

Advanced Alloy Design Concepts for High-Temperature Fossil Energy Applications (FEAA114)

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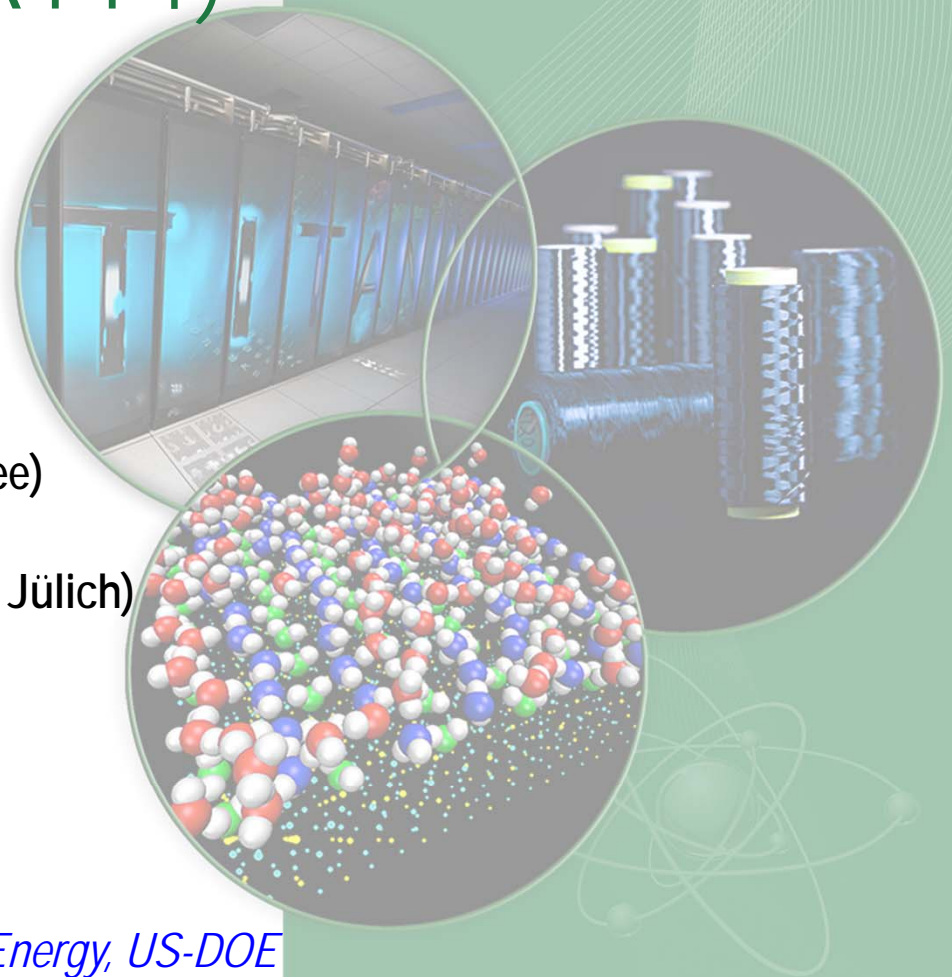
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Contents of This Talk

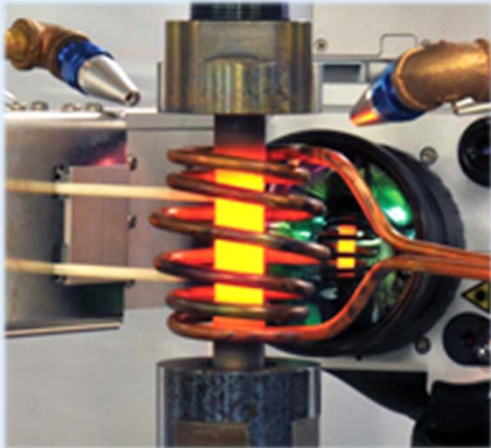
- **Backgrounds/Motivation:**
 - *High-Cr containing FeCrAl alloy development*
- **Update on FY15/16**
 - *Microstructure characterization of crept specimens*
 - *Oxidation update*
 - *Effect of alloying on Laves-phase solvus and size*
 - *Effect of alloying on yttrium effect*
 - *Trial weld results*
 - *Scale-up efforts*
- **Summary**
- **Future Activities**

Project objective

- To identify and apply breakthrough alloy design concepts and strategies for incorporating **improved creep strength, environmental 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.

High-Cr containing FeCrAl ferritic alloy

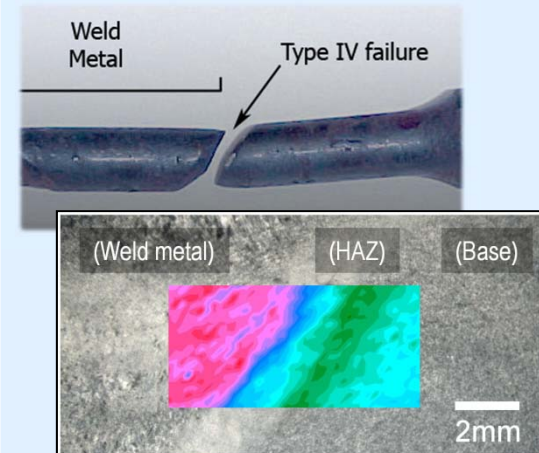
High-temp. Strength



Oxidation/Corrosion



Weldments

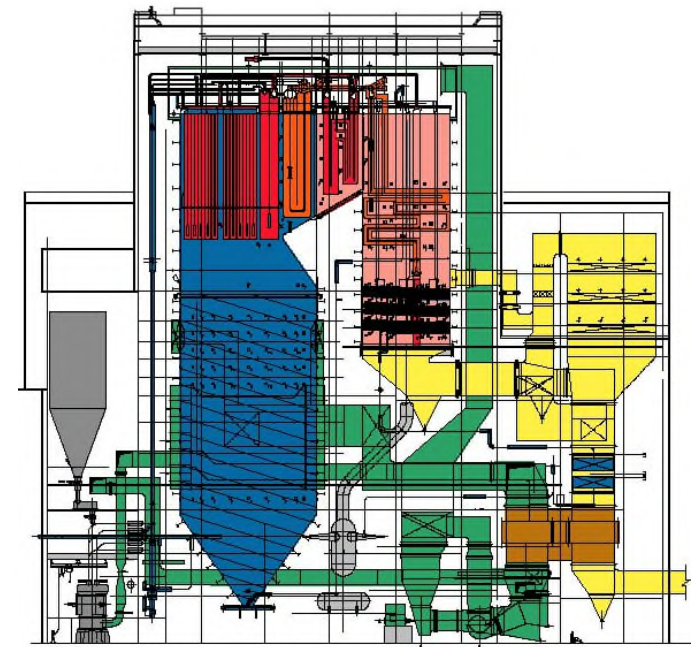
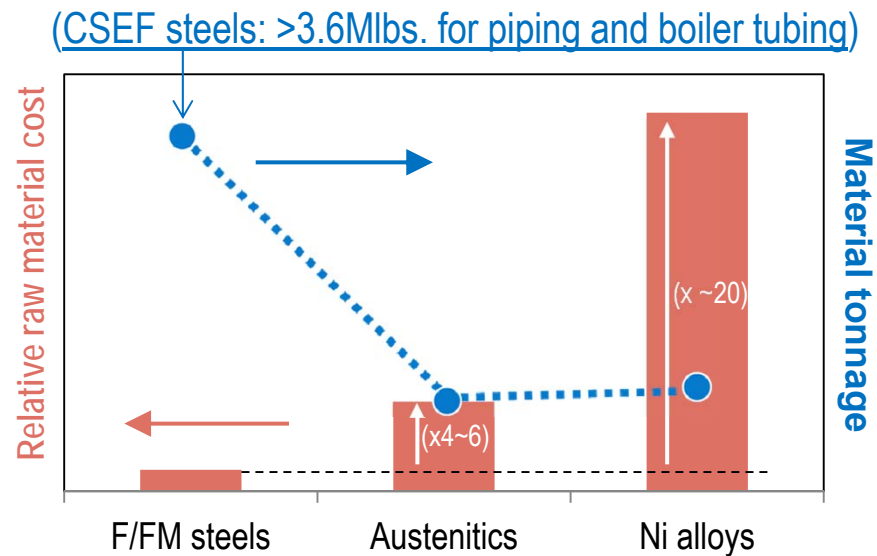


<https://mts.com/en/products/industry/materials-testing/index.htm>
<http://www.cci-online.com/prioritization-of-issues-improves-hrsg-reliability-performance/>

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

Type IV Issues of F-M Steels in Fossil Energy Applications

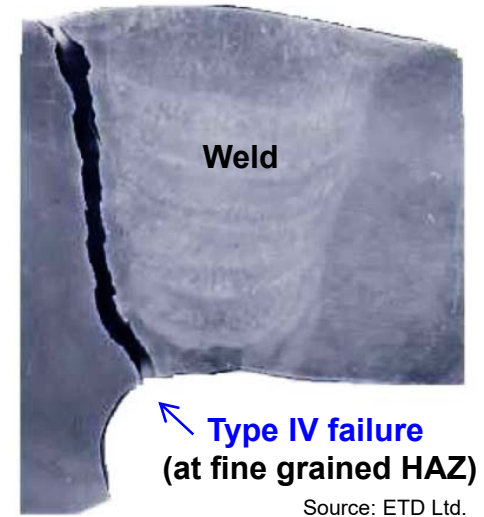
- **Life of weldments shorter than Base Metal**
 - **Type IV failure** shortens the material life, caused by weakened microstructure at the heat affected zone (HAZ)



- **Type IV failure of traditional F-M steel weldments unavoidable**

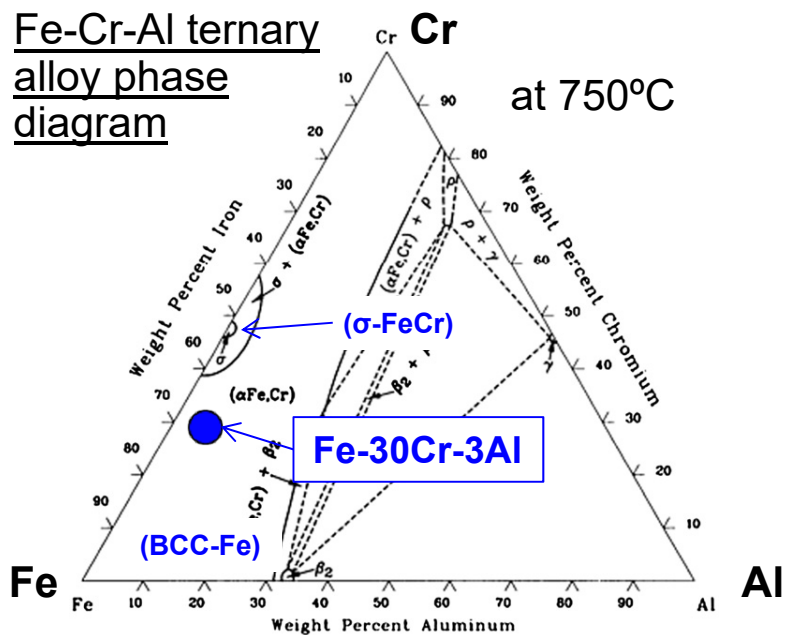
- To minimize: **Optimization of heat treatment (FEAA107, ~FY13)**
- To eliminate: **New alloy development (FEAA114, FY14~)**
 - No Type IV failure (= no phase transformation) → Increase upper limit temperatures
 - Improved mechanical properties AND oxidation/corrosion resistances in single alloy
 - Maintain competitiveness with existing structural materials (cost, fabricability, weldability)

→ Fe-30Cr-3Al with Nb addition

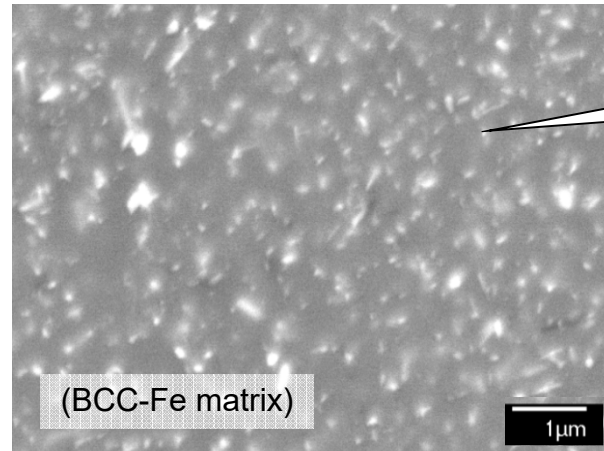


New Approach to Develop Heat-Resistant High-Cr FeCrAl +Nb Alloys

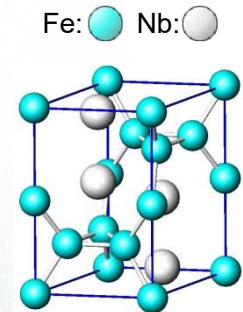
- ❑ **No phase transformation in Fe-Cr binary alloys with > ~13 wt.% Cr**
 - The higher Cr addition the better oxidation/corrosion resistance (>25 wt.%)
- ❑ **Improved steam oxidation resistance by Al addition**
 - Also destabilize brittle σ -FeCr phase
- ❑ **Require to strengthen the alloys at elevated temperatures**
 - Nb addition to expect Fe_2Nb -Laves phase precipitation for HT strengthening



SEM-BSE
(Fe-30Cr-3Al + Nb, W, Si; aged at 700°C)



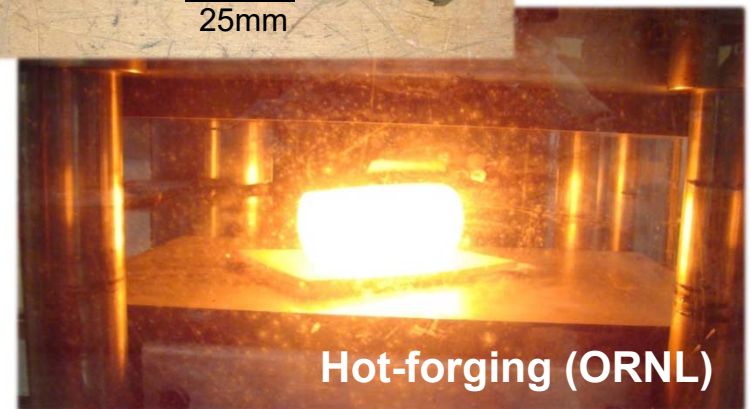
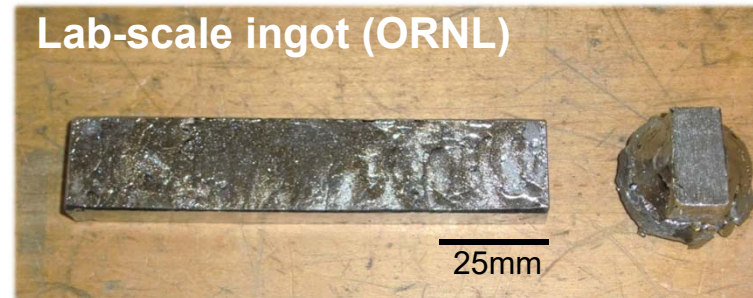
C14: Laves- Fe_2Nb



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

Properties Need To Be Evaluated

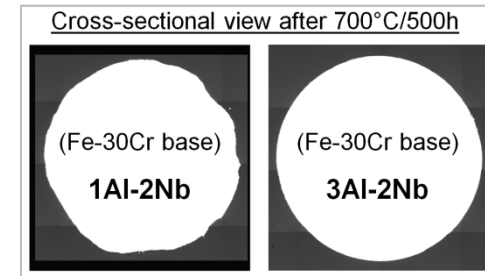
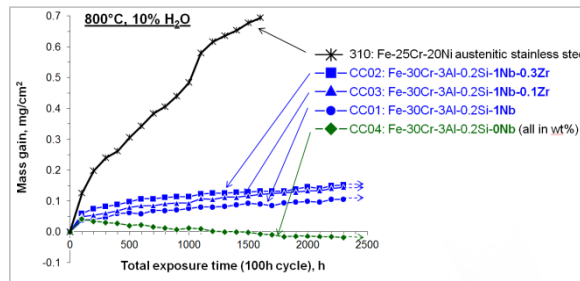
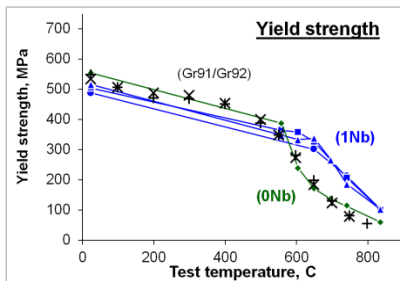
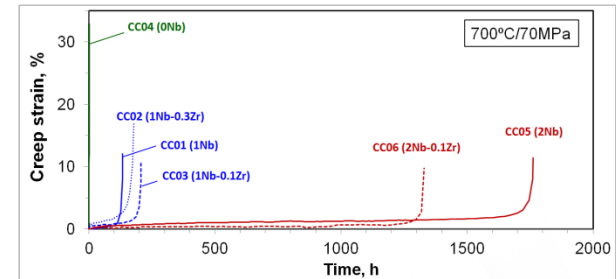
- **Thermo-mechanical Treatments:**
 - *Homogenization*
 - *Solution heat-treatment*
 - *Hot-forging/ -rolling*
 - *Annealing*
- **Microstructure characterization:**
 - *As hot-processed*
 - *Solution treated and Aged*
 - *Creep-ruptured*
 - *Cross-welded*
- **Mechanical properties:**
 - *RT/HT tensile properties*
 - *Creep-rupture properties*
 - *Hardness*
 - *Toughness*
- **Environmental compatibilities:**
 - *Oxidation test in Air + 10% H₂O*
 - *Ash-corrosion test*
- **Weldability:**
 - *E-beam weld*
 - *Gas Tungsten Arc Weld*



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, 40~110MPa)

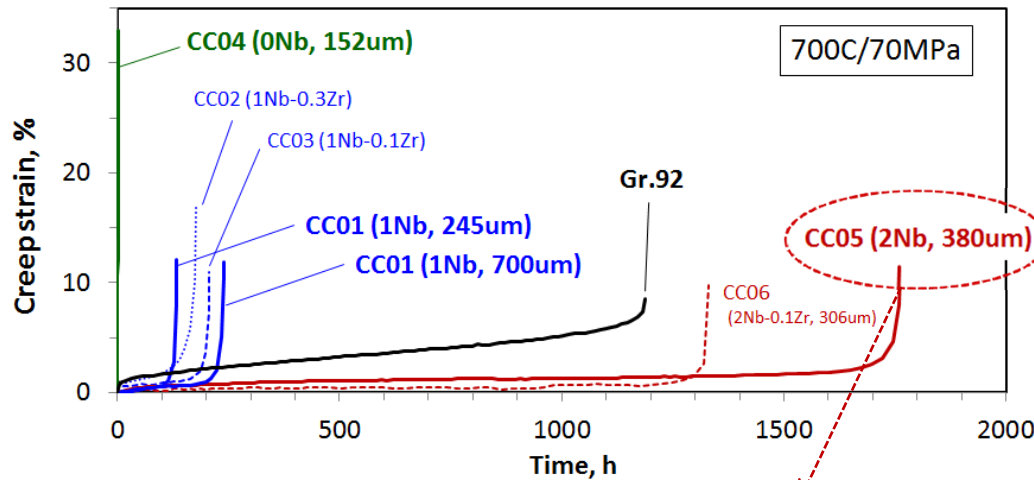


- **2nd series: Fe-30Cr-3Al with (0.5~2)Nb + W, Mo, Ti, or Y**

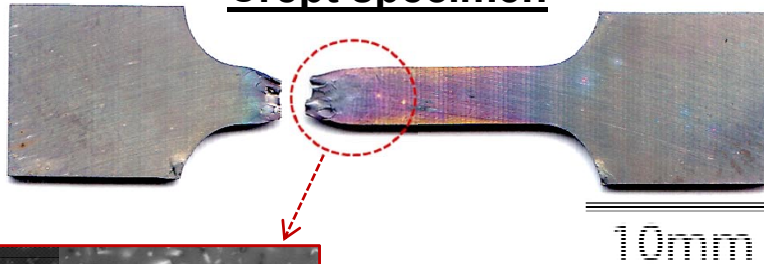
- Solvus temperature control
- Size stability of Lave-phase particle at 700°C
- Size stability of grain structure at 1200°C
- Trial E-beam weld
- Scale-up effort

Improved Creep Properties in 2Nb Alloys

Creep-rupture curves

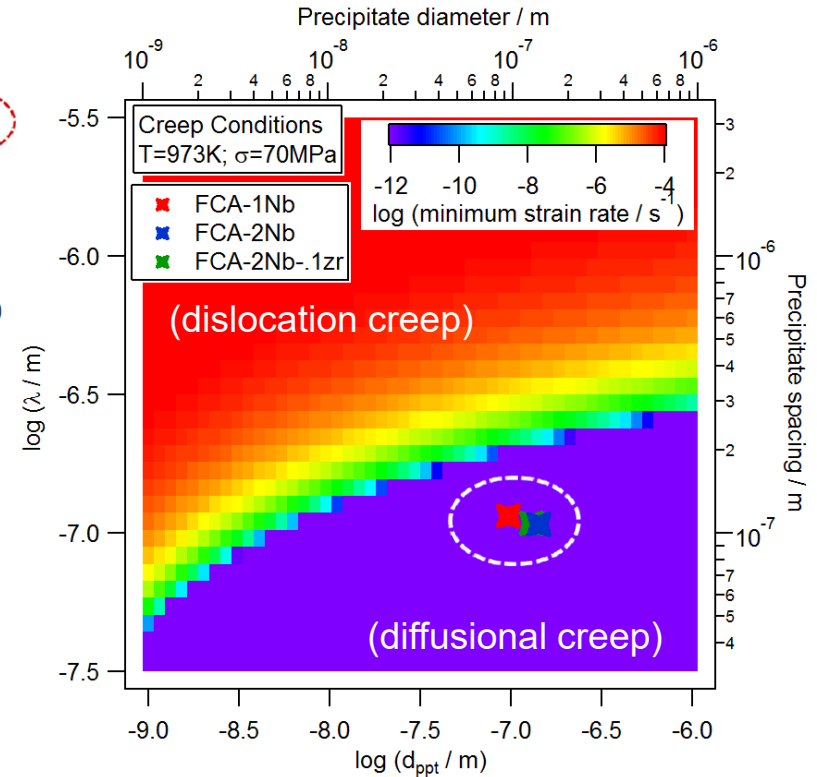


Crept specimen



$\dot{\epsilon}_{min}$: $1.47 \times 10^{-7} \text{ s}^{-1}$
 Particle size: $1.4 \times 10^{-7} \text{ m}$
 Particle spa.: $1.0 \times 10^{-7} \text{ m}$

Calc. minimum creep-rate map at given particle distribution

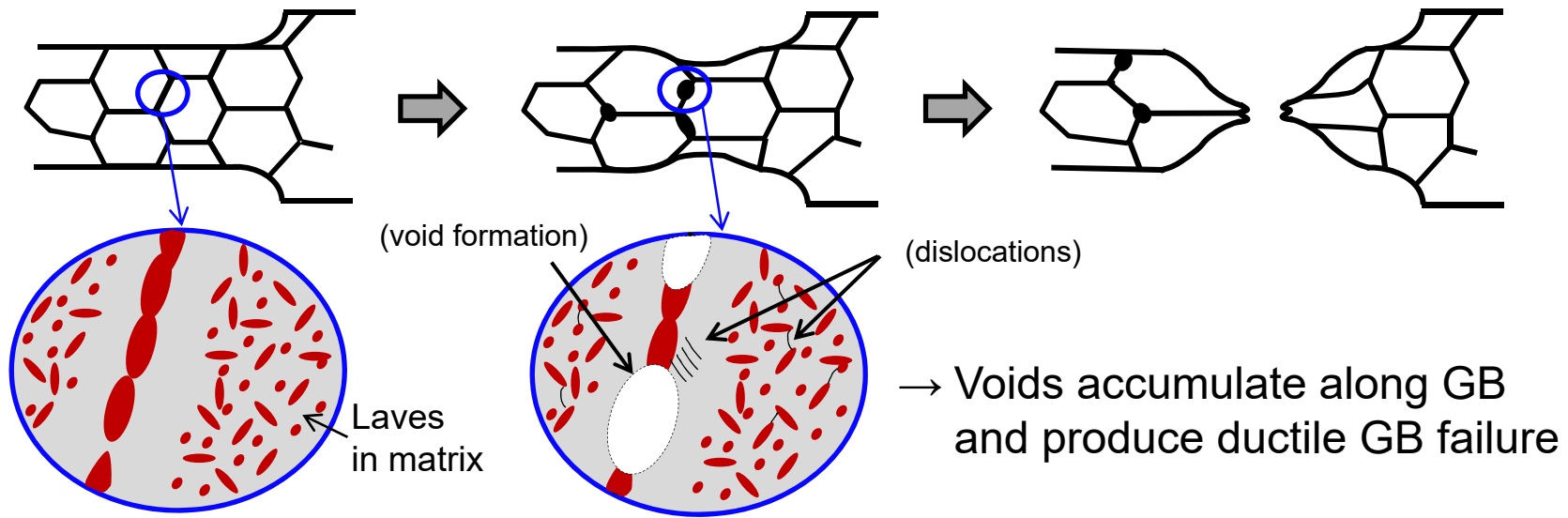


*Used Bird-Mukherjee-Dorn (BMD) model

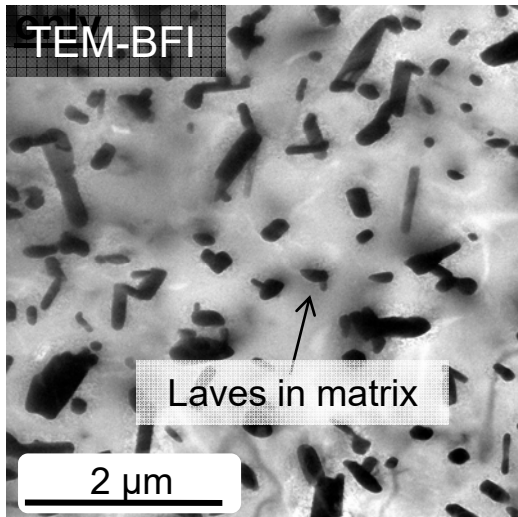
$$\frac{\dot{\epsilon}_m kT}{DEb} = A_{Dis} \left(\frac{\sigma_a - \sigma_{th}}{E} \right)^n$$

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

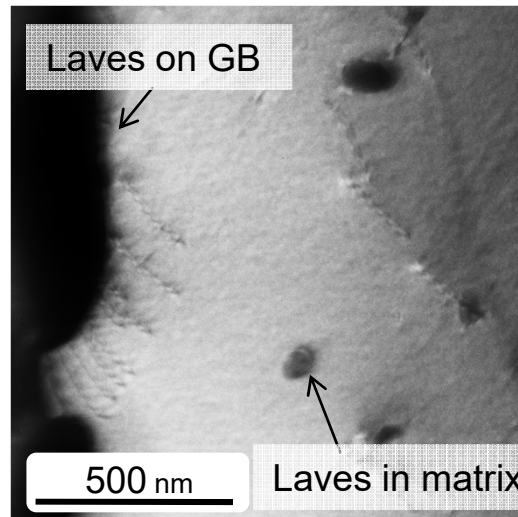
Creep-Failure Mechanisms Near GB



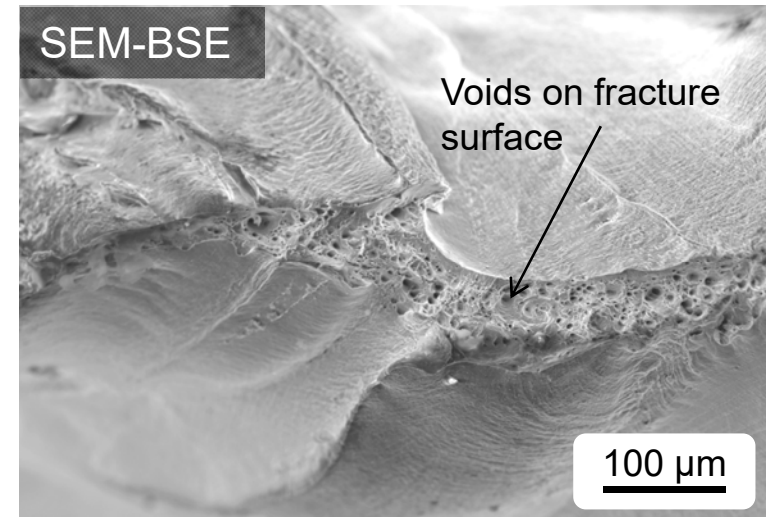
Matrix



Near GB

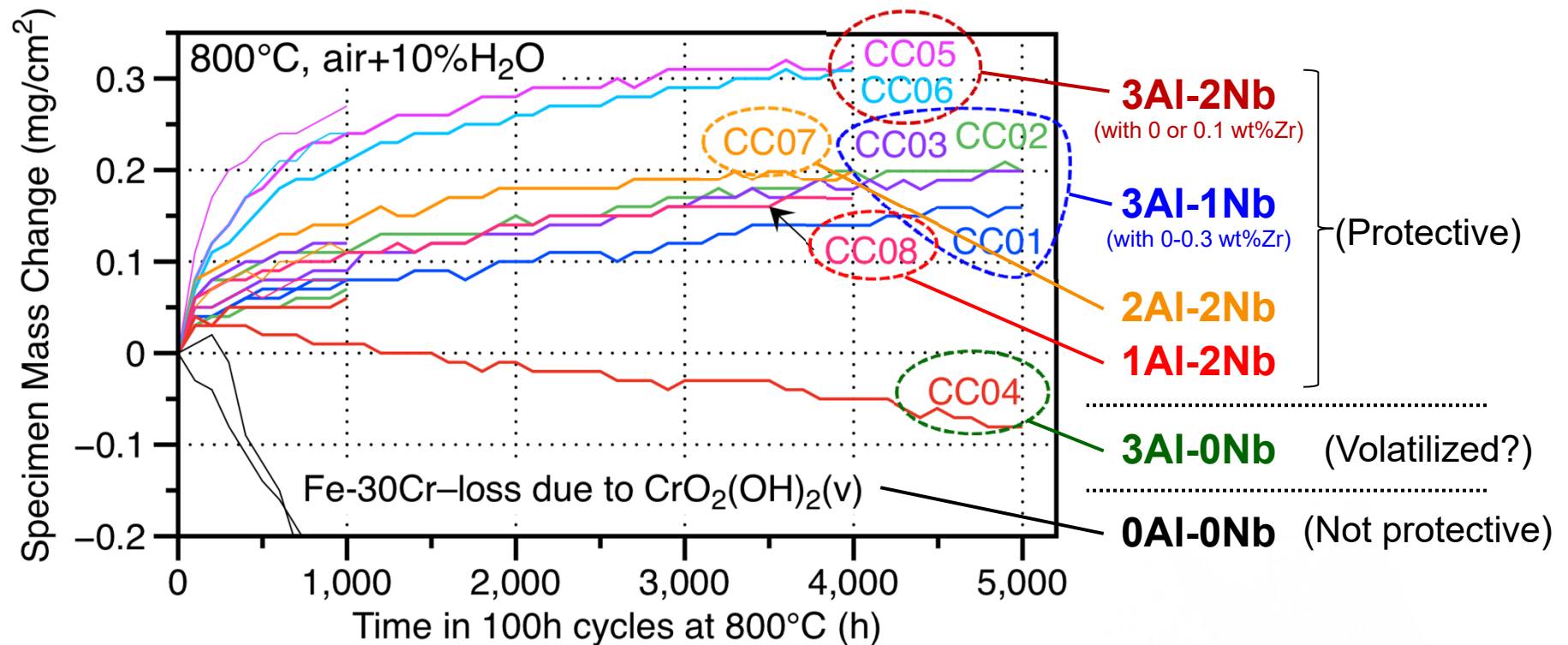


Creep rupture surface



(Creep ruptured specimen (2Nb alloy) tested at 700C and 70MPa)

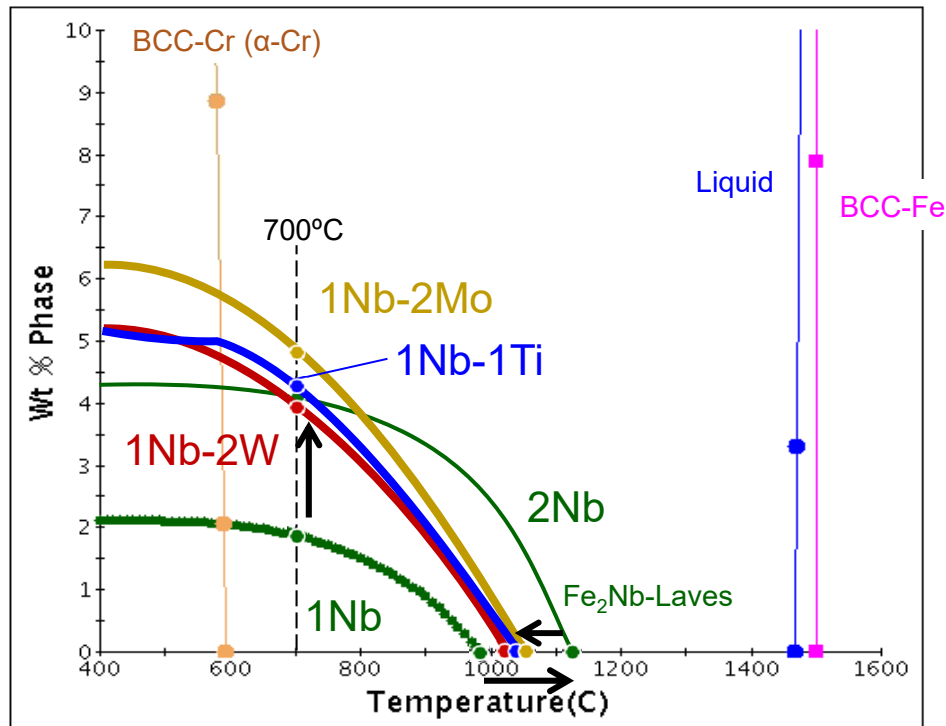
Strong Benefit of Al+Nb Additions on Slow Oxidation Kinetics in Air+10%H₂O



- *No significant impact from the Zr addition (0.1-0.3 wt.%)*
- *Ash-corrosion test at 700°C revealed improved protective characteristics by the combined additions of Al+Nb (FY15)*

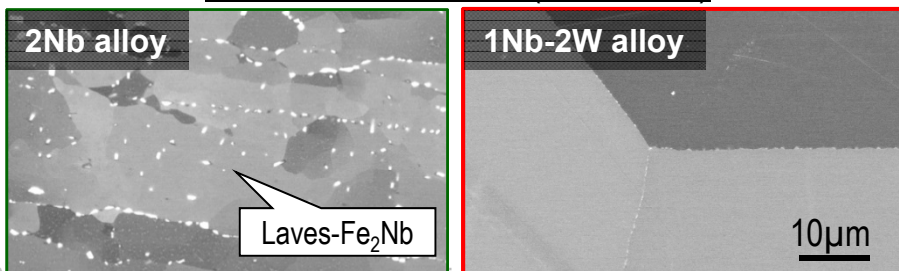
Impact of "Third Additional Elements" on Microstructure

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

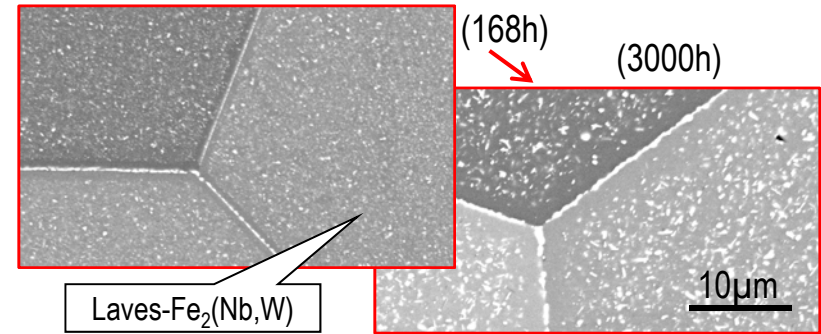


*calculated by JMatPro

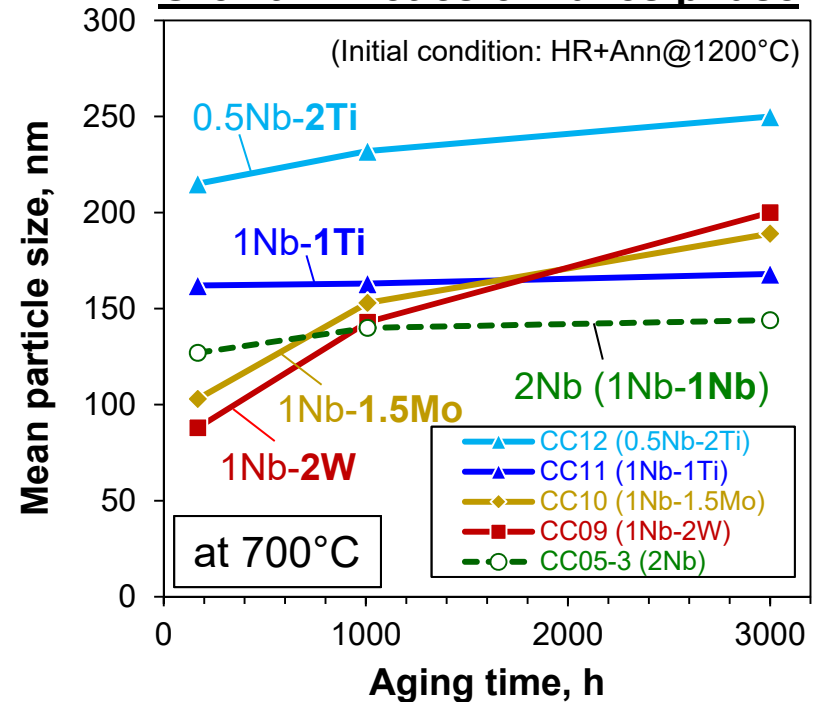
Annealed at 1200°C (SEM-BSE)



1Nb-2W alloy, aged at 700°C (SEM-BSE)

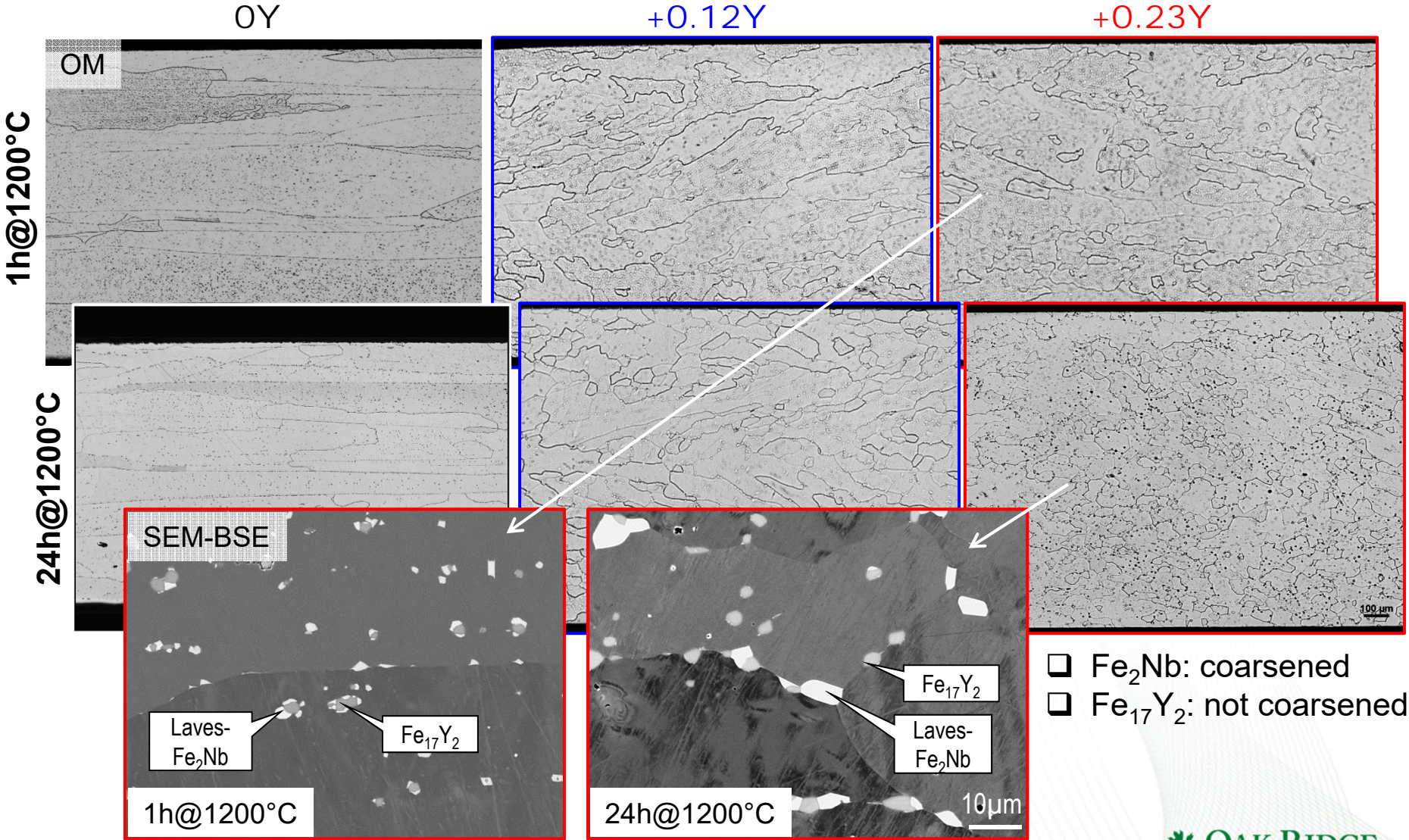


Growth kinetics of Laves phase

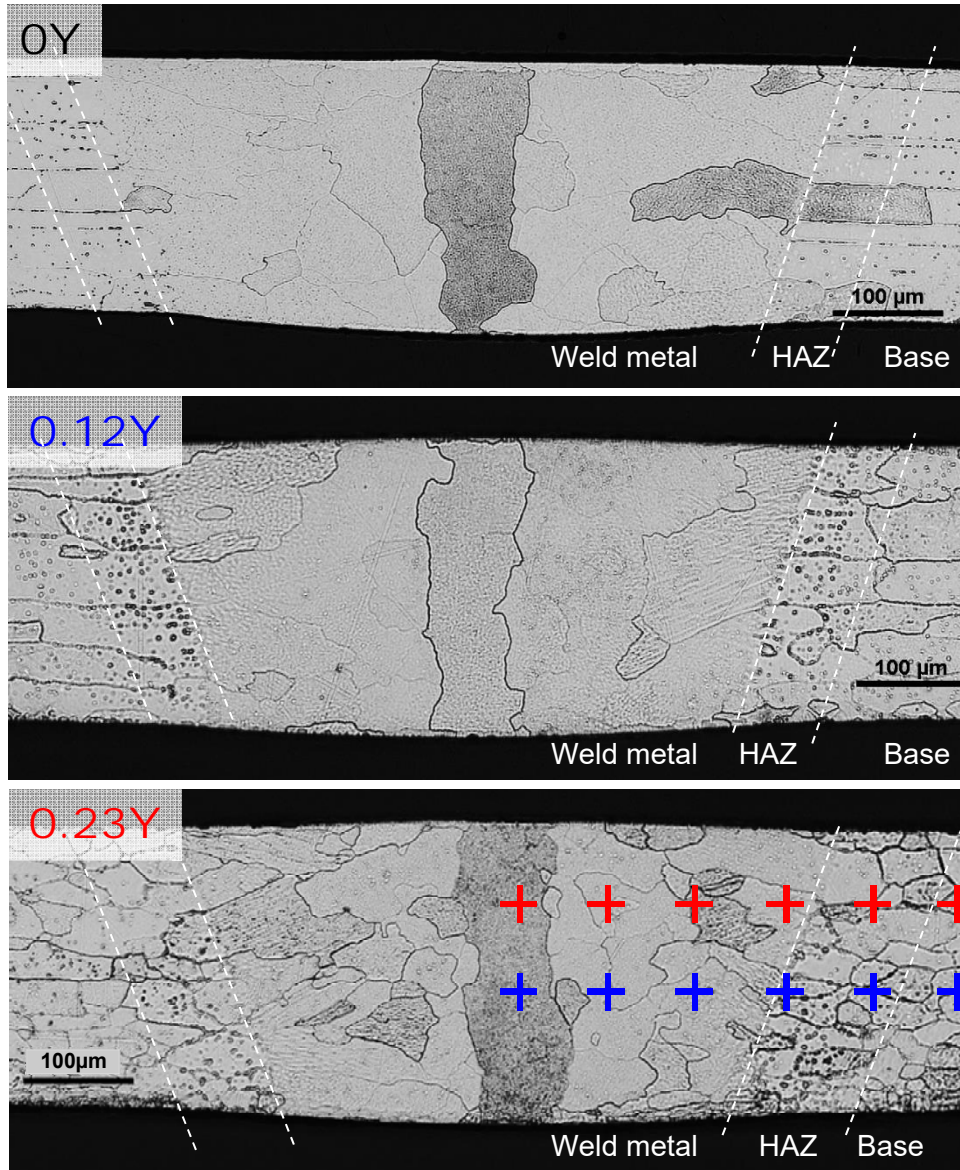


Stabilized Grain Size Through Y Addition

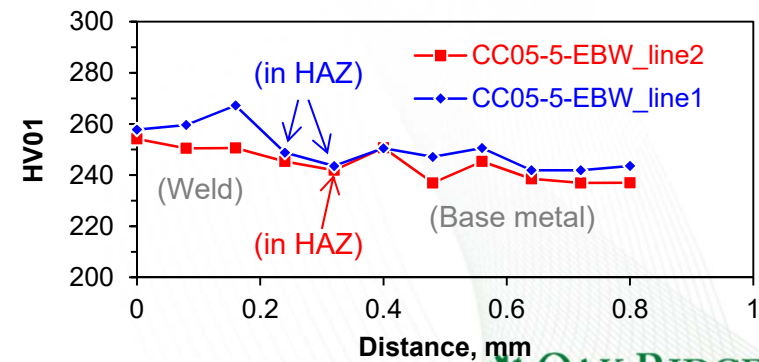
Fe-30Cr-3Al-2Nb + Y, Hot-rolled at 800°C + annealed at 1200°C



Y Addition Also Beneficial on Weld (EBW)

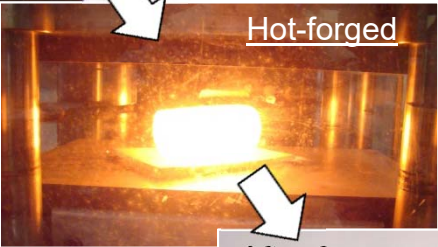
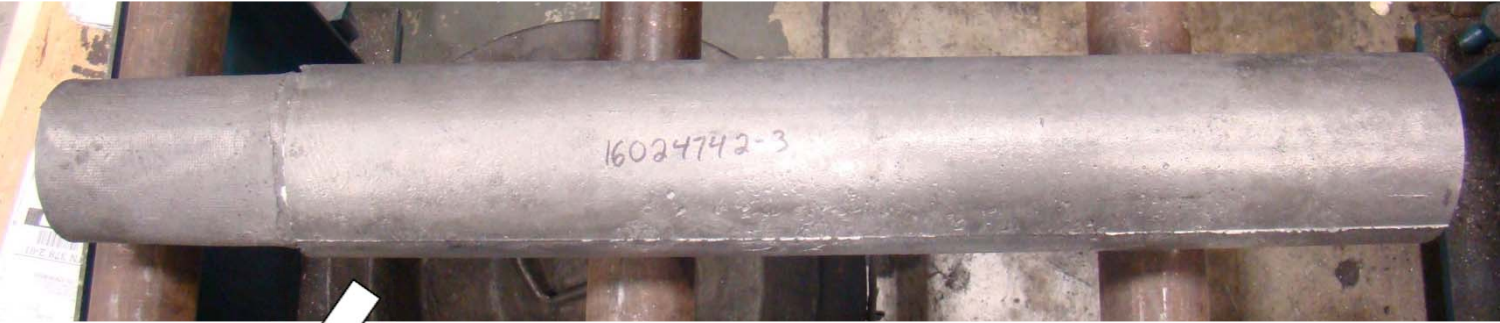


- High Y addition (0.23 wt.%) effectively refine the grain size inside weld metal
- No obvious grain coarsening nor hardness drop at HAZ
- Uniform hardness profile across the weld/HAZ/base metal



Scale-up Effort Initiated

VIM ingot: 4" diameter x 26" length (off-spec, Fe-30Cr-2.6Al-2Nb+Y)



- Cracks already exist in the as-cast ingot (not formed during hot-process)
- Hot-isostatic press has successfully eliminated the cracks

Summary

Creep-resistant high-Cr FeCrAl alloy development in progress

- **Microstructure characterization of crept specimens:**
 - *Creep-rupture specimens → discussed creep-deformation mechanism*
 - **Oxidation test up to 5,000h completed:**
 - *Found the benefit of Al + Nb combined additions*
 - *Corrosion test of the scale-up batches is planned*
 - **Effect of third element additions on thermal stability:**
 - *Laves-phase formed elements (W, Mo, and Ti) → further optimization would be suggested to balance the solvus temperature and particle stability*
 - *Y additions on high temperature grain size stability → potential advantage of hot-workability and weldability*
 - **Trial e-beam weld of Y containing alloys:**
 - *Potential advantage of Y addition to avoid unfavorable coarse grains*
 - **Scale-up effort initiated:**
 - *Plan to have two 80lbs VIM ingots (on-spec. and off-spec.)*
 - *Process development in progress*
-
- **Communication with Forschungszentrum Jülich (FZJ) in progress:**
 - *For high-Cr fully ferritic steel development (Hiperfer, Fe-17Cr base)*
 - *ORNL supports process and weld development*

Future Activities

- **Complete thermo-mechanical treatment of the scale-up heat:**
 - *Screening basic properties (tensile, hardness, microstructure)*
 - *Intermediate/long-term creep-rupture test at or above 700°C*
 - *Ash-corrosion resistance evaluation at 700°C*
 - *GTAW screening*
- **Communicate with ASME Boiler and Pressure Vessel code committee for potential determination of code case:**
 - *Initiated to contact with the Section II committee members*

Thanks for your attention

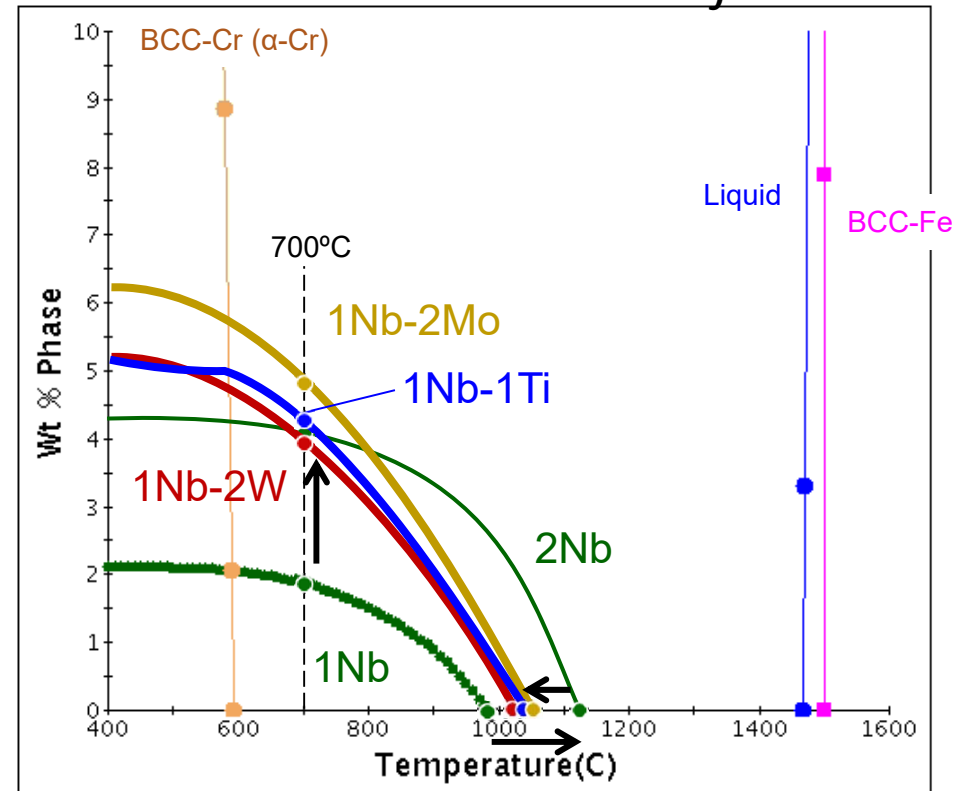
Preparation of Materials

- **Down-selected alloys to be evaluated:**
 - 12 alloys based on **Fe-30Cr-3Al + Nb, Zr, W, Mo, Ti, and Si**
 - Expected Fe_2Nb type Laves-phase precipitates for strengthening
 - Used computational thermodynamic tools for downselect

Table: Nominal composition of the alloys studied

wt%	Fe	Cr	Al	Nb	Zr	W	Mo	Ti	Si
CC01	Bal.	30	3	1	0				0.2
CC02	Bal.	30	3	1	0.3				0.2
CC03	Bal.	30	3	1	0.1				0.2
CC04	Bal.	30	3	0	0				0.2
CC05	Bal.	30	3	2	0				0.2
CC06	Bal.	30	3	2	0.1				0.2
CC07	Bal.	30	2	2	0.1				0.2
CC08	Bal.	30	1	2	0.1				0.2
CC09	Bal.	30	3	1		2			0.2
CC10	Bal.	30	3	1			1.5		0.2
CC11	Bal.	30	3	1				1	0.2
CC12	Bal.	30	3	0.5				2	0.2

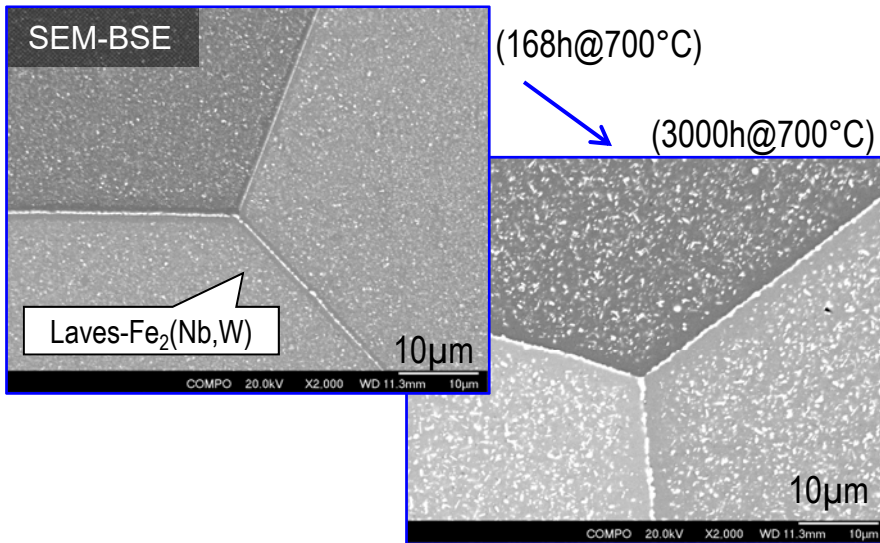
Fe-30Cr-3Al-0.2Si base alloys*



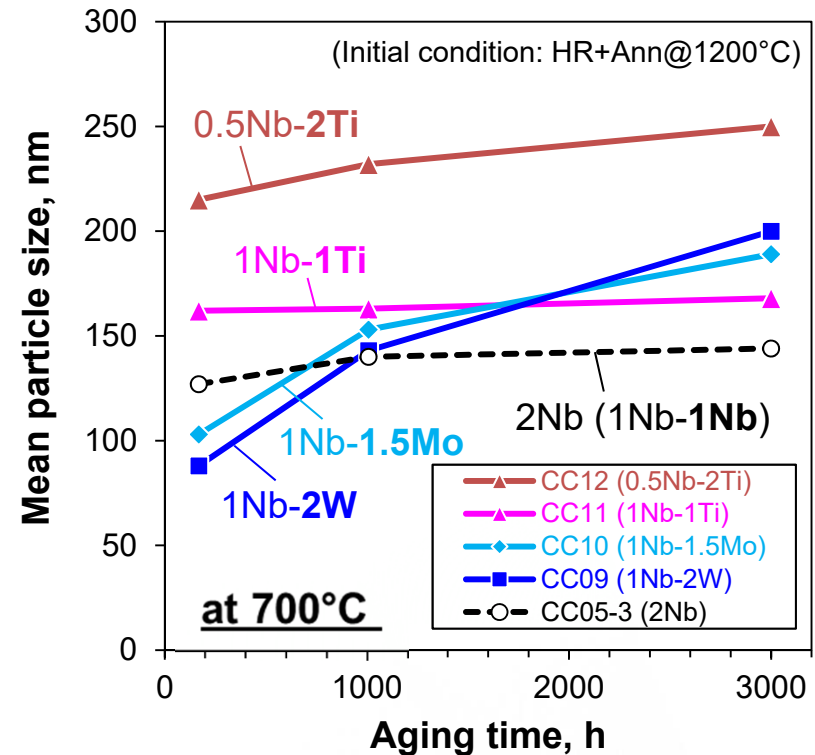
*calculated by JMatPro

Negative Impact of "Third Element Additions" on Precipitate Size Stability

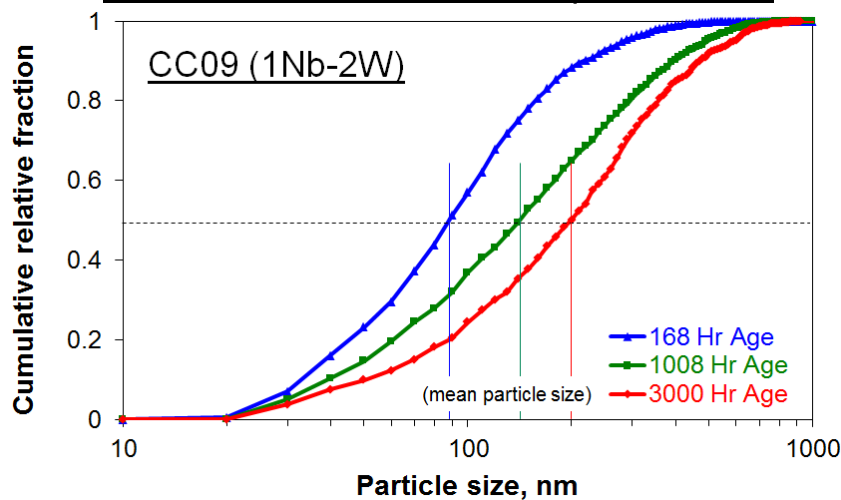
1Nb-2W alloy, aged at 700°C



Growth kinetics of Laves phase



Cumulative relative fraction of particle sizes



Third element effects:

- Solvus of Fe_2Nb in BCC successfully lowered (not shown)
- Less positive effect on size stability during aging at 700°C

Bird-Mukherjee-Dorn (BMD) Model

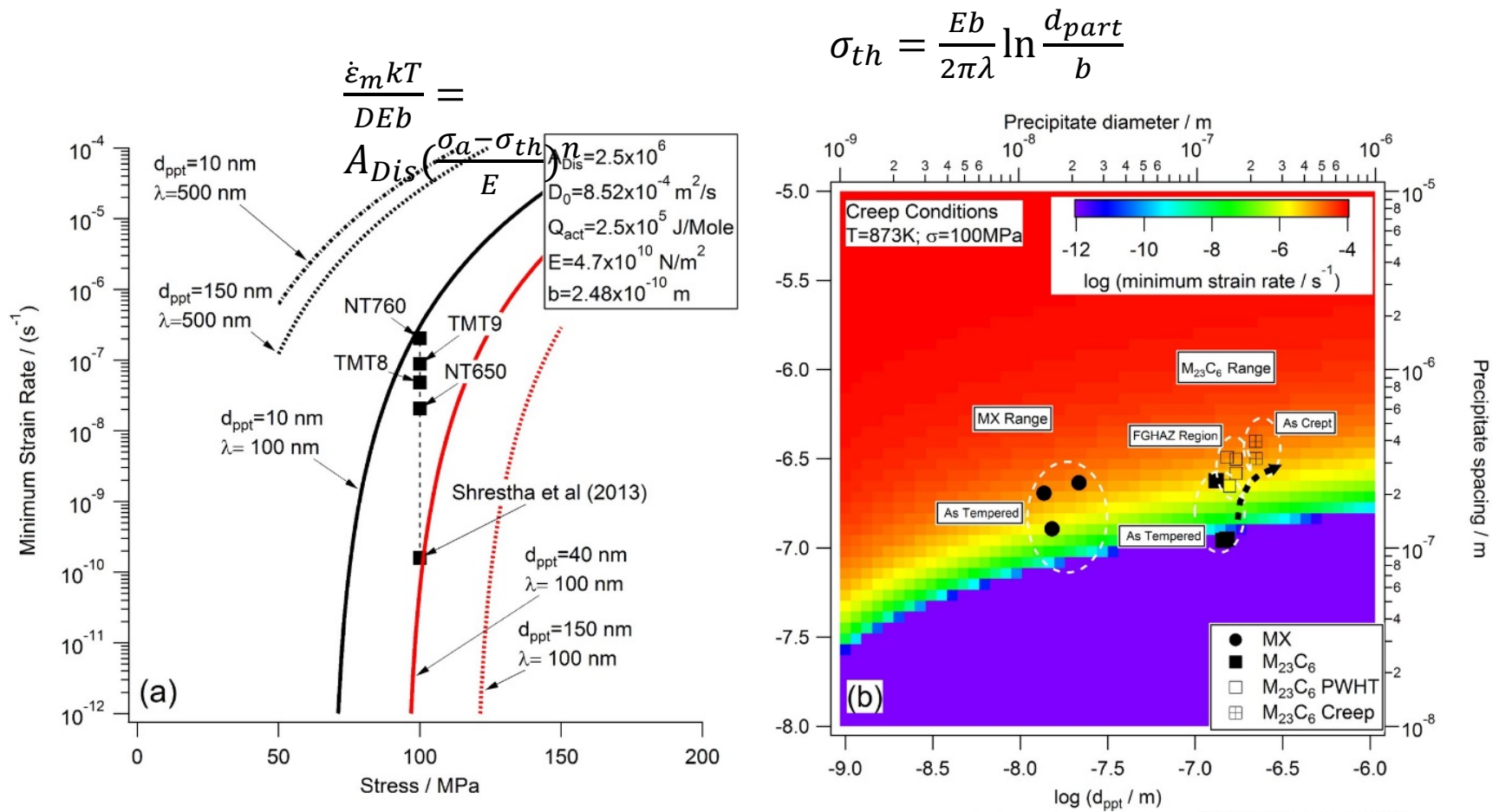


Figure: Results from parametric calculations of minimum creep rate using BMD phenomenological model as a function of (a) stress and (b) precipitate characteristics. (B. Shassere, et al. MMTA, 2016)