Intermetallic Strengthened Alumina-Forming Austenitic Steels for Coal-Fired Power Systems

Bin Hu, Ian Baker

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

DOE grant DE-FE0008857

Acknowledgement

- Dr. Charles Daghlian
- Ms Geneva Trotter

- Dr. Yukinori Yamamoto
- Dr. Michael Brady
- Dr. Michael Miller

- Dr. Si Chen
- Dr. Zhonghou Cai

- Funded by the U.S. Department of Energy
  NETL Award DEFG2612FE0008857

Outline

- Introduction
  - Motivation
  - Background
- Results and Discussion
  - Microstructural analysis
  - Thermo-mechanical treatments
  - SEM & TEM characterization
  - XRD analysis
  - Room temperature tensile tests
  - High temperature tensile tests
- Summary

New Materials for High Temperature Applications

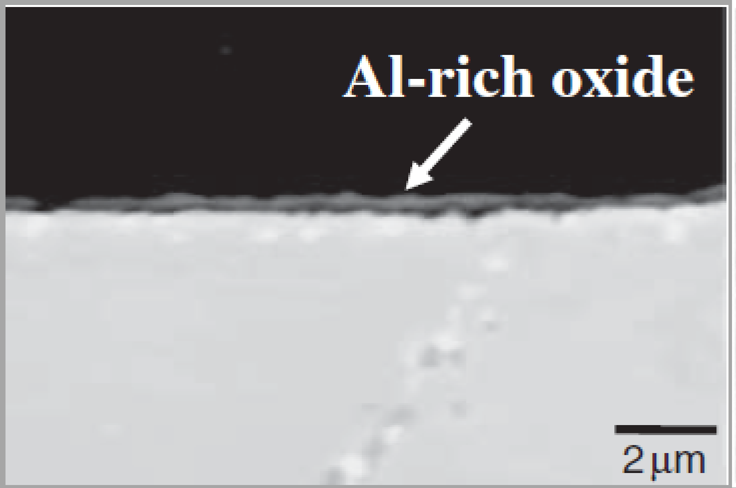
- **Motivation**: Develop materials which can be used at higher temperature (>700 °C) and pressure (>100 MPa) to enhance efficiency (>50 %) and reduce CO_2 emissions in fossil fired boiler/steam turbine power plants

- **Solutions:**
  - Ni-Base Superalloys: too costly
  - FeCrAl alloys: bcc structure, weak >500 °C
  - Al_2O_3 coatings or surface treatments
  - Alumina-Forming Austenitic Steels
    - Combination of creep and oxidation resistance
    - Lower cost (Lower nickel content)

www.siemens.com
Yamamoto, Y., et al.: Science, 2007, vol. 316(5823), pp. 433–36.
Yamamoto, Y., et al., Metallurgical and Materials Transactions A, 2011. 42(4): p. 922-931.

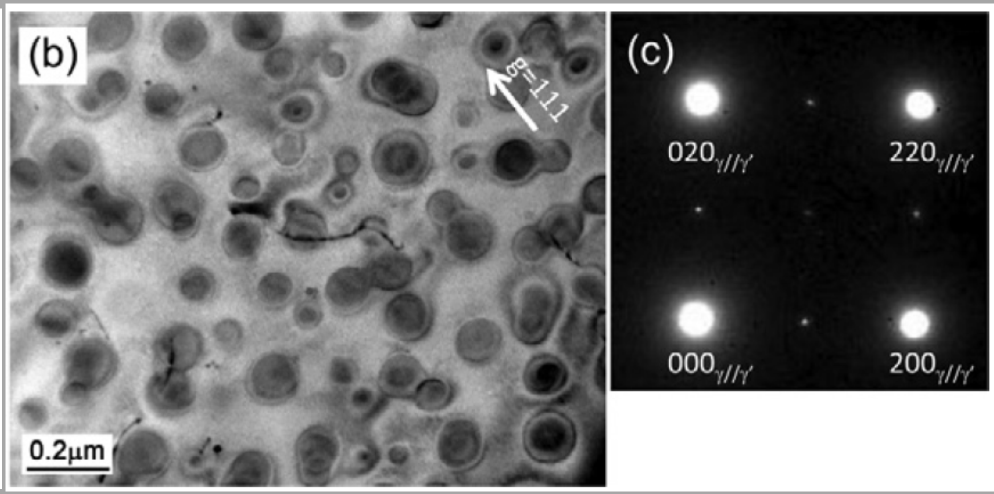
Alumina-forming Austenitic (AFA) Stainless Steels

- Combination of good oxidation & creep resistance
  - Oxidation resistance achieved by the formation of protective, external alumina scale. (~3 wt.% Al)
  - f.c.c. matrix with intermetallic strengthening (Ni_3Al etc.)



Fe-14Cr-20Ni-0.95Nb-2.5Al-2.5Mo wt. % base alloy (initial developed AFA)

BSE image after 72 hours of oxidation at 800°C in air



Fe-14Cr-32Ni-3Nb-3Al-2Ti wt.% base alloy (recent developed AFA)

TEM BF images of the alloys and SAD pattern

Yamamoto, Y., et al.: Science, 2007, vol. 316(5823), pp. 433–36.
Yamamoto, Y., et al., Scripta Materialia, 2013, 69(11–12), P.816–819.

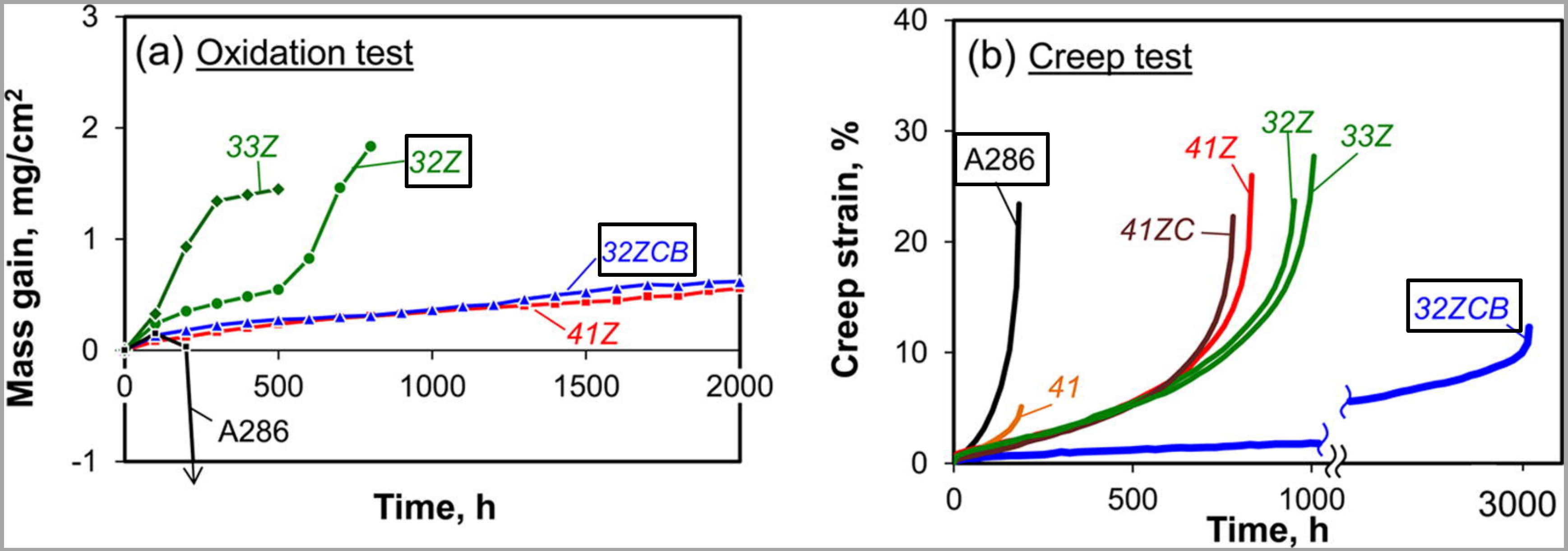
Oxidation Resistance and Creep Performance of AFA Steels

- Alumina formation in AFA alloys
  - Others: Ti content, C and B addition
- The best alloy has >7 times longer creep life than A286

32ZCB: Fe–14Cr–32Ni–3Nb–3Al–2Ti-0.27Zr-0.14Si (wt.%)
41Z: Fe–14Cr–32Ni–3Nb–4Al–1Ti -0.27Zr-0.12Si (wt.%)

A286: Fe–14Cr–25Ni–2Ti-0.15Al (wt.%)

(Iron-base superalloy)



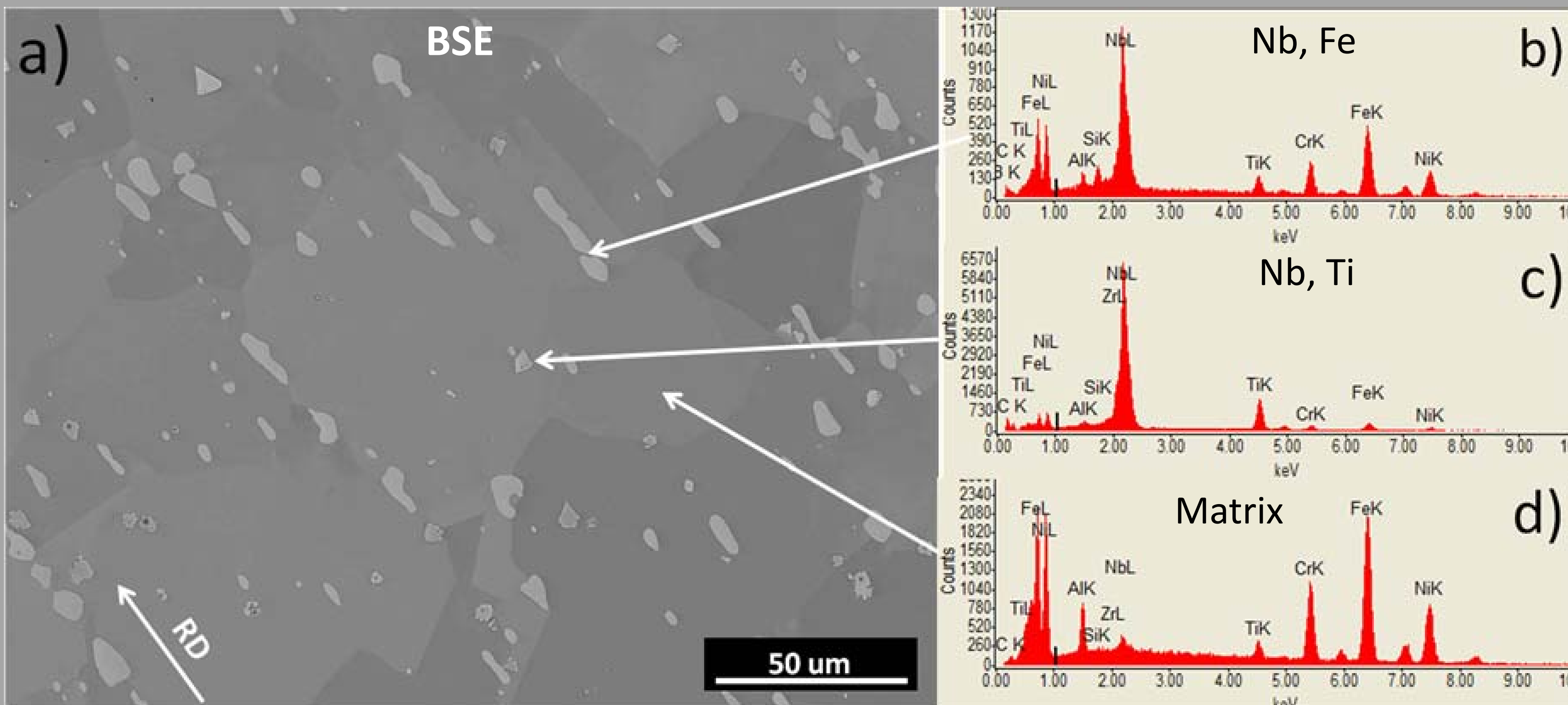
Cyclic oxidation test results at 800 °C in 10% water vapor

creep-rupture curves at 750 °C and 100 MPa.

Yamamoto, Y., et al., Scripta Materialia, 2013, 69(11–12), P.816–819.

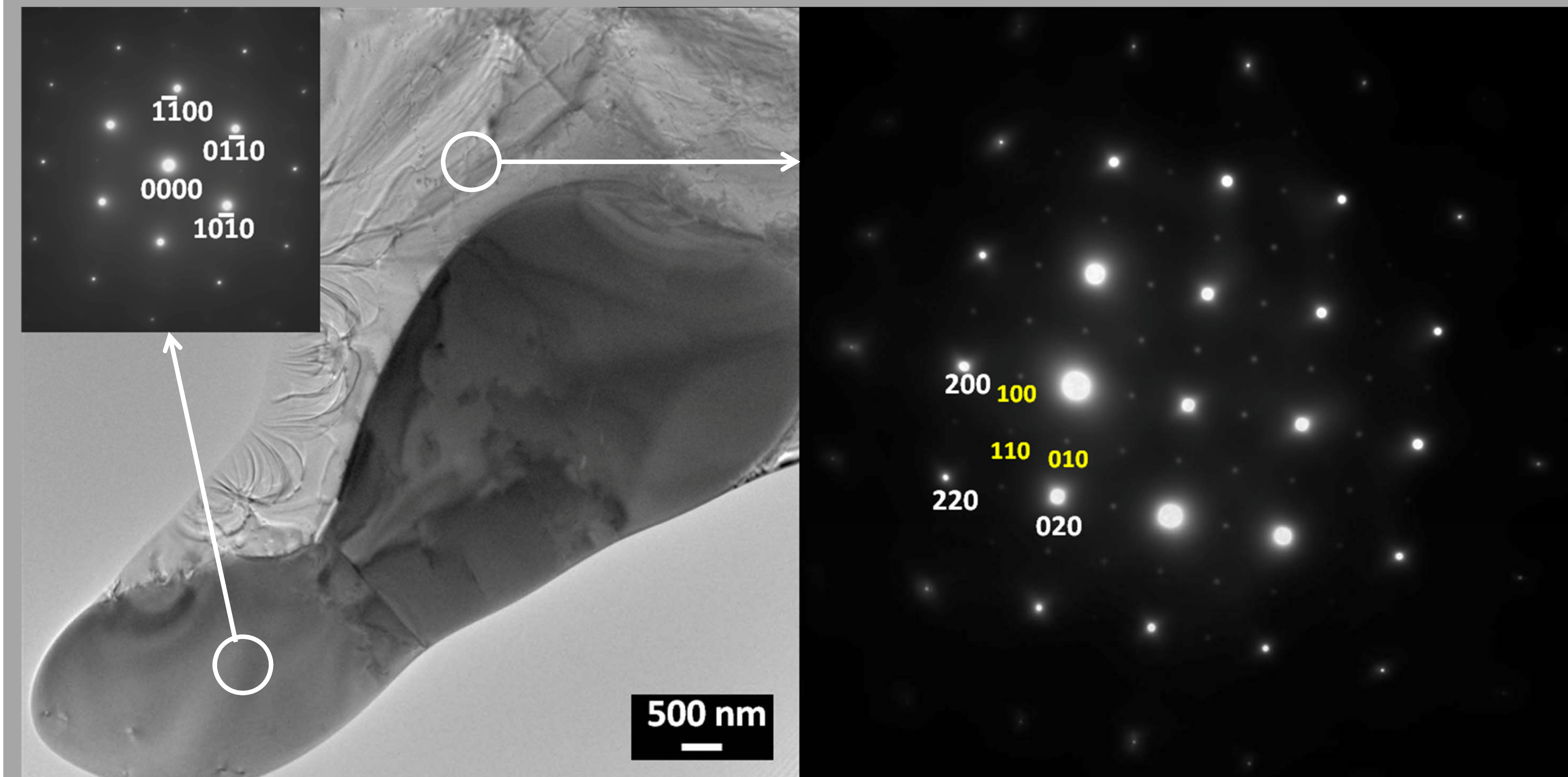
BSE Image and EDS Results of DAFA29

- DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-0.1C-0.01B (wt.%) (as-hot-rolled)
  - Nb enrich precipitates and grain size ~40 µm



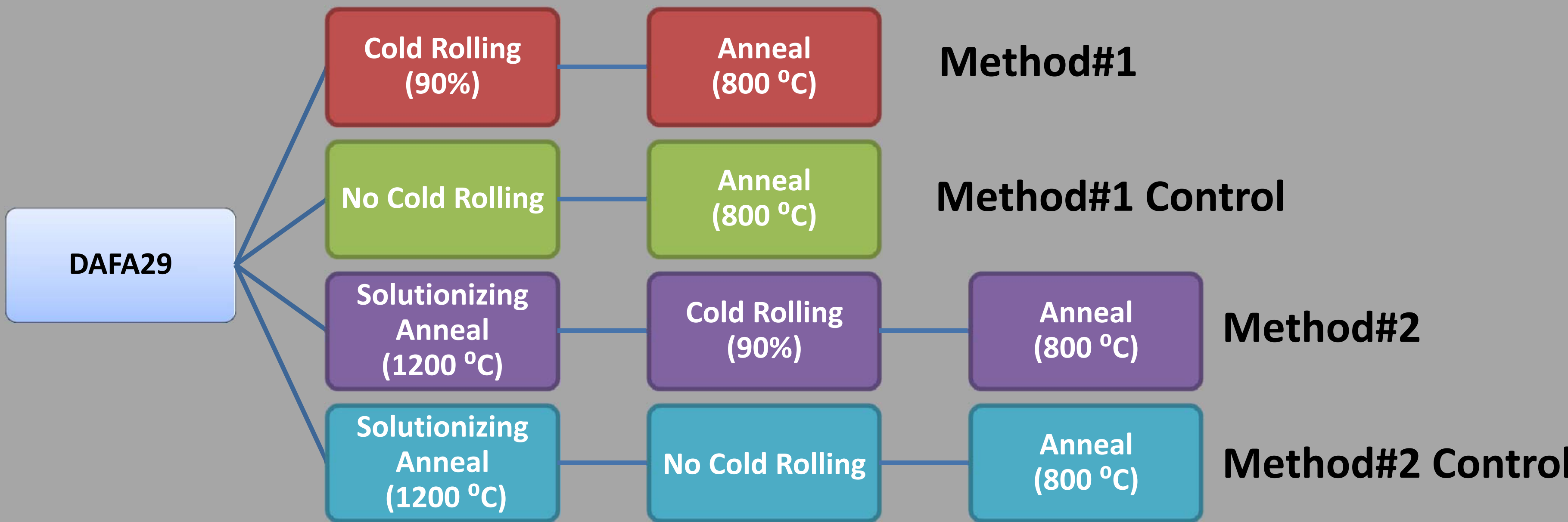
BF&SAD of Precipitates in DAFA29

- DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-0.1C-0.01B (wt.%) (as-hot-rolled)
  - Fe_2Nb Laves phase precipitates + $L1_2$ precipitates in f.c.c. matrix



Thermo-mechanical Treatments (TMT) Procedures

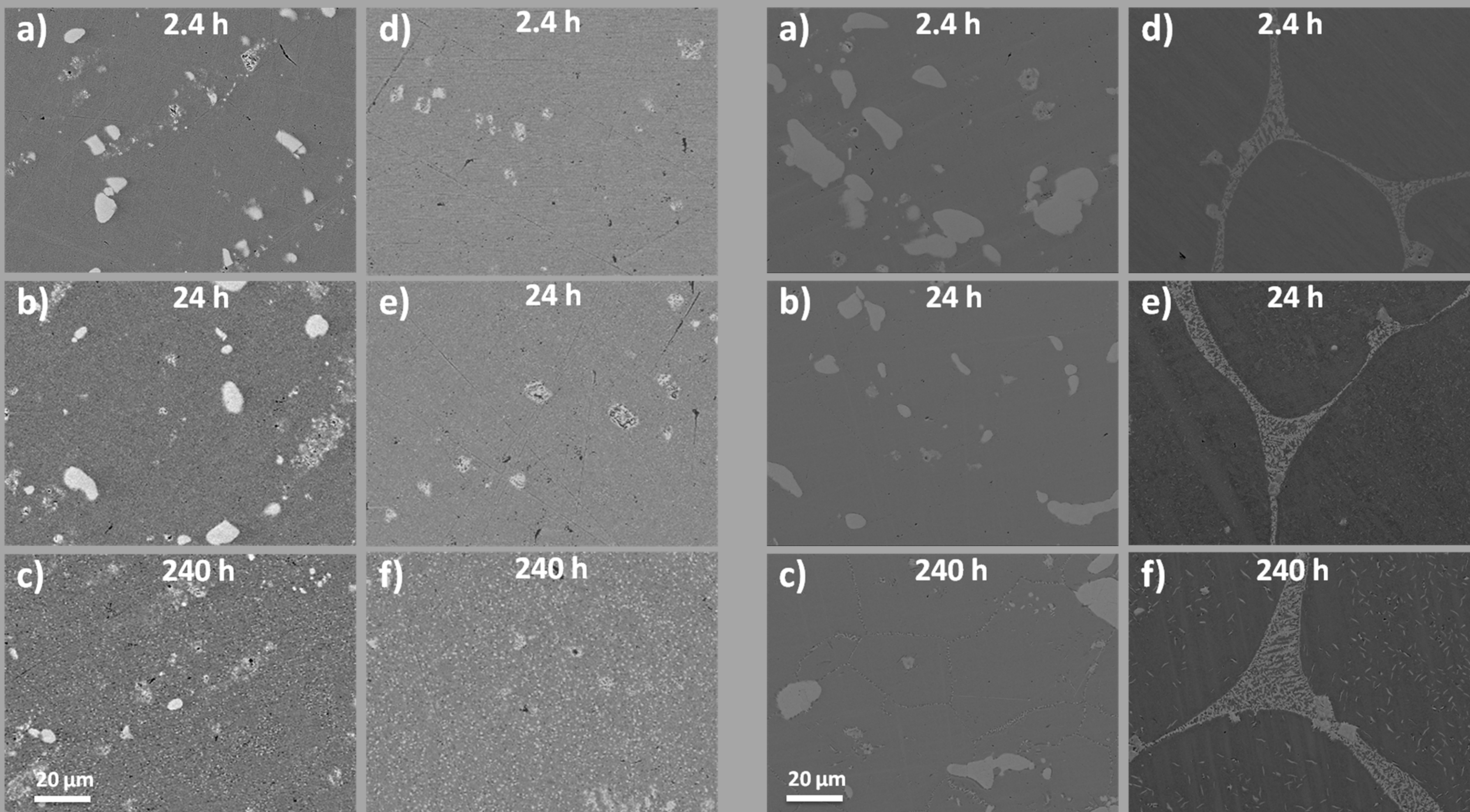
DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-0.1C-0.01B (wt.%) (recent developed)



- Cold rolling 90 % thickness reduction (~4.5 % reduction per pass)
  - ❖ Enhance the creep properties
  - ❖ Introduce dislocations which will act as nucleation sites for fine precipitates

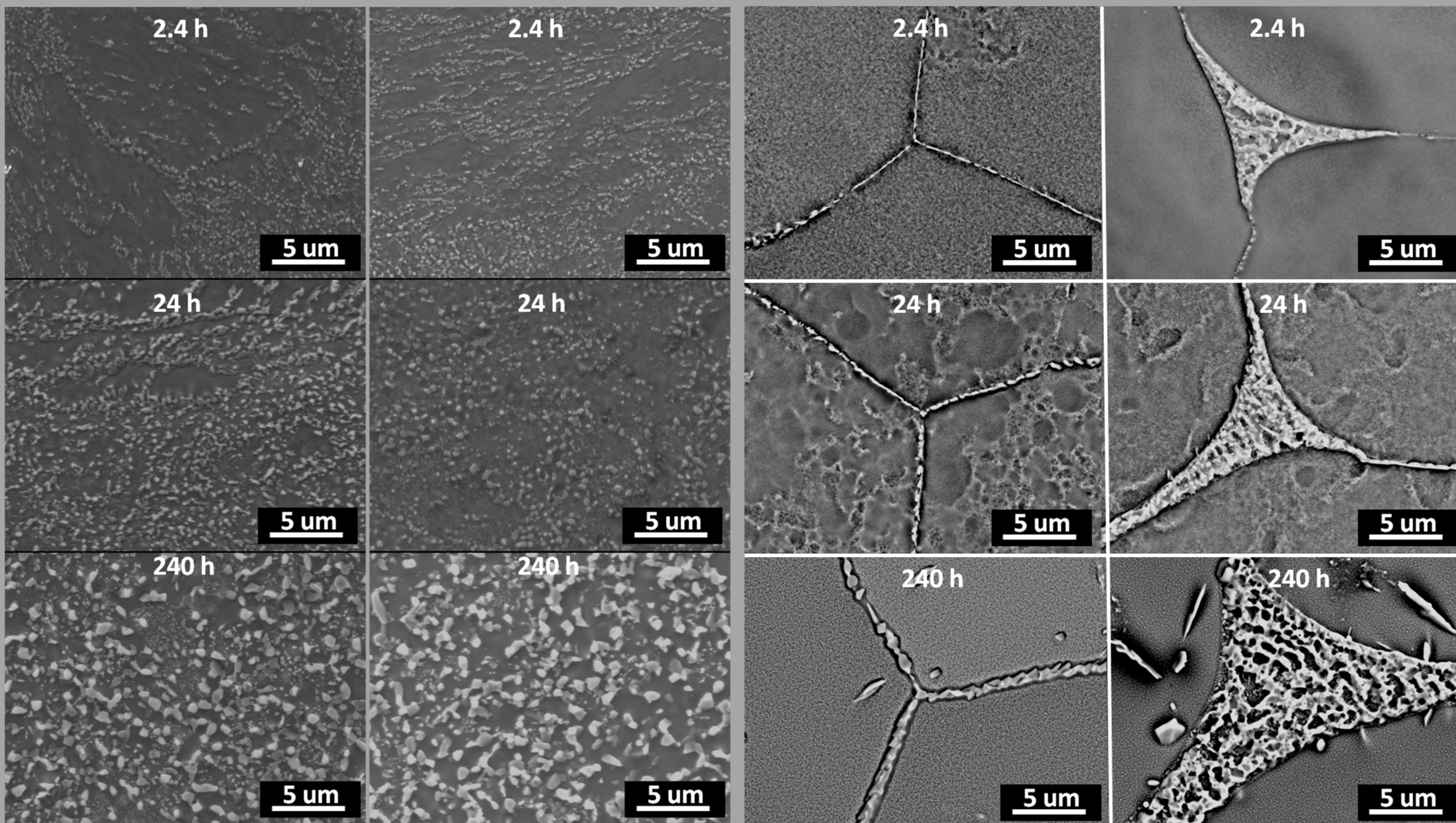
The Effects of Cold Rolling on The Microstructures of TMT DAFA29

Method #1	Method #2	Method #1 Control	Method #2 Control
Cold rolling + 800 ^oC	1200 ^oC + Cold rolling + 800 ^oC	800 ^oC	1200 ^oC + 800 ^oC



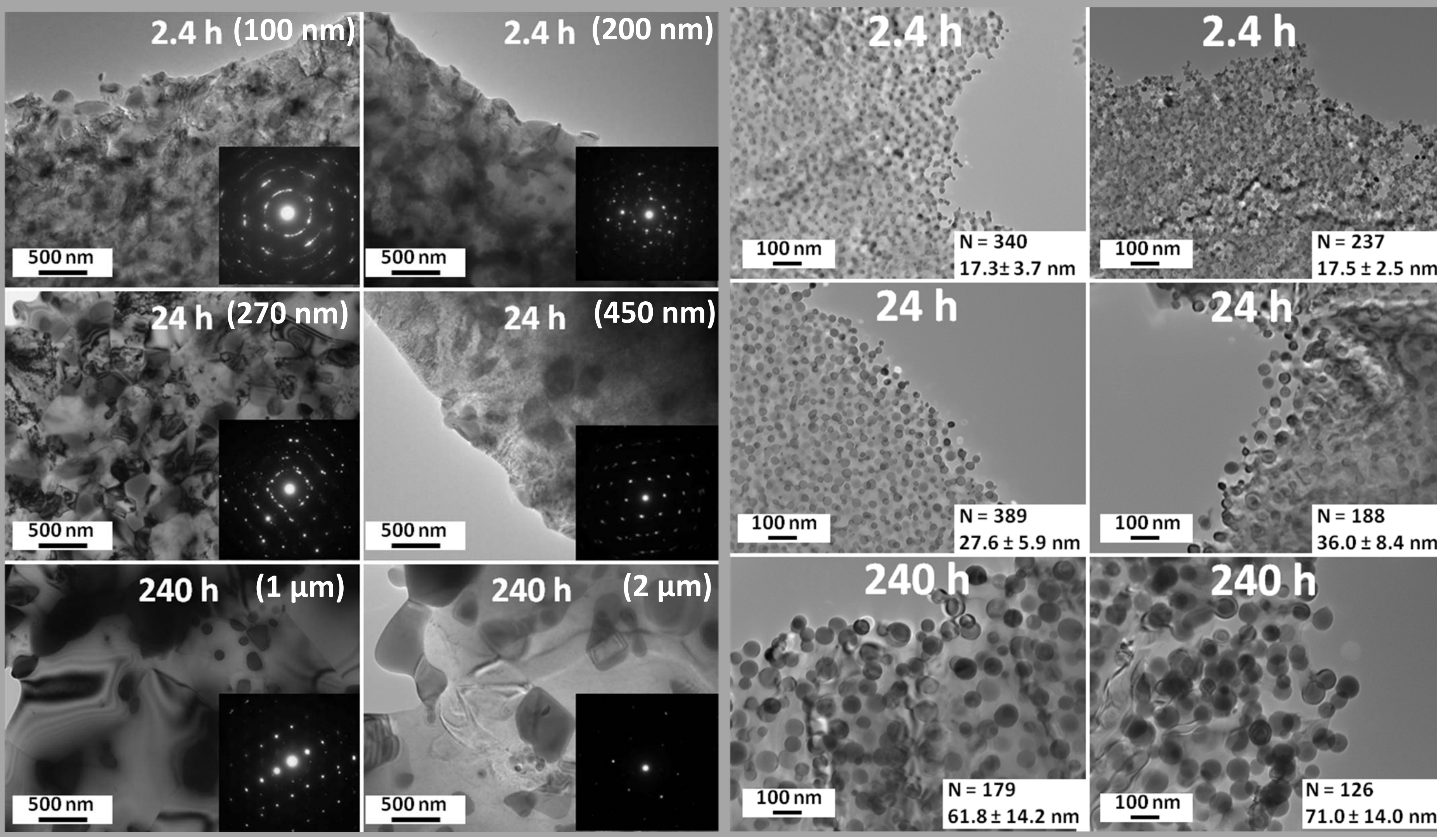
The Effects of Cold Rolling on The Microstructures of TMT DAFA29

Method #1	Method #2	Method #1 Control	Method #2 Control
Cold rolling + 800 ^{o}C	1200 ^{o}C + Cold rolling + 800 ^{o}C	800 ^{o}C	1200 ^{o}C + 800 ^{o}C



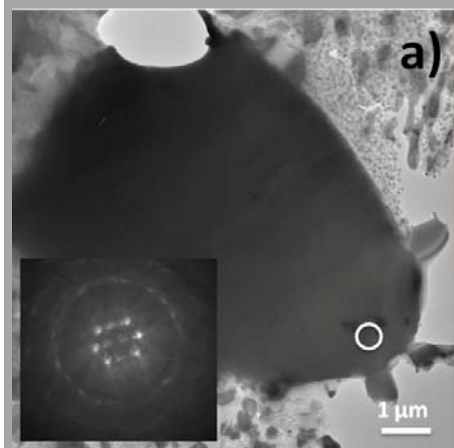
BF Images and SAD of DAFA29 after Thermo-mechanical Treatments

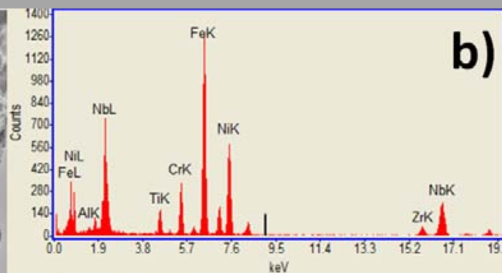
Method #1	Method #2	Method #1 Control	Method #2 Control
Cold rolling + 800 ^{0}C	1200 ^{0}C + Cold rolling + 800 ^{0}C	800 ^{0}C	1200 ^{0}C + 800 ^{0}C



BF TEM Image, EDS and CBED of Different Precipitates in TMT DAFA29

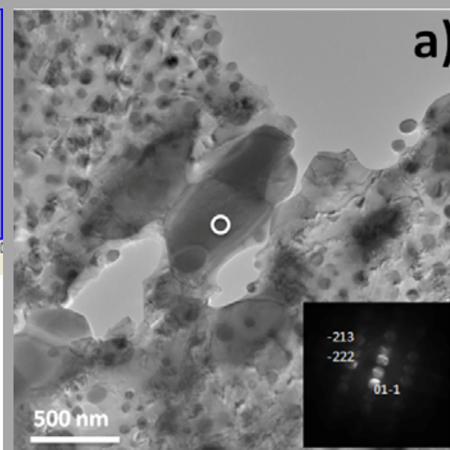
Laves-Fe_2Nb (4%)

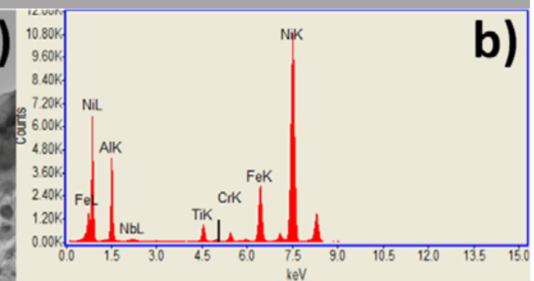




Elem	Weight %	Atomic %
AlK	0.6	1.5
TiK	3.2	4.3
CrK	7.7	9.5
FeK	36.2	41.5
NiK	17.9	19.5
ZrK	6.8	4.8
NbK	27.7	19.1
Total	100	100

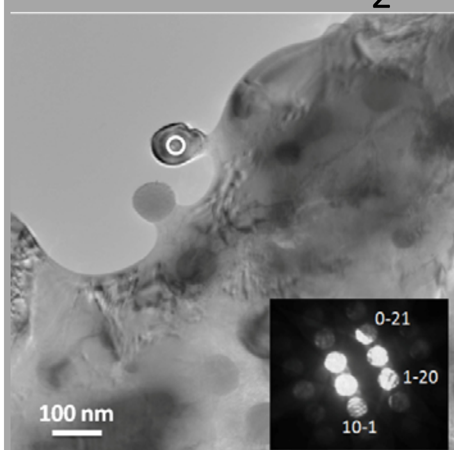
B2-NiAl (2%)

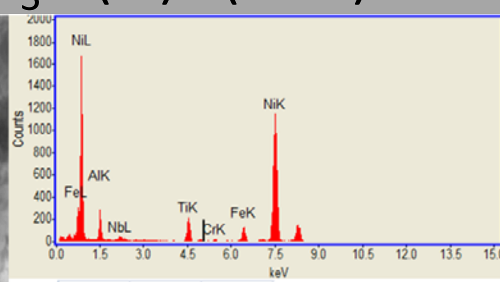




Elem	Weight %	Atomic %
AlK	14.1	26
NbL	1.2	0.6
TiK	3.5	3.7
CrK	1.9	1.8
FeK	13	11.6
NiK	66.3	56.2
Total	100	100

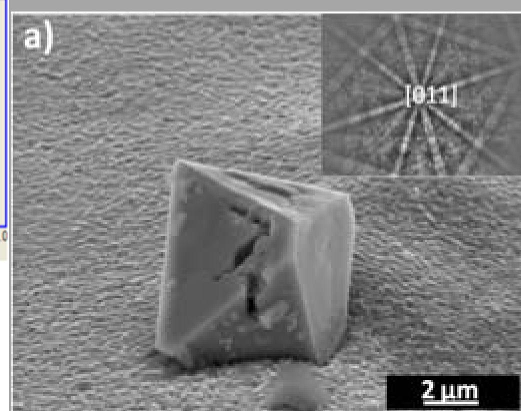
$L1_2$-$Ni_3Al(Ti)$ (17%)

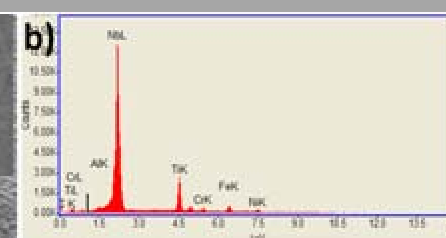




Elem	Weight %	Atomic %
AlK	9.2	17.9
TiK	8.7	9.5
CrK	0.6	0.6
FeK	5.5	5.2
NiK	73.1	65.2
NbK	2.8	1.6
Total	100	100

MC (M:Nb,Ti) (1%)

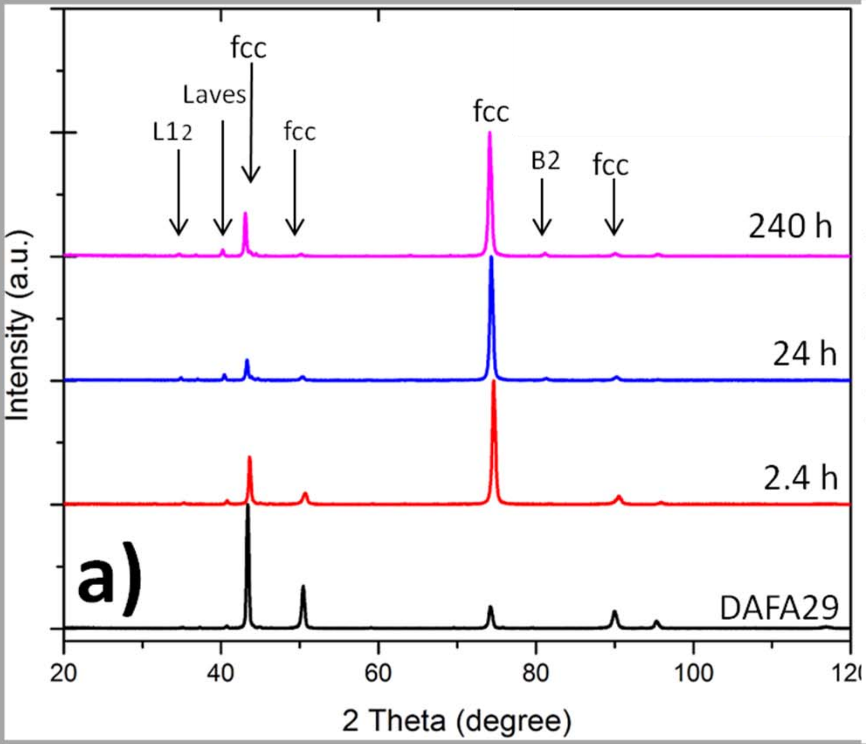




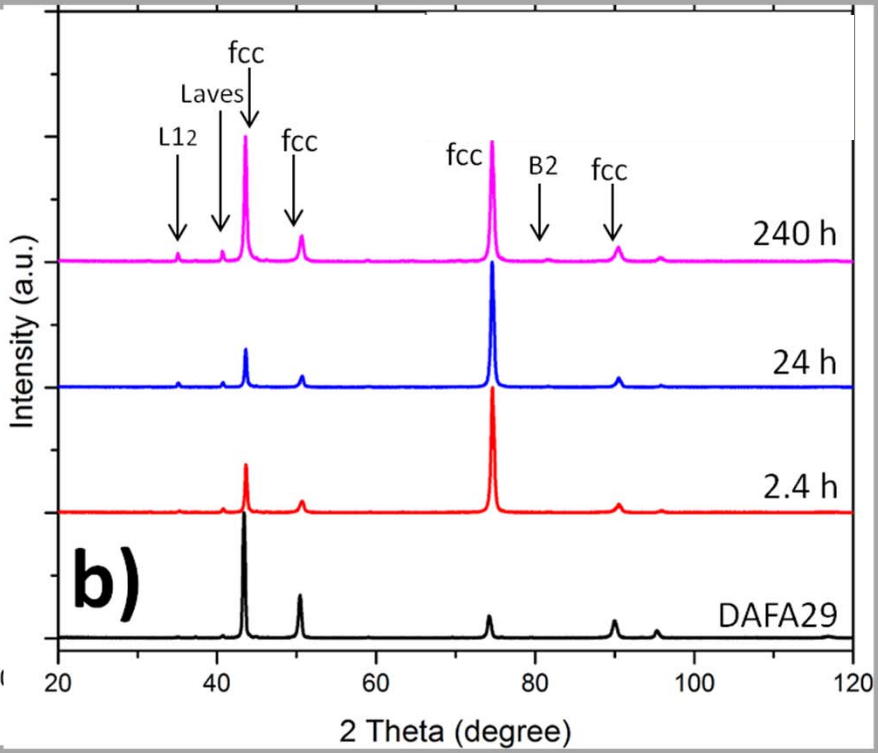
Element	Wt %	At %
C K	6.5	30.79
NbL	71.48	43.76
TiK	18.1	21.49
CrK	0.58	0.64
FeK	1.92	1.96
NiK	1.41	1.37
Total	100	100

Synchrotron XRD Results

Method#1:
Cold rolling + 800 ^oC



Method#2:
1200 ^oC + Cold rolling + 800 ^oC



Lattice parameters

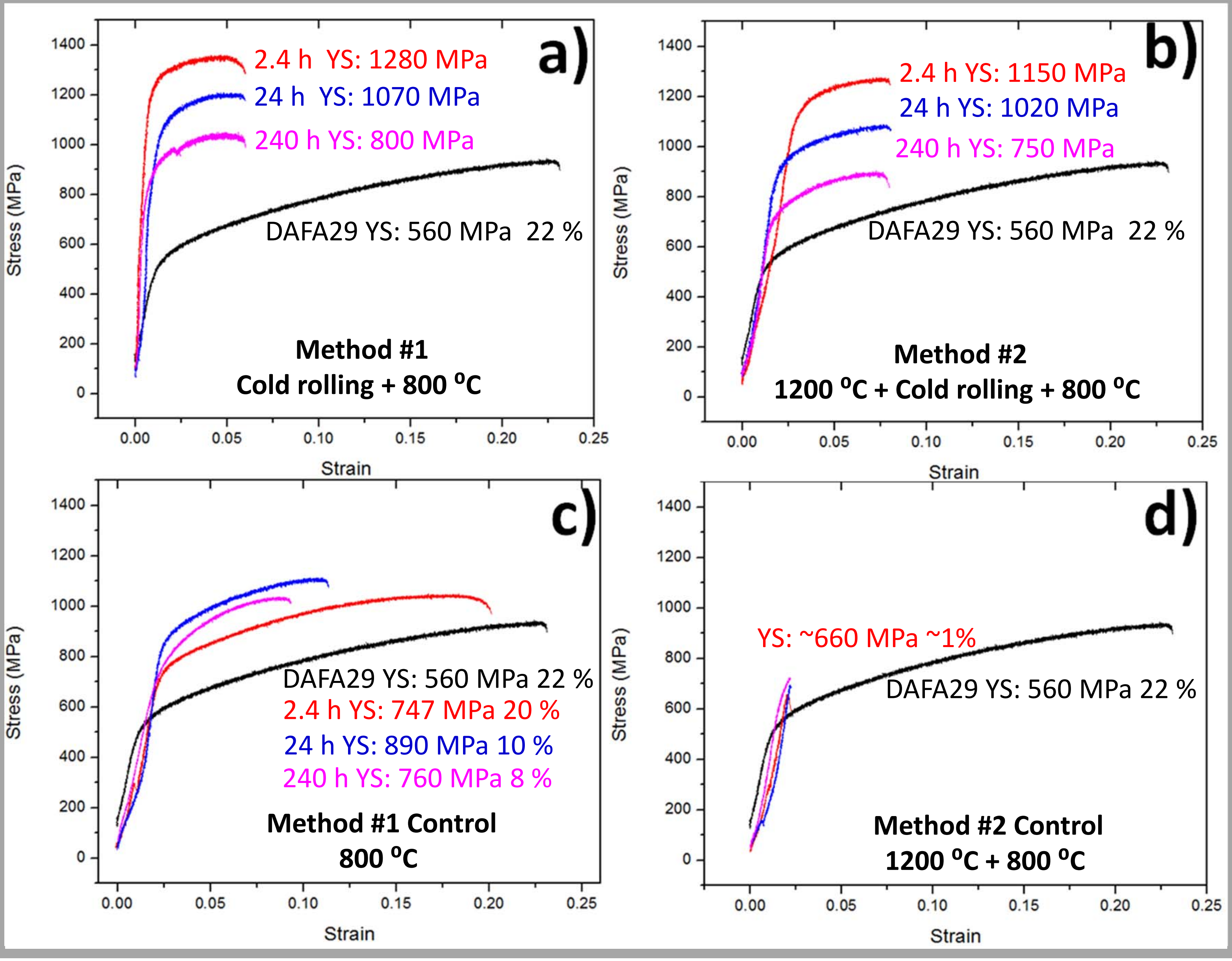
		Fe-f.c.c.	Fe_2Nb (a)	NiAl	Ni_3Al
	DAFA29	3.611	4.820	2.888	3.604
Method #1	**2.4 h**	3.599	4.812	2.883	3.590
	24 h	3.601	4.853	2.895	3.591
	240 h	3.597	4.881	2.900	3.587

Lattice parameters

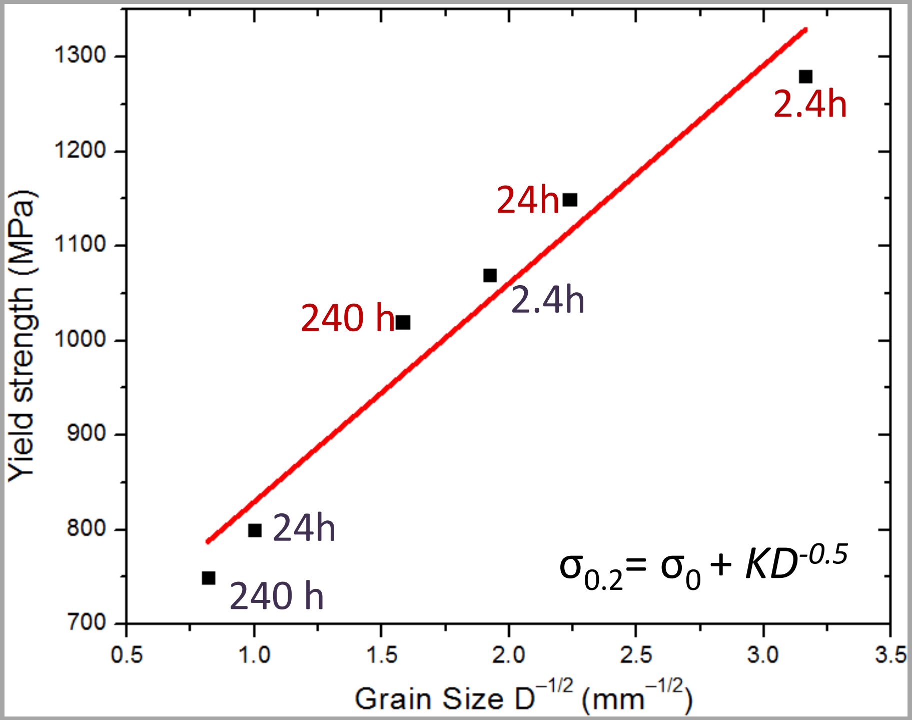
		Fe-f.c.c.	Fe_2Nb (a)	NiAl	Ni_3Al
	DAFA29	3.611	4.820	2.888	3.604
Method #2	**2.4 h**	3.601	4.812	2.883	3.591
	24 h	3.601	4.817	2.888	3.594
	240 h	3.601	4.820	2.890	3.591

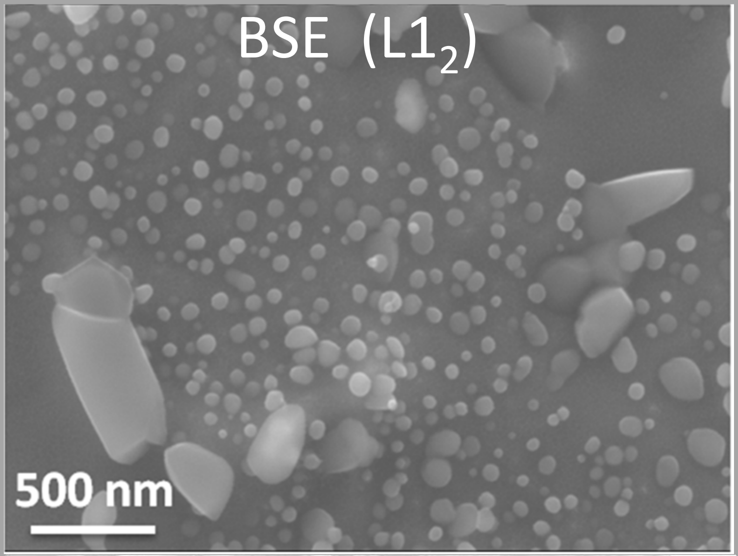
Lattice misfit of $L1_2$ phase with f.c.c. matrix is calculated to be only **~0.28%** for both treatments

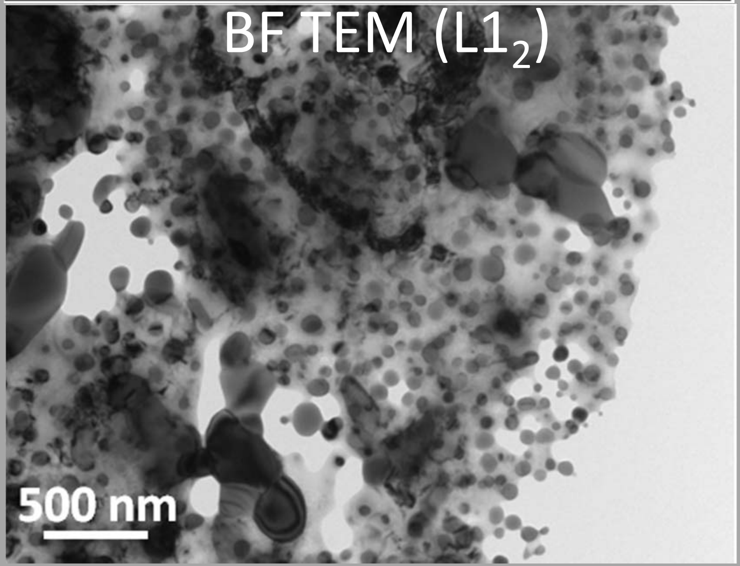
Room Temperature Tensile Tests



Hall-Petch Relationship for TMT DAFA29







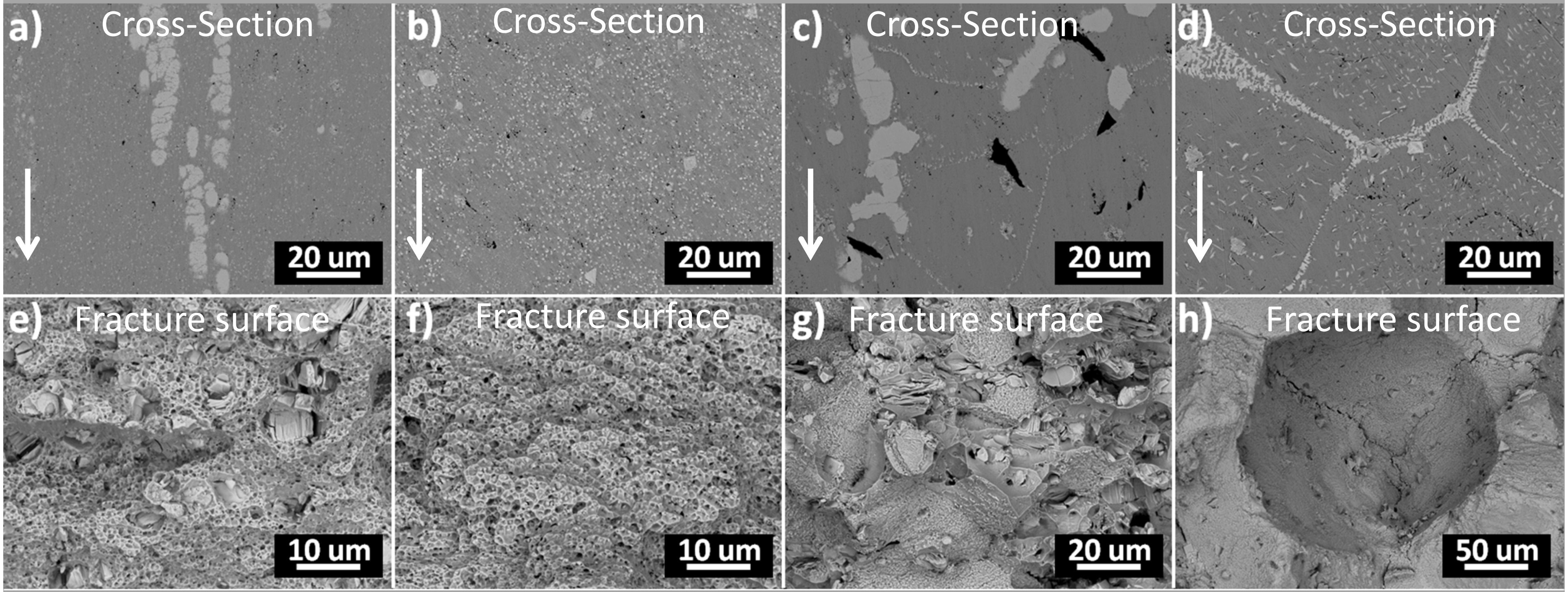
Hall-Petch: $\sigma_{0.2} = \sigma_0 + KD^{-0.5}$,

where $\sigma_0 = 600$ MPa , $K = 230$ MPa•$\mu m^{-0.5}$

$\sigma_0 = \sigma_{ppt} + \sigma_d + \sigma_{ss}$

Cross-Sections and Fracture Surfaces for Samples Treated by TMT Methods

Method #1	Method #2	Method #1 Control	Method #2 Control
Cold rolling + 800 ^oC	1200 ^oC + Cold rolling + 800 ^oC	800 ^oC	1200 ^oC + 800 ^oC

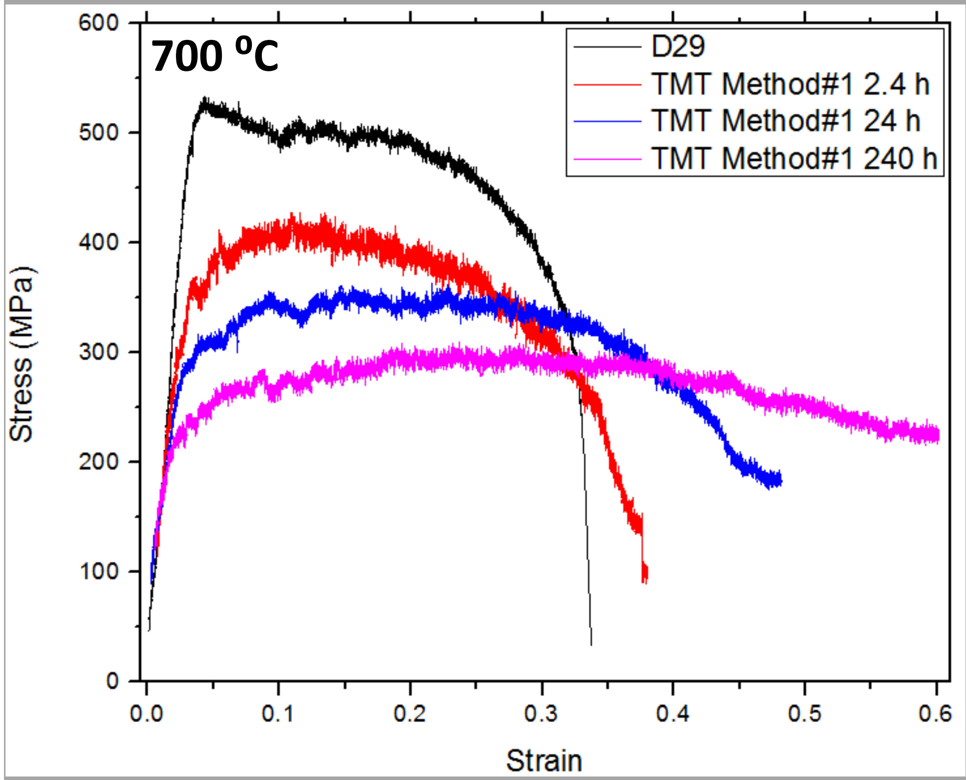


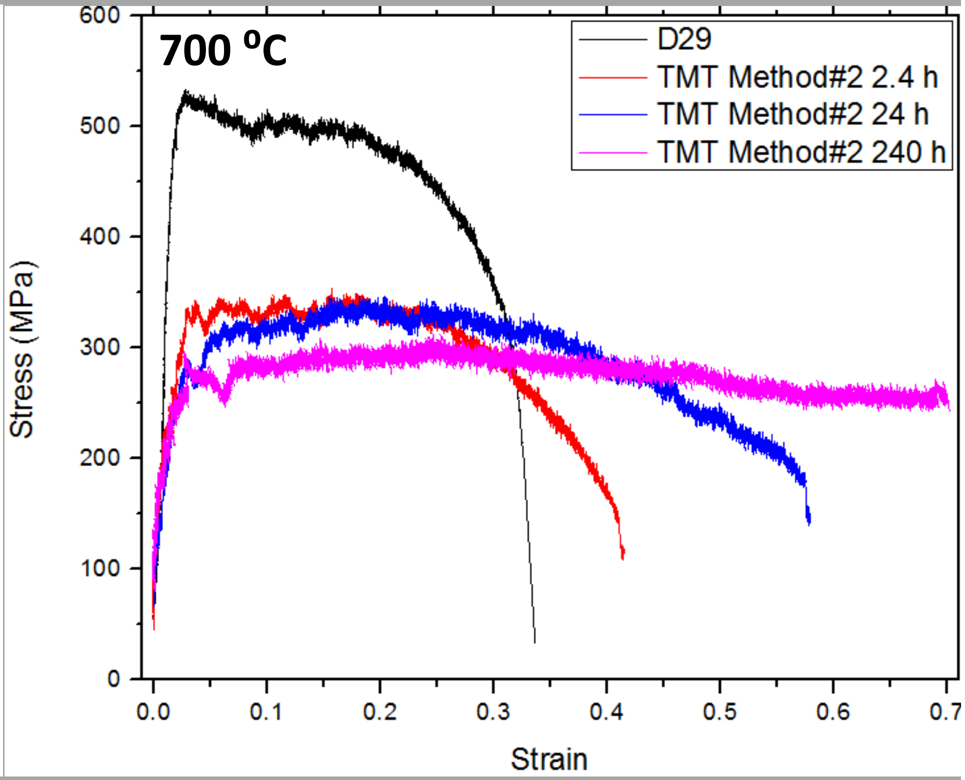
240 h	240 h	240 h	240 h
YS: 800 MPa	YS: 750 MPa	YS: 760 MPa	YS: 660 MPa
Elongation: 5.1 %	Elongation: 6.2 %	Elongation: 8.0 %	Elongation: 1.0 %

Tensile Tests at 700 ^oC

Method #1
Cold rolling + 800 ^oC

Method #2
1200 ^oC + Cold rolling + 800 ^oC

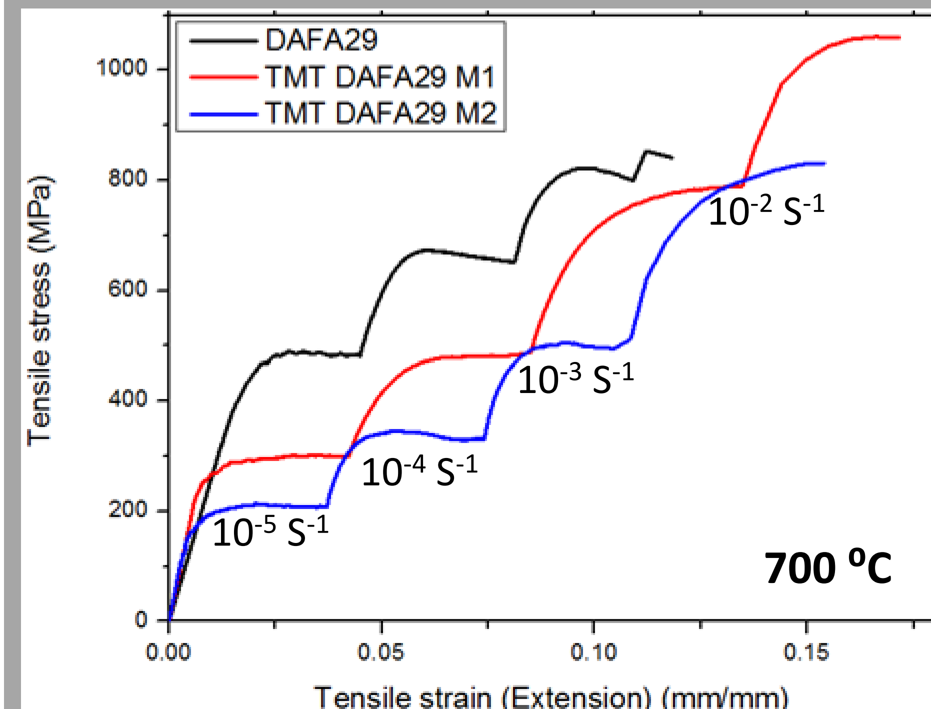


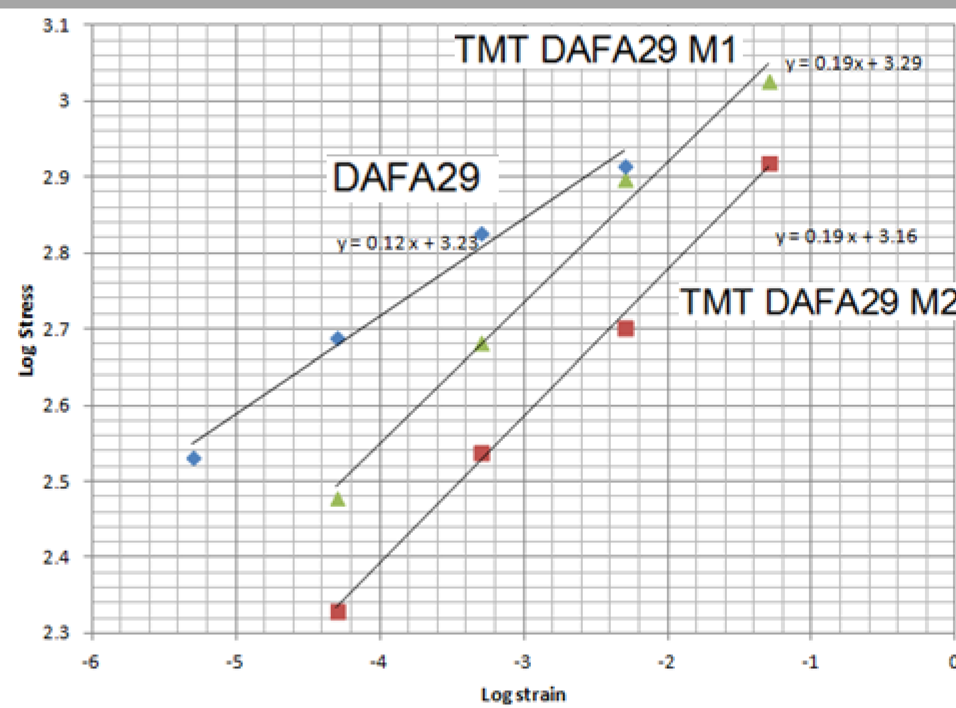


Materials	Yield Strength (MPa)	Elongation (%)
DAFA29	510	31
TMT 2.4h	384	35
TMT 24h	289	46
TMT 240h	218	59

Materials	Yield Strength (MPa)	Elongation (%)
DAFA29	510	31
TMT 2.4h	337	39
TMT 24h	290	55
TMT 240h	262	68

Strain Rate Jump Tests at 700 ^oC





$$\sigma_y = C(\dot{\epsilon})^m$$

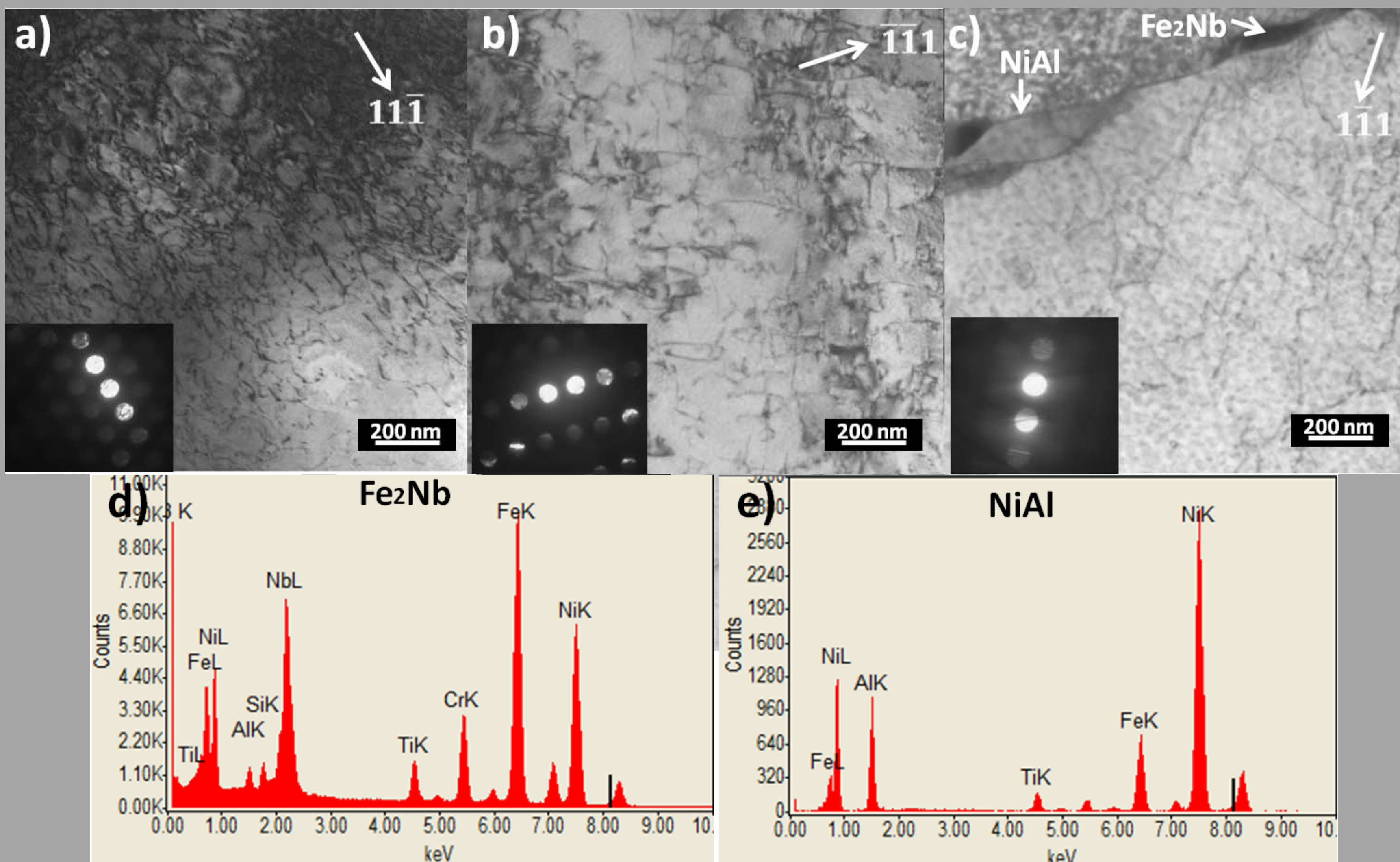
$$m = \frac{\partial ln\sigma(\epsilon)}{\partial ln(\dot{\epsilon})}$$

As-received DAFA29: *m*= 0.12

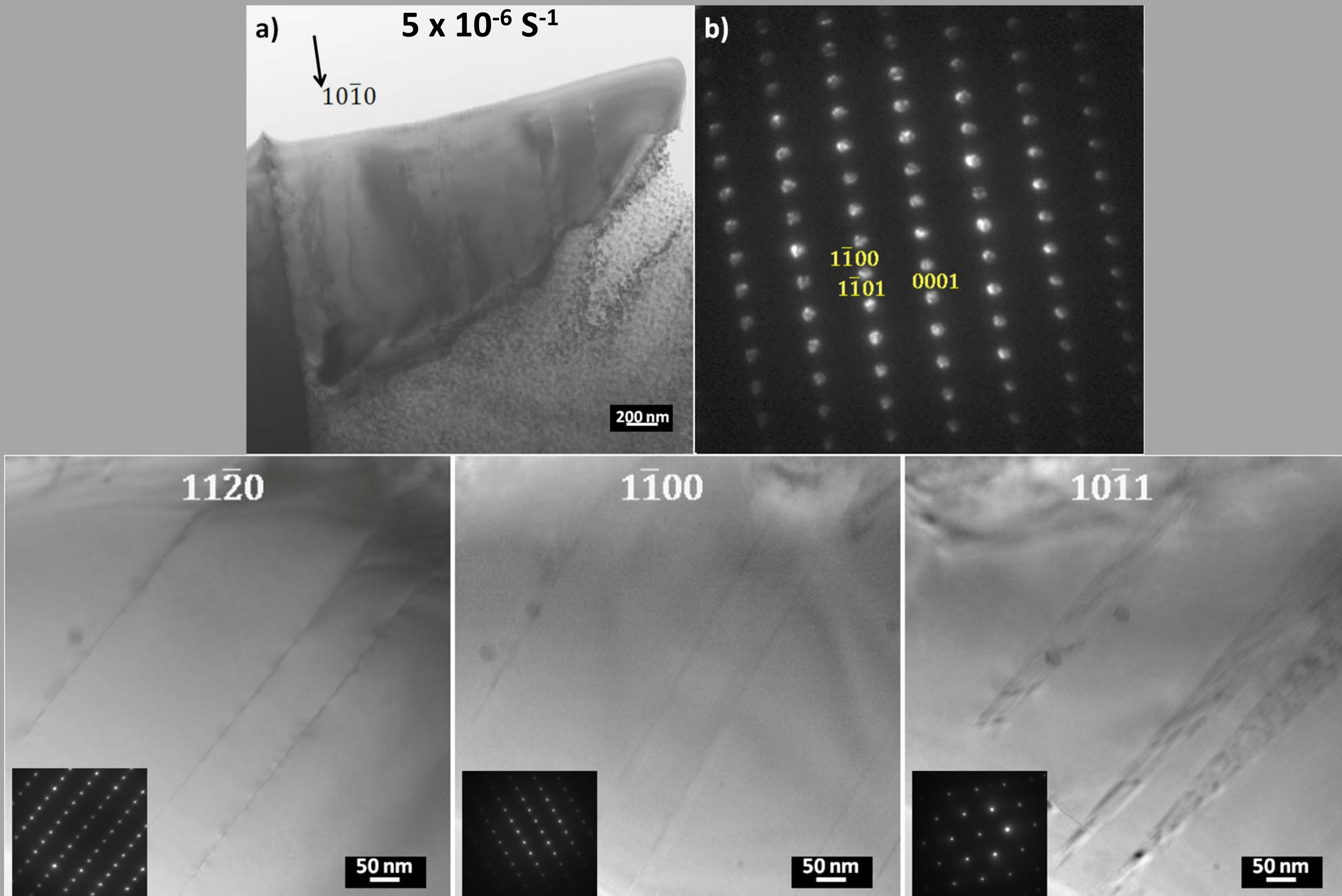
TMT DAFA29: *m*= 0.19

Dislocations in DAFA29 Tested in Different Strain Rates at 700 ^oC

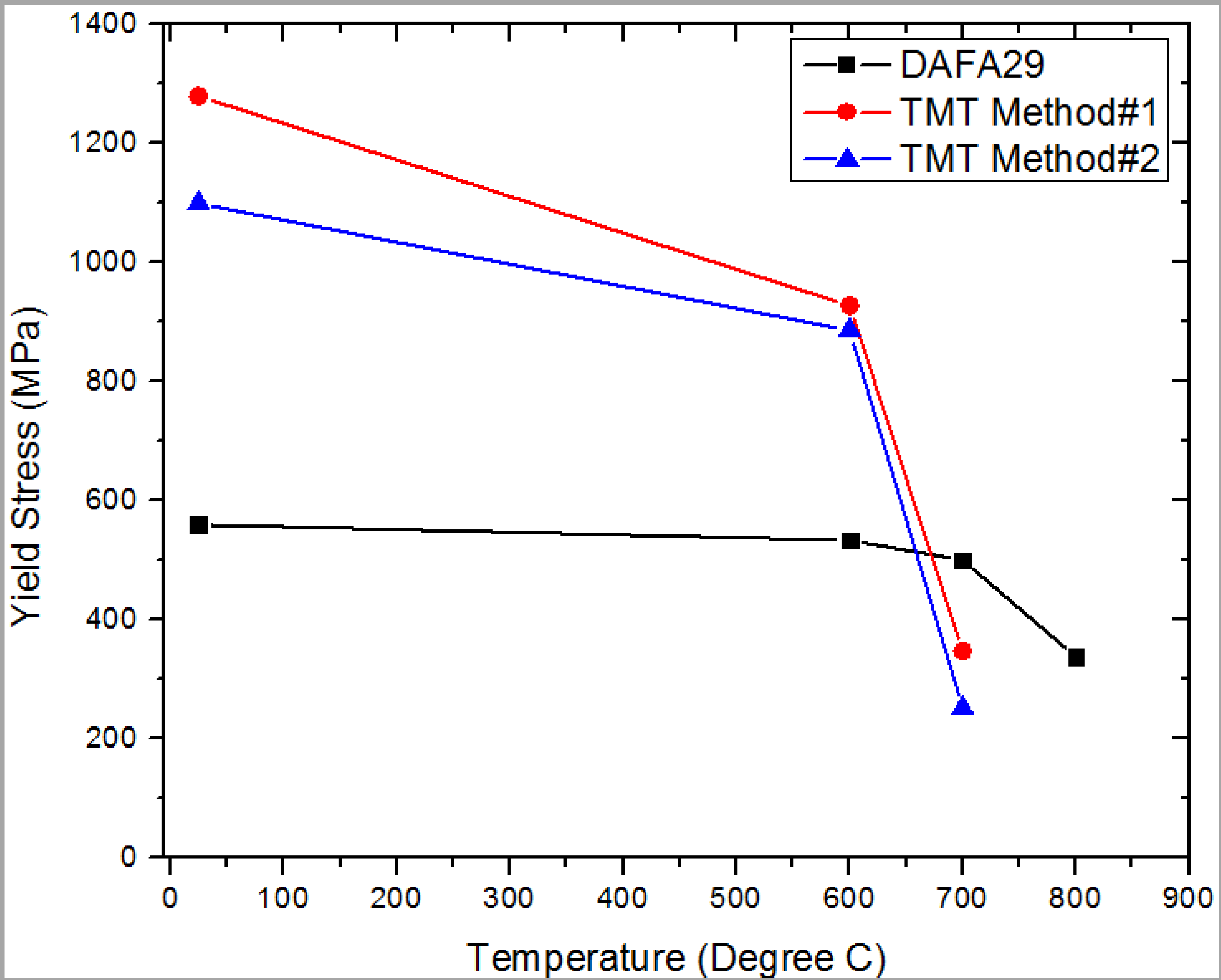
$5 \times 10^{-2}\ S^{-1}$ **$5 \times 10^{-4}\ S^{-1}$** **$5 \times 10^{-6}\ S^{-1}$**



Stacking Faults on Grain Boundaries
Laves Phase Precipitates



Stress Versus Temperature for as-received and TMT DAFA29



Summary

- A solutionizing anneal at 1200^{o}C followed by cold rolling and annealing at 800^{o}C can be used to generate a finer-scale and more uniform distribution of Laves phase precipitates.

- Cold rolling produces a high density of dislocations, which act as nucleation sites for Laves phase, B2, and $L1_2$ precipitates

- Nanocrystalline steels processed through 90% cold rolling exhibit a dramatic increase in yield strength up to 1280 MPa at RT. The TMT alloys loss stress at 600 -700^{o}C.

- The yield strength of TMT AFA steels exhibits a Hall-Petch relationship with a large value for σ_0 that likely arises from precipitate strengthening (σ_{ppt}).

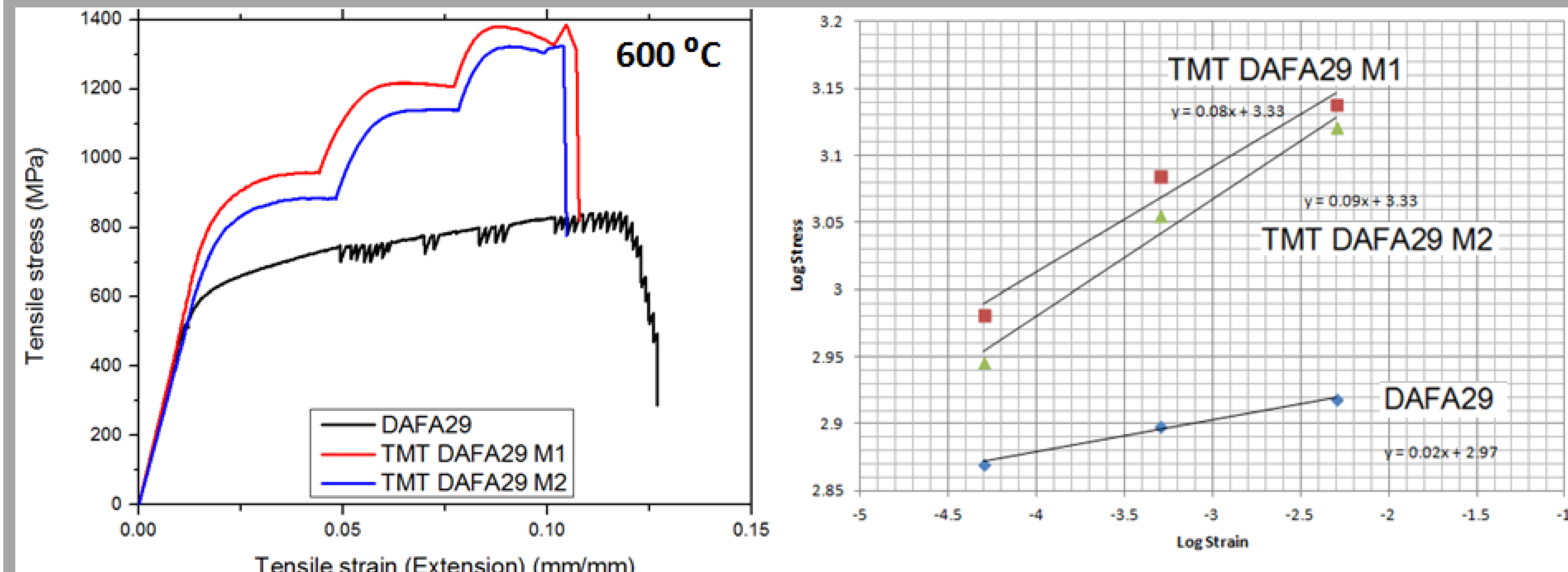
- The high temperature strength of both as-received and TMT DAFA29 are strain rate dependent at 700 ^{o}C

Future Work

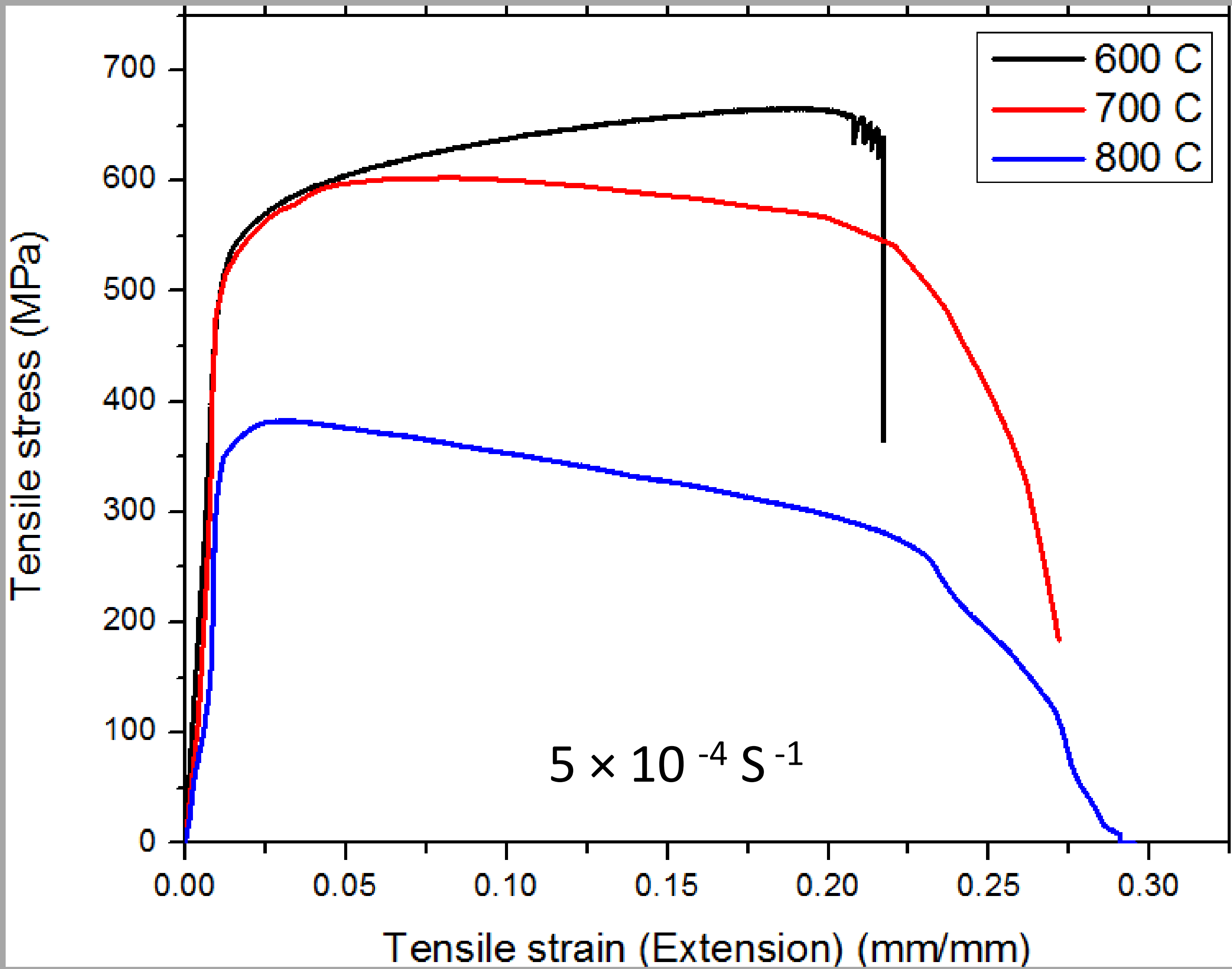
- Continue high temperature tensile tests
  - Tests at different temperatures (600-800 ^{o}C)
  - Fracture behavior analysis

- Creep tests of TMT DAFA29
  - Study the creep mechanisms for as-received D29
  - Characterize the deformed creep samples
  - Determine dislocation/precipitate interactions

Strain Rate Jump Tests at 600 ^oC



Tensile Tests of D29 at Different Temperatures



Stress vs Temperature for DAFA29