Laves Phase-Strengthened Austenitic Steels for Coal-Fired Power Systems

Ian Baker, Bin Hu, Geneva Trotter

Thayer School of Engineering, Dartmouth College, Hanover, NH 03755

DOE grant **DE-FE0008857**

Wednesday, June 12th, 2013

Outline

- Motivation
- Introduction to alumina-forming austenitic stainless steels
- Fe-20Cr-30Ni-2Nb-5Al
- Characterization of as-hot-rolled DAFA 26
- Characterization of processed DAFA 29

Motivation

Power generation plants need to operate at higher temp

Current boiler temperatures: T_H ~600° C

Desired temperatures: T_H up to 760° C

Efficiency gains of at least 8-10% possible

(National Energy Technology Laboratory, Advanced Materials for Ultra Supercritical Boiler Systems 2012)

Motivation

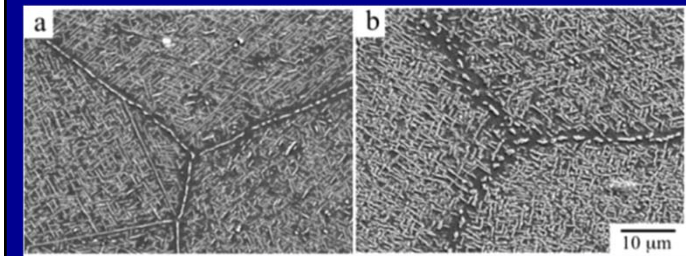
Desired operational environment in power generation plants is demanding:

- •Decades-long service life
- •High temperature (700° C+), high pressure (35MPa+)
  - *•Requires excellent high-temperature creep strength*
- •High H_2O vapor, S, C concentrations
  - *•Requires excellent corrosion resistance*

Current boiler elements are made from:

- •Ferritic stainless steels ($)
- •Austenitic stainless steels ($$)
- •Ni-base superalloys ($$$)

Motivation



Laves phase in a Fe-20Cr-30Ni-2Nb (at.%) steel after a creep test at 700° C and 120 MPa: (a) boron-doped steel, and (b) boron-free steel (Takeyama et al.)

Courtesy Ji-Cheng Zhao

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Alumina-forming Austenitic Stainless Steels

Alumina-Forming Austenitic Stainless Steels
- •Cheap w.r.t. Ni-based alloys
- •Form Al_2O_3 surface oxide rather than Cr_2O_3
  - •*Superior high-temp corrosion resistance*

However, creep resistance has typically been poor
- •Strengthened by carbides or nitrides
  - •*However, coarsen over time at high temperature → brittle fracture*

Alternatives:
1. Strengthen with coherent $L1_2$ Ni_3Al precipitates
2. Strengthen with intermetallic precipitates such as Fe_2Nb Laves Phase
   - •Could pin dislocations, preventing creep
     - •*Requires fine dispersion of <100 nm particles in the matrix*
   - •However, most Fe_2Nb forms in coarse (500-700 nm) precipitates

---

Careful Balancing of Alloy Element Additions Needed to Achieve Combination of Properties

- ❑ Additions of sufficient Al essential for development of stable external alumina scale
  - – More than 2.5 wt% Al required for alumina scale formation
- ❑ Nb additions are key for alumina scale formation
  - – More than ~0.6-1.0 wt% Nb is also required for alumina-scale formation
- ❑ Too much Al and/or Nb will worsen creep properties (δ-Fe, brittle second-phases, etc.)
- ❑ Solid solution strengthening and precipitation strengthening is needed
  - – How much carbon can be tolerated?
  - – Coherent intermetallic phase?

Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

---

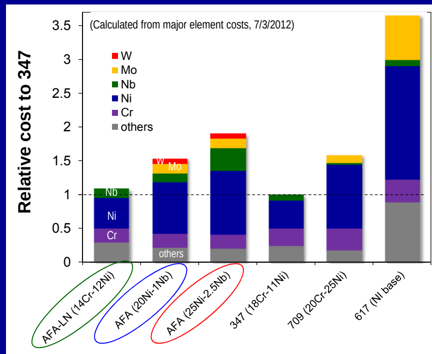
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Oak Ridge alloy DAFA 26 and DAFA 29

Name	Analyzed composition (wt%)										Remarks
	Fe	Cr	Ni	**Al**	Si	Nb	**Ti**	**Zr**	C	B	
#26	45.29	14.00	32.47	**2.95**	0.13	2.93	**1.97**	**0.29**	-	-	3Al-2Ti + Zr
#29	45.36	13.99	32.46	2.97	0.14	2.80	1.88	0.29	0.065	0.005	3Al-2Ti + Zr,C,B
A286	56.2	14.5	25	0.15	0.2	-	2.1	-	0.04	0.006	1.25Mo, 0.3V, 0.2Mn, 0.015P

Alloys supplied by Y. Yamamoto and M. P. Brady, Oak Ridge National Laboratory

Inexpensive Raw Material Cost



Major Elements	USD/KG* (July 2012)
W	43.4
Mo	44.7
Nb	81.9
Ni	23.0
Cr (from Ferro-Cr)	9.0

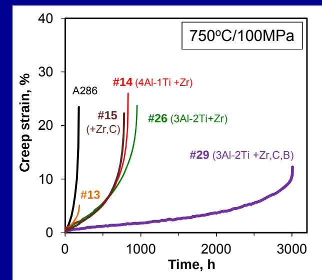
*from http://www.metalprices.com/

- Comparable or even less than the competitors.

Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

B+C Additions Improves Properties Drastically

Creep curves

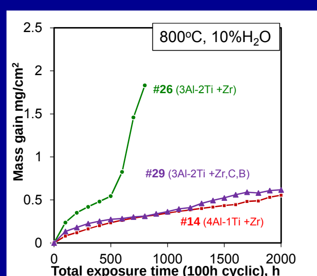


- Alloy #29 showed excellent properties of oxidation and creep resistances.
- The B addition increases creep resistance significantly.

Courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

B+C Additions Improves Properties Drastically

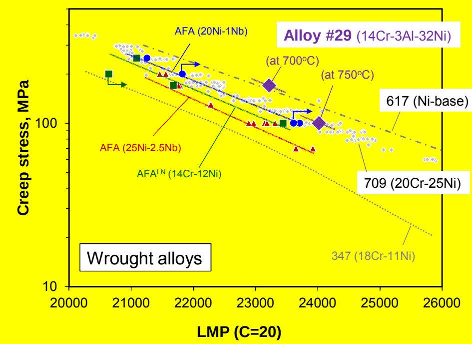
Oxidation-curves



- Alloy #29 showed excellent properties of oxidation and creep resistances.
- The C addition improves oxidation resistance

Courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

Comparable to Ni-base alloy 617 at 700°C

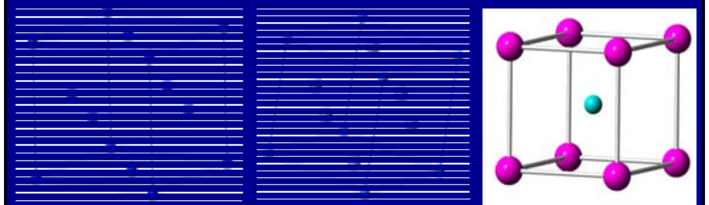


- Strong advantage at relatively lower temperatures (from LMP).

Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

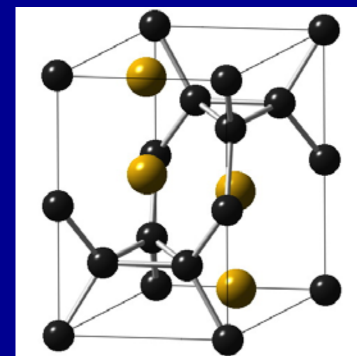
Crystal structures present



f.c.c. matrix | $L1_2$ $Ni_3(Al,Ti)$ precipitates | B2 NiAl precipitates

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Fe_2Nb

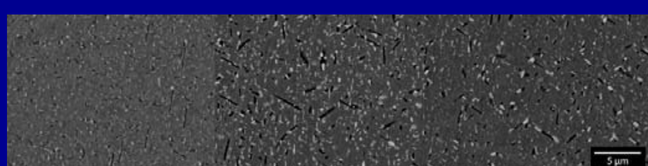


Hexagonal C14 Laves phase structure adopted by many AB_2 compounds. The yellow spheres represent the "A" atoms; the black spheres represent the "B" atoms.

Fe-20Cr-30Ni-2Nb Takeyama et al. Laves-phase stainless steel

Fe-20Cr-30Ni-2Nb-5Al (at.%) annealed 800° C

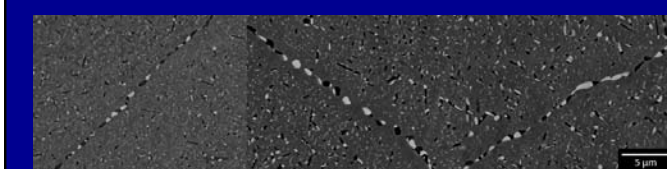
Solutionized + Quenched | 2.4h | 24h



240 h | 480h | 1128h

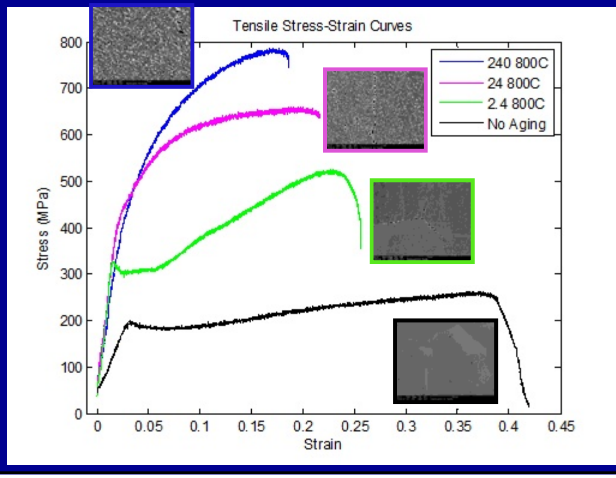
Fe-20Cr-30Ni-2Nb-5Al(at.%) annealed at 800° C

As-Quenched | 2.4h | 24h

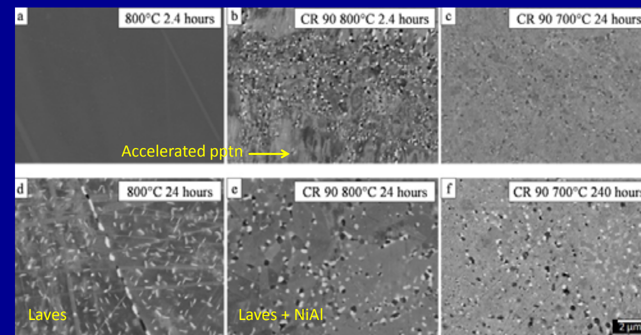


240 h | 480h | 1128h

Fe-20Cr-30Ni-2Nb-5Al (at. %)



Cold rolling accelerates precipitation of both Laves phase and NiAl



BSE micrographs of aged Fe-20Cr-30Ni-2Nb-5Al a) 800°C 2.4 hours no cold roll; b) 800°C 2.4 hours 90% cold roll; c) 700°C 24 hours 90% cold roll; d) 800°C 24 hours no cold roll; e) 800°C 24 hours 90% cold roll; and f) 700°C 240 hours 90% cold roll. Images b, c, e and f all show refined, higher-volume fraction second-phase structures as compared with the non-cold-rolled specimens in a and d.

(Garrett Rayner's MS thesis, 2011)

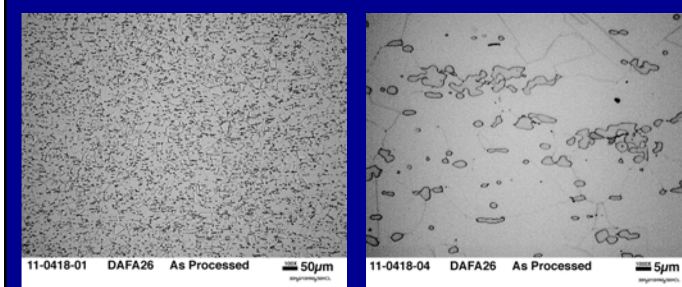
1867 THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Characterization of as-processed material

DAFA 26 Preparation

- Arc-melted 600g ingot by using pure element feedstock.
- Drop cast into 1" x 1" x 3" bar shape die.
- Soaked at 1100°C for 2 h in Ar + 4% H_2 gas
- Hot-rolled the ingot along longitudinal axis for up to 80% thickness reduction (~15-20% thickness reduction per pass).
- Anneal the plate at 1100°C for 30 min in Ar + 4% H_2 gas, followed by air cooling.

DAFA26, Hot-rolled at 1100°C, OM

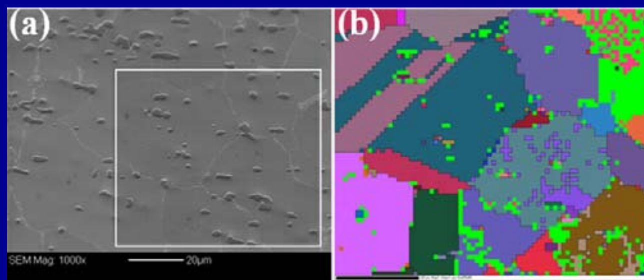


Optical micrographs showing Laves phase distribution

Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

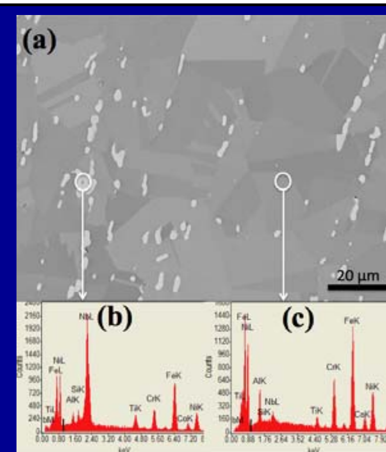
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

EBSD map of Laves Phase-Strengthened Austenitic Steel



THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

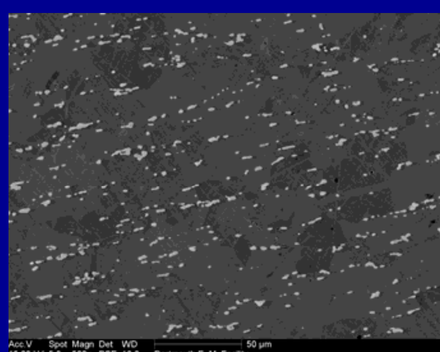
DAFA 26
as-hot-rolled



(a) BSE image of as-hot-rolled DAFA 26 showing Laves phase precipitates aligned along rolling direction; EDS of (b) (white) Laves phase precipitates, and (c) austenitic matrix

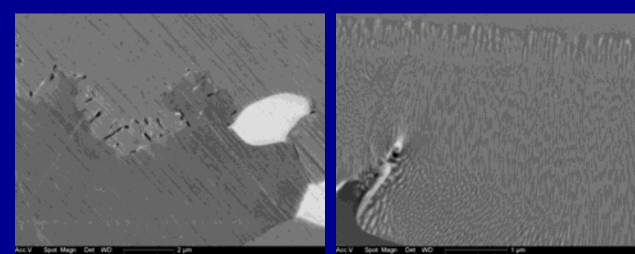
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE image of DAFA 26 after 1h at 750^{o}C



THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

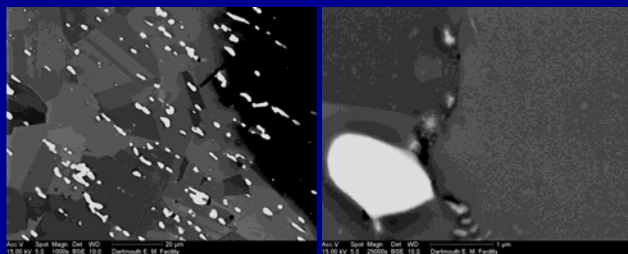
BSE image of DAFA 26 after 1h at 750^{o}C



Unusual Precipitation at grain boundaries

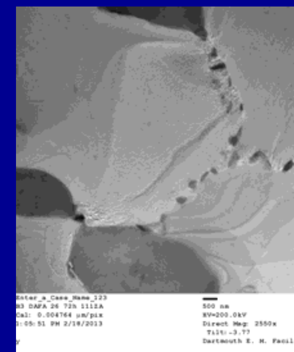
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE image of DAFA 26 after 2h at 750^{o}C



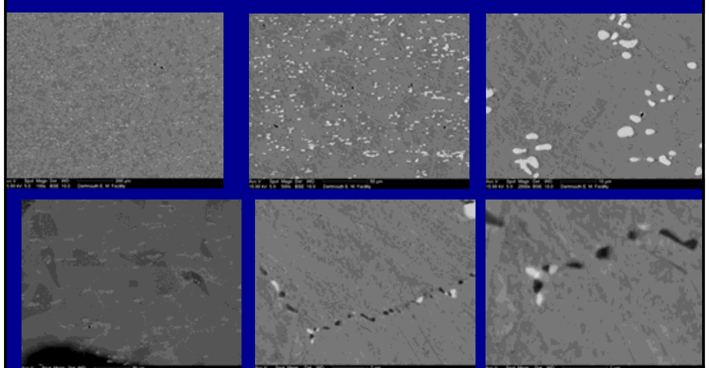
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

TEM BF image of DAFA 26 after 2h at 750^{o}C



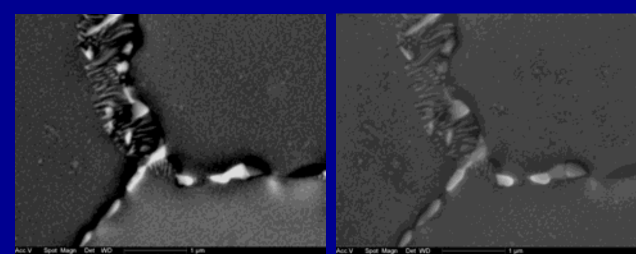
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE image of DAFA 26 after 72h at 750^{o}C



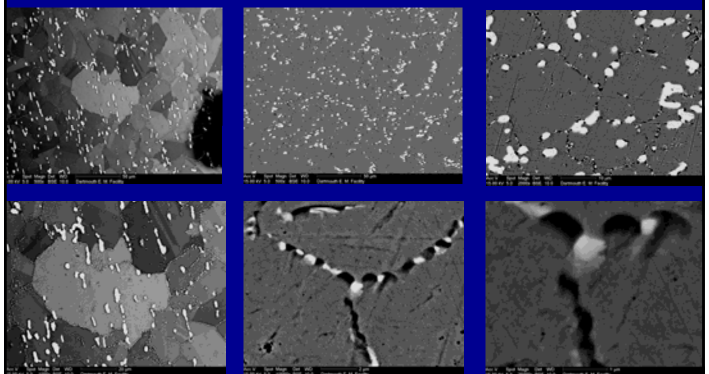
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE image of DAFA 26 after 72h at 750^{o}C



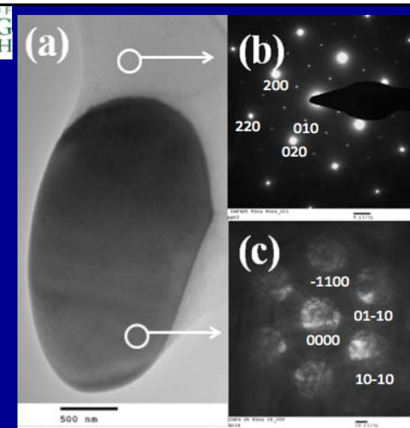
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE image of DAFA 26 after 750h at 750^oC



THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

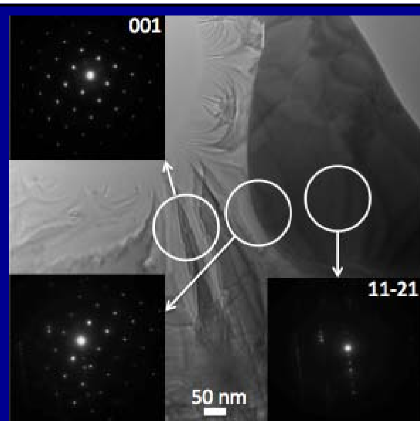
DAFA 26
30 min @ 1100^oC



BF TEM image of Laves phase precipitate, b) [001] SAD pattern of nearby region showing reflections from both the f.c.c. matrix and $L1_2$ precipitates (010), and c) CBED pattern of the Laves phase precipitate after tilting to [0001].

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

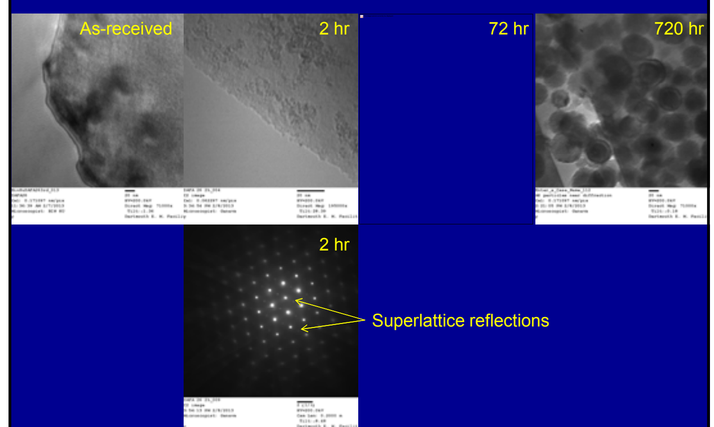
DAFA 29 as hot-rolled



BF TEM image showing Laves-phase precipitate and diffraction patterns from the locations indicated. The orientation relationships between the Laves phase and the matrix was identified to be $(1121)_{Fe2Nb}//(001)_{\gamma}$.

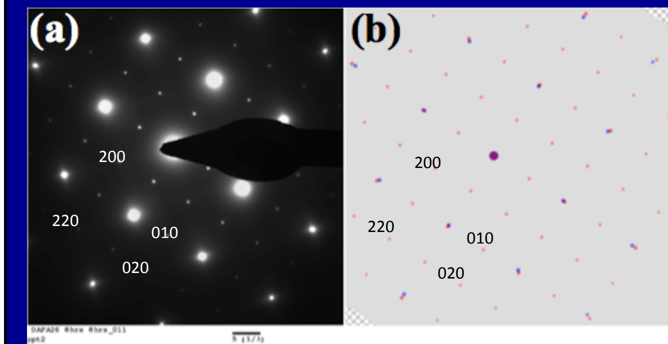
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

TEM:DAFA 26 Annealing at 750^oC



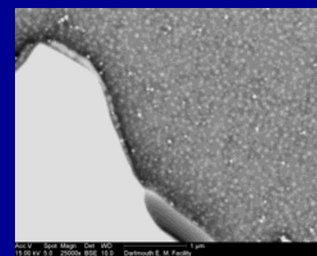
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

DAFA 26

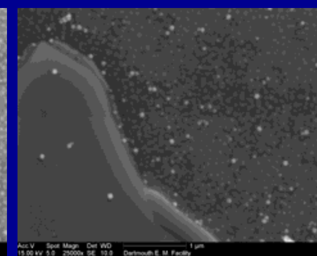


SAD pattern of fcc matrix along [001] showing superlattice reflections from $L1_2$ γ′ precipitates, b) corresponding simulated SAD pattern

DAFA 26 after 720h at 750°C

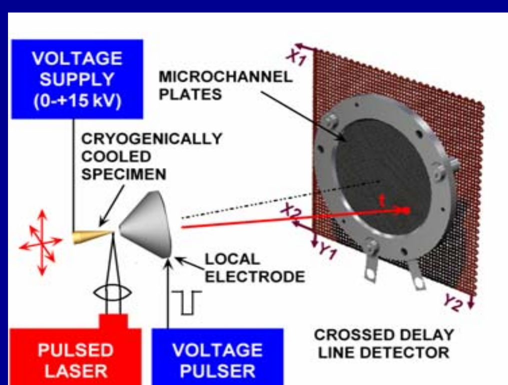


BSE image



SE image

Local Electrode Atom Probe

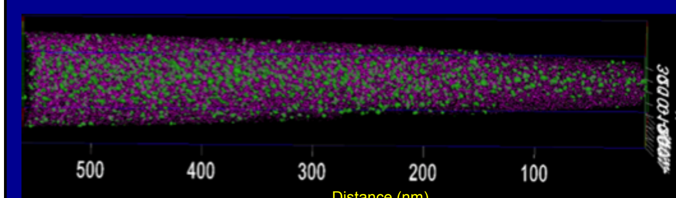


Courtesy Dr. M.K.Miller , Oak Ridge National Laboratory

35

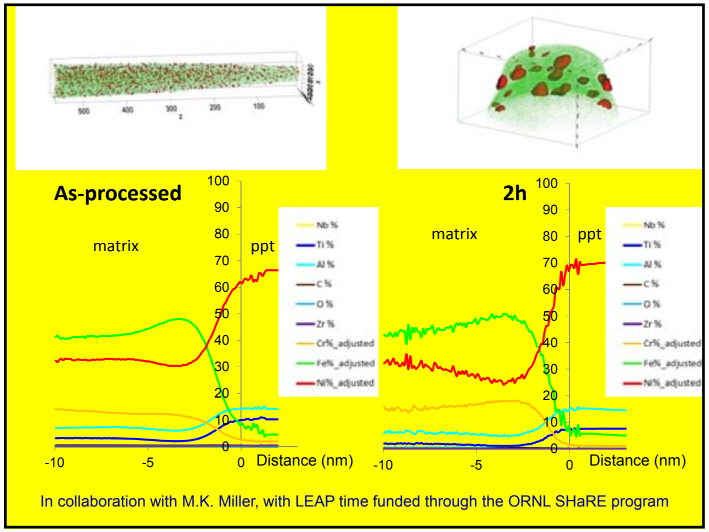
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

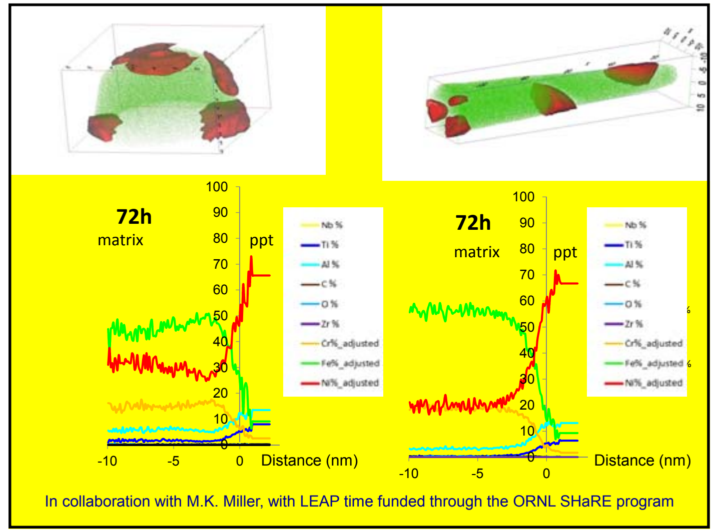
Atom Probe Tomography of as-hot rolled DAFA 26

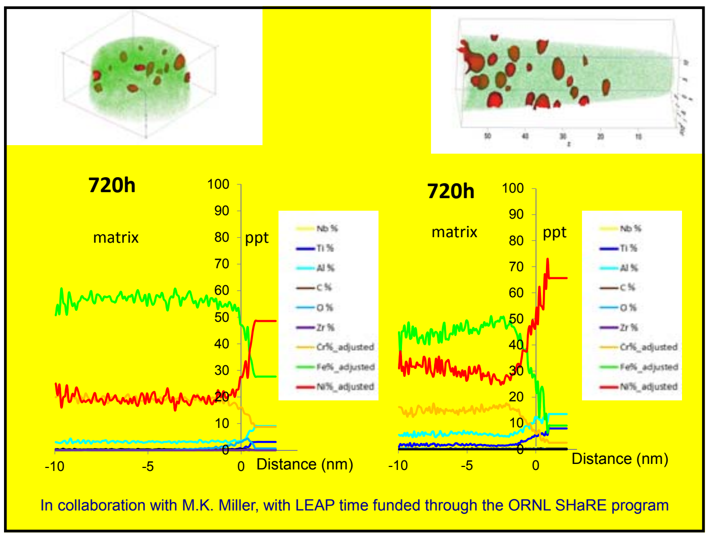


Green regions are Ni-rich $L1_2$ precipitates, the mauve color is the Fe in the matrix

In collaboration with M.K. Miller, with LEAP time funded through the ORNL SHaRE program







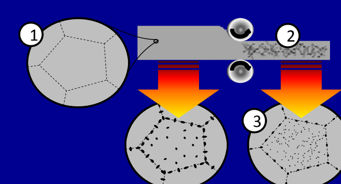
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Goal: Move Fe_2Nb from coarse dispersions on grain boundaries to fine precipitates in the matrix, refine existing matrix precipitates (ideally <100nm)

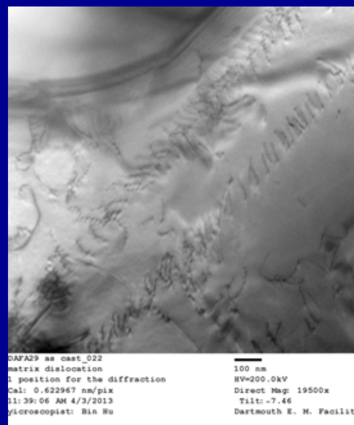
How? Two routes:

1 Cold roll (to introduce dislocations) + anneal ➔ induce precipitate nucleation on dislocations

2 Solutionize Laves Phase + cold roll (to introduce dislocations) + anneal ➔ induce precipitate nucleation on dislocations



TEM BF image of As-cast DAFA 29



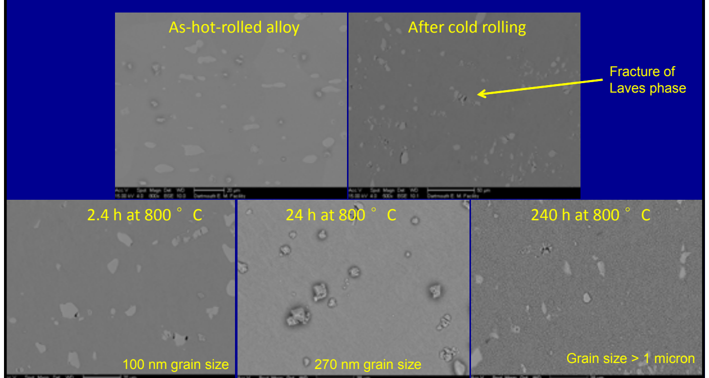
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Thermomechanical Treatment: Method #1

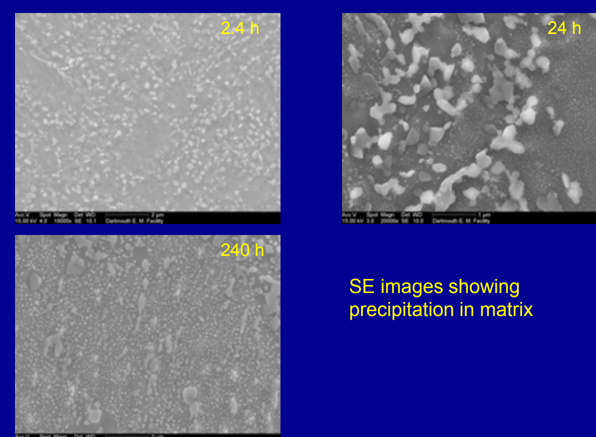
- Room temperature cold rolling (90% reduction)
- Annealing
2.4 h, 24 h and 240 h at 800^{o}C

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE images of Treatment Method #1



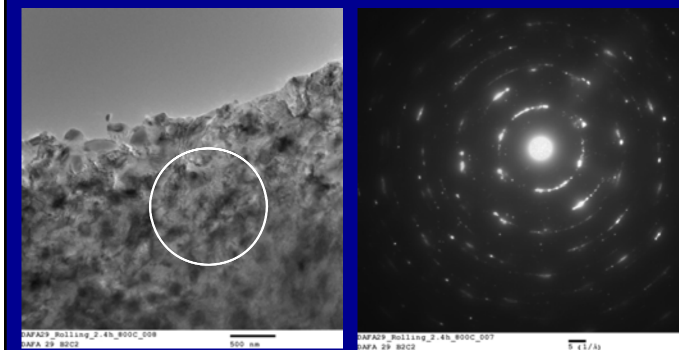
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH



SE images showing precipitation in matrix

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

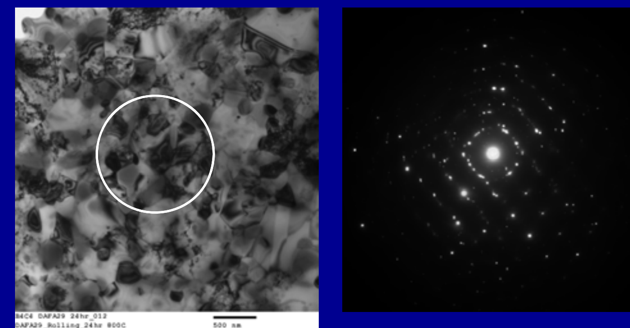
TEM Image and SAD of Sample after anneal at 800 ^{0}C for 2.4 h



Grain size ~ 100 nm

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

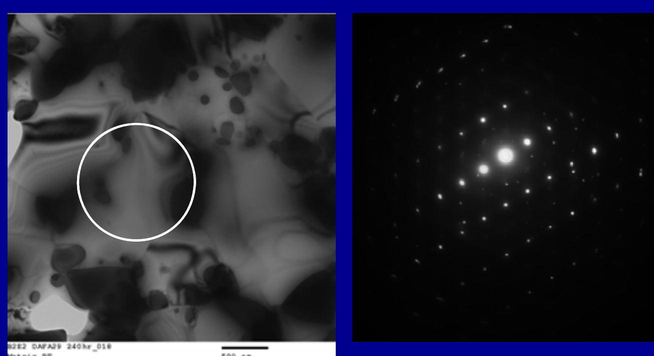
TEM Image and SAD of Sample annealed at 800 ^{0}C for 24 h



Grain size ~ 270 nm

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

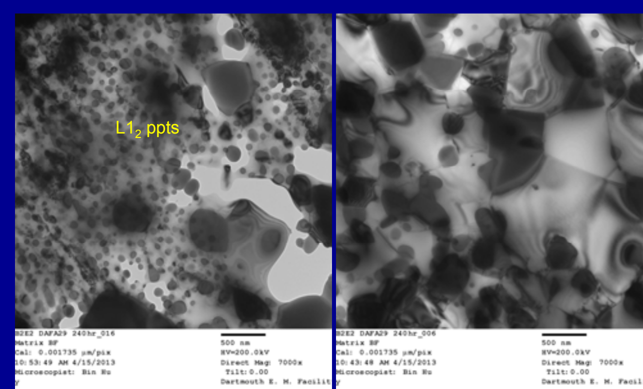
TEM Image and SAD of Sample annealed at 800 ^{0}C for 240 h



Grain size > 1 micron

THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

TEM Images of Sample annealed at 800 ^{0}C for 240 h

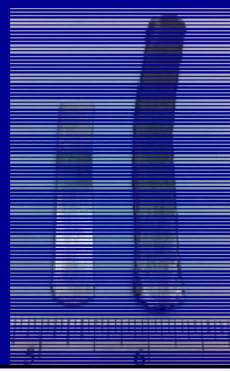


THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

Thermomechanical Treatment Method #2

- Solutionizing anneal for 50 h at 1200°C in Ar
- Room temperature cold rolling (90% reduction)
- Annealing for 2.4 h, 24 h and 240 h at 800°C

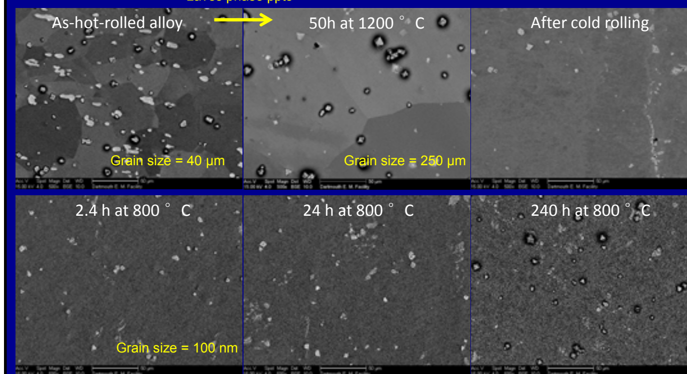
Treatment method # 1 Treatment method # 2



THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

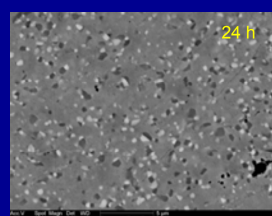
BSE Images of Treatment Method #2

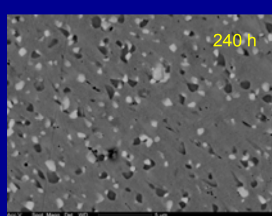
Reduction in no. of Laves phase ppts



THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

BSE Images of Treatment Method #2



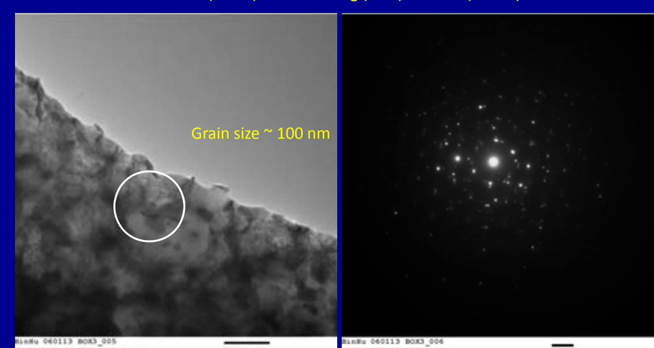


Laves phase + NiAl ppts

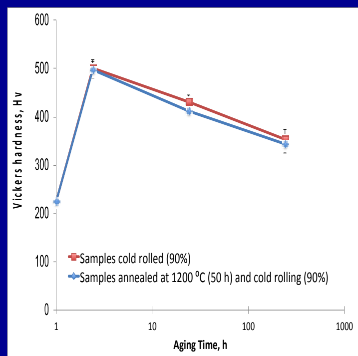
THAYER SCHOOL OF ENGINEERING AT DARTMOUTH

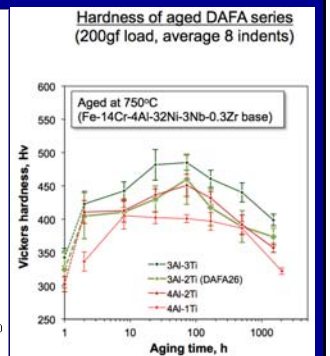
TEM analysis of samples after thermomechanical treatment 2

DAFA29 + 1200C (50hrs) + Cold Rolling (90%) + 800°C (2.4hrs)



52





Courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady

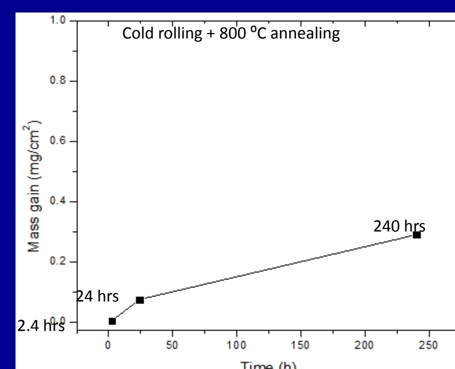
Summary

1. Solutionizing and annealing Fe-20Cr-30Ni-2Nb-5Al produces Laves Phase and NiAl ppts in the matrix and GBs.
2. Hot-processed DAFA 26 contains large (1-5 μm) Laves phase ppts
3. Annealing of DAFA 26 produces $L1_2$ ppts in the matrix and Laves Phase and NiAl at the grain boundaries.
4. Cold-rolling of DAFA 29 fractures Laves Phase ppts.
5. Annealing, cold-rolled DAFA 29 produces a very fine (100 nm) grain structure and $L1_2$ precipitates in the matrix.
6. Solutionizing DAFA 29 followed by cold-rolling and annealing produces a fine grain size (100 nm); Laves Phase and NiAl ppts in the matrix and GBs.

Future work

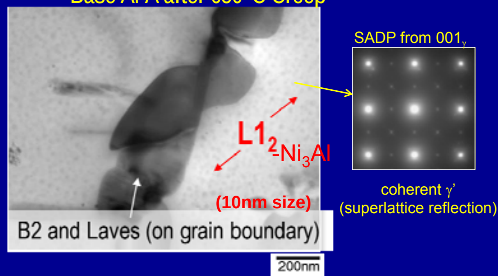
- Complete microstructural characterization of DAFA 29 after processing
  - determine orientation relationships between both Laves phase ppts and NiAl ppts and matrix
  - *Do NiAl ppts nucleate on Laves phase ppts?*
- Tensile tests on as-received and processed DAFA 29
- Creep tests on DAFA 29 in different conditions
- Characterization of precipitates after creep testing

Oxidation in air



Metastable γ'-Ni_3Al Observed at < 700°C for Some AFA Alloy Variants

TEM-Bright Field Image of Fe-25Ni-14Cr-3.5Al-2.5Nb-0.1C wt.% Base AFA after 650°C Creep

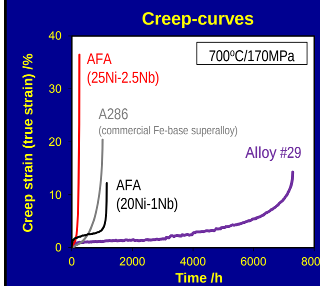


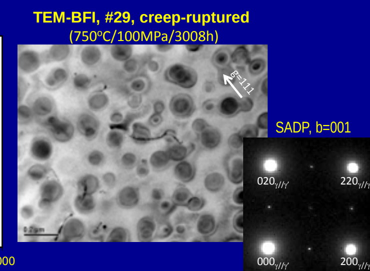
- Favored by increased Nb in the γ-Fe matrix
- Metastable: ~3000 to 10,000 h at < 700°C depending on load (Ni_3Al kinetically favored due to coherency, replaced by stable B2-NiAl)

Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory

Development of Creep-resistant, Fe-base AFA Superalloys

- Optimized AFA alloy compositions to maximize the stability of **coherent γ'-Ni_3Al** precipitates for strengthening.
- The best alloy showed >7 times longer creep-life (700ºC/170MPa) than A286.





Slide courtesy of Y. Yamamoto, G. Muralidharan, M.P. Brady, Oak Ridge National Laboratory