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

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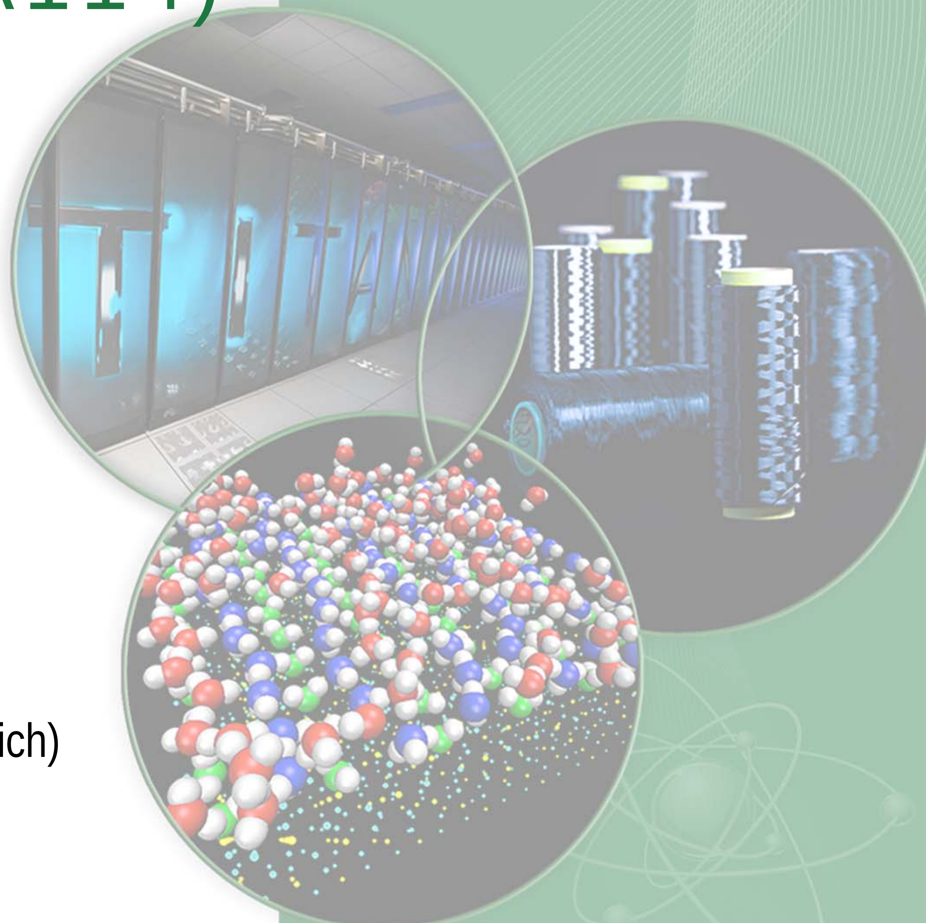

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Why "Improvement" of CSEF required? (FEAA107, ~FY14)

- **Majority of structural components for High-Efficiency Boilers (T23, T/P91, T/P92)**
- **Life of weldments shorter than Base Metal**
  - Type IV failure shortens the material life, caused by weakened microstructure at the heat affected zone (HAZ)

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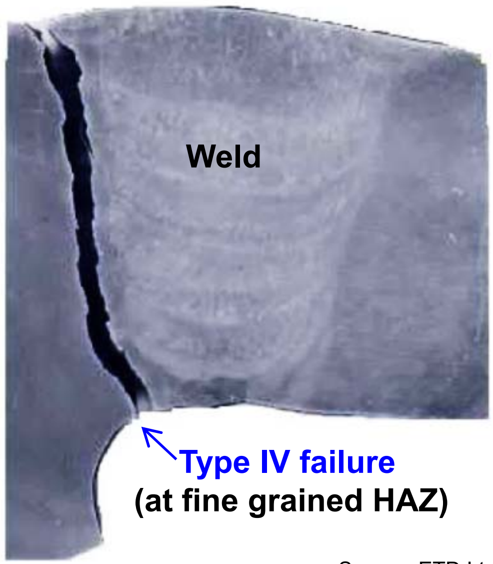
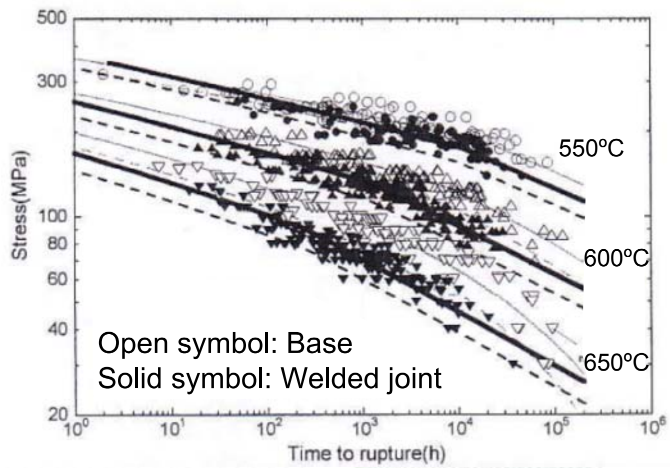
- Type IV failure of traditional F-M steel weldments is unavoidable
  - To minimize: Optimization of heat treatment
  - To eliminate: New alloy development



Source: ETD Ltd.

Creep-rupture lives of P91 Base/Weldments



Source: Yaguchi et al., ASME 2012 PVP

Approaches have been made/to be made

Optimization of HT
(FEAA107, ~FY14)

- Target existing CSEF steel (*e.g. Grade 91*).
- Apply optimized thermo-mechanical heat treatment (*feasible, inexpensive*).
- Based on scientific understanding (*required cumulative efforts*), as well as breakthrough concepts.

New alloy development
(FEAA114, FY14~)

- Target new alloys with optimized properties (e.g. *no Type IV failure = increase upper limit temperature*).
- Improved mechanical properties demand increased corrosion resistance.
- Maintain competitiveness with existing structural materials (*cost, fabricability*).

Industry demands ⟷ Scientific challenges

Target Materials/ Applications

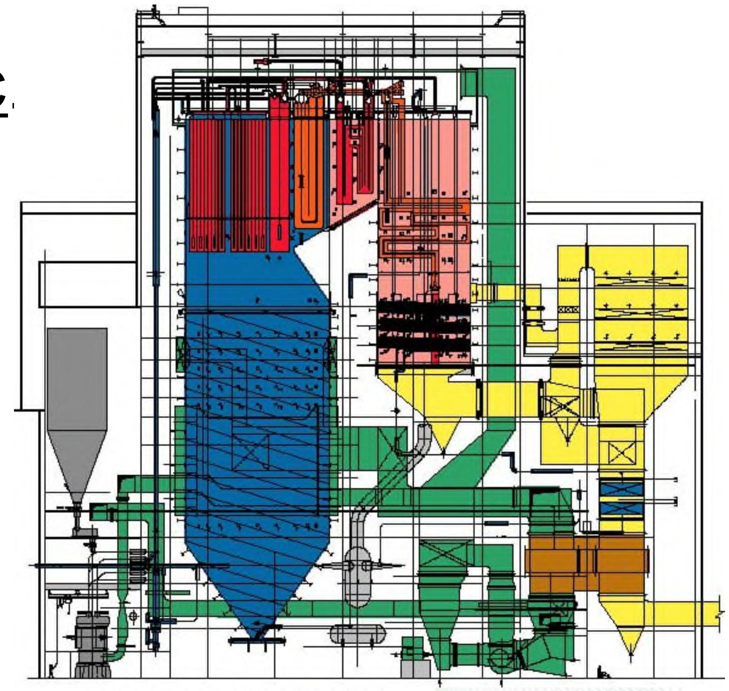
Three different grades of structural materials that are currently available for use by the US electric utility industry:

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.

– Super-heater / re-heater
– Steam piping / tubing
– Etc.



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

Corrosion/Oxidation Resistant Alloys

- **Environmental compatibility AND sufficient mechanical properties are the key for fossil-fired energy application**
  - Fabricability, weldability, and inexpensive material cost are also required
  - Alloy design requires satisfying all demands in one alloy
- **Approach: Follow successful “alumina-forming austenitic (AFA) steel” development strategy**
  - Select the base alloy compositions satisfying steam oxidation resistance (= alumina-scale formability)
  - Apply optimization of strength via solution/precipitation hardening (= creep resistance)

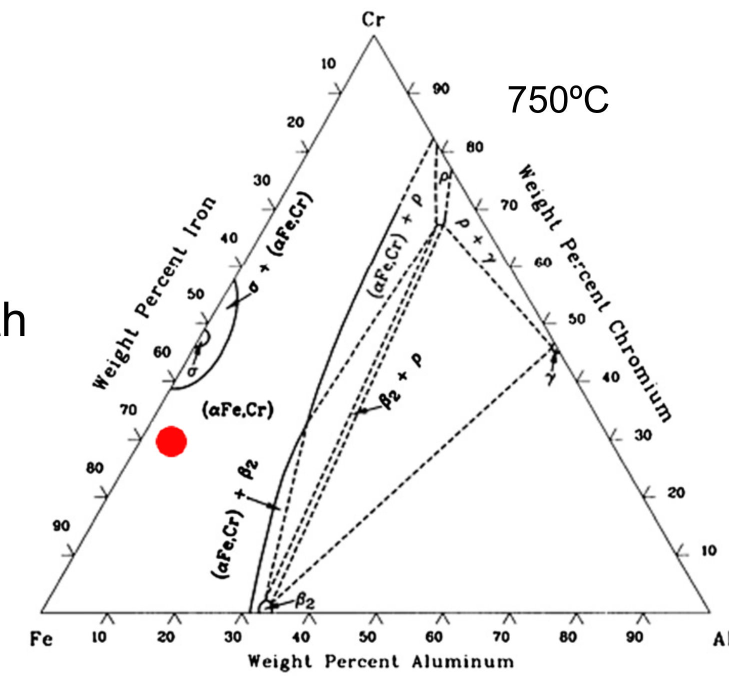
Project objective

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

Starting from Fe-30Cr-3Al base ferritic steel

Why high-Cr FeCrAl?

- **Expected fire-side corrosion resistance**
  - 30 wt% Cr will be required for surface protection
  - Addition of Al allows formation of alumina-scale for steam-side oxidation resistance
- **Advantages:**
  - Essentially free from Type IV failure (no α-γ transformation)
  - Better oxidation/corrosion resistance than advanced austenitic SS or Ni-base alloys with inexpensive cost
  - Al addition destabilizes σ-FeCr phase
- **Potential issues:**
  - Poor processbility due to low RT toughness
  - No carbides/nitrides can be used for strengthening precipitates because of very low C solubility/AlN formation, respectively



H.P. Qu et al. / Materials Science & Engineering A 562 (2013) 9–16

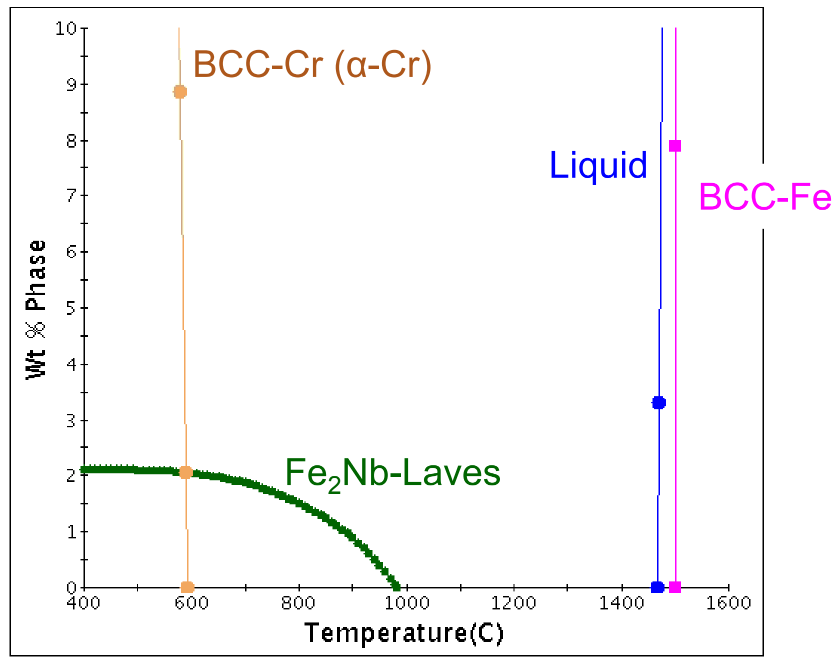
Preparation of Materials

- Down-selected alloys to be evaluated:
  - 8 model alloys based on **Fe-30Cr-3Al + Nb, Zr, 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	Si
CC01	65.8	30	**3**	**1**	0	0.2
CC02	65.5	30	**3**	**1**	0.3	0.2
CC03	65.7	30	**3**	**1**	0.1	0.2
CC04	66.8	30	**3**	**0**	0	0.2
CC05	64.8	30	**3**	**2**	0	0.2
CC06	64.7	30	**3**	**2**	0.1	0.2
CC07	65.7	30	**2**	**2**	0.1	0.2
CC08	66.7	30	**1**	**2**	0.1	0.2

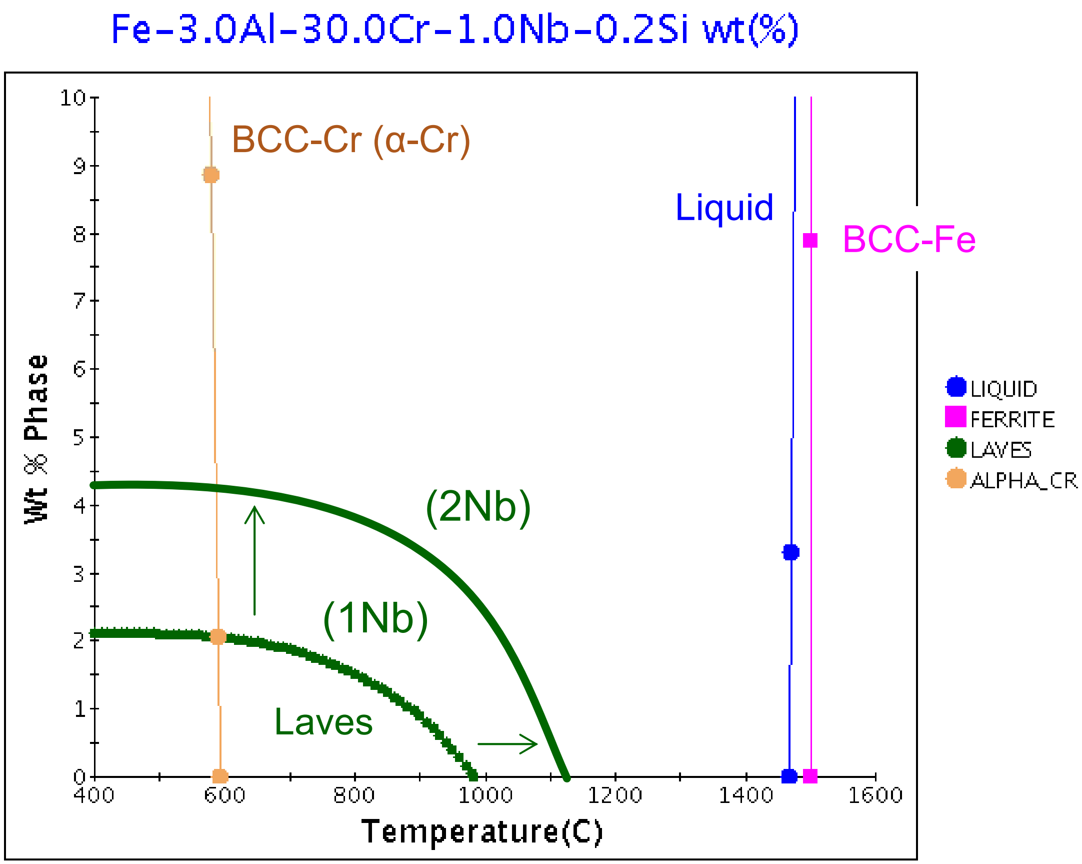
Calculated phase equilibrium* (CC01)



*calculated by JMatPro

Consideration of Phase Equilibrium

- **High Nb addition**:
  - Advantage: increase the amount of Laves phase precipitates for strengthening
  - Disadvantage: raise the solution limit temperature (difficult to be processed)

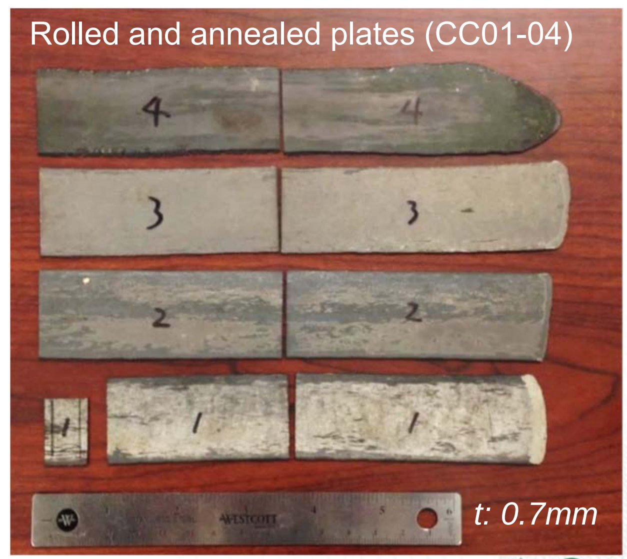


*calculated by JMatPro

Preparation of Materials (cont'd)

- **Melted / Processed the lab-scale heats**:
  - Arc-melted and drop-cast to make ~500g bar ingots
  - Hot-forged and -rolled to make sheet samples
    - *CC01-04: Warm-rolled at 300ºC + annealed at 1100-1200ºC*
    - *CC05-08: Hot-rolled and annealed at 1300ºC*
- **Prepared specimens for evaluations**:
  - Dogbone shape sheet specimens for tensile/creep testing
  - Coupons for oxidation testing
  - Bar samples for corrosion testing

As cast ingot (CC01 and CC02)

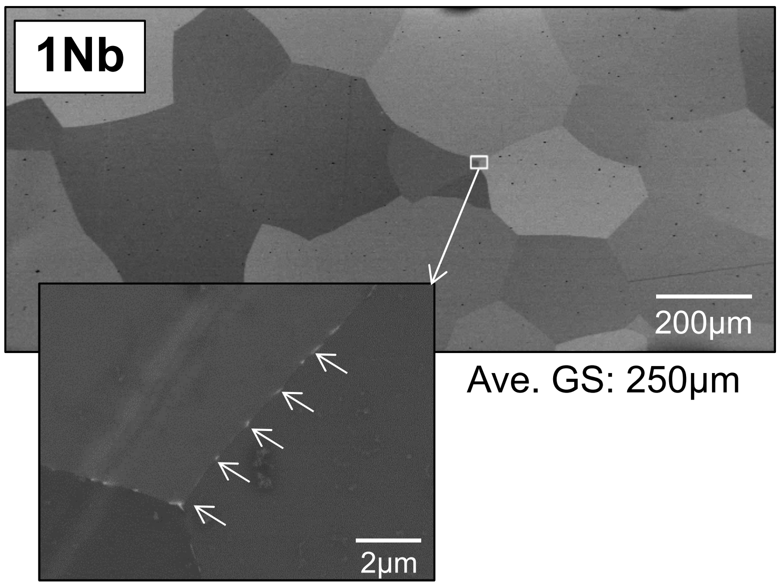


Rolled and annealed plates (CC01-04)

Gap Between Calculation and Experiment

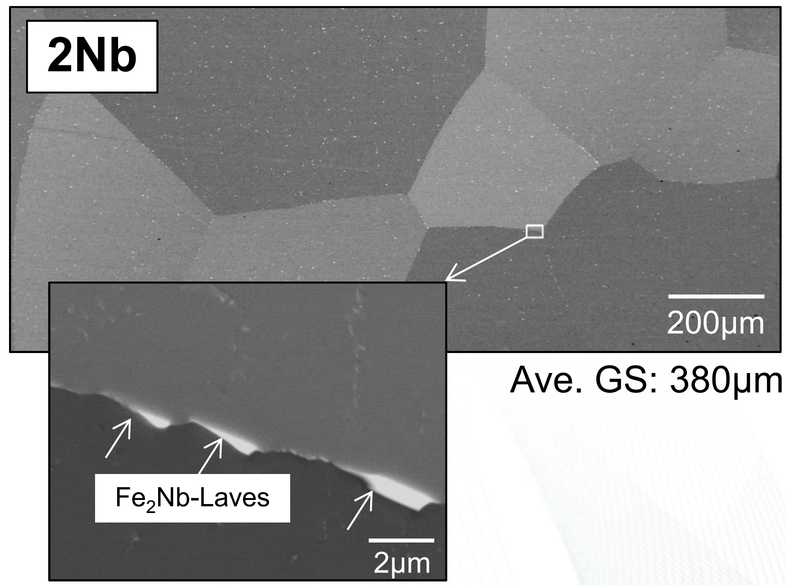
- **Controlled grain structure with solution heat-treated condition**
  - CC01-04: Most of the second-phase (Laves) dissolved at 1100-1200ºC
  - CC05-08: Laves-phase still remained even after 1300ºC processing

CC01 (1Nb)
WR@300ºC + 1100ºC/30min + 1200ºC/5min



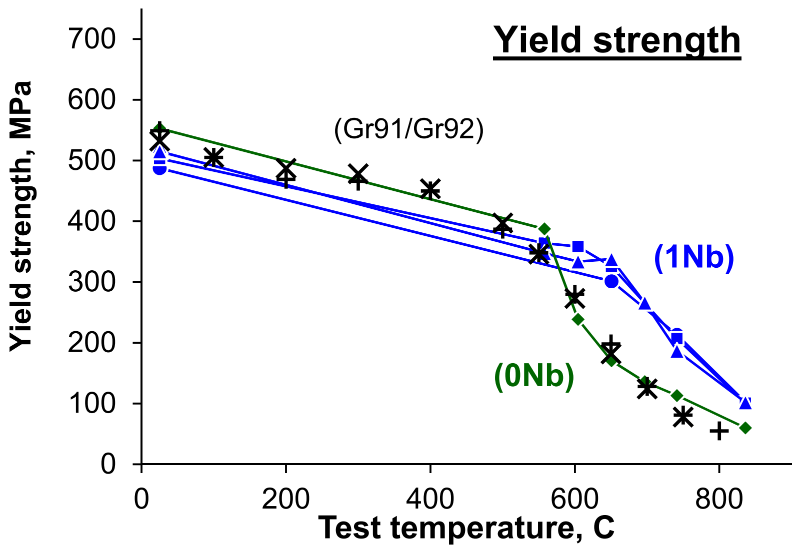
Ave. GS: 250µm

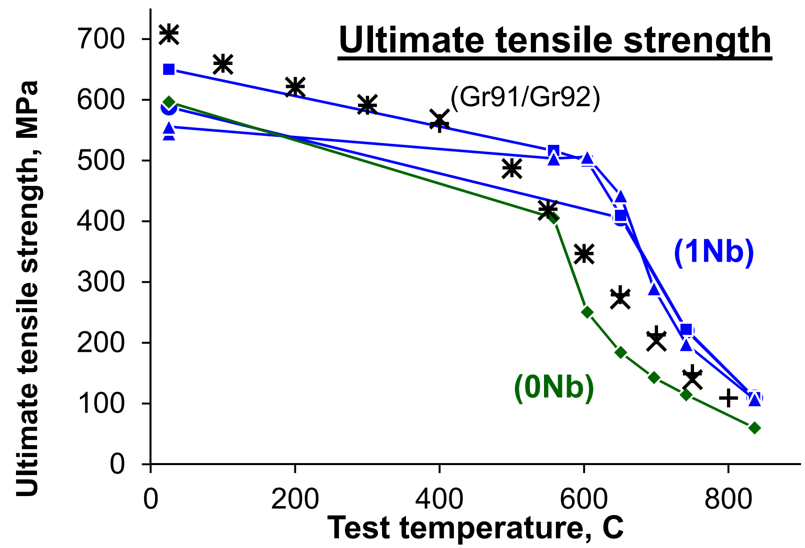
CC05 (2Nb)
HR@1300ºC + 1300ºC/10min

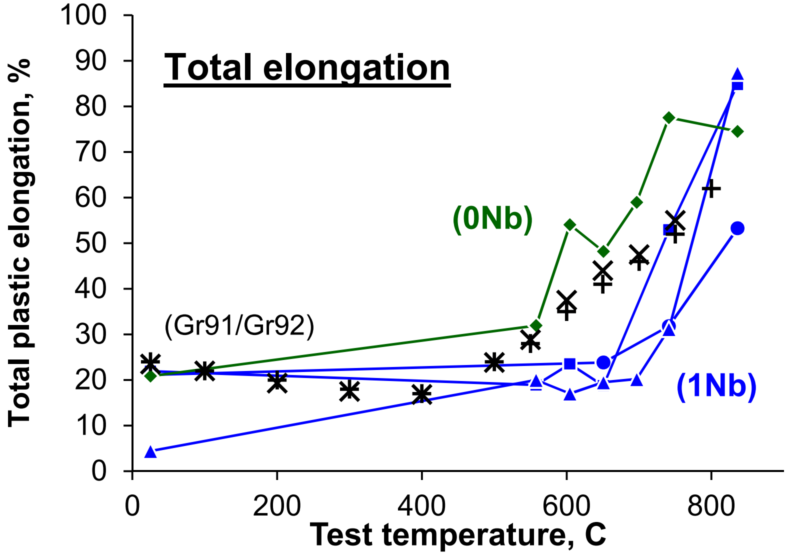


Ave. GS: 380µm

Improved Tensile Properties Superior to Grade 91/92 Steels (Above 600°C)

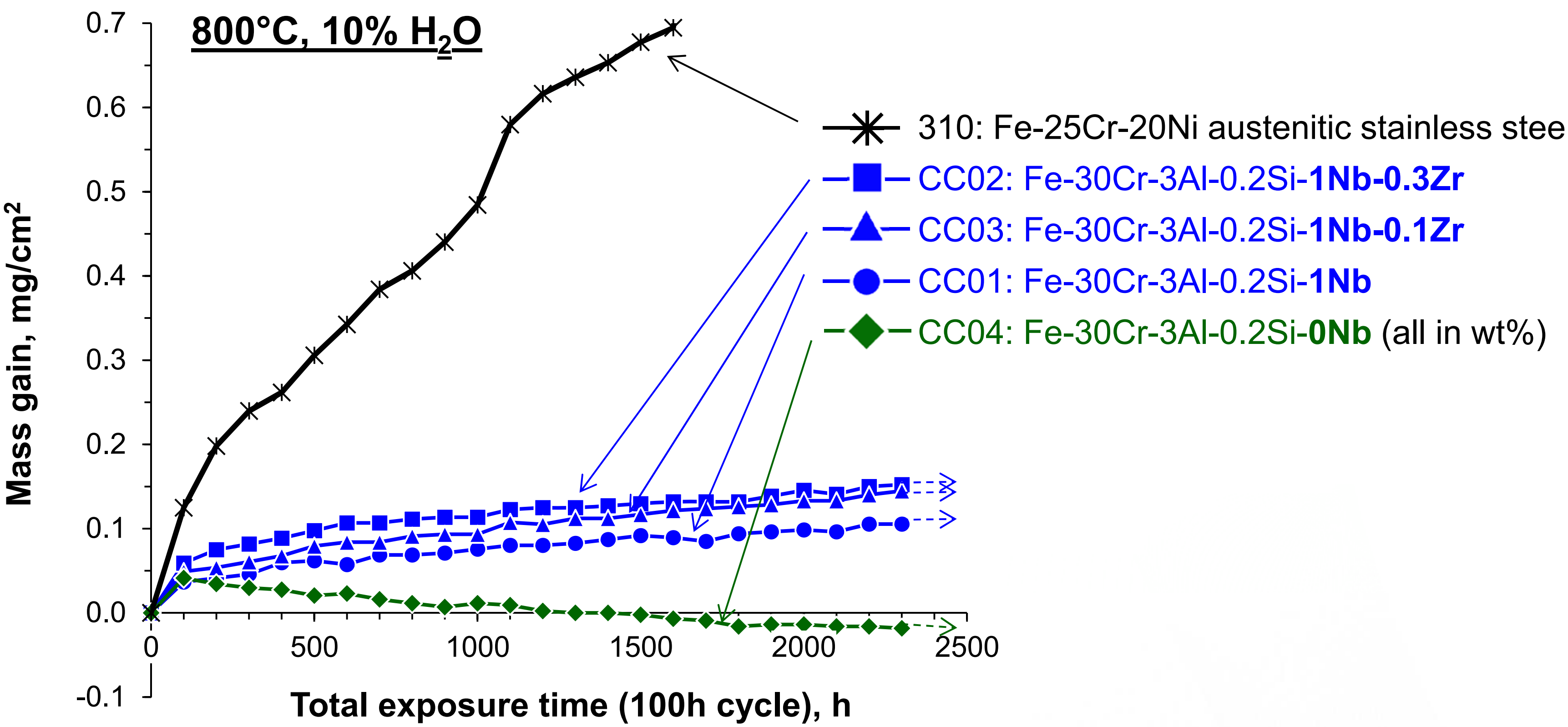






- CC01: Fe-30Cr-3Al-0.2Si-**1Nb**
- CC02: Fe-30Cr-3Al-0.2Si-**1Nb**-0.3Zr
- CC03: Fe-30Cr-3Al-0.2Si-**1Nb**-0.1Zr
- CC04: Fe-30Cr-3Al-0.2Si -**0Nb** (all in wt%)
- + × Gr91 and 92: from NIMS creep datasheet

Better Steam Oxidation Resistance than 310 Stainless Steel



- 1Nb alloys show slow oxidation kinetics
- Tests for CC05-08 (2Nb alloys) have also been initiated

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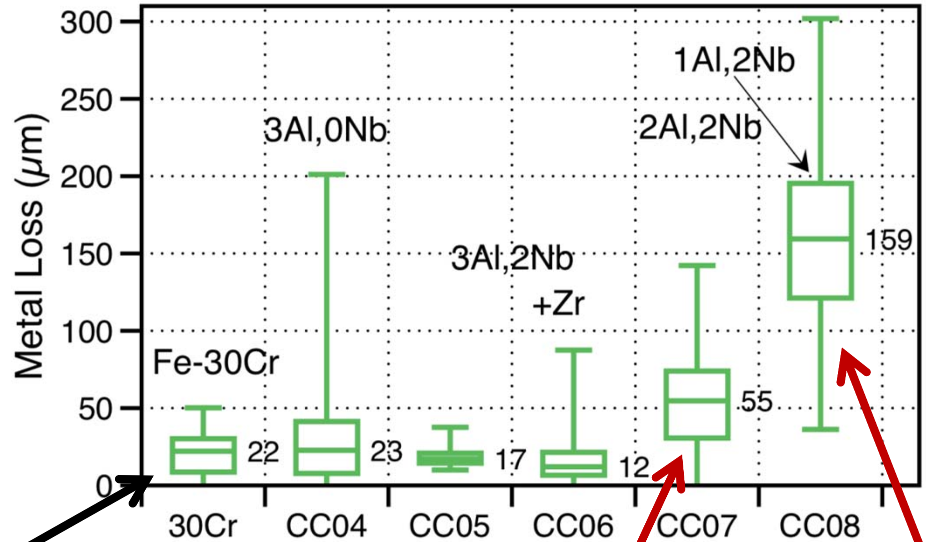
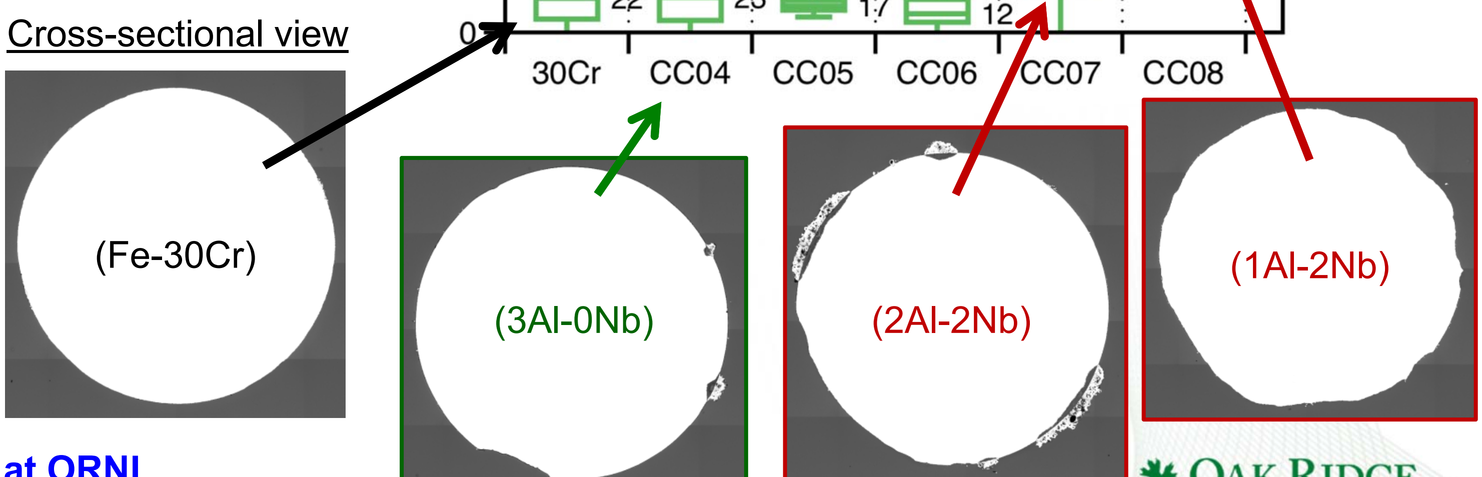
3Al-2Nb Alloys Showed Less Metal Loss Compared to Fe-30Cr in Coal Ash

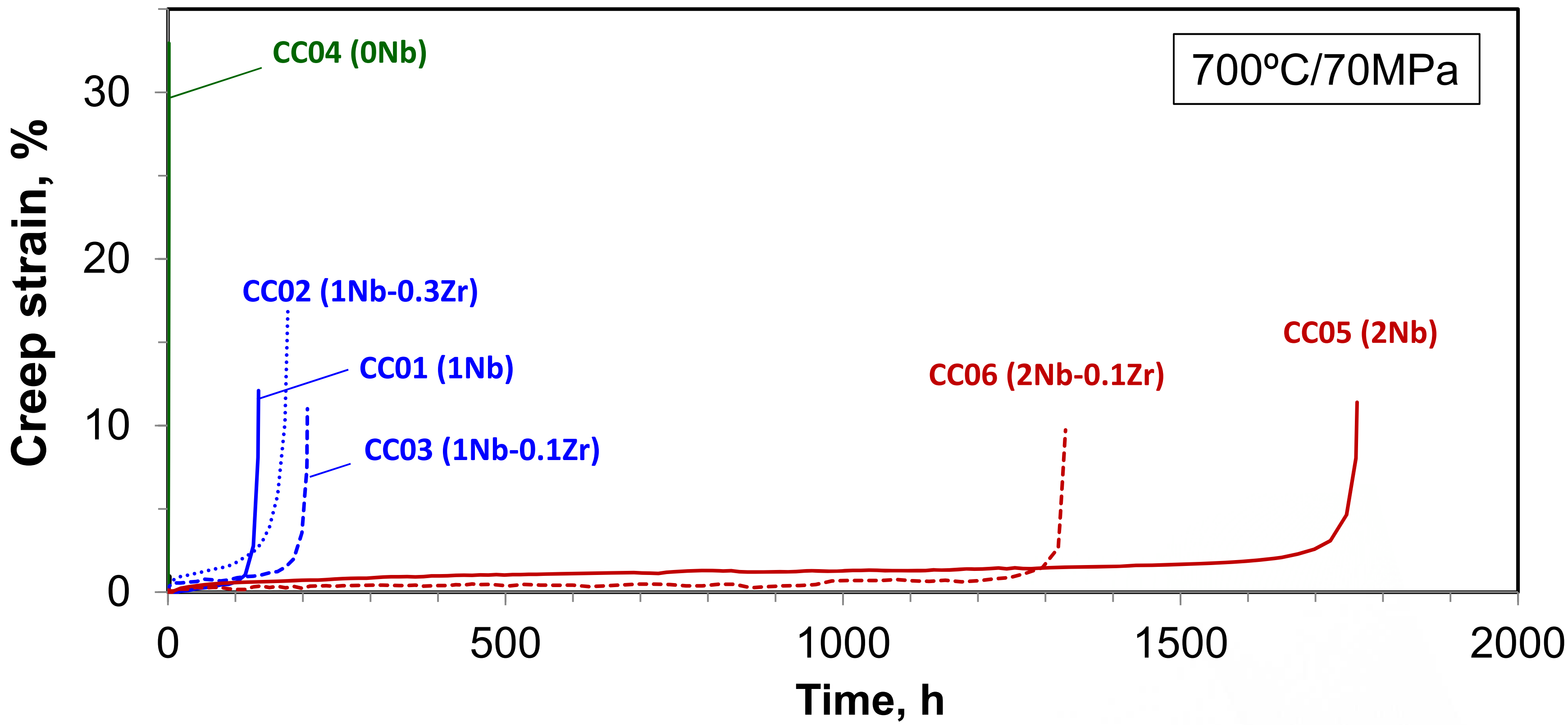
- Ash: 30%Fe_2O_3-30%Al_2O_3-30%SiO_2-5%Na_2SO_4-5%K_2SO_4
- Gas: 61%CO_2-30%H_2O-3%O_2-0.45%SO_2
- at 700ºC for 500h
  - CC04: 3Al-**0Nb**
  - CC05: 3Al-**2Nb**
  - CC06: **3Al**-2Nb-0.1Zr
  - CC07: **2Al**-2Nb-0.1Zr
  - CC08: **1Al**-2Nb-0.1Zr





Courtesy: B. Pint at ORNL

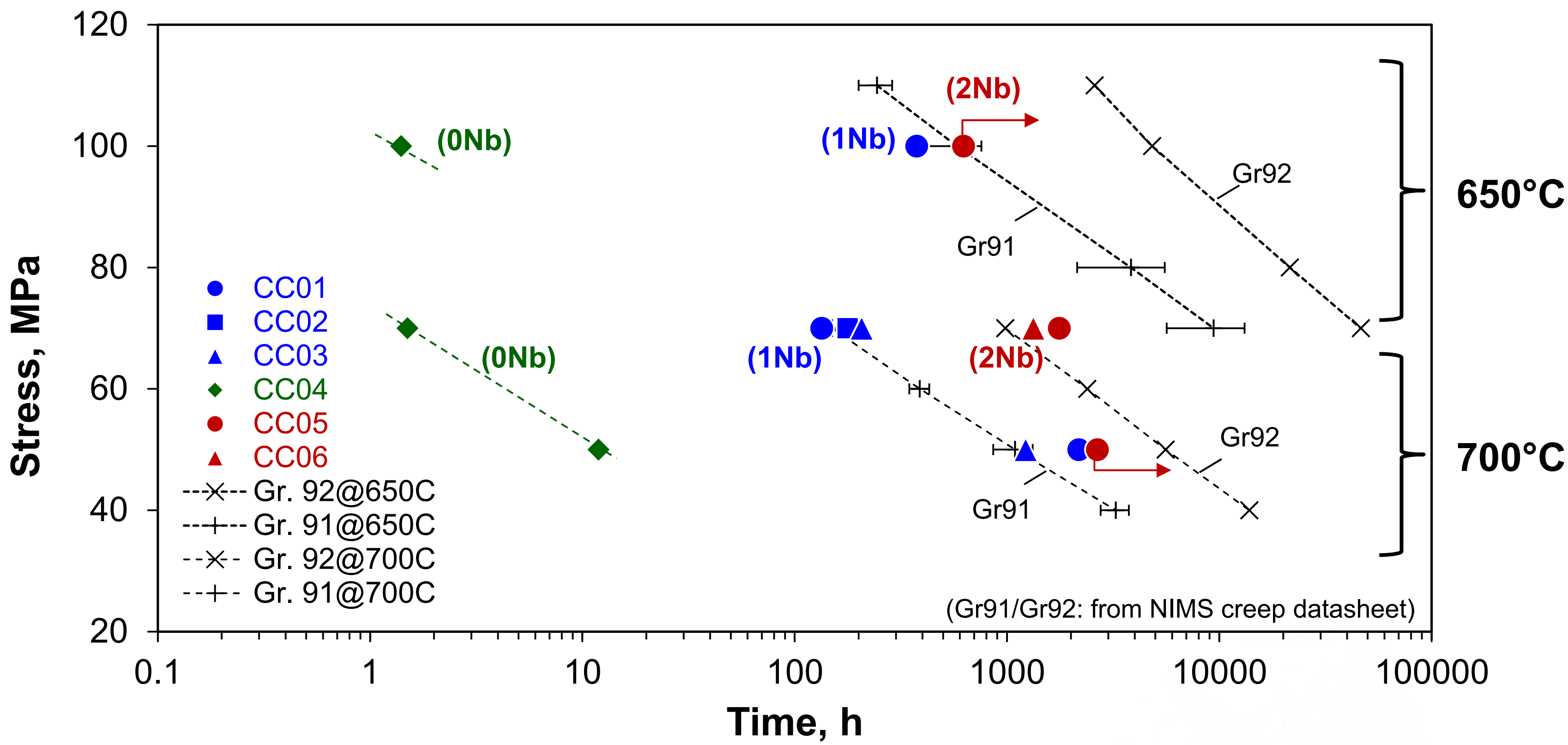
Creep Curves at 700ºC and 70MPa



Calculated weight percent of Laves phase:

– **1Nb alloys: ~2.0 wt%; 2Nb alloys: ~4.2 wt%**

Creep-rupture Properties (at 650-700ºC)



- Creep-rupture lives increase monotonically with increasing the Nb additions:

  → **Amount of Laves-phase precipitates is the key**

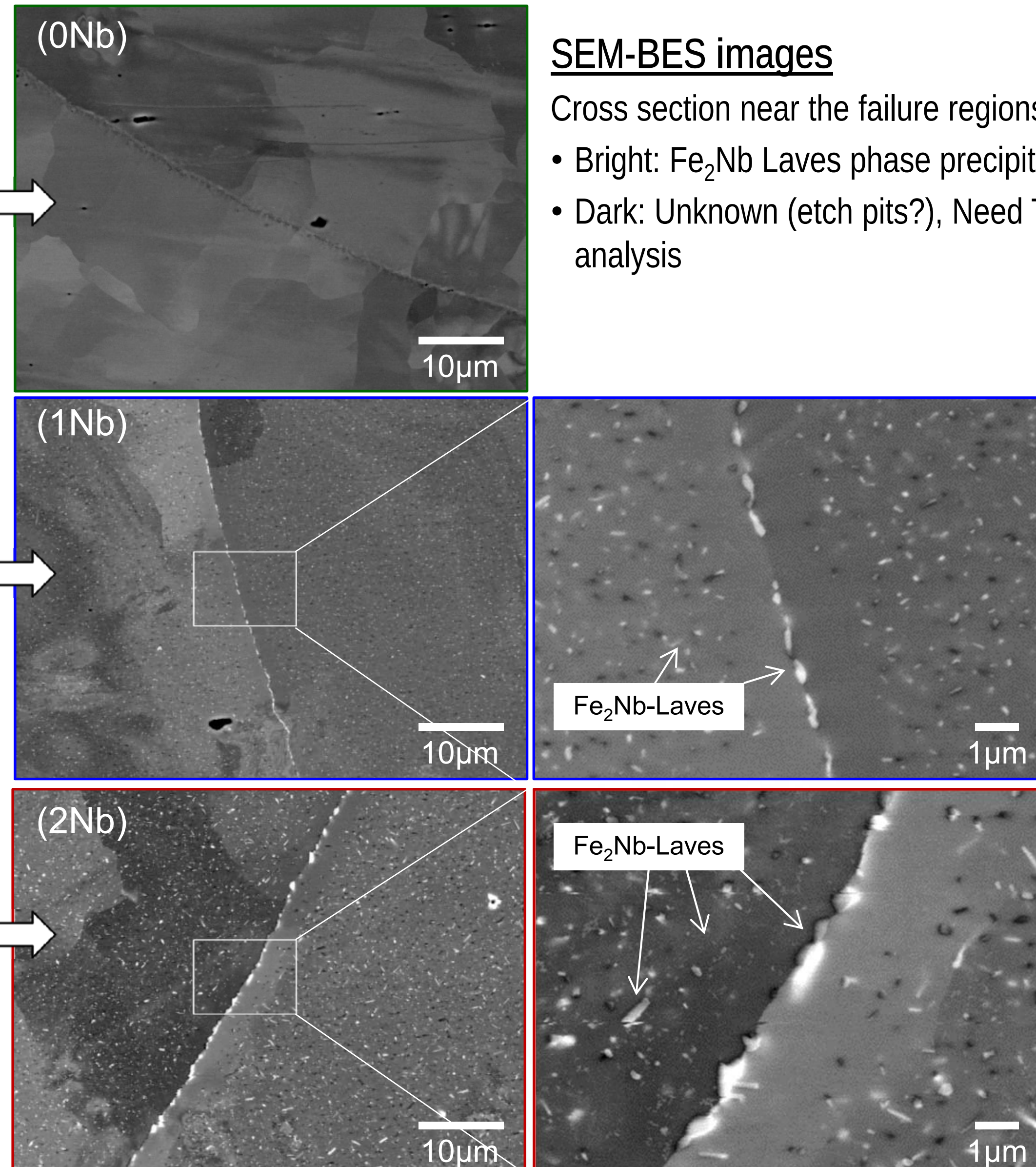
Dense and Fine Precipitates in Matrix

<u>Creep-ruptured specimens (700ºC/70MPa)</u>

CC04 (0Nb), Creep-life:1.5h, EL: 41%

CC01 (1Nb), Creep-lie: 134h, EL: 14%

CC05 (2Nb), Creep-life: 1762h, EL: 15%



<u>SEM-BES images</u>

Cross section near the failure regions;

- Bright: Fe_2Nb Laves phase precipitates
- Dark: Unknown (etch pits?), Need TEM analysis

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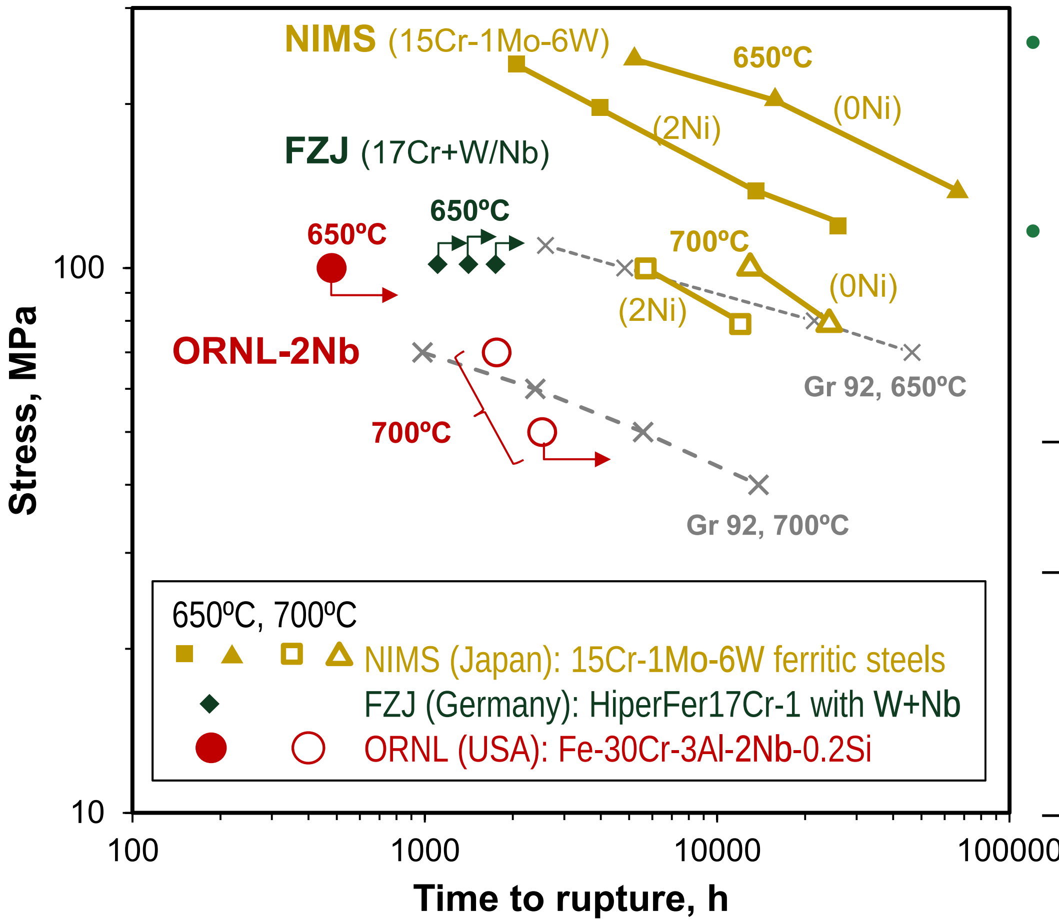
Other Laves-phase Strengthened Ferritic Steel Development



- NIMS alloys show >one order of magnitude longer creep-lives (at 700ºC) than ORNL-2Nb alloys
- ORNL alloys still have advantage of oxidation/corrosion resistance

Table: Calculated amount of Laves phase

Alloy	Cal. Laves phase, wt%	
	650ºC	700ºC
NIMS (15Cr-1Mo-6W)	9.5	10.2
FZJ (17Cr+W/Nb)	3.4	4.0
ORNL (30Cr-3Al-2Nb)	4.1	4.2
ORNL (30Cr-3Al-1Nb)	1.9	2.0

*calculated by JMatPro

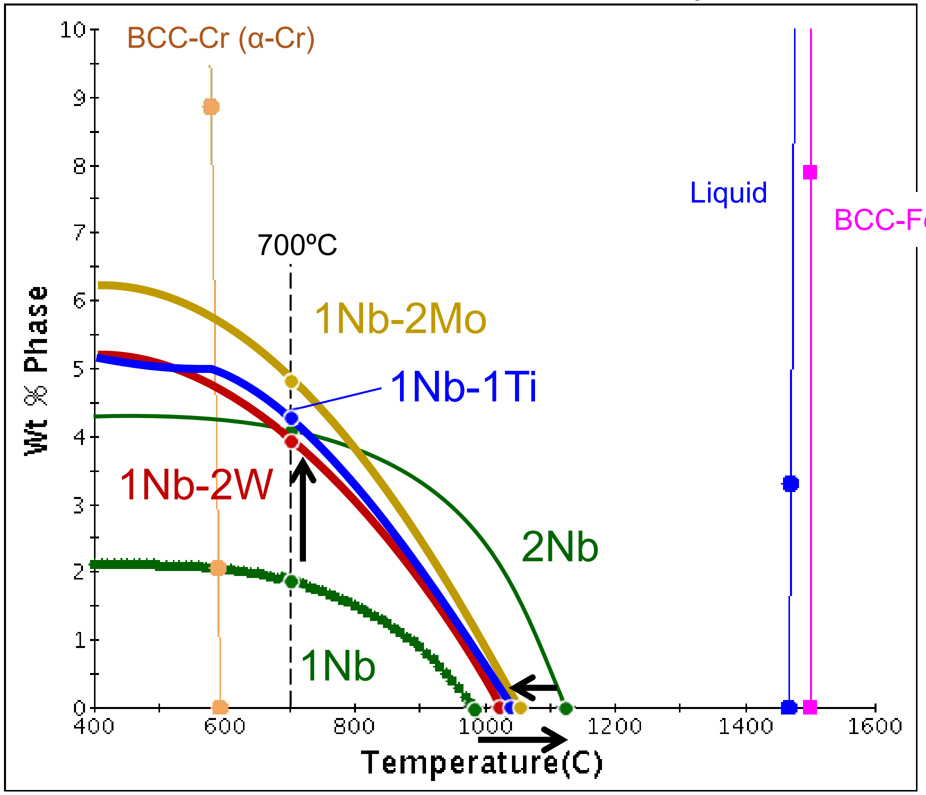
* Toda, et al., *Proceedings of the 10th Liège Conference on Materials for Advanced Power Engineering*, 2014

** M. Talik and B. Kuhn, Presentation at Workshop on Coordinated FZJ-ORNL Materials Research for Energy Applications

Re-consideration of Phase Equilibrium

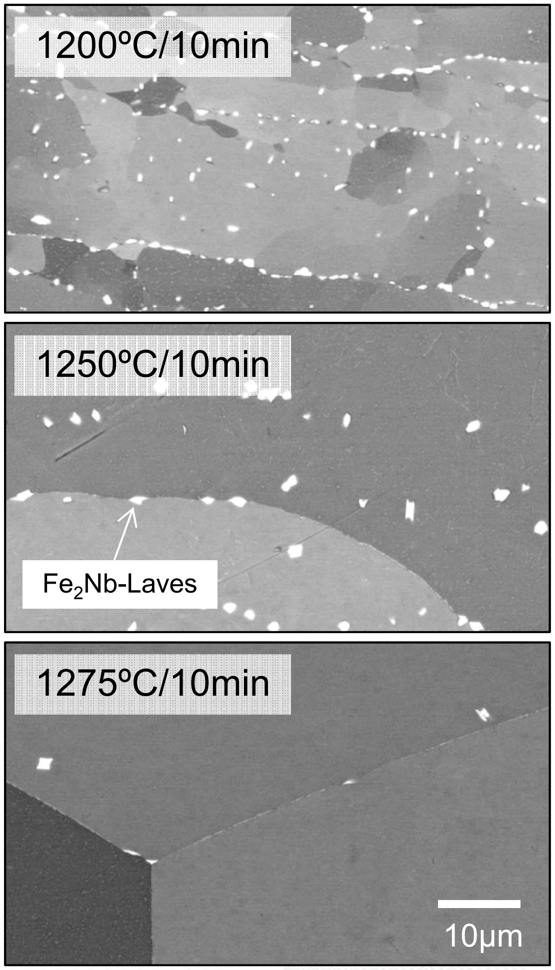
- Increasing the amount of Laves phase was effective in improving creep-rupture life
- For making the thermo-mechanical process easier, “third element” addition is proposed

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



*calculated by JMatPro

CC05 (2Nb), Annealed



Concern about Raw Material Cost

As of 3/6/2015

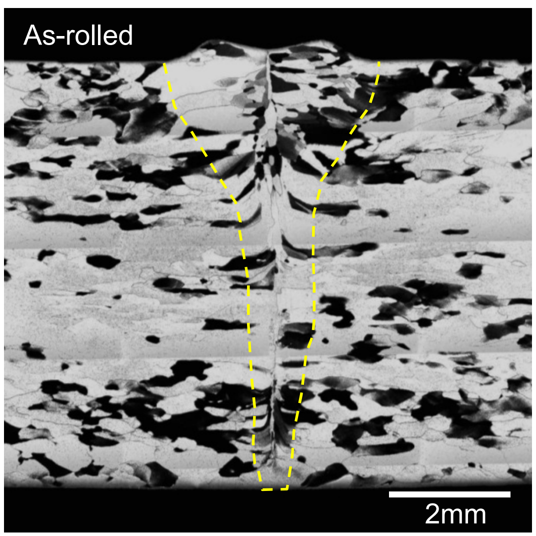
Element	Price for pure element, USD/LB	Source product
Cr	3.64	Ferro-chrome 60-65% Cr + Low C
Ta	146.40	Tantalum scrap 99.9%
W	30.00	Ferrotungsten 75% W
Nb	**21.91**	**Ferro-Niobium 66% Nb**
Zr	13.67	Zirconium Sponge 99.4% Zr + Hf
Mo	12.30	Ferro-Molybdenum 60% Mo
Ti	4.05	Ferro-titanium 70% minimum Ti
Si	0.87	Ferro-silicon 75% Si

(ref.: www.metalprice.com)

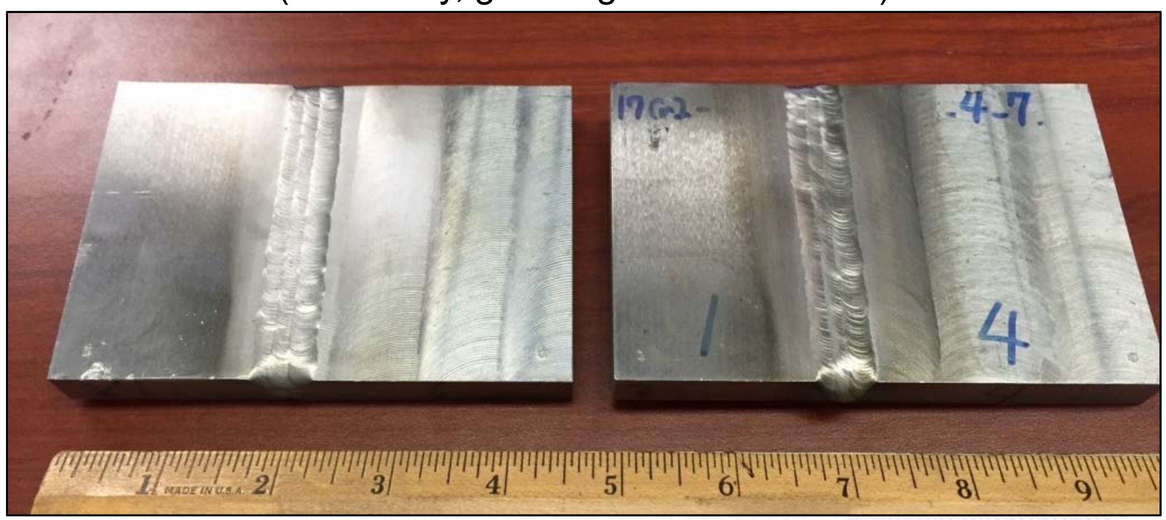
Collaboration with Forschungszentrum Jülich for High Cr Ferritic Steel Development

- Task: Weld development of 17Cr base ferritic steels (Hiperfer-17Cr with W+Nb)
- Progress: Completed e-beam welds, and performed butt welds with two different filler metal wires. Property screenings (microstructure characterization, bend test, and cross-weld creep test) are planned.

Cross-weld microstructure
(17Cr alloy, e-beam welded)



Picture of welded plates with filler metal
(17Cr alloy, gas tungsten arc welded)



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Milestone Status

- **FY2014**:
  - Complete computational screening of first iteration of candidate creep-resistant FeCrAl alloys (March 2014, Met).
  - Complete preliminary property assessments (oxidation, tensile, and creep) of down-selected candidate alloys (January 2015, Met).
  - Complete characterization of e-beam welded high-Cr Ferritic steels prepared under collaboration with Jülich Research Centre (September 2014, Met).
- **FY2015**:
  - Evaluate oxidation resistance of the FeCrAl alloys to provide feedback to the alloy design process (March 2015, Met).
  - Complete a second iteration of computational thermodynamic assessment to optimize alloy composition suitable for dense and fine second-phase precipitation dispersion (April 2015, in progress).
  - Down-select one or two creep-resistant FeCrAl alloys and initiate creep-rupture testing (June 2015).
  - Submit a journal paper on the new FeCrAl alloy design study (September 2015).

Future Activities

- **Assessment of corrosion resistance of the alloys:**
  - Preliminary results indicated a potential improvement by the Al+Nb additions
  - Detailed characterization is currently in progress
- **Detailed microstructure characterization of annealed/creep-ruptured specimens:**
  - Investigate the effect of Nb additions on microstructure
  - Interpret the role of second-phase on creep strength
- **Evaluate new alloy compositions:**
  - Effect of “third element” additions on microstructure, thermal stability, and creep performance
  - Initiate weld study including evaluation of cross-weld creep properties
- **Communicate with FZJ (every 6 weeks) to update the progress:**
  - E-beam weld for screening
  - GTAW filler metal development
  - Cross-weld property evaluation of GTAW samples

Summary

Creep-resistant high-Cr FeCrAl alloy development:

- Selected Fe-30Cr-3Al base alloys for potentially better oxidation and corrosion resistance, and the Nb addition for Laves phase precipitate strengthening
- Combined additions of Al and Nb resulted in improved properties of both oxidation resistance and mechanical properties
- Creep-rupture life increased with increasing the Nb additions (= the amount of Laves-phase), although high Nb addition required very high solution treatment temperature
- Second iteration of computational thermodynamic assessment for optimized alloy design was initiated through the “third element” addition for potentially improved strength and processbility

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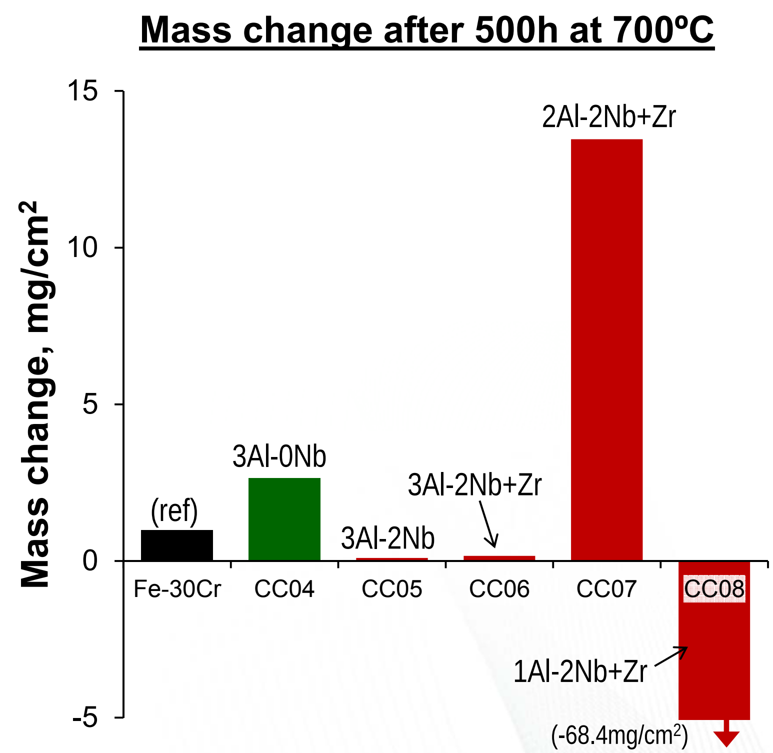
Thanks for your attention

3Al-2Nb Alloys Showed Lower Mass Change than Fe-30Cr in Coal Ash at 700ºC

- **Five selected alloys were exposed in a coal ash corrosive environment (Ash: 30%Fe_2O_3-30%Al_2O_3-30%SiO_2-5%Na_2SO_4-5%K_2SO_4; Gas: 61%CO_2-30%H_2O-3%O_2-0.45%SO_2) at 700ºC;**
  - CC04: 3Al-0Nb
  - CC05: 3Al-2Nb
  - CC06: 3Al-2Nb-0.1Zr
  - CC07: 2Al-2Nb-0.1Zr
  - CC08: 1Al-2Nb-0.1Zr



- The combined additions of Al + Nb (3Al-2Nb) potentially improved the corrosion resistance
- Detailed characterization is required to understand the mechanism (in progress)

Courtesy: B. Pint at ORNL