Advanced Alloy Design Concepts for High-Temperature Fossil Energy Applications

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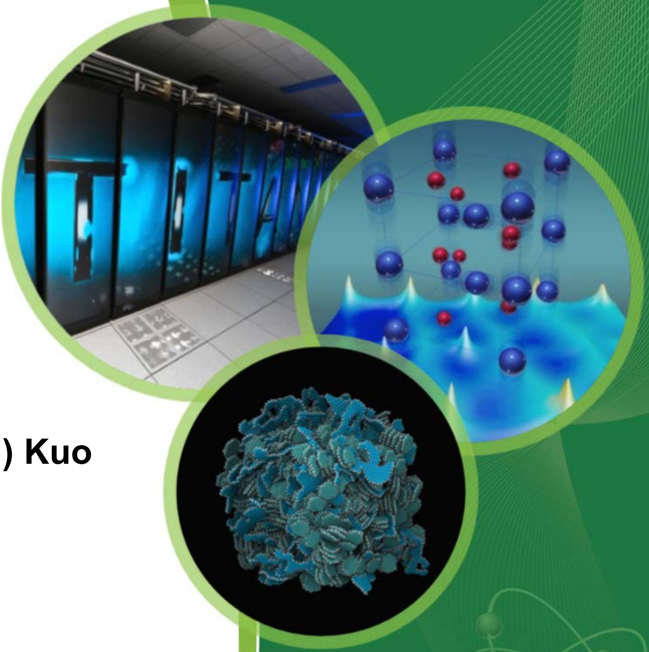

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Project Goals and Objectives

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 (FY2017):

1. *Complete intermediate-term oxidation and creep testing of scale-up heats of “model alloy” (Met)*
2. *Submit a journal paper summarizing the new FeCrAl alloy design study (In Progress)*
3. *Initiate computational screening of next generation advanced alumina-forming austenitic and Ni-base alloys for improved strength and corrosion resistance (In Progress)*

Presentation Outline

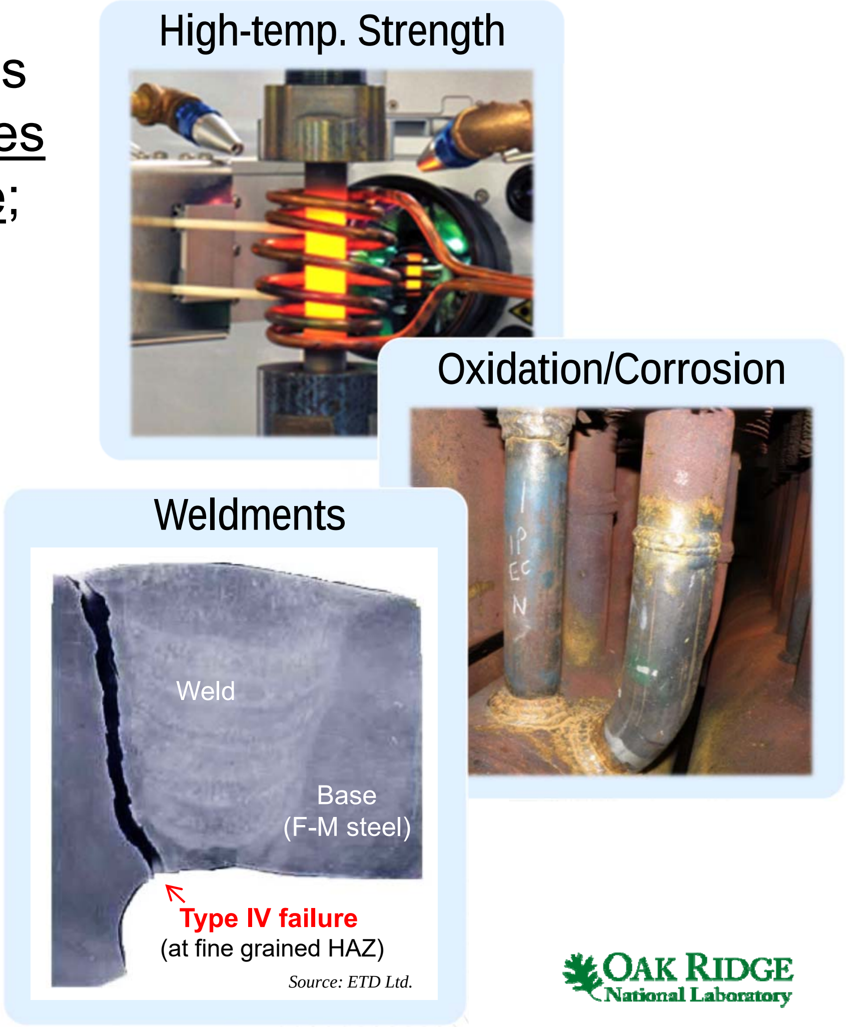
- Backgrounds/Motivation:
  - *Concepts of "Advanced Alloy Design"*
  - *High-Cr containing FeCrAl "ferritic" alloy development*
- Update on FY16/17
  - *Effect of alloying on Laves-phase solvus and stability*
  - *Creep property evaluation*
  - *Oxidation/ash-corrosion tests*
  - *Scale-up efforts*
- Summary
- Future Activities

Backgrounds: Advanced Alloy Design

Strong demands on new high-temperature materials with improved properties for upper limit temperatures higher than that of the materials currently in service;

- *High-temperature strength (tensile, creep)*
- *Environmental compatibilities (oxidation, corrosion)*
- *Minimized weld-related issue for final components*
- *RT toughness (Charpy)*
- *Processibility (including microstructure control)*
- *Inexpensive materials cost (raw elemental costs, process routes, etc.)*

High-Cr containing FeCrAl ferritic alloy (Fe-30Cr-3Al base, wt/%)


High-temp. Strength

Oxidation/Corrosion

Weldments

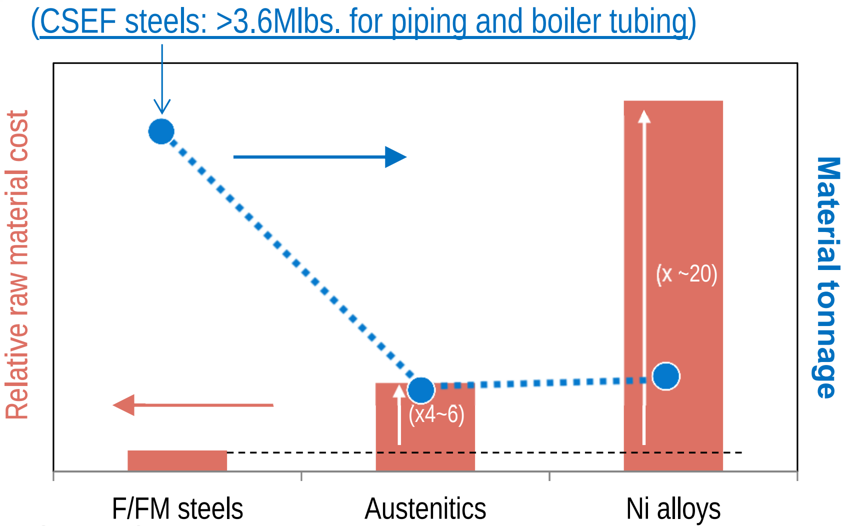
Source: ETD Ltd.

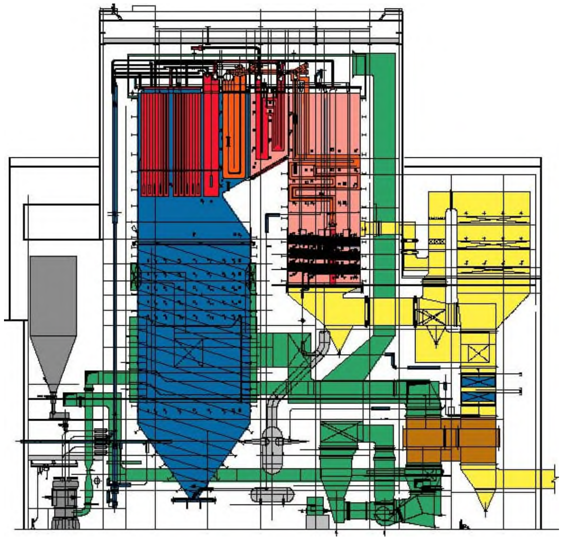
https://mts.com/en/products/industry/materials-testing/index.htm
http://www.ccj-online.com/prioritization-of-issues-improves-hrsg-reliability-performance/`

Target Materials/ Applications

Three different grades of structural materials that are currently available for use by the US electric utility industry:

1) **Ferritic steels** for temperatures up to 600 °C, with **ferritic-martensitic** versions (F-M steels) having increased strength up to 600-620 °C;
2) **Austenitic stainless steels** with strength and environmental resistance up to 650 °C; and
3) **Ni-base alloys** for temperatures > 700 °C.



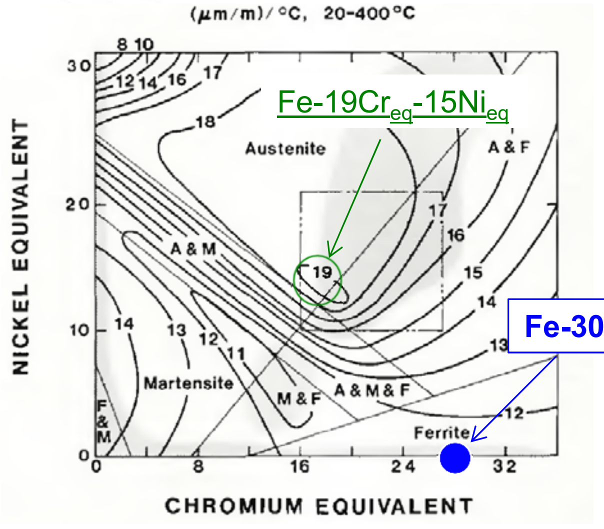


Alstom USC and AUSC Power Plants – J. Marion - NTPC/USAID Int. Conf. SC Plants - New Delhi, India, 22 Nov. 2013 – P 8

Why High Cr Containing FeCrAl Ferritic Alloy?

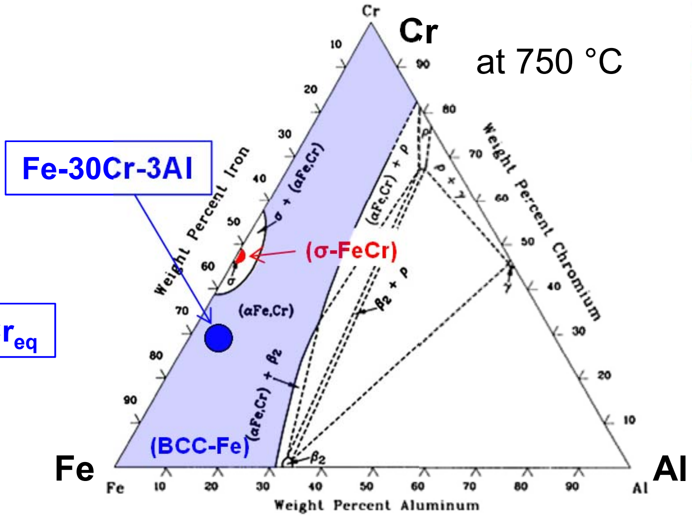
- High surface protection in both steam and ash-corrosion environments
- Less thermal expansion and high thermal conductivity
- Suppress brittle σ-FeCr formation by Al additions
- No Type IV failure because of no BCC-FCC transformation during welding

Mean coefficient of thermal expansion



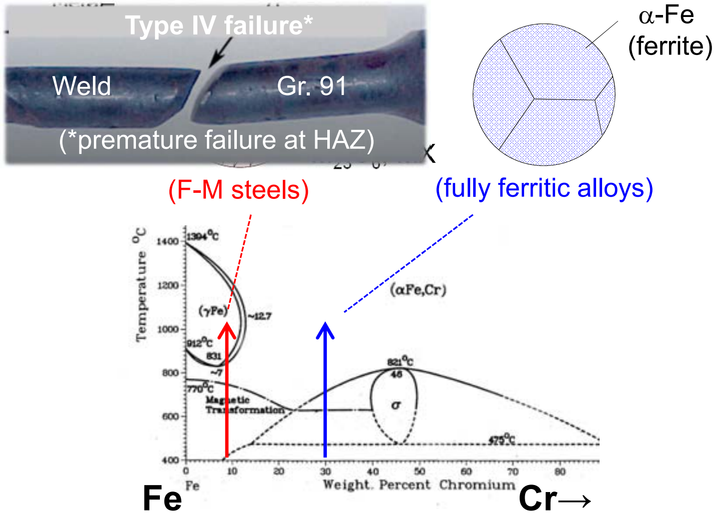
Ref. Welding Research Supplement (1982)

Fe-Cr-Al ternary alloy phase diagram



Ref. ASM international, Ternary alloy phase diagrams

Fe-Cr binary alloy phase diagram



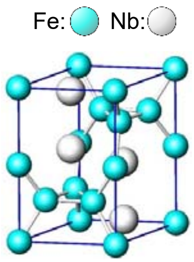
Ref. ASM international, Binary alloy phase diagrams

What is the Challenge in High Cr Containing FeCrAl Ferritic Alloy?

- Poor high-temperature strength due to BCC matrix
- Rapid grain coarsening causes poor ductility at low temperature

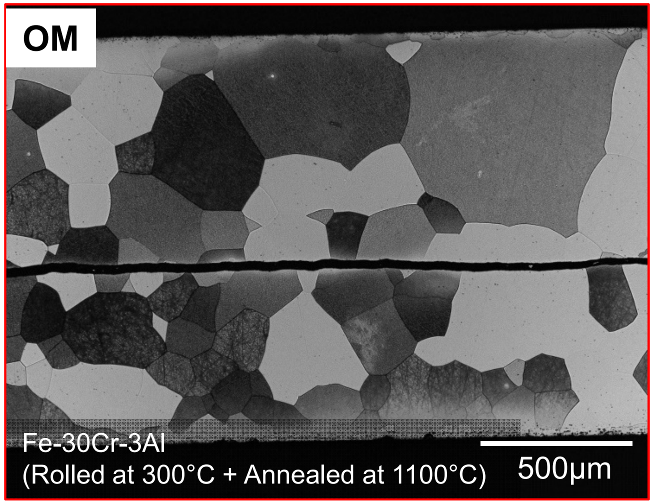
→ ***Use alloying additions for GS stability and strengthening (e.g. Nb for Laves-phase formation)***

C14: Laves-Fe_2Nb

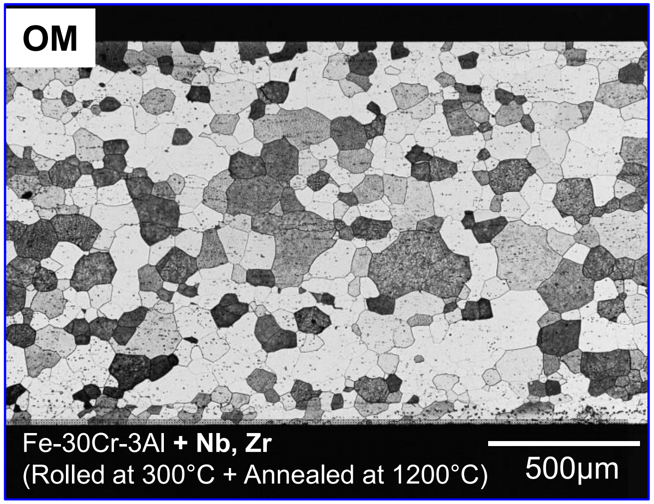


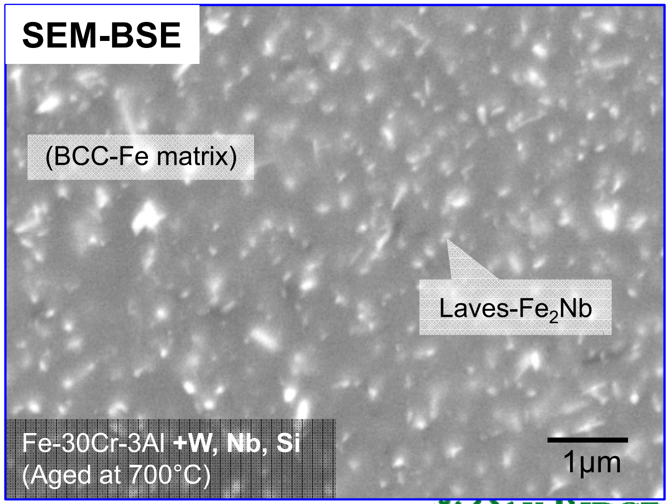
http://www.geocities.jp/ohba_lab_ob_page/structure5.html

No optimization



After optimization



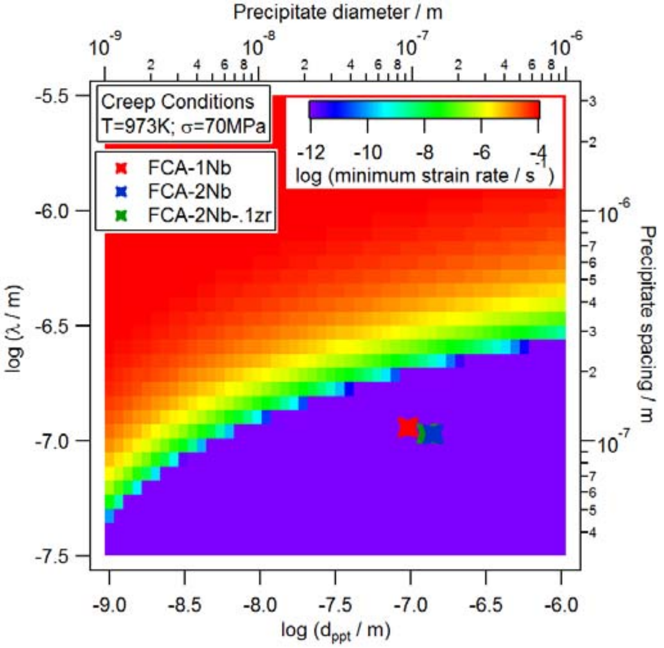


Alloy Development in Progress

- **1st series**: **Fe-30Cr-3Al with (0~2)Nb-(0~0.3)Zr (in wt.%)**
  - *Optimization of thermo-mechanical treatment*
  - *Tensile test (RT~800°C)*
  - *Oxidation test (800°C, in air + 10%H_2O)*
  - *Ash corrosion test (700°C, in ash + corrosive gas)*
  - *Creep-rupture test (650~700°C, 70~100MPa)*

- **2nd series**: **Fe-30Cr-3Al with (0.5~2)Nb + W, Mo, Ti, and Y**
  - *BCC solvus temperature control*
  - *Size stability of Lave-phase particle at 700°C*
  - *Oxidation/Ash-corrosion resistance*
  - *Property evaluation*
  - *Scale-up effort*

Calc. minimum creep-rate map



*Used Bird-Mukherjee-Dorn (BMD) model

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

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

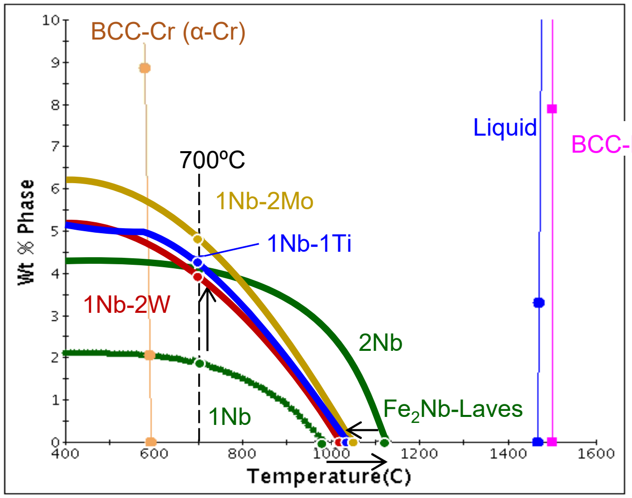
Major Concerns in FY17

- Effect of third element addition on microstructural stability, mechanical properties, and oxidation/ash-corrosion resistance:
  - *Nb, W, Mo, and Ti (Laves-phase forming elements)*
  - *Mn, Si, C (simulate engineering alloys with the level of industrial impurities)*
- Scale-up efforts of high-Cr FeCrAl alloy

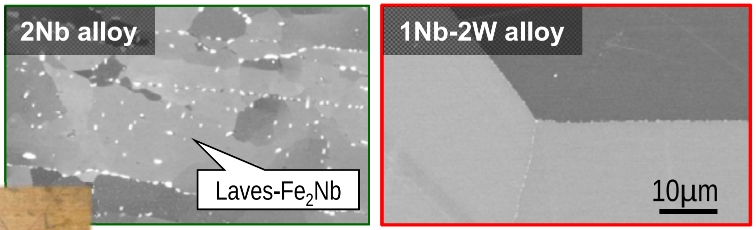
Experimental Procedure

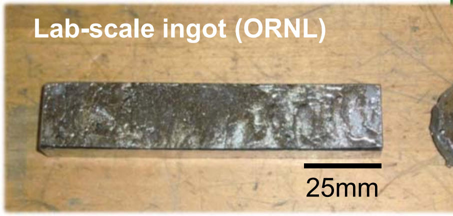
- **Alloys to be evaluated:**
  - *<u>Fe-30Cr-3Al base</u> with (or without) Nb, Si, W, Mo, Ti, Y, Mn, and C, wt.%*
  - *Used thermodynamic computational tool (JMatPro, v.8-9) for downselection*
- **Lab-scale heat preparation:**
  - *Arc-melt and drop-cast the bar ingots (13 x 25 x 125 mm)*
- **Thermo-mechanical treatment:**
  - *Homogenization, forging, rolling, annealing*
  - *Water-quenching*
- **Microstructure analysis:**
  - *OM, SEM*
- **Property evaluations:**
  - *Creep, oxidation, ash-corrosion*

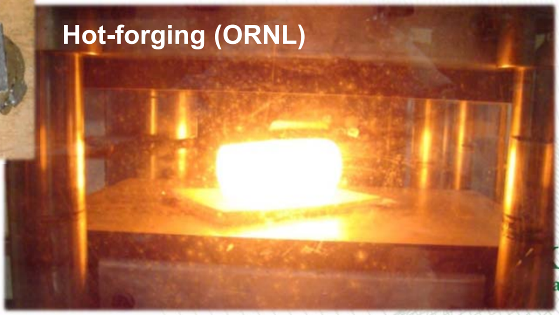
Fe-30Cr-3Al-0.2Si base alloys



Annealed at 1200°C (SEM-BSE)



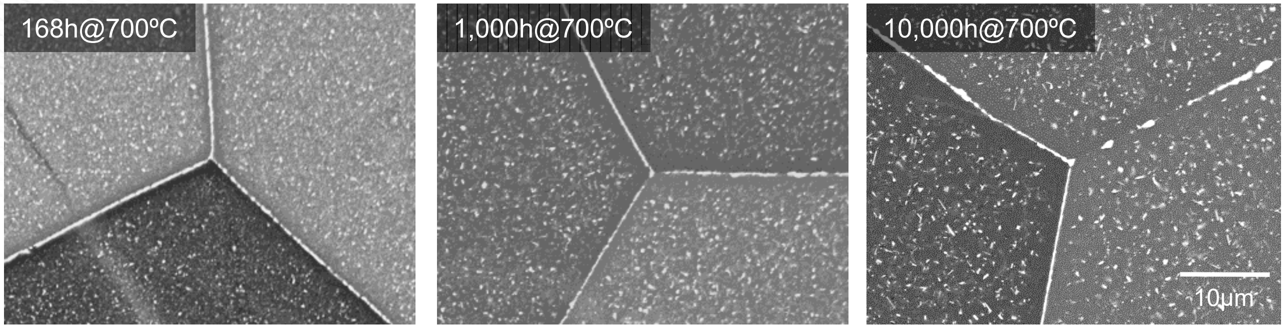




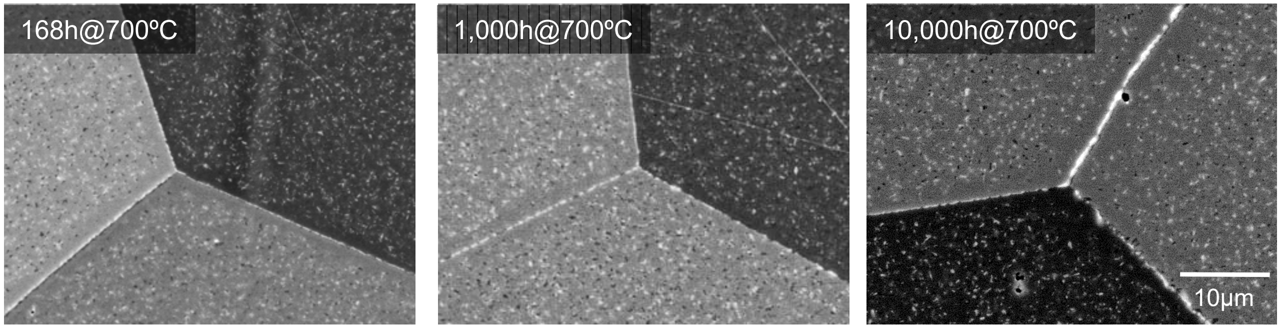
Impact of “Third Additional Elements” on Microstructure

- Fine particle size maintained even after 10,000h at 700°C

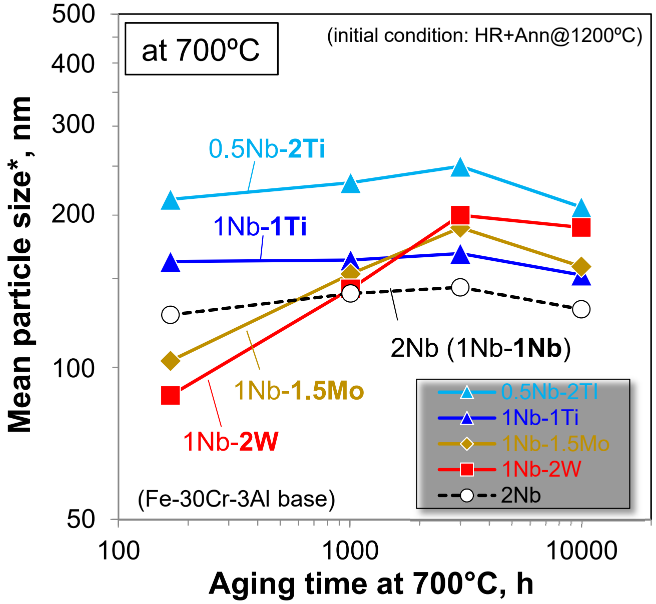
Fe-30Cr-3Al-1Nb-2W



Fe-30Cr-3Al-1Nb-1Ti

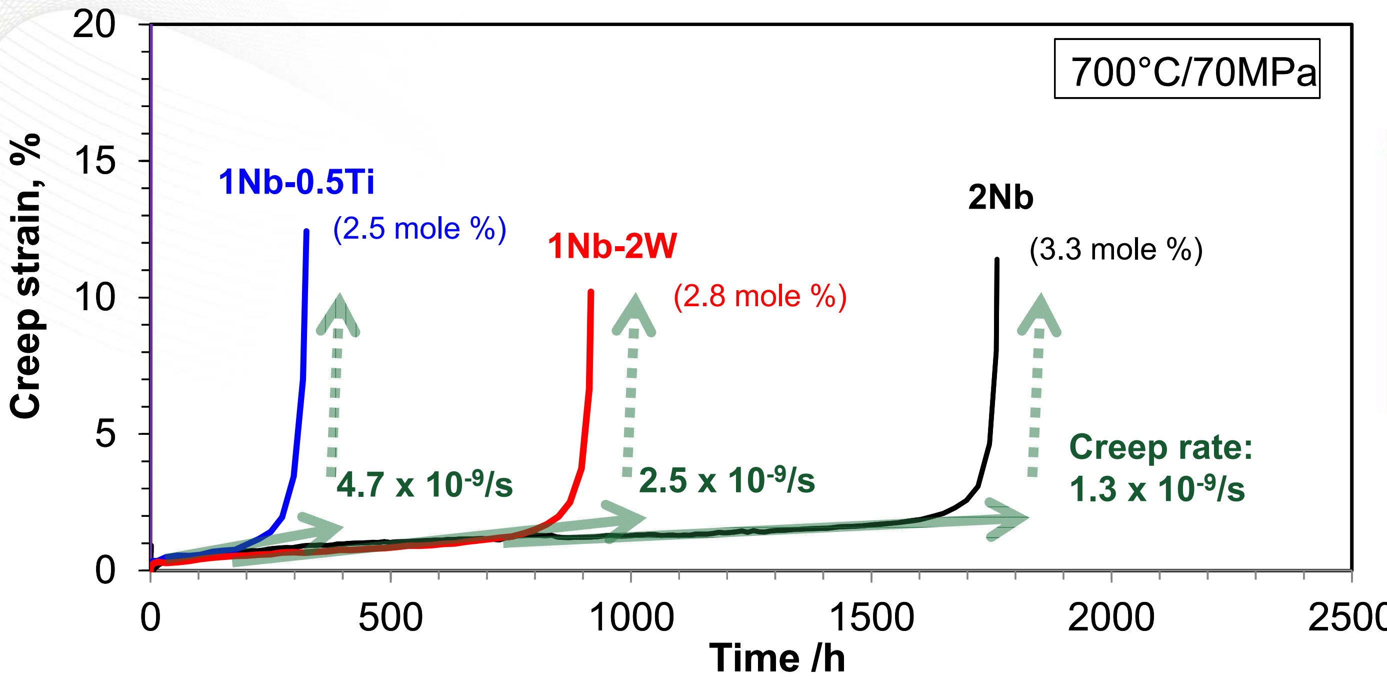


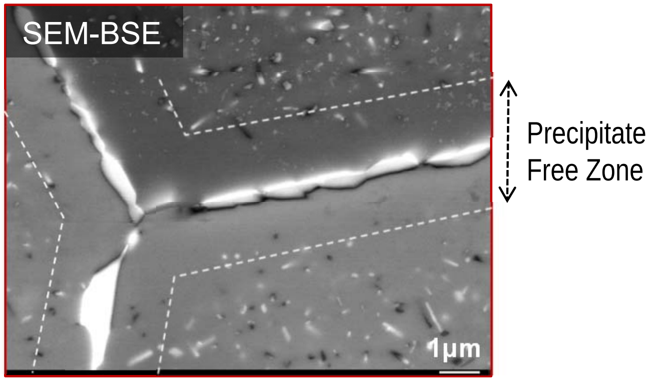
Growth kinetics of Laves phase



*assumed the normal distribution

Third Element Addition Was Effective As Expected



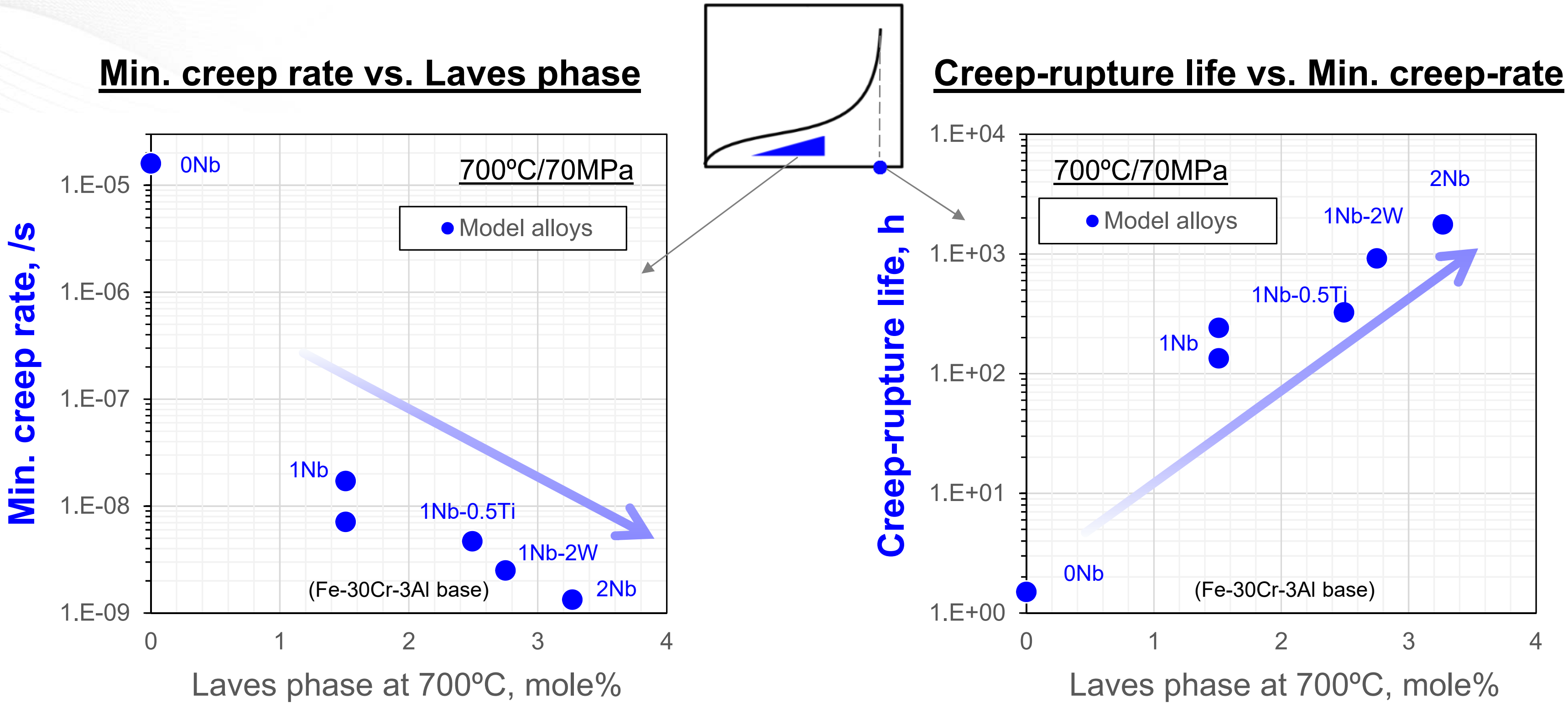


- Grain Boundary Zone Strength Factor:

$$\frac{\text{Grain boundary precipitate coverage}}{\text{Width of precipitation free zone}}$$

B. Shassere et al. (to be submitted)

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

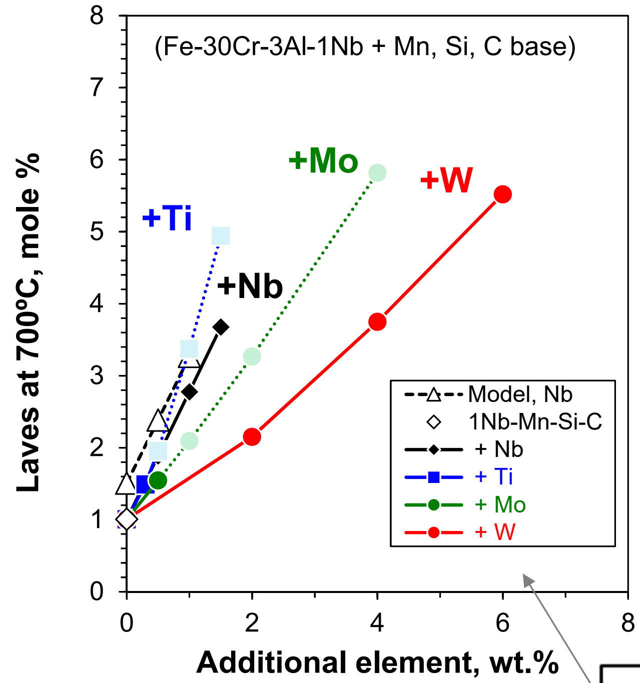

Min. creep rate vs. Laves phase

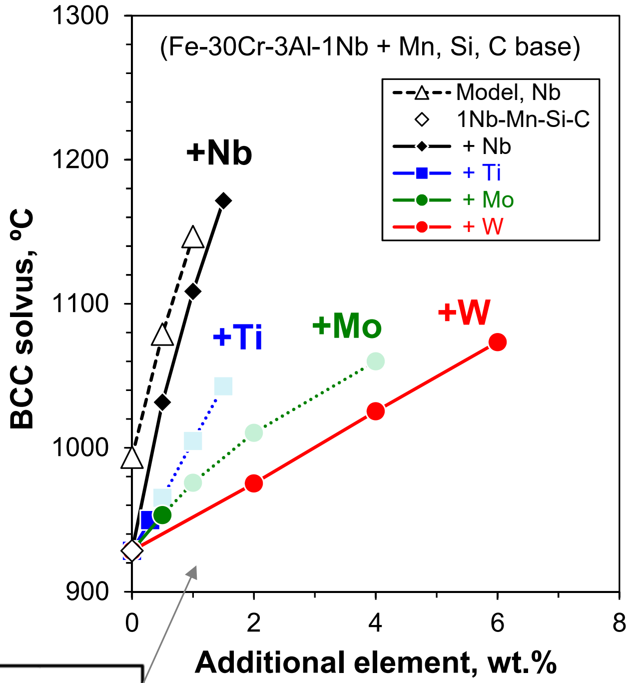
Creep-rupture life vs. Min. creep-rate

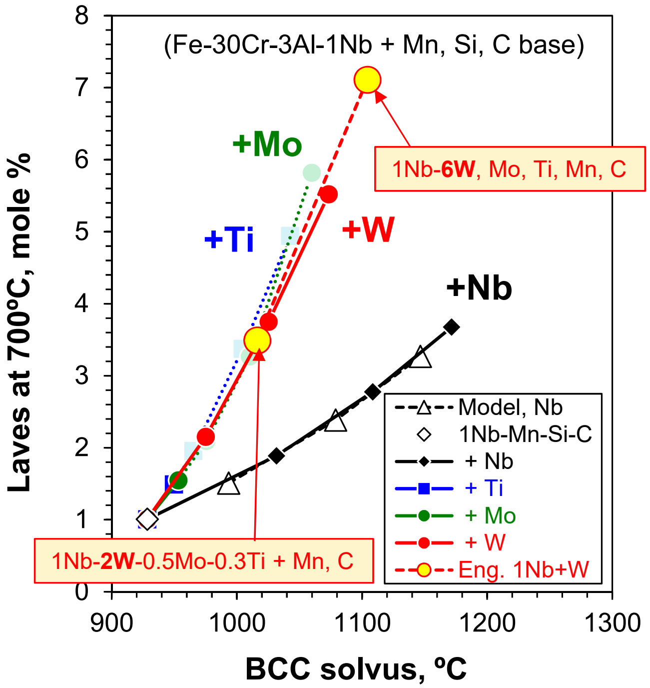
Moving toward Engineering Alloys

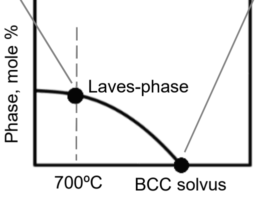
- Optimized the combination of Nb, W, Mo, and Ti:
  - *Maximize Laves phase formation combined with reasonably low BCC solvus temperature (for Laves phase)*
- Considerations of industrial quality chemistry:
  - *Mn, Si, and C were intentionally added to simulate commercial steels*
  - *P, S, and N still need to be minimized for better weldability and oxidation resistance*

BCC Solvus Temperature Control



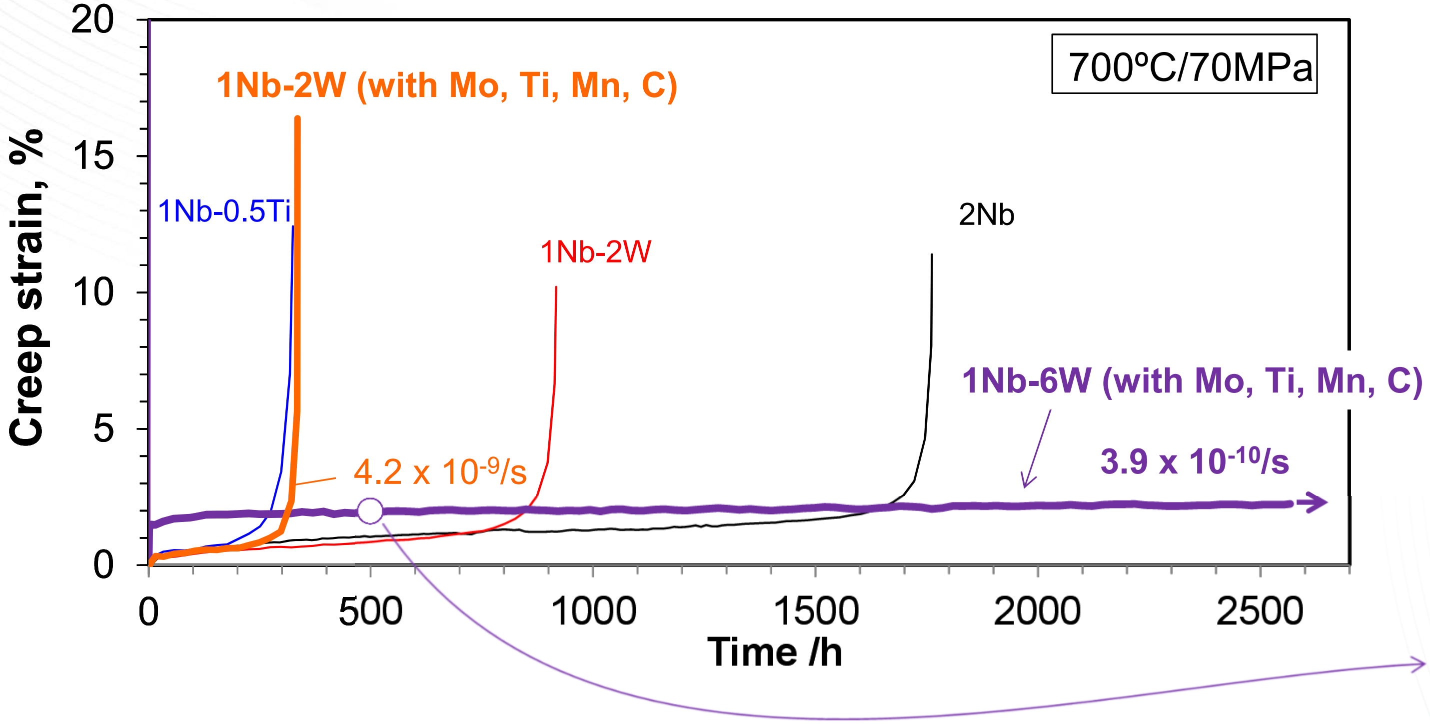


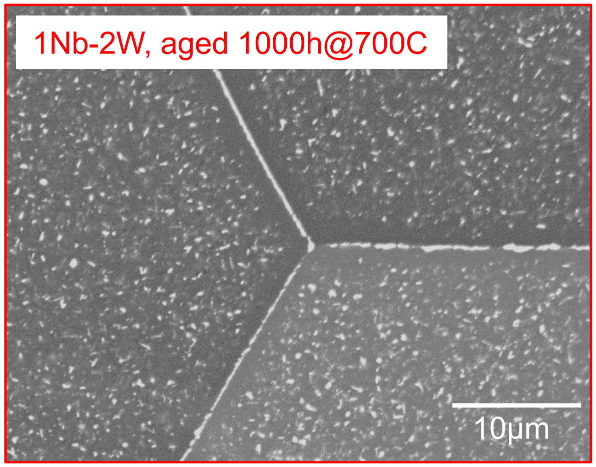


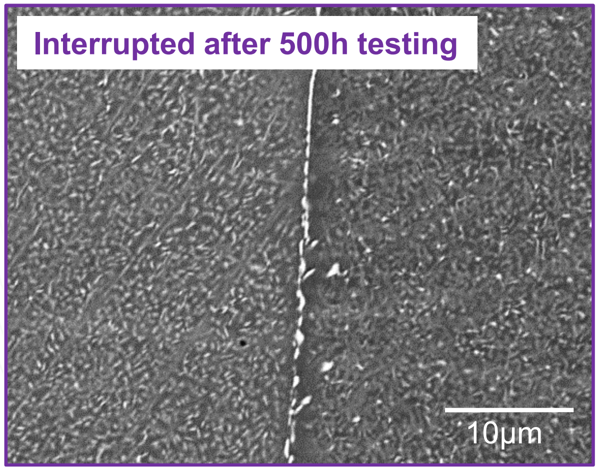


- Ti: $\leq$ 0.3 wt.% for better oxidation resistance
- Mo: $\leq$ 0.5 wt.% to avoid σ-FeCr or χ-FeCrMo formation

Improved Creep Resistance by Increased Volume Fraction of Laves-phase Precipitates



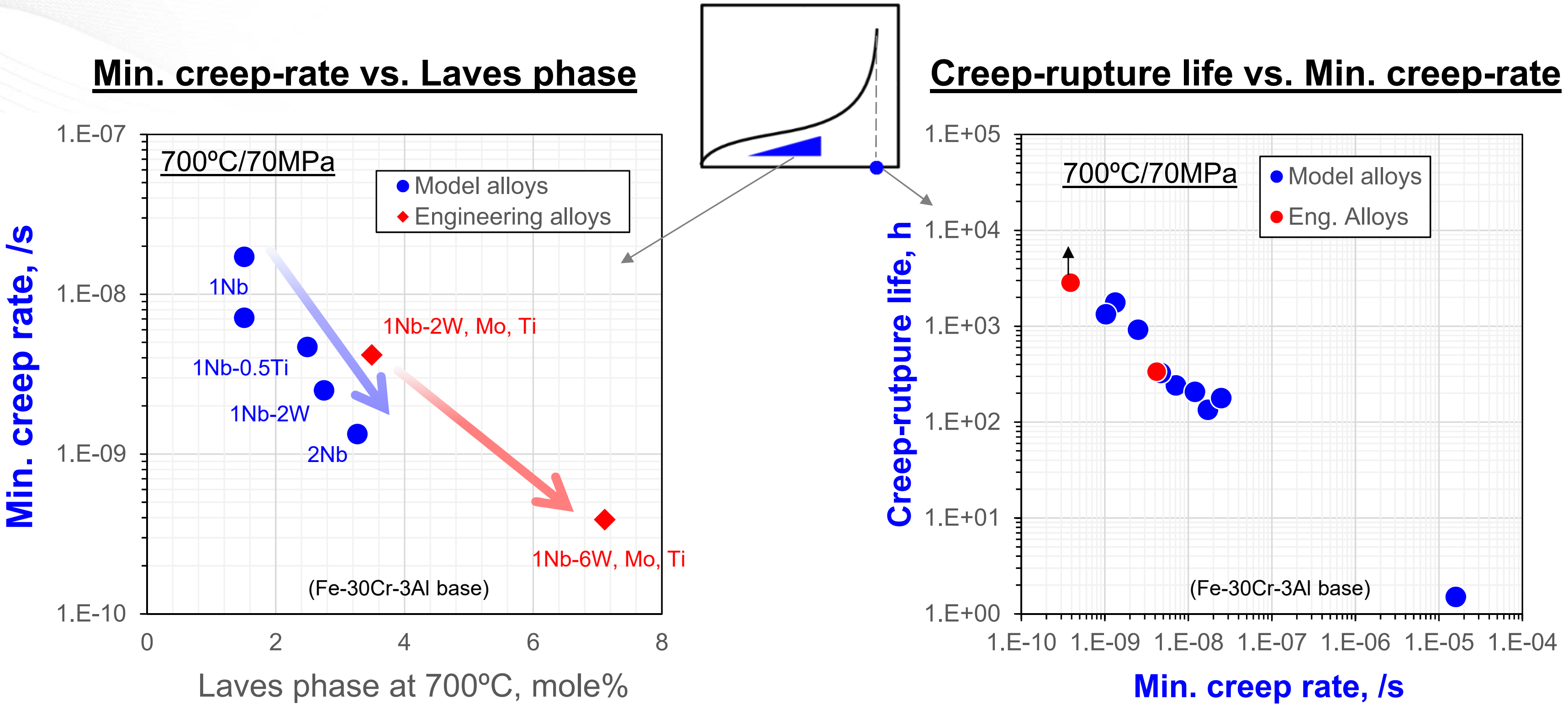




Min. Creep Rate / Creep-rupture Life Depend On Fraction of Laves Phase Precipitates

Min. creep-rate vs. Laves phase

Creep-rupture life vs. Min. creep-rate



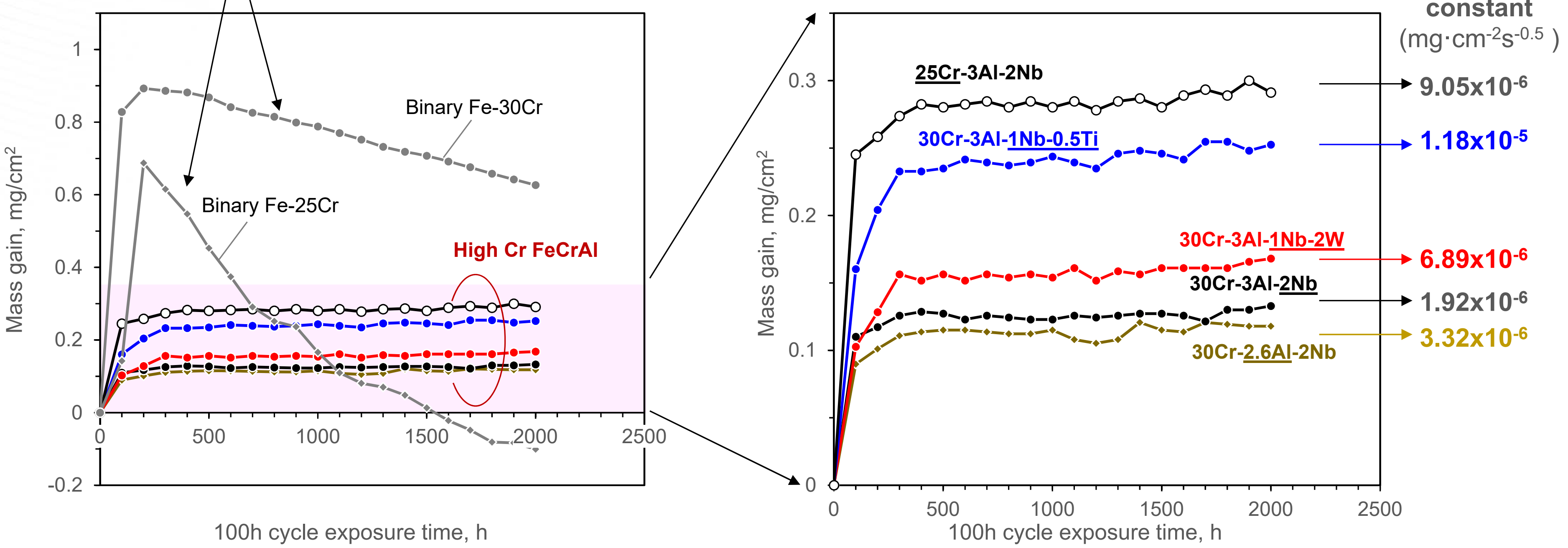
Important Role of Al Addition on Oxidation Resistance

- Slow oxidation kinetics indicates protective alumina scale formation

Volatarization of chromia scales:
1/2 Cr_2O_3 + 3/4 $O_2(g)$ + $H_2O(g)$ = $CrO_2(OH)_2(g)$

800ºC, 10% water vapor, 100h cycle

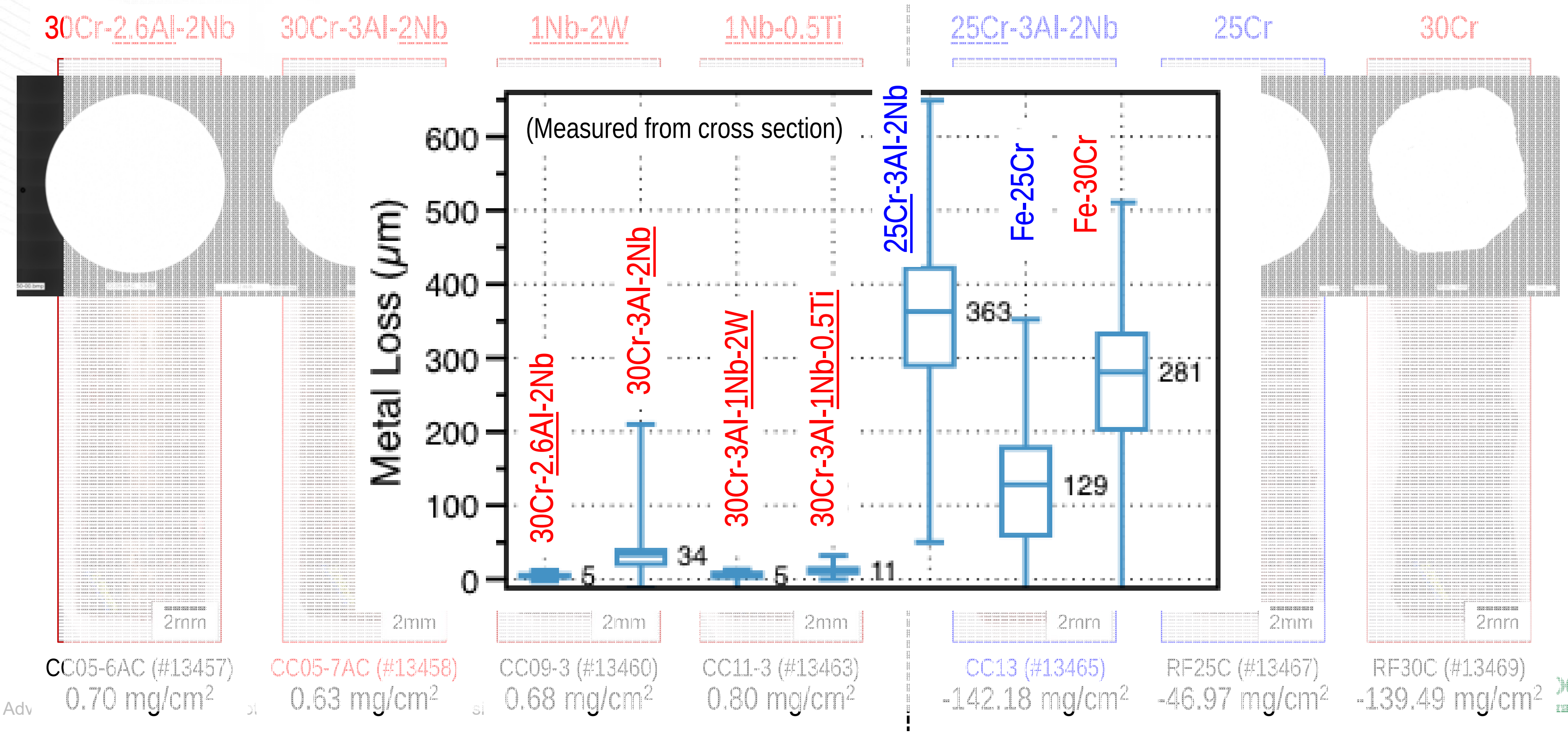
Parabolic rate constant
($mg \cdot cm^{-2} s^{-0.5}$)



Ash-corrosion Tested at 700ºC for 500h

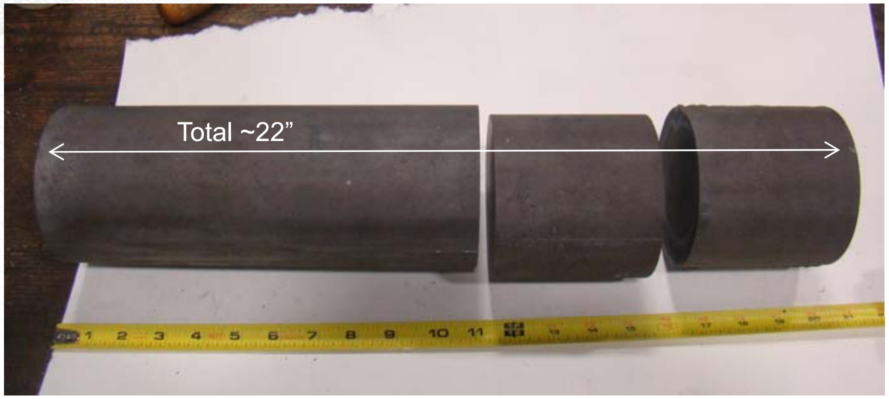
Ash: Al_2O_3 16.9%, SiO_2 22.6%, CaO 0.9%, Fe_2O_3 7.8%, KOH 1%, TiO_2 0.6%, MgO 0.2%, $Fe_2(SO_4)_3$ 19.8%, $MgSO_4$ 10.1%, K_2SO_4 4.8%, Na_2SO_4 15.1%

Gas: Synthetic gas simulating combustion environment in a steam plant (suggested by B&W/EPRI)



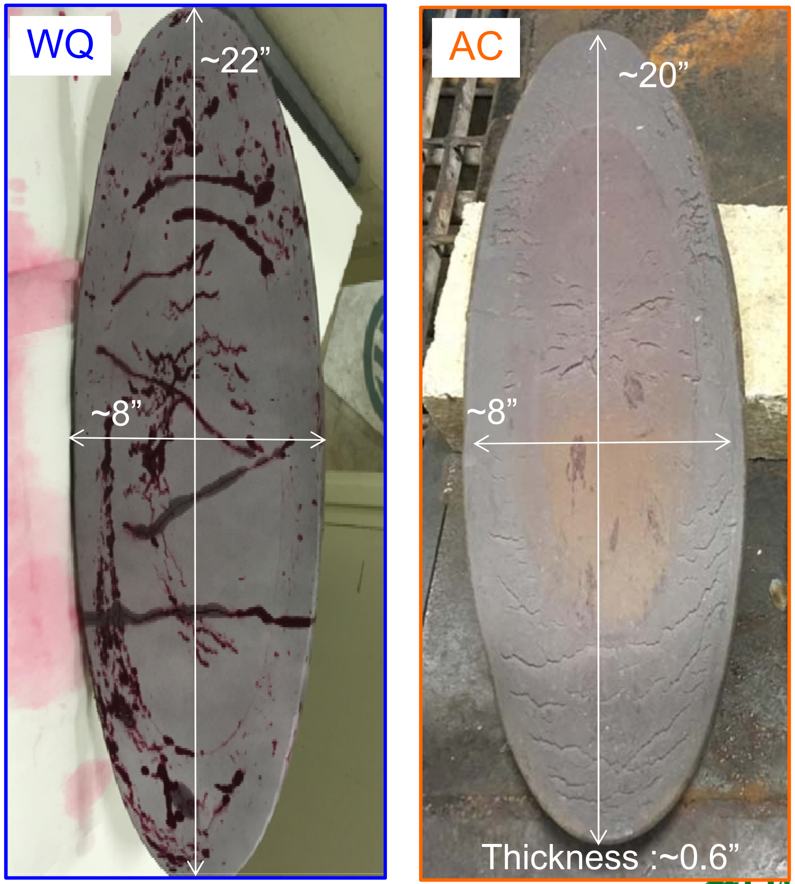
Scale-up Efforts (Fe-30Cr-3Al-2Nb-0.2Si-0.12Y)

VIM ingot (4” dia.) after HIPing

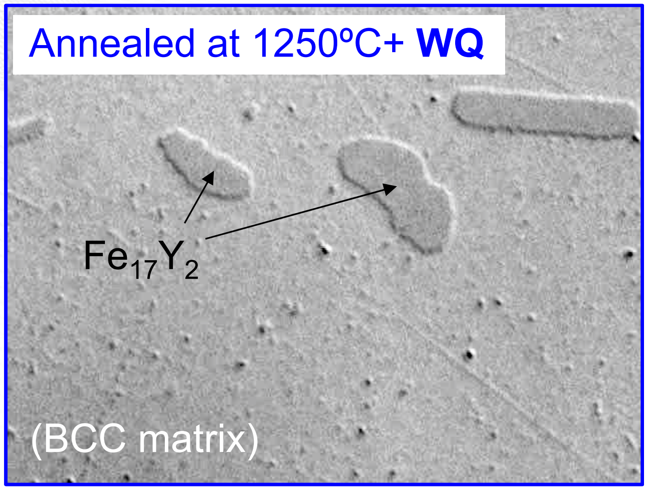


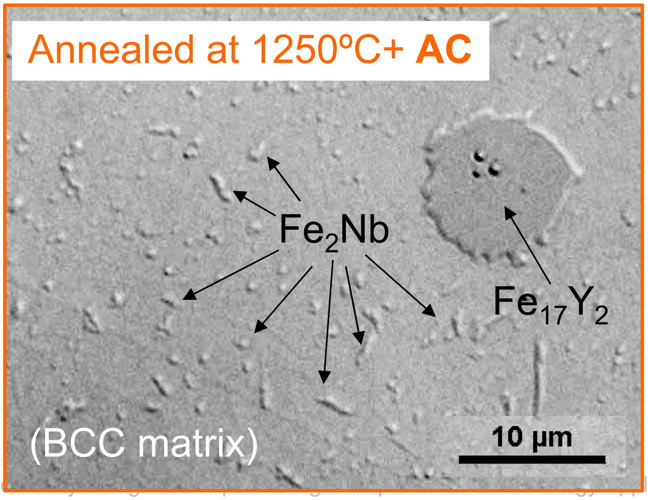
Forged at 1250ºC

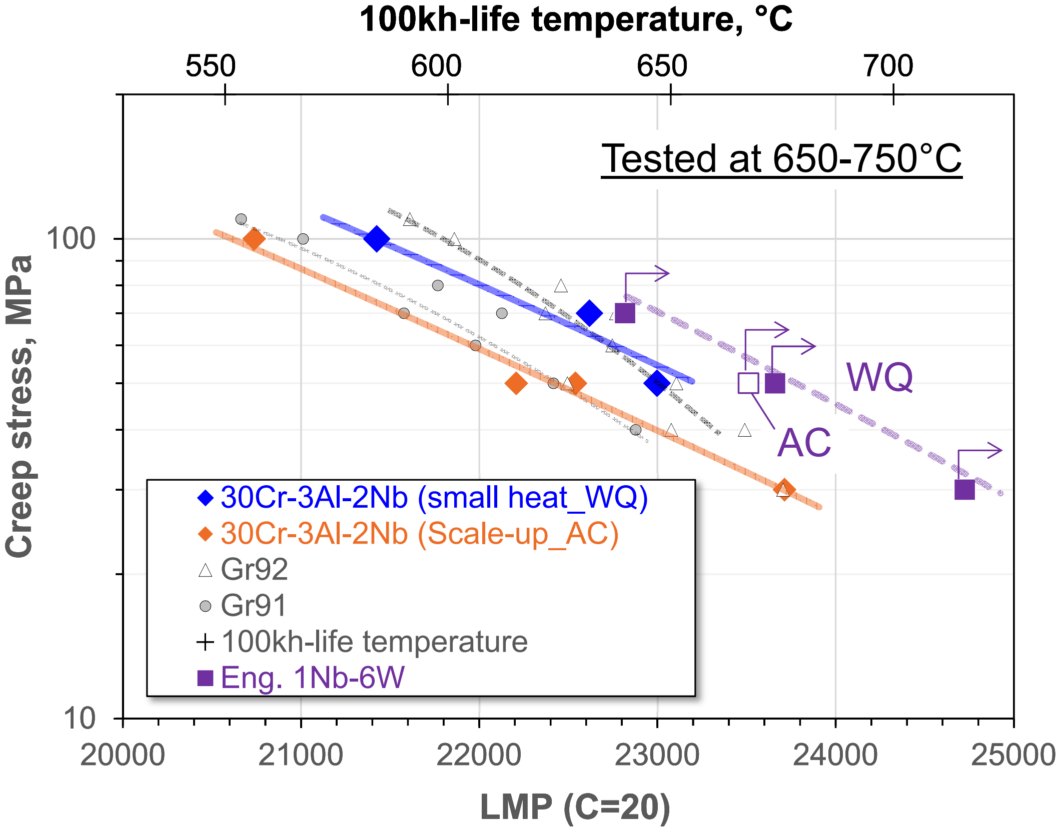
Rolled (and annealed) at 1250ºC



Effect of Cooling Rate after Solution Annealing







Summary

- Effect of third element additions in Fe-30Cr-3Al base alloy on “microstructural stability” and “various high-temperature properties”:
  - W, Mo, and Ti additions are;
    - *Effective to lower the BCC solvus temperature*
    - *Detrimental to microstructure stability during creep deformation*
  - The larger volume fraction of Laves phase precipitate, the better for the creep resistance
  - Oxidation and ash-corrosion resistance are more sensitive to the amounts Cr and Al (and Nb) than the others
- Scale-up efforts in progress
  - Move to engineering alloys (based on 1Nb-6W +Mo, Ti, Mn, and C)
  - Require improvement of better processibility (against thermal shock, etc.)

Future Activities

- **Property evaluation the second scale-up heat:**
  - *Screening basic properties (tensile, hardness, microstructure)*
  - *Intermediate/long-term creep-rupture test at or above 700ºC*
  - *Ash-corrosion resistance evaluation at 700ºC*
  - *GTAW screening*
- **New efforts on alumina-forming austenitic steels and Ni-base alloys**
  - *Target the applications in various extreme conditions (coking, metal dusting, sCO_2, etc.)*
  - *Communications with industrial partners initiated*

Thanks

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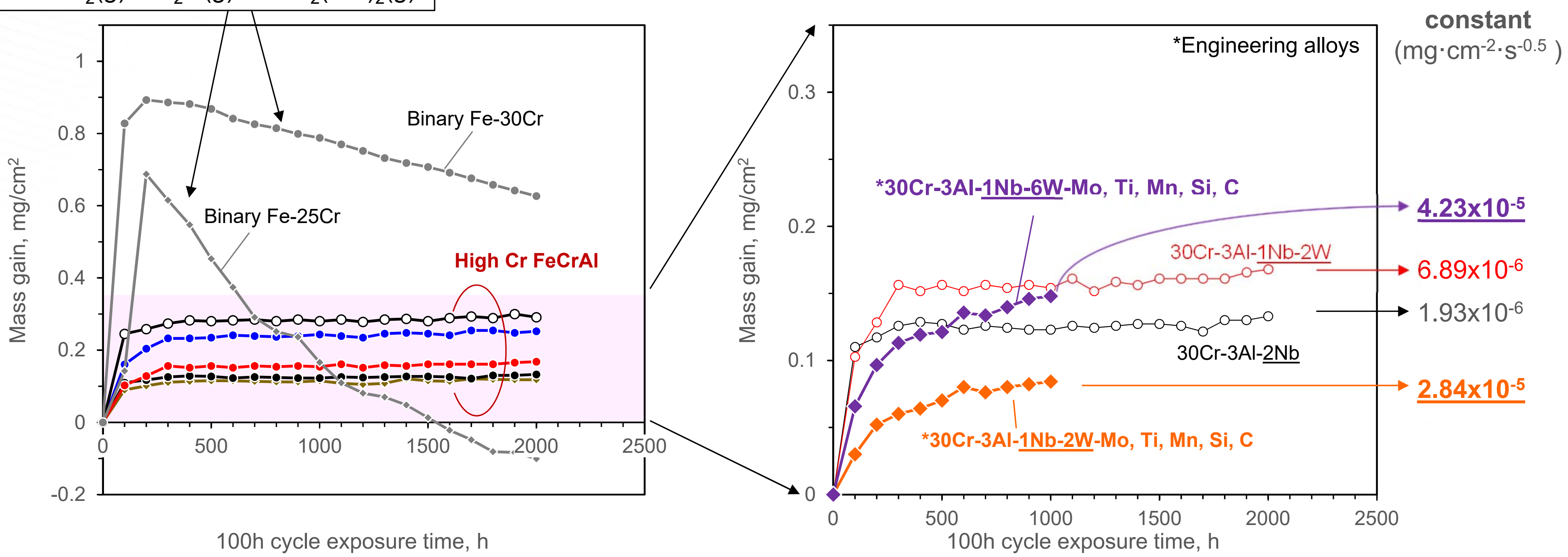
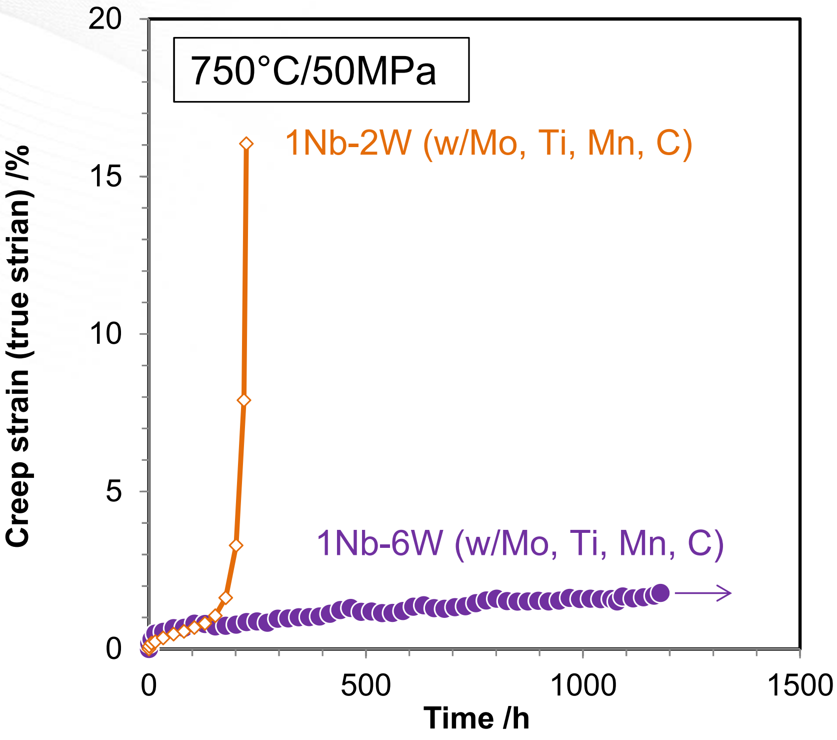
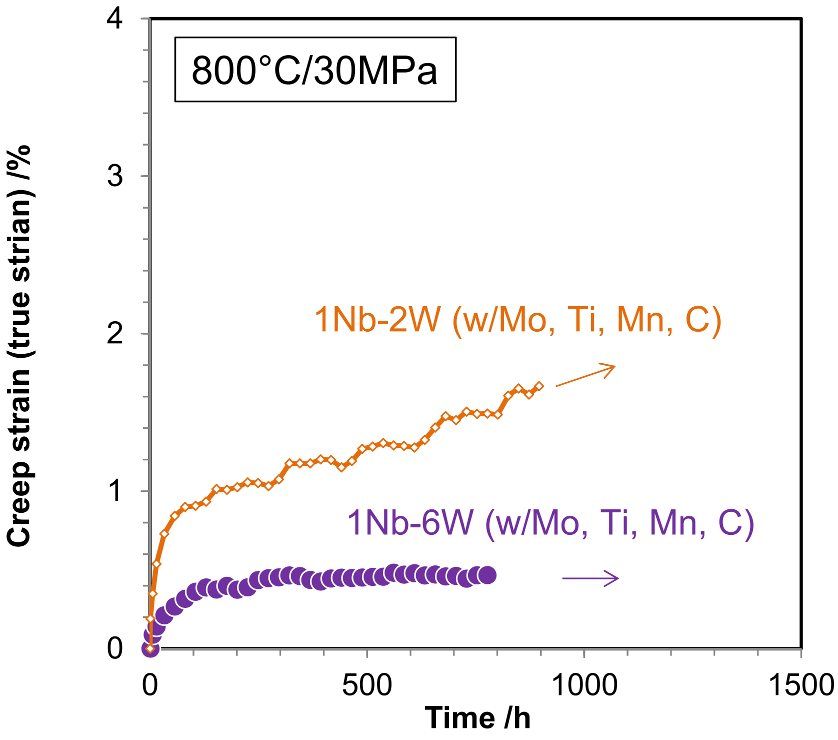


Higher Temperature Tests In Progress (750 & 800 °C)





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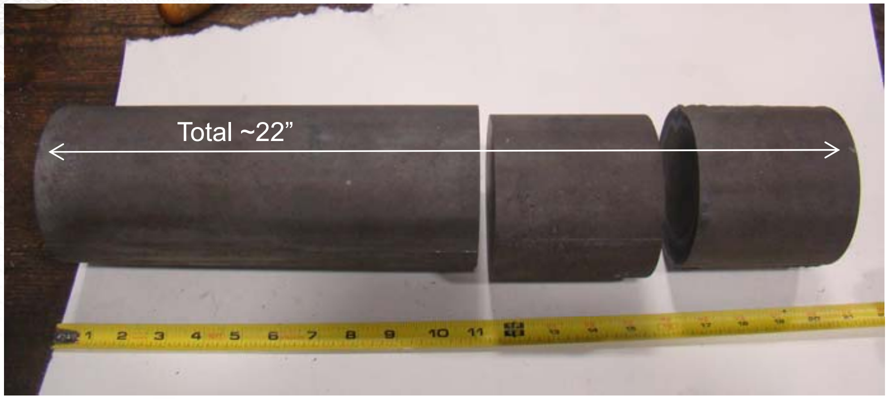


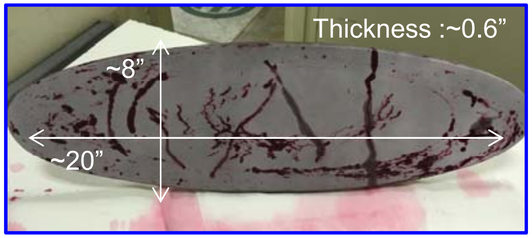
Forged at 1250ºC

Rolled

at 800ºC

at 1000ºC

at 1250ºC
+ WQ



at 1250ºC
+ AC