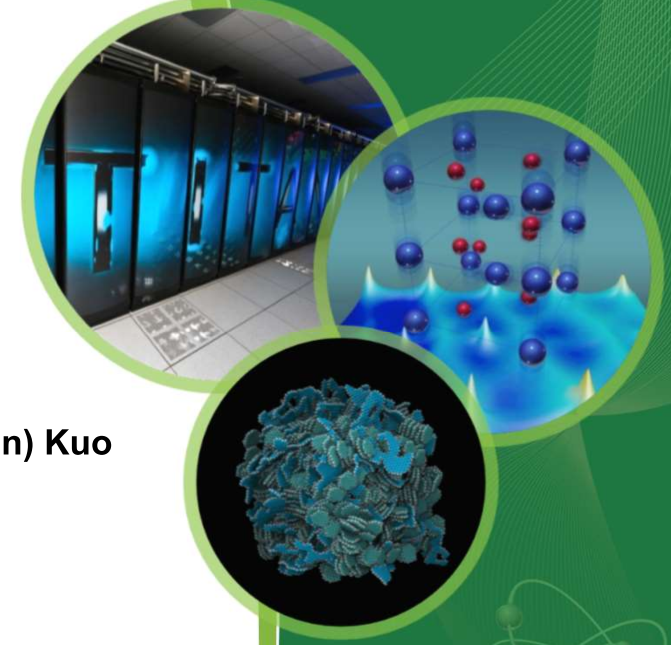
Advanced Design Concepts for Steels and Alloys Tailored for High-Temperature Fossil Applications



PI: Yukinori Yamamoto
Oak Ridge National Laboratory, Oak Ridge, TN 37831
E-mail: yamamotoy@ornl.gov

Co-investigators:
Bruce A. Pint
Oak Ridge National Laboratory, Oak Ridge, TN

Sudarsanam Suresh Babu, Benjamin Shassere*, Chih-Hsiang (Sean) Kuo
University of Tennessee, Knoxville, TN
(*Currently at Oak Ridge National Laboratory)

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2018 Crosscutting Research Portfolios Review
Pittsburgh, PA, April 10-12, 2018

OAK RIDGE
National Laboratory

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U.S. DEPARTMENT OF ENERGY | NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

Presentation Outline

- Backgrounds/Motivation:
  - *Concepts of "Advanced Alloy Design"*
- Update on FY17/18
  - *Development and optimization of "alumina-forming" high Cr FeCrAl ferritic alloys*
  - *Progress in "alumina-forming" austenitic stainless steels*
- Summary and Future works

Project Goals and Objectives

Goals: To identify and apply breakthrough alloy design concepts and strategies for incorporating improved creep strength, environmental compatibility/resistance, and weldability into three classes of alloys (ferritic, austenitic, and Ni-base) intended for use as heat exchanger tubes in fossil-fueled power generation systems at higher temperatures than possible with currently available alloys

Objectives: To develop and propose new creep-resistant, “alumina-forming”, cost-effective structural materials with guidance of computational thermodynamic tools

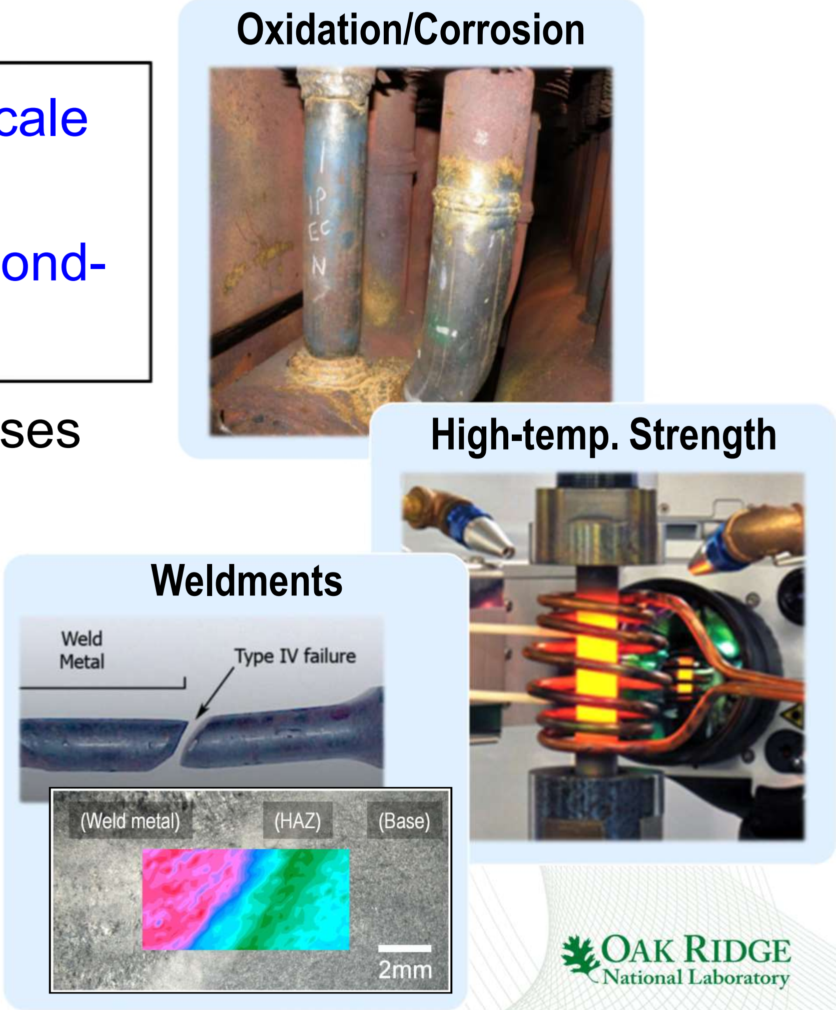
- Milestones (FY2018):

1. *Prepare at least one hot-rolled plate of the second scale-up heat of “alumina-forming” high Cr FeCrAl ferritic alloy with high W content (December 2017, Met)*
2. *Complete microstructural characterization and map hardness analysis of GTAW plate of the second scale-up heat (May 2018, in progress)*
3. *Complete cross-weld Charpy impact test, fracture toughness test, and short-term creep test (up to 2,000h) of the second scale-up heat (August 2018, in progress)*
4. *Complete alloy preparation and initial property screening including oxidation and ash-corrosion tests and fracture toughness test of proposed austenitic and Ni-based alloys (September 2018, in progress).*

Propose New Alloy Design Concepts for Heat Resistant Steels and Alloys

- ❑ "Compositional guide" to form stable alumina-scale for surface protection in extreme environments
- ❑ High temperature strength through multiple second-phase precipitate strengthening

- ➢ Apply the design strategy to three different classes of fossil energy structural materials
  - – **Ferritic (~600°C), Ferritic-Martensitic (~600-620°C)**
    - ➔ **high Cr containing FeCrAl alloys**
  - – **Austenitic (up to 650°C)**
    - ➔ **Alumina-Forming Austenitic stainless steels**
  - – **Ni-base (>700°C)**
    - ➔ Alumina-Forming Ni-base alloys

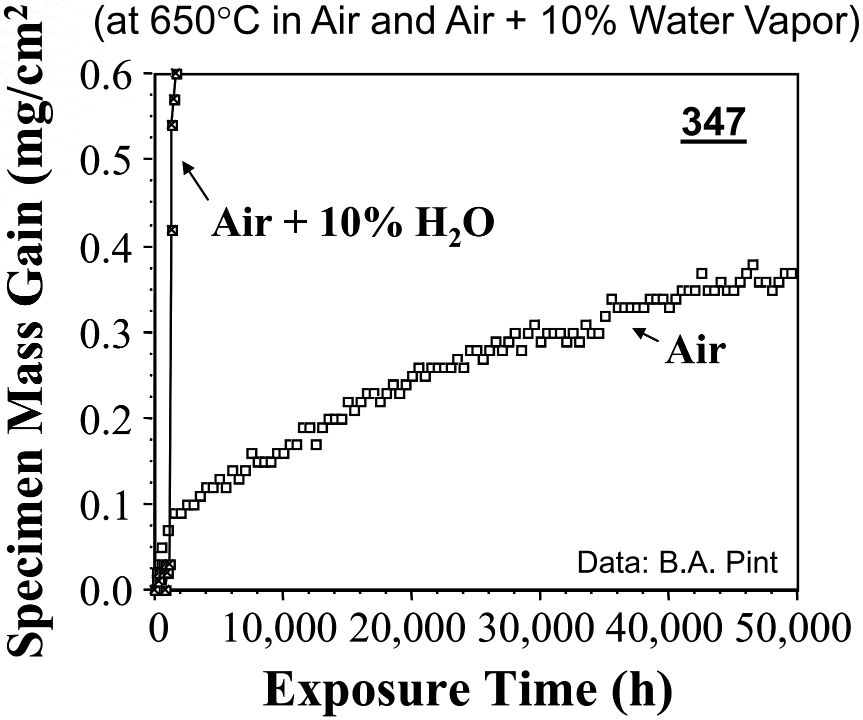


https://mts.com/en/products/industry/materials-testing/index.htm
http://www.ccj-online.com/prioritization-of-issues-improves-hrsg-reliability-performance/`

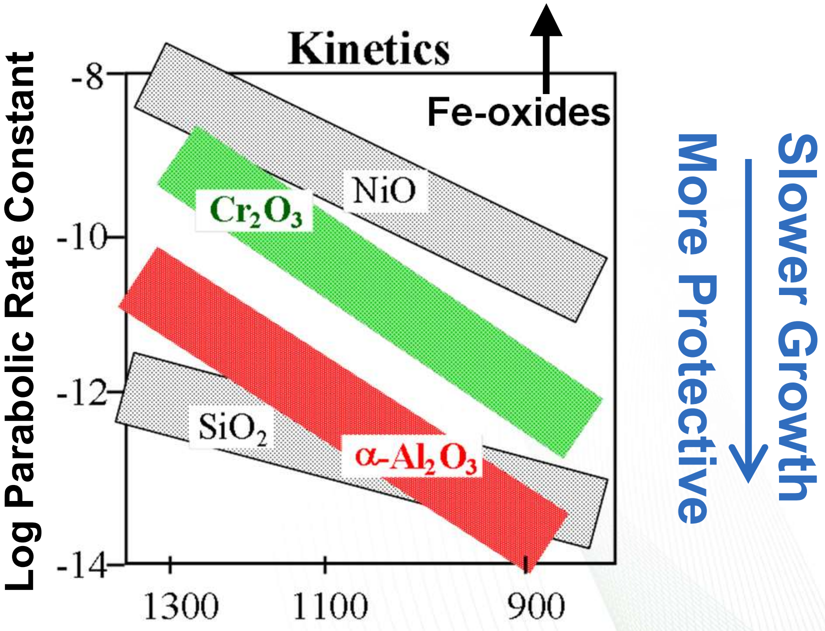
Alumina-scale is Attractive for High-temperature Use with Water-vapor Containing Environments

Oxidation Data for Chromia-forming 347 SS (18Cr-11Ni)

(at 650°C in Air and Air + 10% Water Vapor)



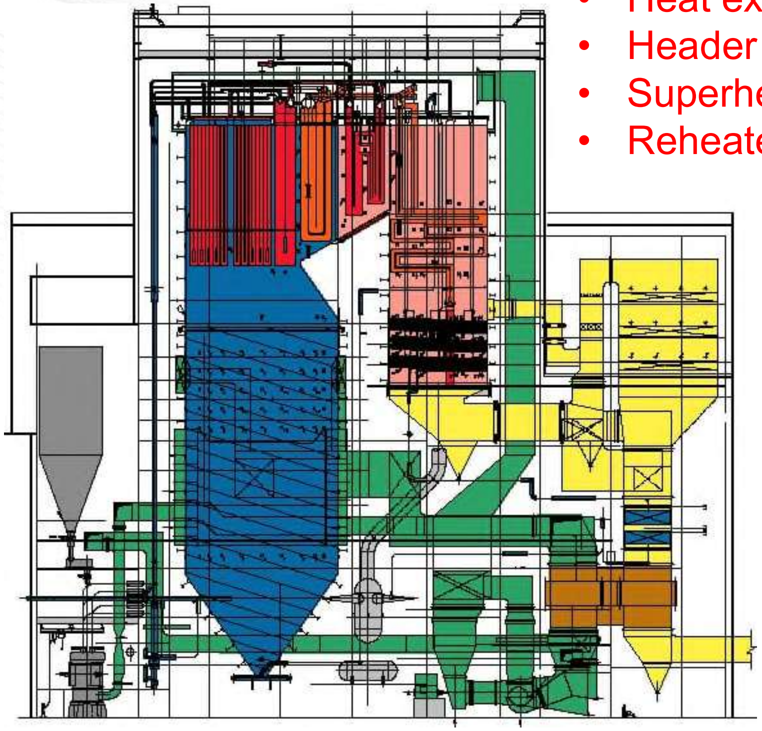
Parabolic Rate Constant of Oxide Scales



- x10 slower oxidation kinetics than chromia

Targets: Increase Service Temperature for Higher Efficiency

- Boiler
- Heat exchanger
- Header
- Superheatrer
- Reheater

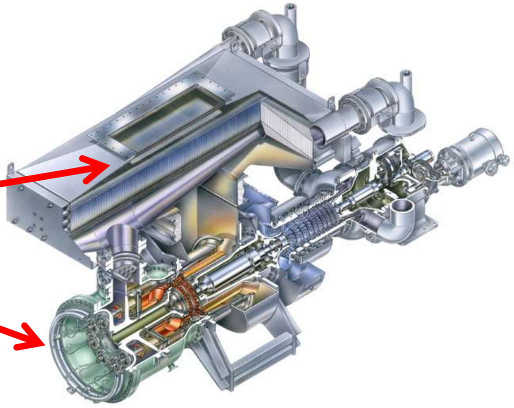


Alstom USC and AUSC Power Plants – J. Marion - NTPC/USAID Int. Conf. SC Plants - New Delhi, India, 22 Nov. 2013 – P 8

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

- Boiler Tubing
- Steam Turbine

- Recuperator
- Casing



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

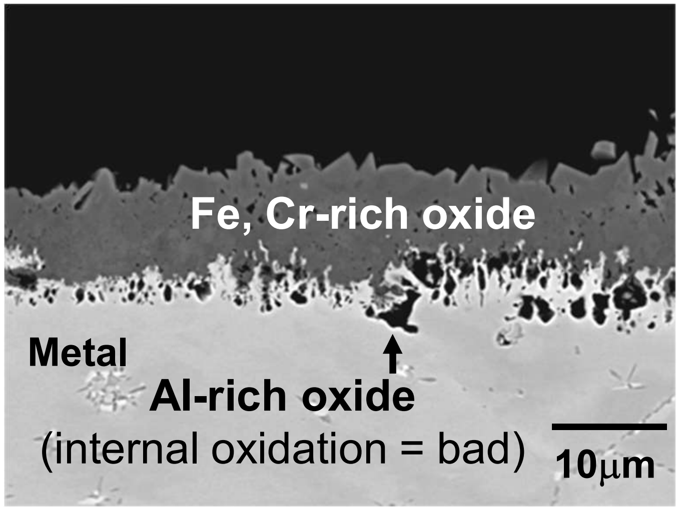
Currently Available Alumina-forming Alloys

- **Ni-base superalloys**:
  - Ni matrix (FCC) with intermetallic second-phase precipitate strengthening (e.g. coherent $L1_2$-Ni_3Al)
  - Attractive for high temperature use, but expensive
- **FeCrAl**:
  - Ferritic steels (BCC), mainly used as heating elements (e.g. Kanthal®)
  - Inexpensive, but weak at elevated temperature
  - PM-ODS approach improved high-temperature properties, but expensive
- **AFA (Alumina-Forming Austenitic) steels**:
  - Austenitic steels (FCC), developed as heat resistant steels at ORNL
  - Combined alumina-scale formability and multi second-phase strengthening
  - Fill the temperature gap between "Ferritic steels" and "Ni-base alloys"

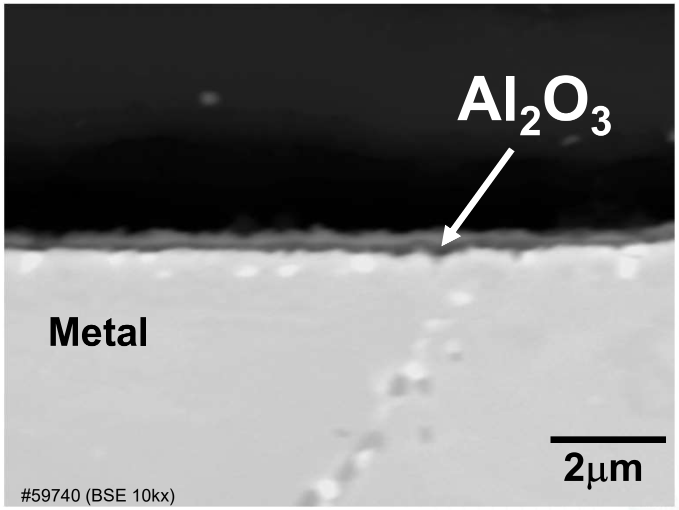
Effect of Minor Alloying on Alumina-scale Formation (AFA)

SEM Cross-Sections After 72 h at 800°C in Air

Fe-14Cr-20Ni-**2.5Al**-0.5V-0.3Ti-0.1C



Fe-14Cr-20Ni-**2.5Al**-0.9Nb-0.1C

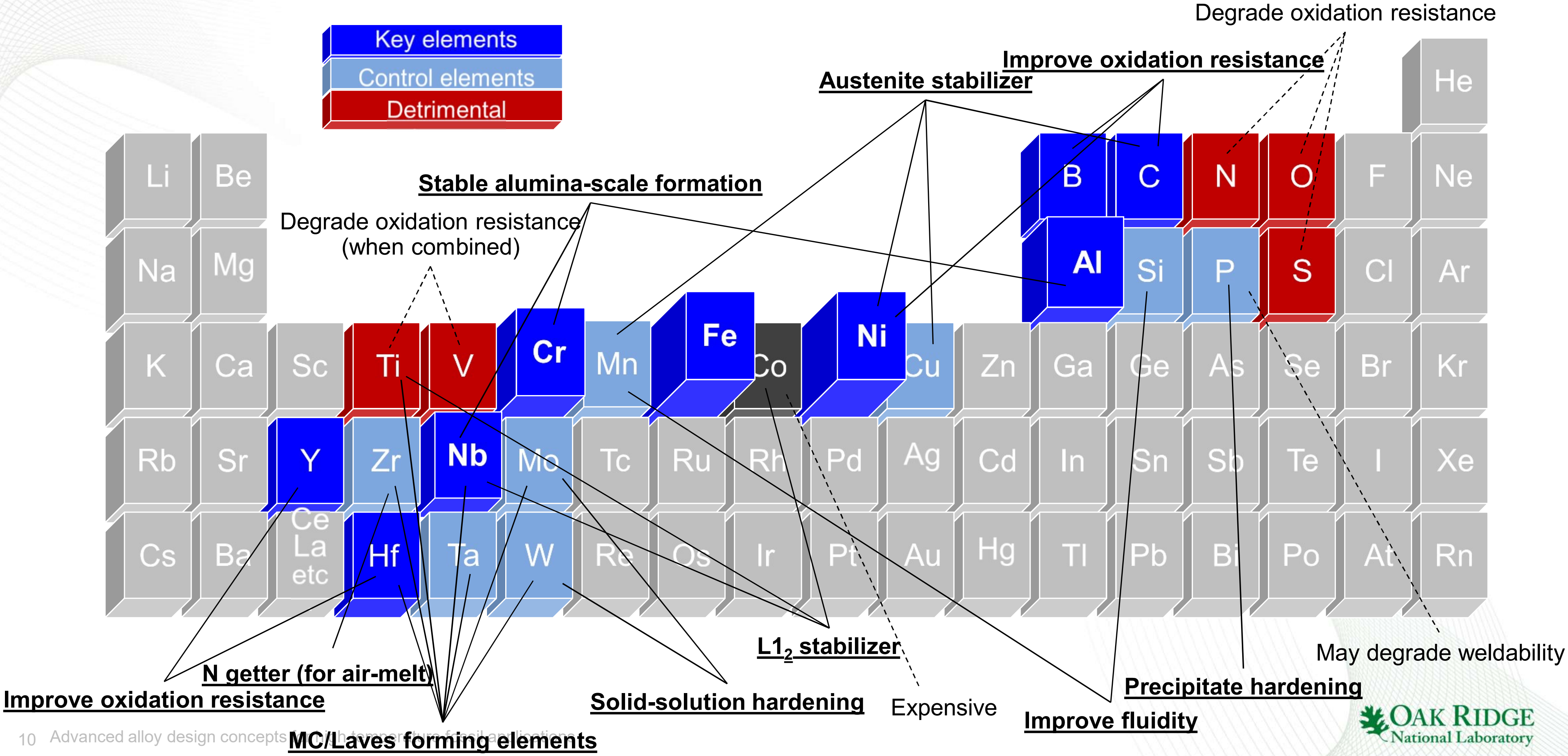


Note: 5x Higher Magnification for Alloy with Nb

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

Yamamoto et al. Science, 316 (2007) 433-436
Brady et al. JOM, 60 (2009) 12-18

Positive/Negative Effects on Alumina-forming Alloys



Key elements

Control elements

Detrimental

Degrade oxidation resistance

Improve oxidation resistance

Austenite stabilizer

Stable alumina-scale formation

Degrade oxidation resistance
(when combined)

$L1_2$ stabilizer

N getter (for air-melt)

Improve oxidation resistance

Solid-solution hardening

Expensive

May degrade weldability

Precipitate hardening

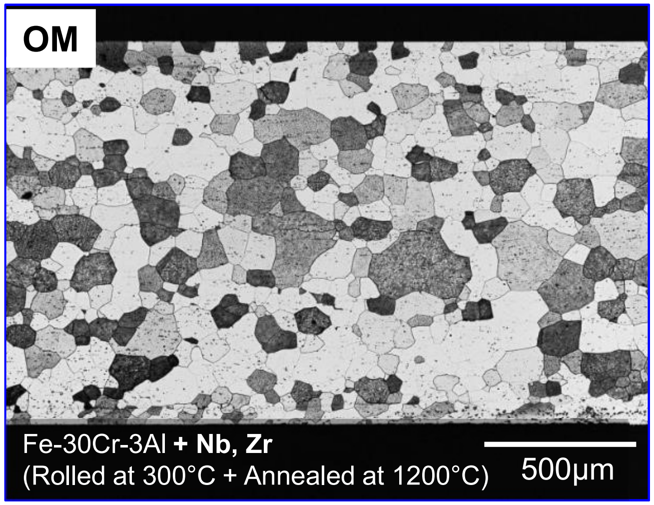
Improve fluidity

MC/Laves forming elements

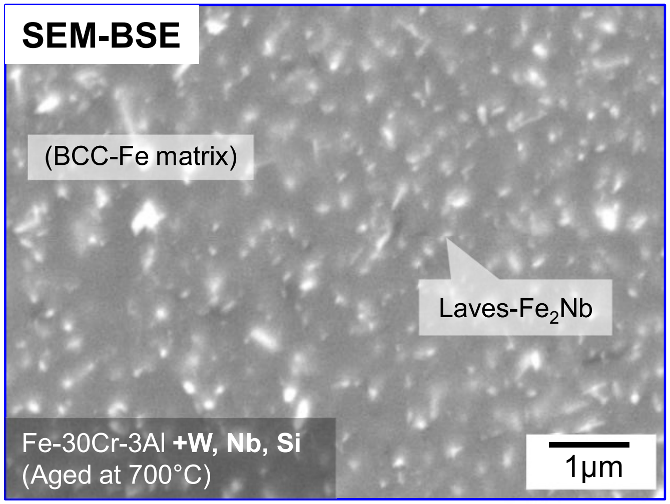
Alumina-Forming Ferritic Steels (High Cr containing FeCrAl alloys)

Design Corrosion/Oxidation/Creep Resistant Ferritic Steels

Fe-30Cr-3Al base alloys

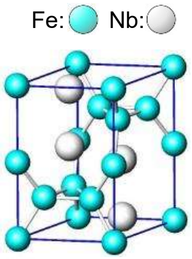


Fe-30Cr-3Al **+ Nb, Zr**
(Rolled at 300°C + Annealed at 1200°C)



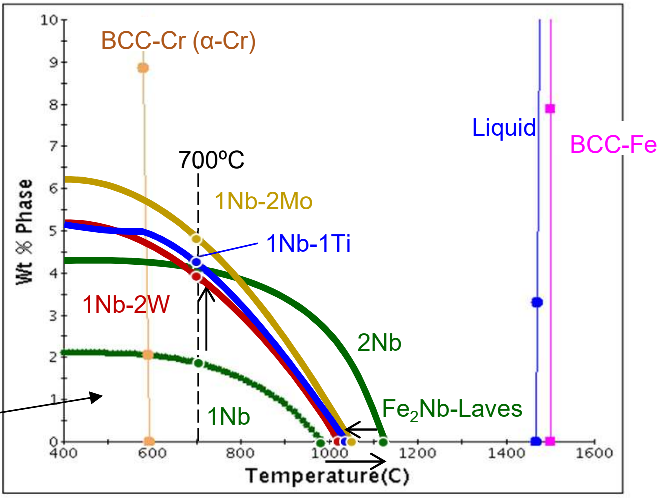
Fe-30Cr-3Al **+W, Nb, Si**
(Aged at 700°C)

C14: Laves-Fe_2Nb



http://www.geocities.jp/ohba_lab_ob_page/structure5.html

Phase equilibrium
(JMatPro v.8)



Fe-30Cr-3Al-0.2Si-1Nb

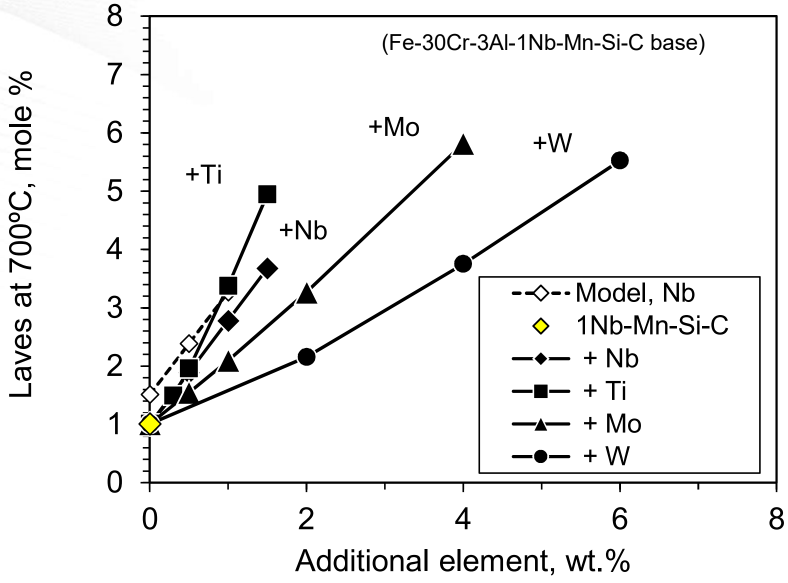
Important design factors for creep:

- *Fraction of Laves phase at 700°C*
- *BCC solvus temperature*

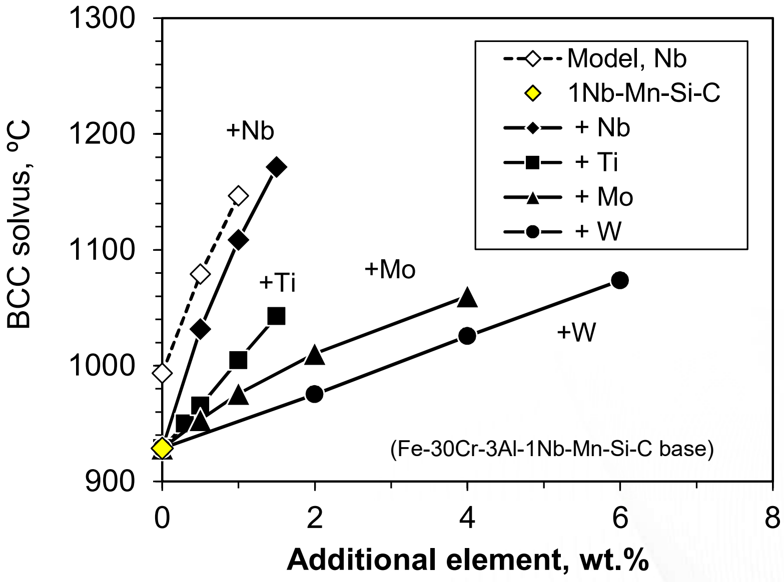
Yamamoto et al. TMS2017

Proposed Alloy Composition Ranges

Mole fraction of Laves phase at 700°C



BCC solvus temperature

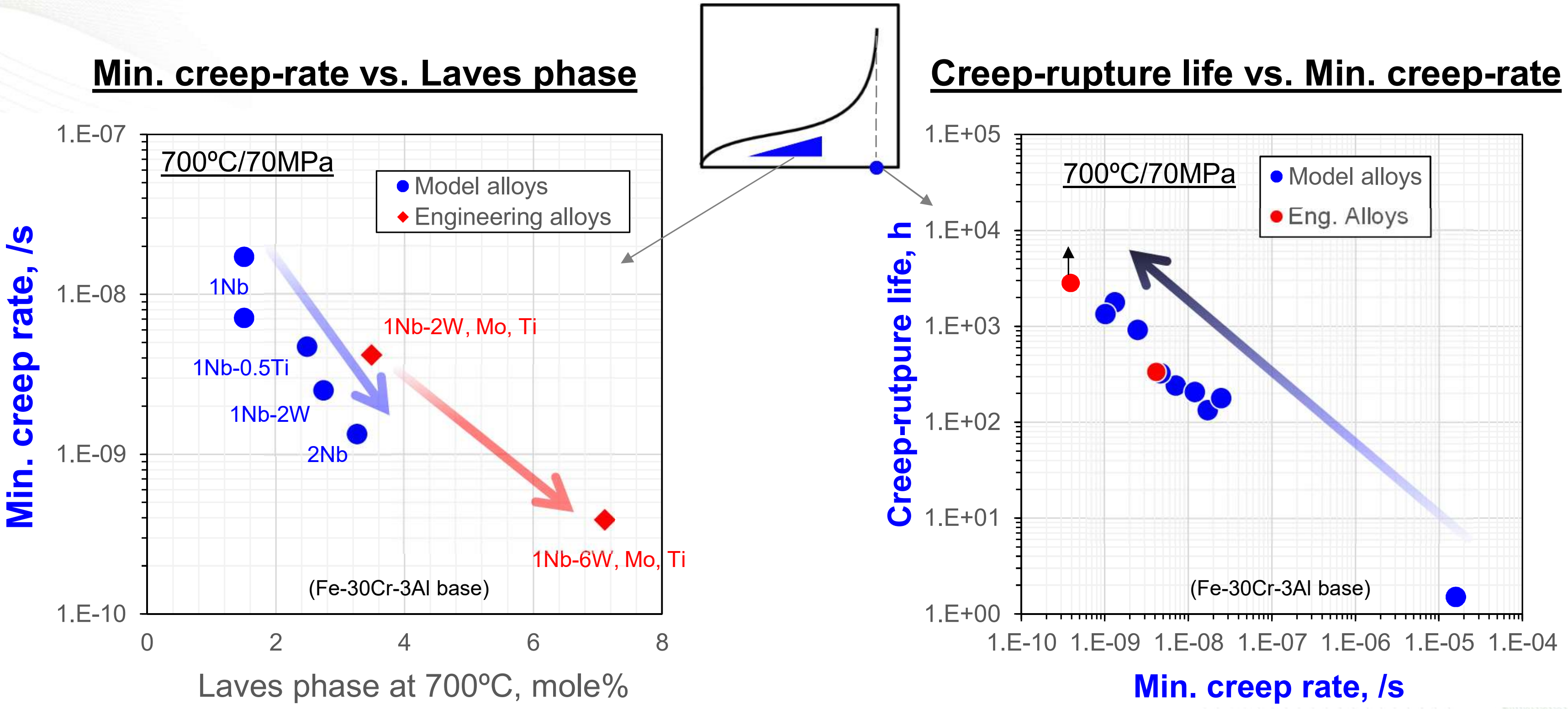


Model alloys: **Fe-30Cr-3Al-0.2Si-1Nb + (Nb, Ti, Mo, W, Zr), wt.%**

Engineering alloys: **Fe-30Cr-3Al-0.15Si-1Nb-6W-0.5Mo-0.3Ti-0.3Ni-0.4Mn-0.03C-0.05Y**

Yamamoto et al. ASME-ETAM 2018 (to be published)

Min. Creep Rate / Creep-rupture Life Depend On Fraction of Laves Phase Precipitates

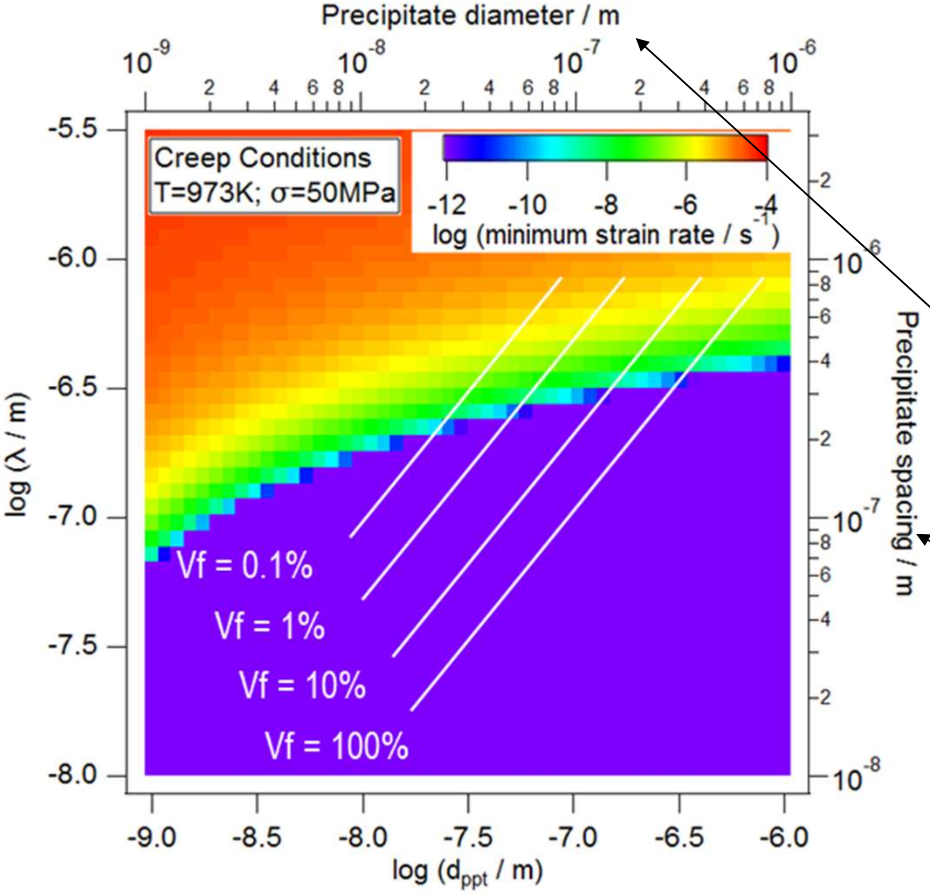


Min. creep-rate vs. Laves phase

Creep-rupture life vs. Min. creep-rate

Yamamoto et al., Crosscutting research program review meeting, 2017

Minimum Creep Rate Prediction
(Ferritic Fe-30Cr-3Al+Nb base, 700°C/50MPa)



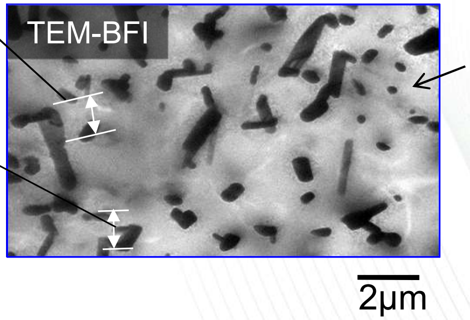
*Used Bird-Mukherjee-Dorn (BMD) model

$$\frac{\dot{\varepsilon}_m kT}{DEb} = A_{Dis}\left(\frac{\sigma_a - \sigma_{th}}{E}\right)^n$$

$$\sigma_{th} = \frac{Eb}{2\pi\lambda}\ln\frac{d_{ppt}}{b}$$

2Nb model alloy

(crept at 700C/70MPa/1750h)



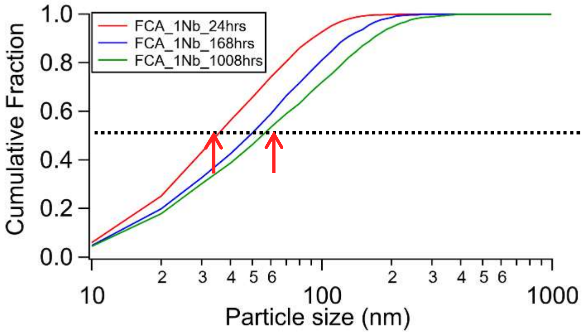
Laves in BCC-matrix

Shassere et al. Met. Mat. Trans. A (2017)

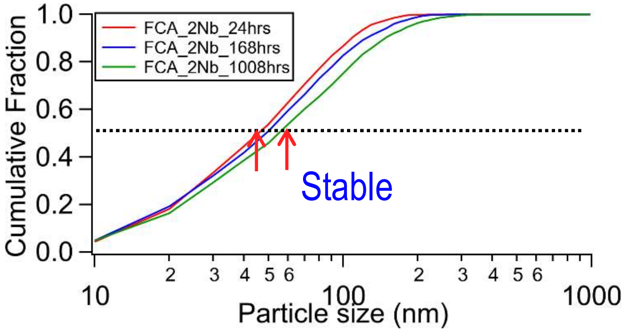
Slow Coarsening Kinetics in 2Nb and 1Nb-6W Alloys

X axis: particle diameter; Y axis: Cumulative Fraction, FCA = Fe-30Cr-3Al base, wt.% (model alloys)

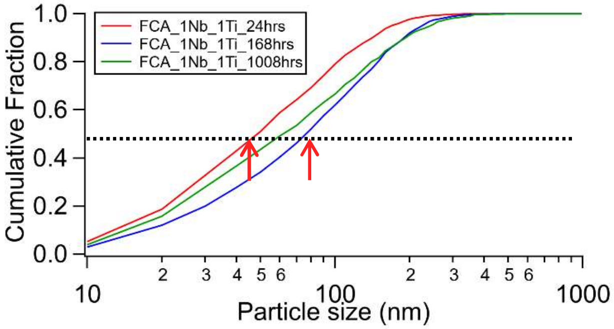
FCA-**1Nb**



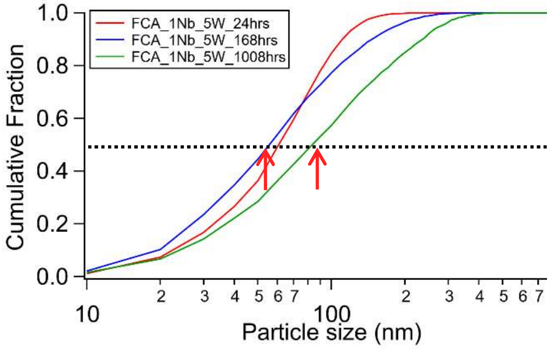
FCA-**2Nb**



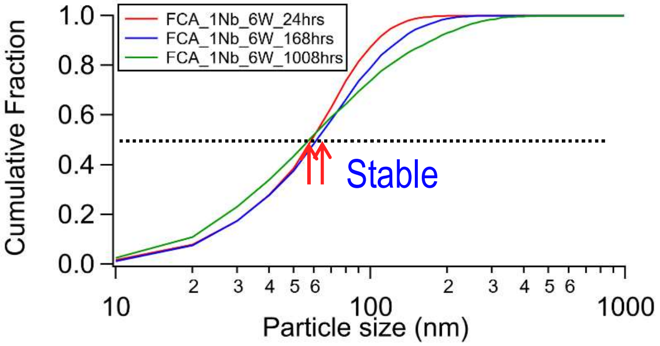
FCA-**1Nb-1Ti**



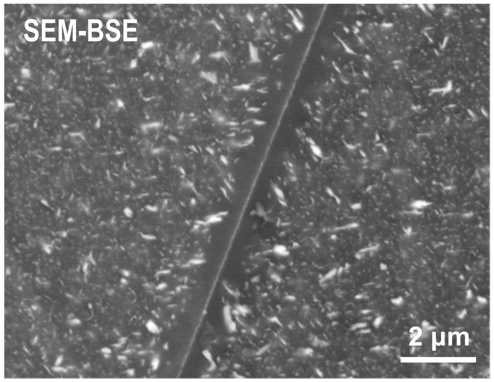
FCA-**1Nb-5W**



FCA-**1Nb-6W**



FCA-1Nb-6W, 700°C/1000h

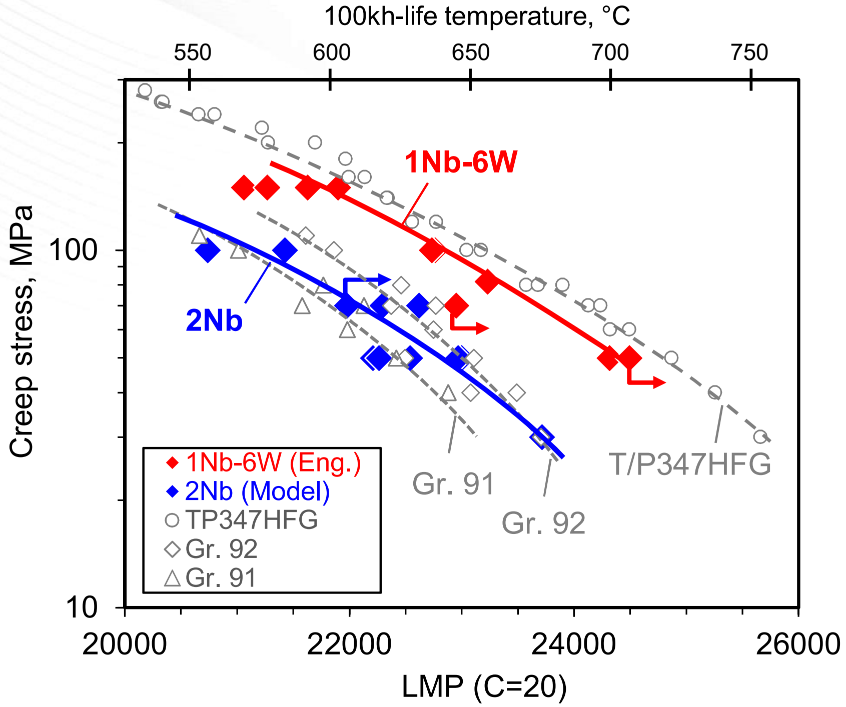


Kuo et al. TMS 2018

Creep Performance / Oxidation Resistance

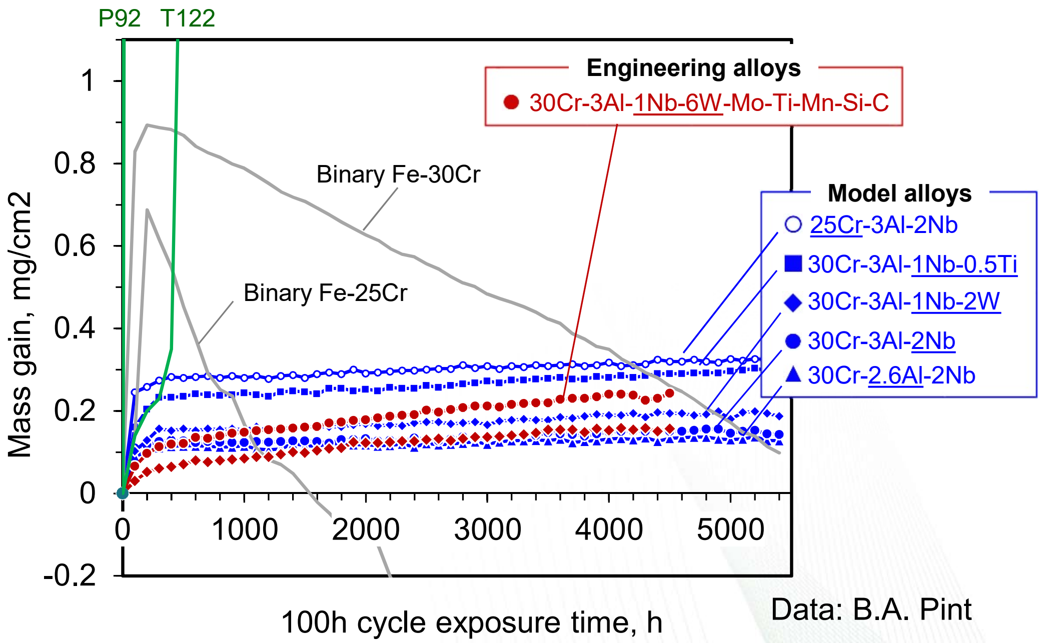
Larson-Miller Parameter Plot

(tested at 650-800°C and 30-150MPa)



Cyclic oxidation test

(100h cycle, at 800°C in 10% water vapor)



Data: B.A. Pint

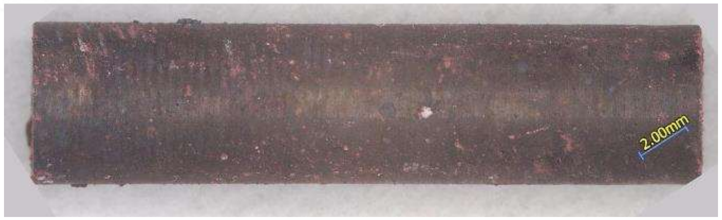
(3.3 mole % for 2Nb, and 7.1 mole% for 1Nb-6W-0.5Mo-0.3Ti)

Yamamoto et al. Proceedings of ASME-ETAM 2018 (to be published)

High Surface Protection in Ash-Corrosive Environments

2Nb (CC05-7, 2000h)

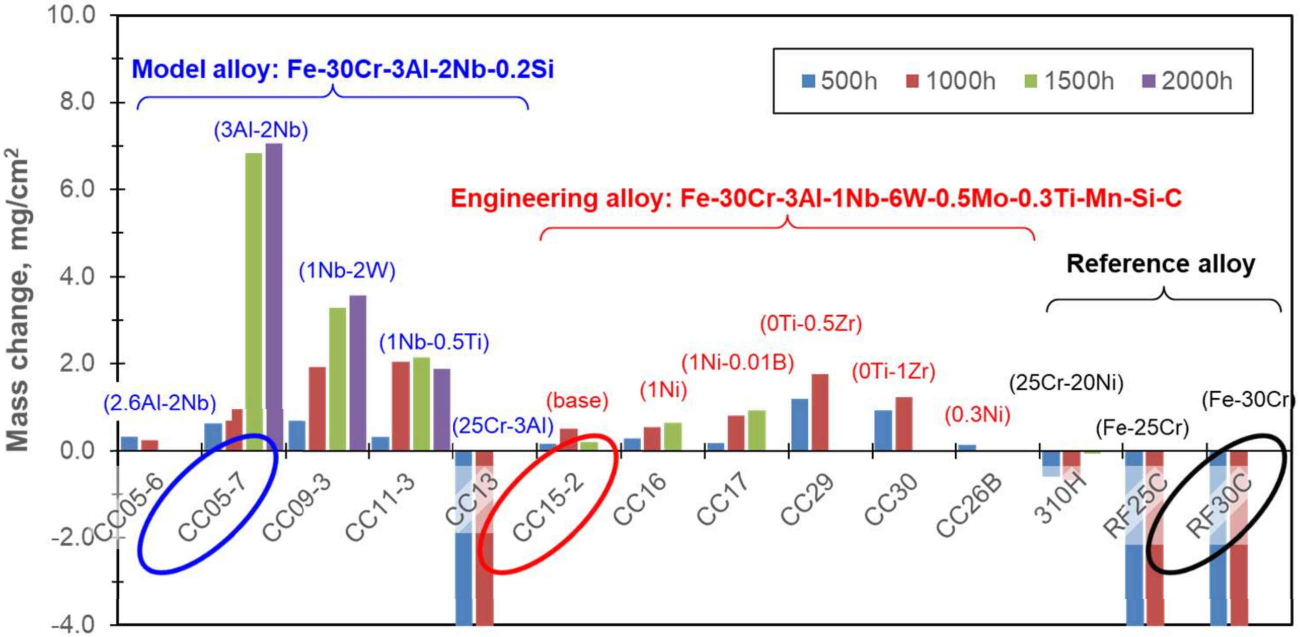
1Nb-6W (CC15-2, 1500h)



Binary Fe-30Cr (RF30, 500h)

Ash-Corrosion Test at 700°C, 500h Cycles

Ash	Al_2O_3 16.9%, SiO_2 22.6%, CaO 0.9%, Fe_2O_3 7.8%, KOH 1%, TiO_2 0.6%, MgO 0.2%, $Fe_2(SO_4)_3$ 19.8%, $MgSO_4$ 10.1%, K_2SO_4 4.8%, Na_2SO_4 15.1%
Gas	N_2, CO_2, H_2O, O_2, SO_2

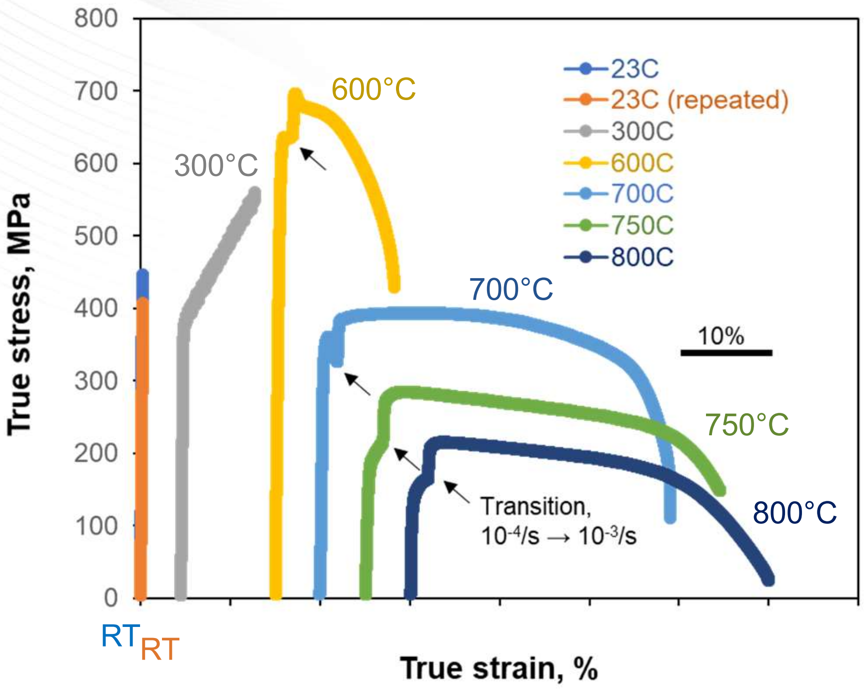


Data: B.A. Pint

Yamamoto et al. ASME-ETAM 2018 (to be published)

Potential Issues with Low Ductility at RT

1Nb-6W Engineering alloy, SS curves

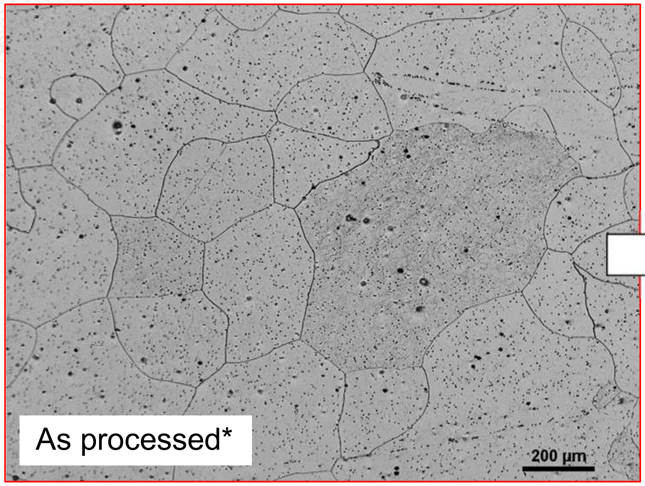


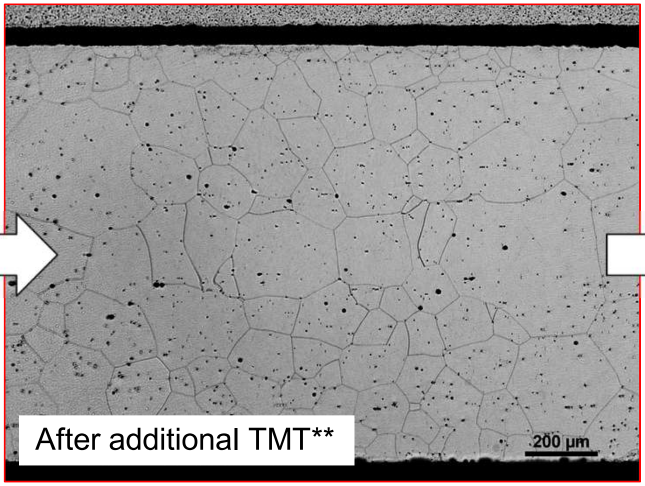
RT RT 300°C 700°C 750°C 800°C

Cold/Warm deformation → ← Hot deformation

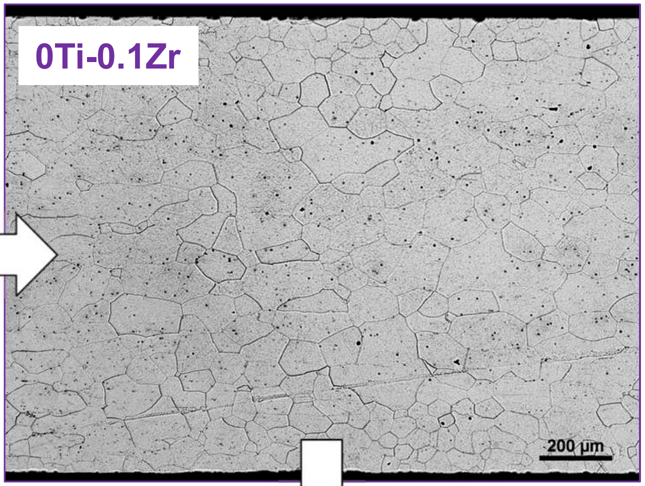
Process/Alloy Optimization for Grain Refinement in Progress

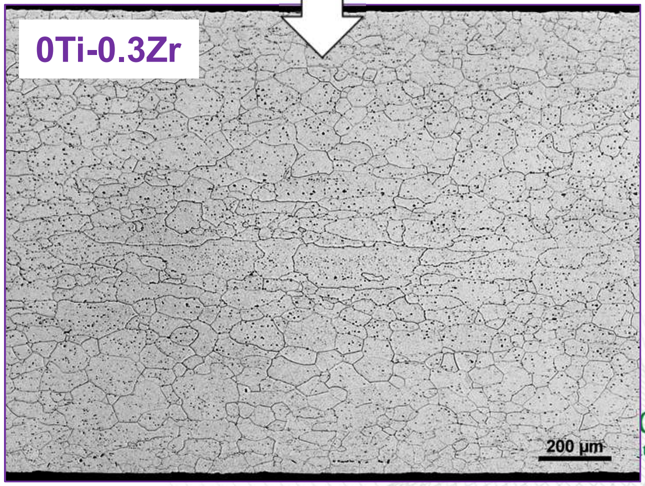
1Nb-6W-0.5Mo-0.3Ti (Base)


As processed*


After additional TMT**

1Nb-6W-0.5Mo-0Ti+Zr (Modified)


0Ti-0.1Zr


0Ti-0.3Zr

Alumina-Forming Austenitic Stainless Steels

Initiated Property Screening of Newly Proposed Advance AFA alloys

$M_{23}C_6$ + MC strengthening (CA01 and CA02):

Fe-14Cr-25Ni-4Al-Mn-Nb-C with Cu, Hf, Y

Fe_2W + $M_{23}C_6$ strengthening (CA03-CA05):

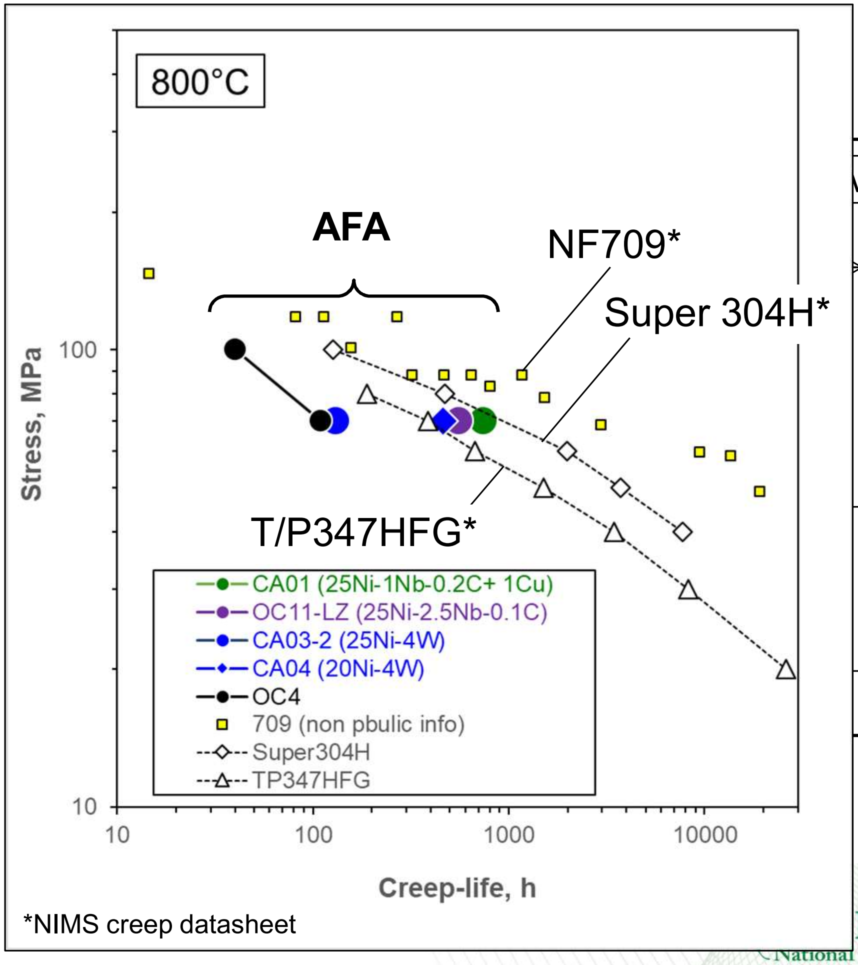
Fe-14Cr-(16-25)Ni-(3-4)Al-Mn-Nb-C with W, Cu, Hf, Y

High Cr containing AFA (CA06 and CA07):

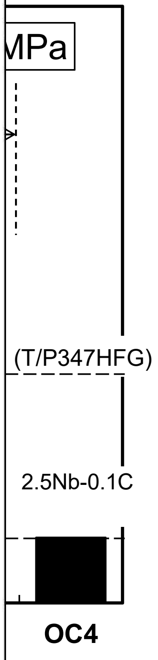
Fe-18Cr-25Ni-4Al-Mn-Nb-C with W, Cu, Hf, Y

Reference AFA (OC4):

Fe-14Cr-25Ni-3.5Al-2.5Nb-0.1C base



*NIMS creep datasheet



Summary

Successfully demonstrated "New Alloy Design Concepts for Creep-resistant, Alumina-forming Alloys for High-temperature Fossil Applications" through development of two different classes of Fe-base alloys:

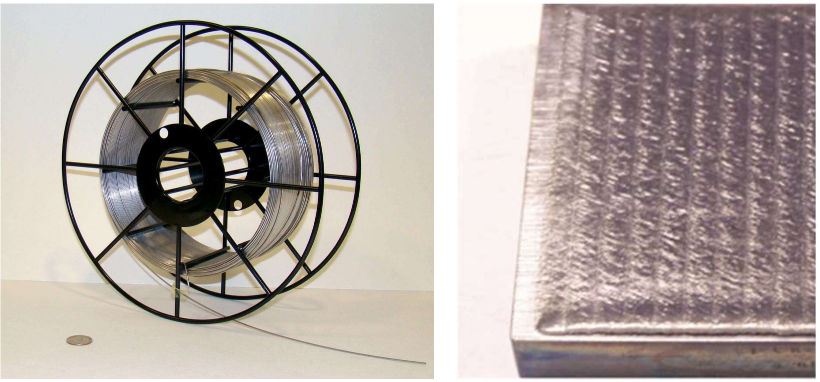
High Cr containing FeCrAl Ferritic alloy (Fe-30Cr-3Al-1Nb-6W base):

- Designed with computational thermodynamic tools
- Promising high-temperature properties
  - *Creep-rupture tests*
  - *Good surface protection in both steam containing environment and fire-side corrosive circumstances*
- Optimization of processability/toughness is in progress
  - *Searching for potential applications in various industries*

Alumina-forming Austenitic alloys (Fe-Cr-Ni-Al-Nb-C-W-Cu-Hf-Y):

- Proposed three different alloy designs (by following compositional guideline)
- Property screening in progress
  - *creep-rupture test at 750/800°C*
  - *oxidation at 800°C in 10% water vapor*

Future Works



http://www.titanovalaser.com/titanova-c_benefits.html

High Cr containing FeCrAl alloys:

- Cross-weld property evaluation:
  - *A metal-core weld filler wire production was completed*
- Seek potential applications:
  - *Thin plate/sheet/foil products for heat exchangers*
  - *Cladding (weld overlay) for protective coating; additively manufactured production*

Alumina-Forming Austenitic Stainless Steels:

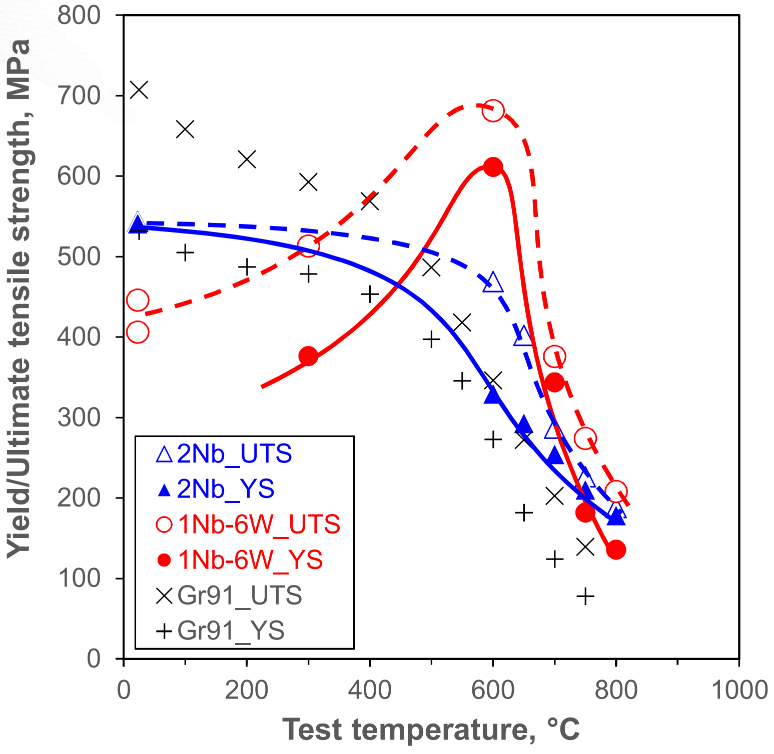
- Continue property evaluation of new AFA alloys with various strengthening second-phases:
  - *List potential candidate microstructural designs for near-future developmental efforts (e.g. EEM)*
- Seek potential applications:
  - *Various industries are interested in the AFA alloys; communications are in progress*

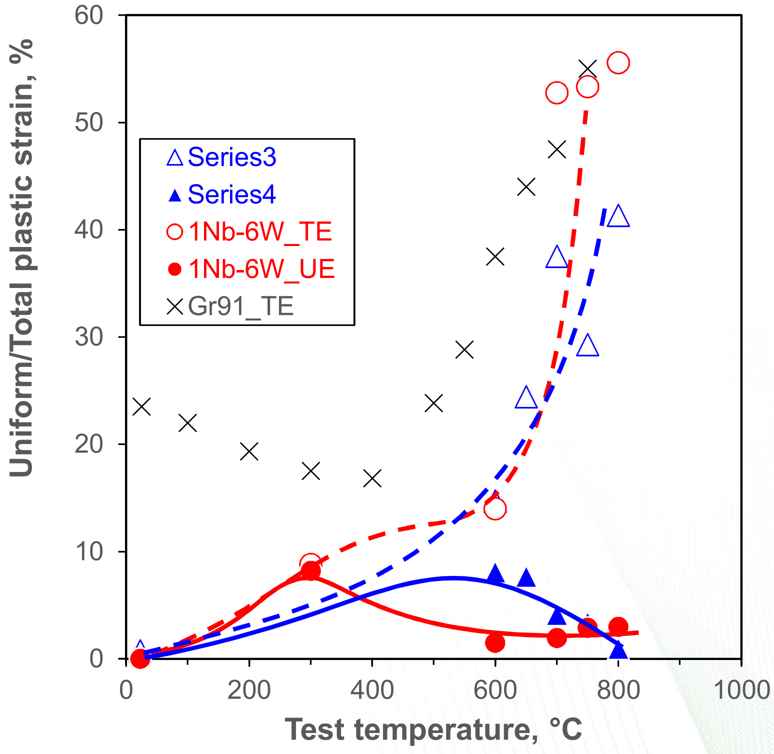
Alumina-Forming Ni-base alloys:

- Leveraged with other DOE-funded projects for wrought alumina-forming Ni-base alloys:
  - *Evaluation of coherent L12 strengthening high-temperature Ni-Fe base wrought alloy is in progress*

Thanks

Tensile Properties Compared to F-M Steel (Grade 91)

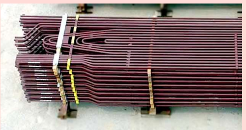




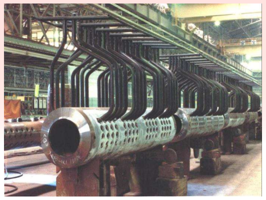
History of "Heat-Resistant/Stainless Steel Development"

Heat-resistant steels and alloys

- **Carbon steels**: Steam locomotives, etc.
  - Quench and temper/annealing
  - Tempered martensite / pearlite transformation
- **Low alloy steels**: Supercritical(SC)
  - Normalization/quench and temper/annealing
  - Martensitic/bainitic transformation
- **High Cr (9-12) FM steels**: Ultra-supercritical (USC)
  - Normalization and temper
  - Introduction of MX (VN, NbC)



- **Advanced austenitic steels**: USC
  - Austenite (FCC) matrix, Fe-Ni base
  - Solution hardening/ carbide strengthening
- **Ni-base alloys**: Advanced USC (A-USC)
  - Austenite (FCC) matrix, Ni-base
  - Solution hardening/ carbide or intermetallic strengthening



Stainless steels and alloys

- Fe-P:
  - "non-rusting steel", India, ~B.C. 400

:

- **Fe-Cr** (ferritic stainless steel):
  - Monnartz, Germany, 1911
  - Dantsizen and Becket, USA, 1911-12
- **Fe-Cr-Ni** (martensitic/austenitic stainless steels):
  - Struss and Maurer, "Nirosta", Germany, 1912
  - Haynes, "Martensitic stainless steels", USA, 1912
  - Brearley, "Martensitic stainless steels", UK, 1912

https://railroad.lindahall.org/essays/locomotives.html
http://www.tppboilers.com/super-heaters-coils.php#
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