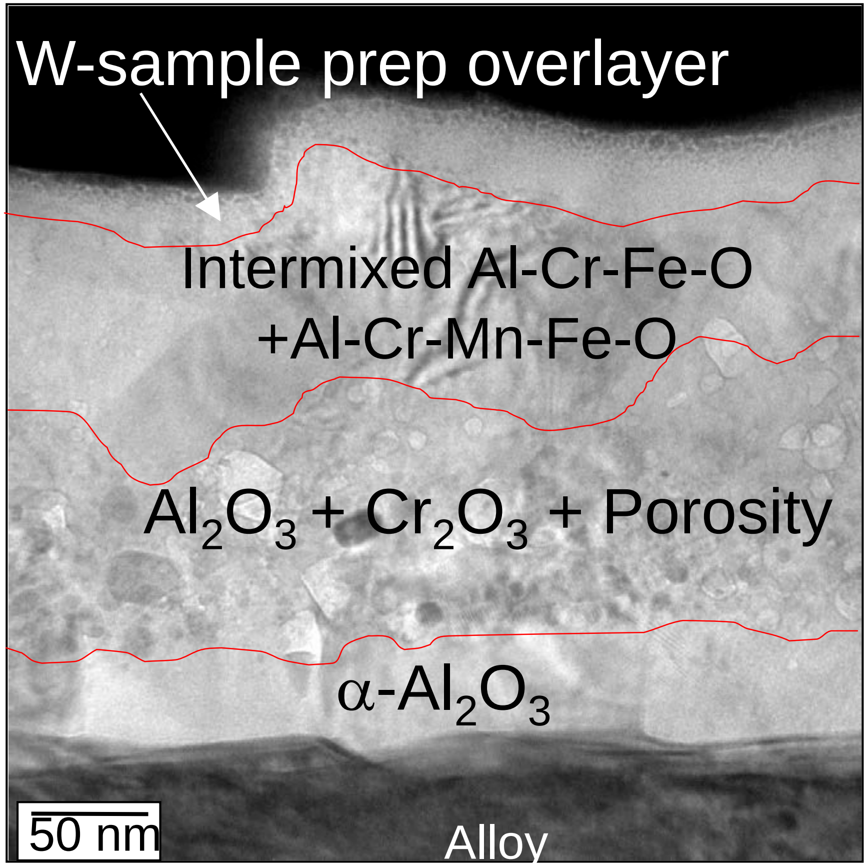


- Creep Strength
  - balance Al, Cr, Ni, to maintain single-phase FCC austenitic matrix
  - Nano NbC and micron/submicron B2-NiAl + Fe_2Nb base Laves precipitates

- To form protective alumina:
  - Ti+V < 0.3 wt.%; Nb > (0.6-1) wt.%; N < 0.02 wt.%

AFA Form Transient Al-Rich Oxide Overlying Inner, Columnar a-Al_2O_3

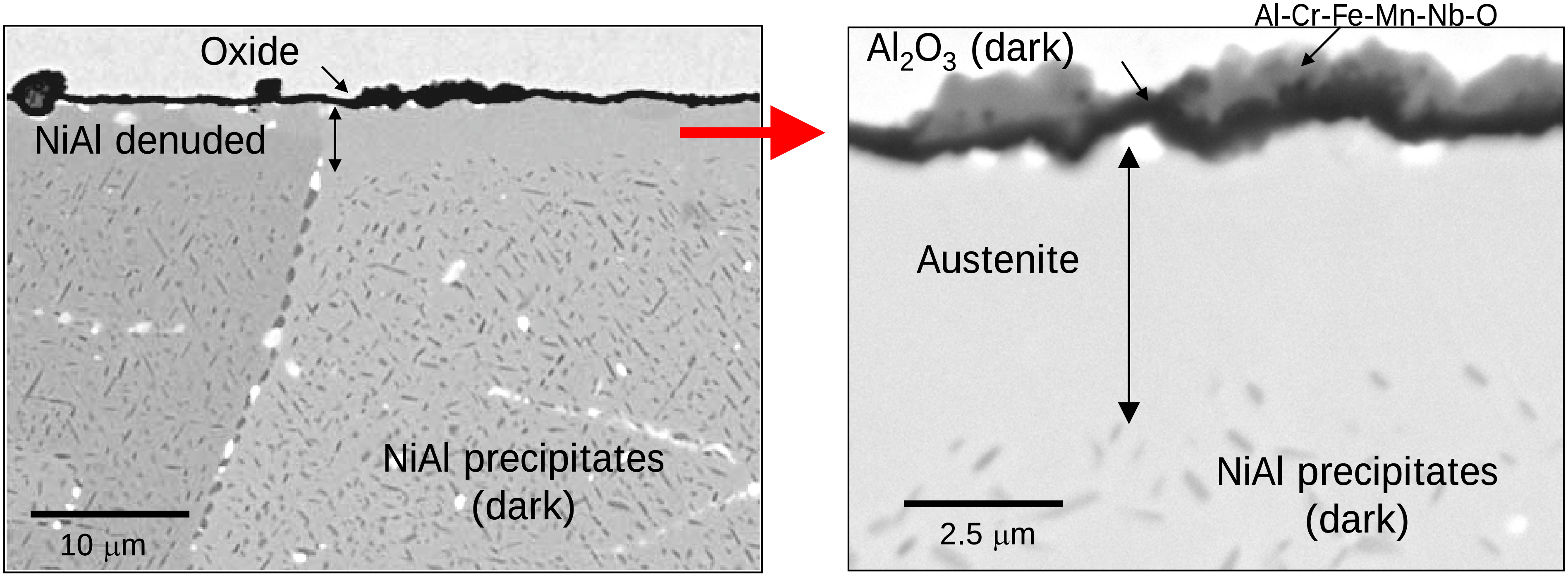
TEM of HTUPS 4 After 1000 h at 800°C in Air + 10% Water Vapor



- α-Al_2O_3 the source of the excellent oxidation resistance
- Occasional transient nodules 0.5-5 μm thick, some Nb-oxide also detected

Austenite Matrix and NiAl Precipitates Key to Establishing and Maintaining Alumina

SEM-BSE Images of Typical Oxidized Cross-Section
for a 4 Al wt.% AFA Alloy (900°C/100h/in air)



- Austenite matrix composition key to forming alumina (Al, C, Cr, Ni)
- NiAl precipitates act as Al reservoir to maintain alumina
- Nb as MC or Laves important in H_2O

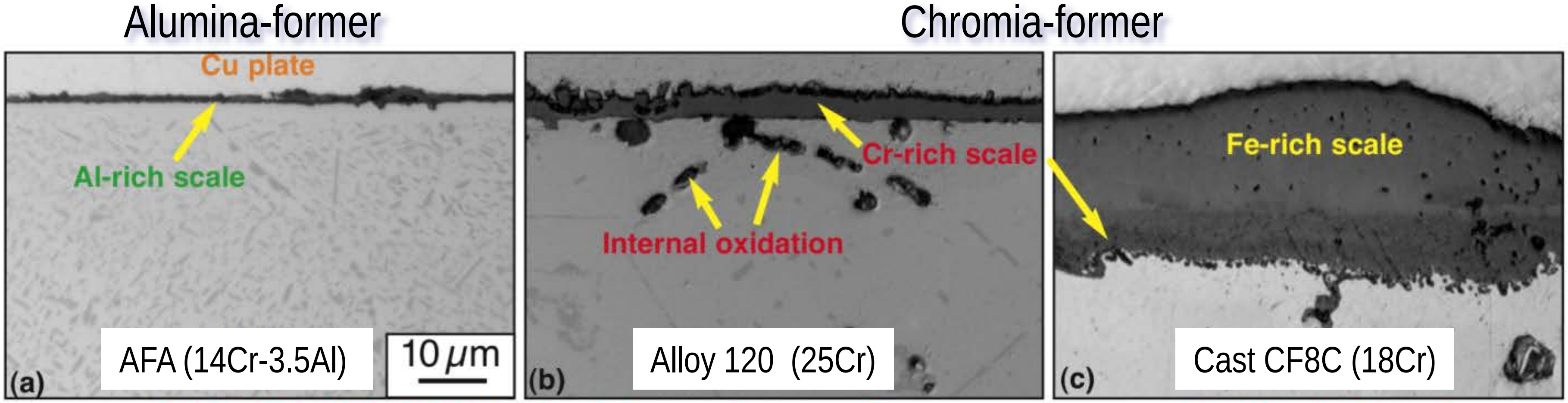
AFA is a Family of Alloys

❑ Three different grades of AFA series (wrought alloys)

- **AFA Grade**: Fe- (14-15)Cr-(2.5-4)Al-(**20-25**)**Ni**-(**1-3**)**Nb** wt.% base
  - *~750-950 ° C temperature limit for Al_2O_3 formation*
  - *higher temperature ranges need higher Ni and Nb + rare earth additions*
  - *MC and $M_{23}C_6$ strengthening*
- **Low Nickel AFA^{LN} :** Fe-14Cr-2.5Al-**12Ni**-0.6Nb-**5Mn**-3Cu wt.% base
  - *~ 650-700 ° C temperature limit for Al_2O_3 formation*
  - *$M_{23}C_6$ strengthening*
- **High Creep resistance γ'-Ni_3Al strengthened AFA**: Fe-(14-19)Cr-(2.5-3.5)Al-(**30-35**)**Ni**-3Nb + wt.% base
  - *~750-850 ° C temperature limit for Al_2O_3 formation*

❑ Cast AFA: *Cast version of AFA alloys*

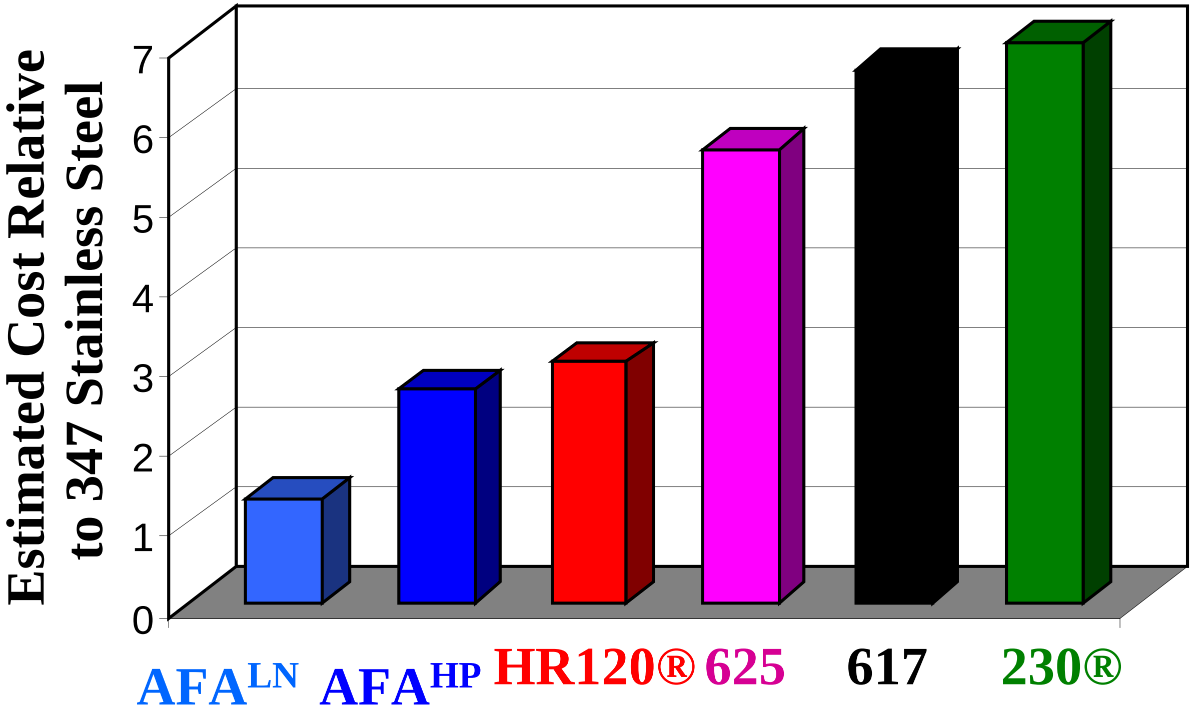
Advantage Compared to Conventional Chromia Scales



800 °C, 10,000 h in laboratory air

5,000 h in air

AFA Lower Raw Material Cost to High-Ni Austenitics/Ni-Base Alloys



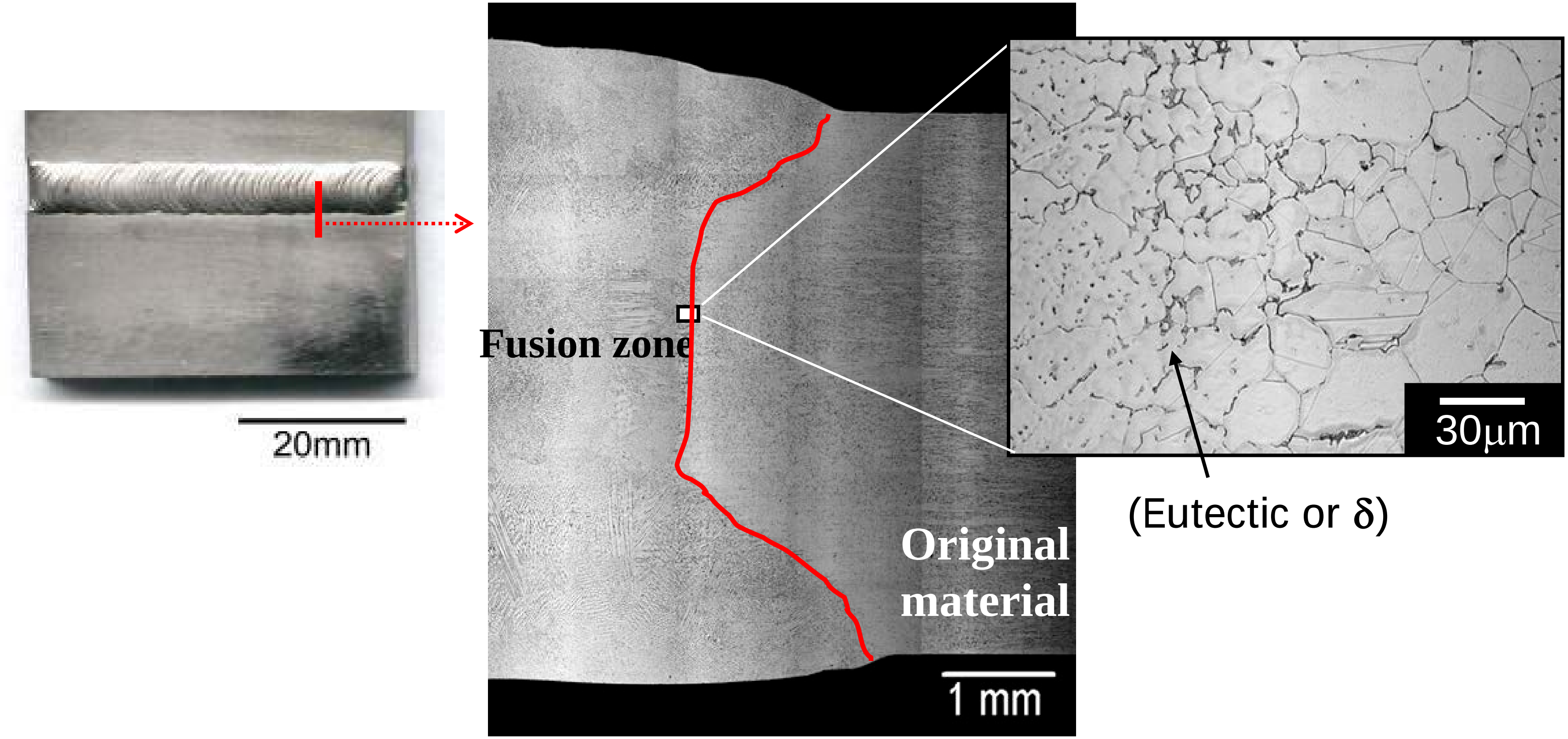
New Alloys (Iron-Base Al_2O_3 formers)

Conventional Nickel-Base Alloys (Cr_2O_3 formers)

AFA Alloys Appear to be Readily Welded (limited data)

Gas Tungsten Arc Weld

(used same alloy as a filler material)

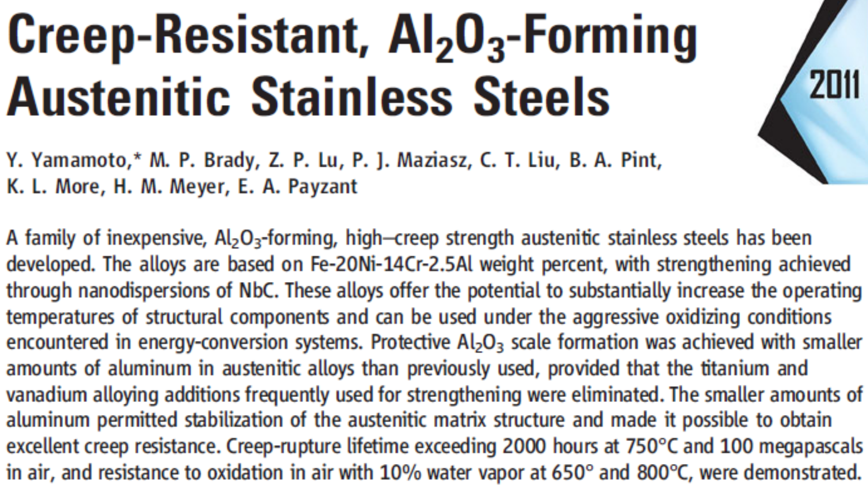


- No cracking at fusion/heat-affected zones

AFA Highlights

Science AAAS

Creep-Resistant, Al2O3-Forming Austenitic Stainless Steels
Y. Yamamoto, *et al.*
Science **316**, 433 (2007);
DOI: 10.1126/science.1137711



Creep-Resistant, Al_2O_3-Forming Austenitic Stainless Steels

Y. Yamamoto,* M. P. Brady, Z. P. Lu, P. J. Maziasz, C. T. Liu, B. A. Pint, K. L. More, H. M. Meyer, E. A. Payzant

A family of inexpensive, Al_2O_3-forming, high–creep strength austenitic stainless steels has been developed. The alloys are based on Fe-20Ni-14Cr-2.5Al weight percent, with strengthening achieved through nanodispersions of NbC. These alloys offer the potential to substantially increase the operating temperatures of structural components and can be used under the aggressive oxidizing conditions encountered in energy-conversion systems. Protective Al_2O_3 scale formation was achieved with smaller amounts of aluminum in austenitic alloys than previously used, provided that the titanium and vanadium alloying additions frequently used for strengthening were eliminated. The smaller amounts of aluminum permitted stabilization of the austenitic matrix structure and made it possible to obtain excellent creep resistance. Creep-rupture lifetime exceeding 2000 hours at 750°C and 100 megapascals in air, and resistance to oxidation in air with 10% water vapor at 650° and 800°C, were demonstrated.

2011 R&D 100

AFA Steel team: Alan Liby, Alexander DeTrana, Mike Brady, Yukinori Yamamoto; Michael Santella, Joseph Marasco, Bruce Pint, Craig Blue

ORNL's AFA licensed to Carpenter Technology Corp.

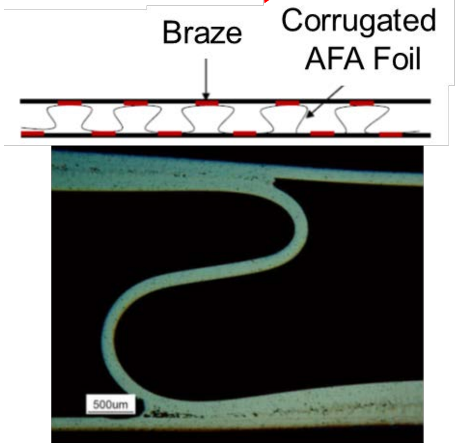
AFA Commercialization:

OC4 (14Cr-3.5Al-25Ni-2.5Nb) Products

Carpenter 10,000lb AFA heat (VIM/VAR)

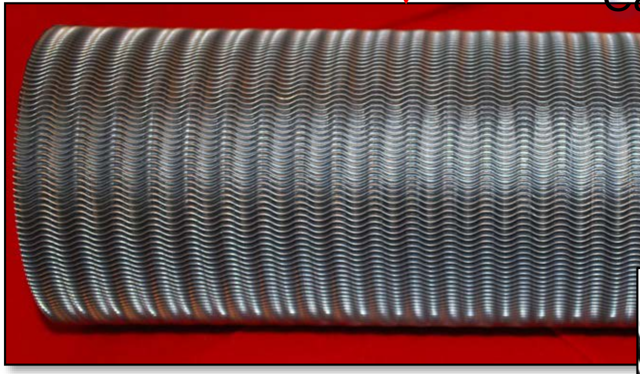
350 lb wire coil
Elgiloy to Capstone

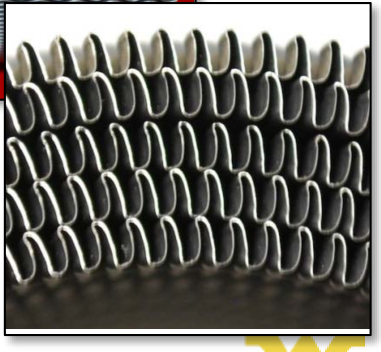
Elgiloy 8” wide, 300 lb, 3.2 mil coil for Capstone



UTRC 6 mil foil subscale brazed heat exchanger (foil by Elgiloy)

15” wide, 4 mil AFA foil for **Solar Turbines** recuperator (Metalwerks 2000lb heat, Haynes, Somers, Elgiloy)





Capstone folded 8” wide 3.2 mil Foil

Project Objectives – Phase I

- Develop and utilize cost-effective alumina forming austenitic steels (AFAs) for balance of plant (BOP) components and pipes in solid oxide fuel cell (SOFC) systems to minimize the Cr-poisoning and improve system stability;

- Systematically investigate the influence of the operation condition, i.e., temperature and moisture, on the oxidation and Cr-release from the AFA steels, and their effects on the degradation of SOFC performance

- Prepare for Phase II of the project, in which we will manufacture and test the related BOP components in industrial SOFC systems

Project Structure

Task 1.0	Project Management and Planning - WVU
Task 2.0	Developing and Manufacturing AFAs - ORNL & Carpenter
Subtask 2.1	AFA Development
Subtask 2.2	Microstructure Characterization
Task 3	Studies on Oxidation Kinetics, and Cr Evaporation in simulated SOFC environments – WVU & ORNL
Subtask 3.1	Oxidation Kinetics – ORNL
Subtask 3.2	Characterization of the oxide scale - ORNL
Subtask 3.3	Cr Evaporation Evaluation – WVU & FCE
Subtask 3.4	Contributions of partial pressure of different Cr species - WVU
Task 4.0	Cr-poisoning of SOFC cathode in associate with BOP materials - WVU
Subtask 4.1	Assembly of SOFCs with BOP Alloys
Subtask 4.2	Electrochemical Investigations
Subtask 4.3	Post-Mortem Analyses
Task 5	Preparation for Phase II – WVU, ORNL, Carpenter and FCE

Project Timeline

I.D.	Task	Year 1				Year 2	
		Q1	Q2	Q3	Q4	Q5	Q6
1.0	Project Management	■◆	■	■	■	■	■
2.0	Developing & Manufacturing AFAs						
2.1	AFA Development	■	■	■	■		
2.2	Microstructure Characterizations		■		■		
3.0	Oxidation and Cr Evaporation in Simulated SOFC Environments						
3.1	Oxidation Kinetics			■		■	
3.2	Scale characterization			■		■	
3.3	Cr Evaporation Evaluation			■		■◆	
3.4	Contributions of partial pressure of different Cr species				■		■
4.0	Investigation on Cr-poisoning of SOFC in associate with BOP Alloys						
4.1	Assembly of SOFCs with BOP Alloys				■		
4.2	Electrochemical Investigations				■	■◆	
4.3	Post-Mortem Analyses					■	■
5.0	Phase II preparation						■◆

Note: ◆ = Decision Points

Project Budget

	Period 1 (Year 1)		Period 2 (6 Months)		Total
	DOE Funds	Cost Share	DOE Funds	Cost Share	
West Virginia University	$ 231,577	$ 47,478	$ 108,422	$ 34,139	$ 421,616
Oak Ridge National Lab	$ 80,000	$ -	$ 50,000	$ -	$ 130,000
Fuel Cell Energy	$ 30,000	$ 7,500	$ -	$ -	$ 37,500
Carpenter Technology	0	$ 40,000	$ -	$ -	$ 40,000
Total	$ 341,577	$ 94,978	$ 158,422	$ 34,139	$629,116.00

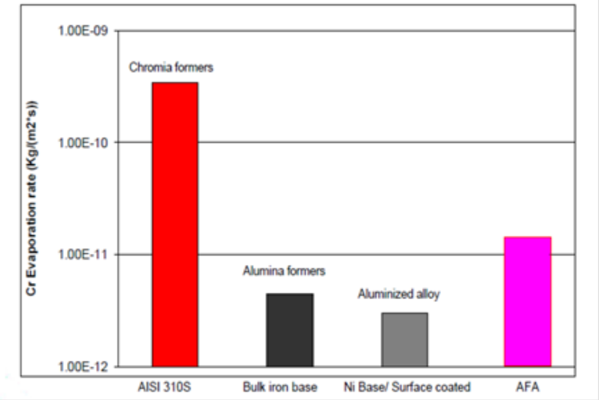
Risk Management

Risk 1		Achieving long-term protective alumina scale formation at the upper end of the SOFC BOP component use temperature range, ~900-950°C.
Risk 1 Mitigation		We have recently identified an AFA composition that can form alumina at 1100°C. This is achieved by higher Al, Cr and Ni levels, which will need to be evaluated for impacts on Cr release rate
Risk 2		The Cr content in the alumina-base surface oxide layer formed by AFA resulting in unacceptably high Cr release rates at both the high-temperature and low-temperature ends of the SOFC BOP component use temperature range.
Risk 2 Mitigation		Transient oxidation and the amount of Cr incorporated into the alumina-base surface layer will be critical. This can be controlled to an extent by minor alloying additions, particularly Hf, Y, Zr, as well as the balance of Al Cr, Ni, and Fe levels. For both issues we will use computational thermodynamic calculations to quickly screen proposed composition changes for feasibility (e.g. maintaining austenitic matrix, second phases formed).

TRL/Commercialization Goals

TRL (Phase I beginning) – 3

TRL (End of Phase I) – 4



Preliminary results on Cr-evaporation rates of AFA and related alloys (ORNL data)

Commercialization Goals –

Developing and Employing AFA in Industrial SOFC Systems

AFA Manufacture – Carpenter Technologies

SOFC Developer – Fuel Cell Energy

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