Development of Alumina-Forming Austenitic (AFA) Stainless Steels

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Stainless Steels with Higher-Temperature Capability Needed

- Driver: Increased efficiencies with higher operating temperatures in power generation systems.

- Key issues are creep and oxidation resistance.

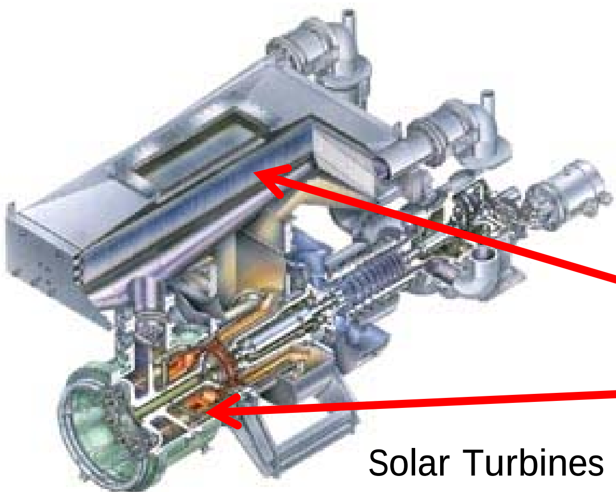
  - Significant gains have been made in recent years for improved creep resistance via nano MX precipitate control (M = Nb, Ti, V; X = C, N).

  - Stainless steels rely on Cr_2O_3 scales for protection from high-temperature oxidation.
    -Limited in many industrial environments (water vapor, C, S)
    -Most frequent solution is coating: costly, not always feasible

Development Effort for Low Cost, Creep and Oxidation-Resistant Structural Alloy for Use from ~600-900°C

- **Approach: Al_2O_3-forming austenitic stainless steels**
  -background and potential advantages
- **Current alloy status for microstructure, mechanical properties, and oxidation resistance**

Initial target(s)



Recuperator, Casing

Solar Turbines 4.6 MW Mercury 50 recuperated low NO_x gas turbine engine

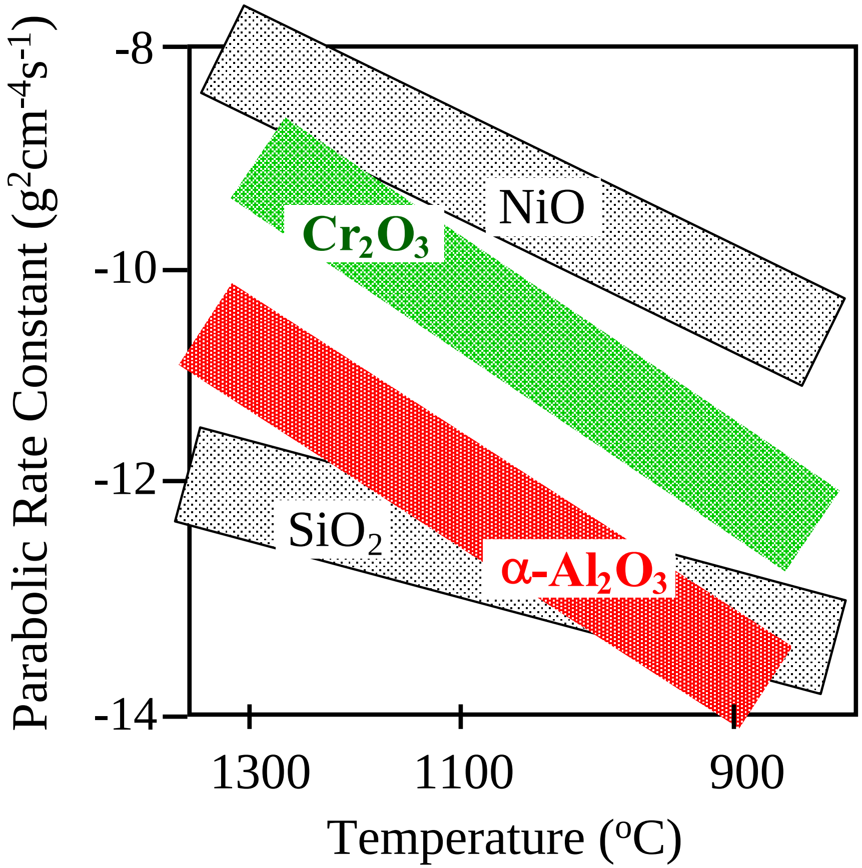
Fossil Power Steam Turbine, Boiler Tubing

HMN-Series (High-, Intermediate- and Low-Pressure) Steam Turbine for Combined-Cycle and Steam Power Plants

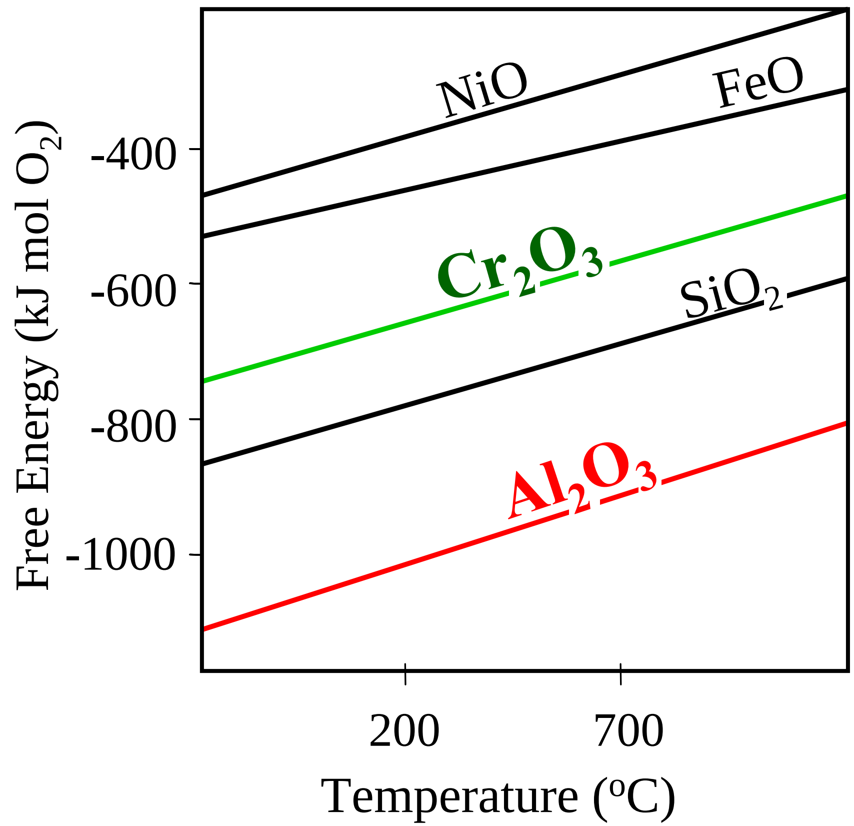
➢ Tubing in chemical/process industry, etc. also targeted.

Al_2O_3 Scales Offer Superior Protection in Many Industrially-Relevant Environments

=Kinetics=
(Growth rate of oxide scales)



=Thermodynamics=
(Ellingham diagram)



- Al_2O_3 exhibits a lower growth rate and is more thermodynamically stable in oxygen than Cr_2O_3.
- Highly stable in water vapor.

Challenge of Alumina-forming Austenitic (AFA) Stainless Steel Alloys

- Numerous attempts over the past ~30 years (e.g. McGurty et al. alloys from the 1970-80's, also Japanese, European, and Russian efforts)

- Problem: Al additions are a major complication for strengthening
  - ➢ strong BCC stabilizer/delta-ferrite formation (weak)
  - ➢ interferes with N additions for strengthening

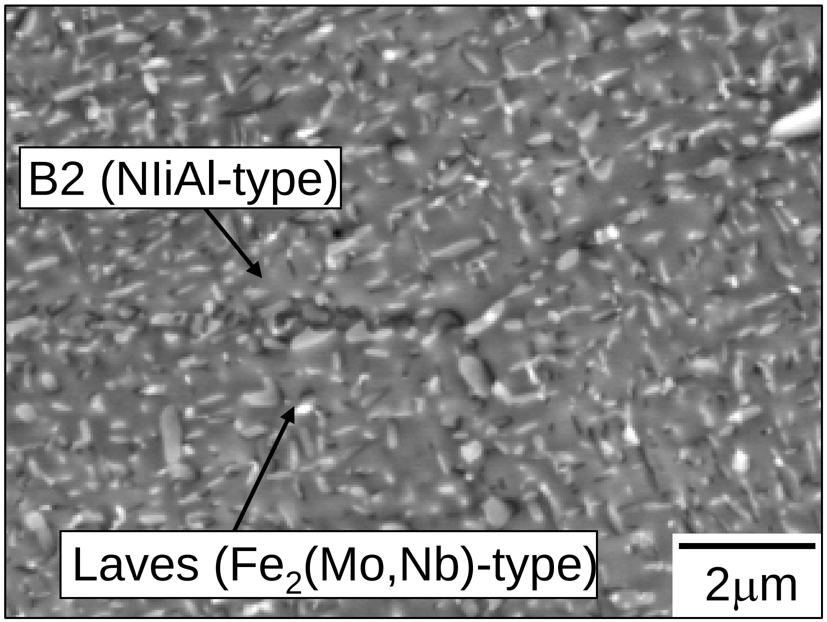
- Want to use as little Al as possible to gain oxidation benefit
  - ➢ keep austenitic matrix for high-temperature strength
  - ➢ introduce second-phase (intermetallics/carbides) for precipitate strengthening

Composition and Microstructure Considerations for AFA Stainless Steels

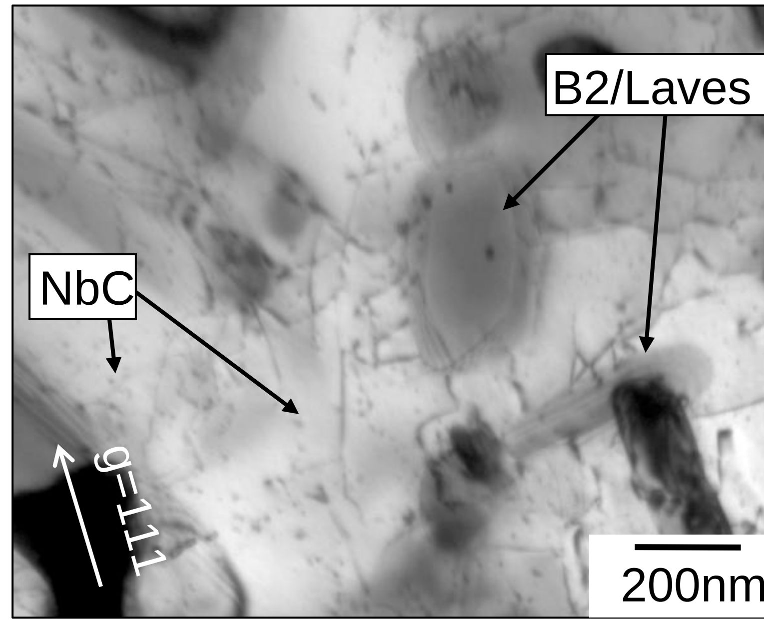
Typical Fe-(20-30)Ni-(12-15)Cr-(2.5-4)Al-(1-3)Nb-0.1C wt.%

Base AFA Alloy Microstructure After Creep

SEM

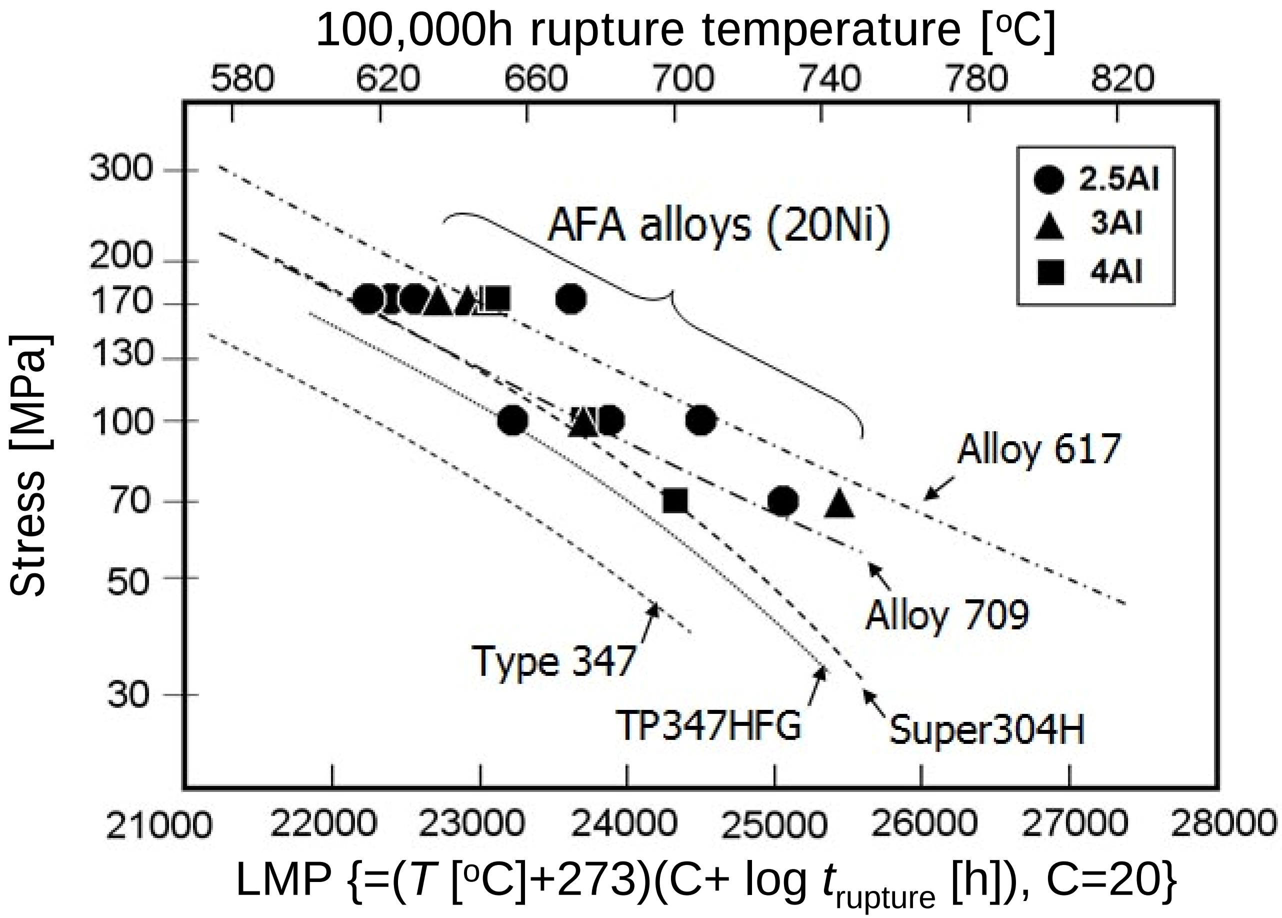


TEM



- Creep Strength
  - balance Al, Cr, Ni, to maintain single-phase FCC austenitic matrix
  - Nano NbC and submicron B2-NiAl + Fe_2Nb base Laves precipitates
- To form protective alumina:
  - Ti+V < 0.3 wt.%; Nb > (0.6-1) wt.%; N < 0.02 wt.%

AFA Exhibits Comparable Creep Strength to Best Commercial Austenitic Stainless Steels



- AFA alloys (20Ni) are in the range between alloy 709 (Fe-20Cr-25Ni base) and alloy 617 (Ni-22Cr-12Co-9Mo base)
- AFA data from small (< 1 kg) laboratory arc-castings, sub-sized screening creep test sample, solution treated + 10% cold work condition

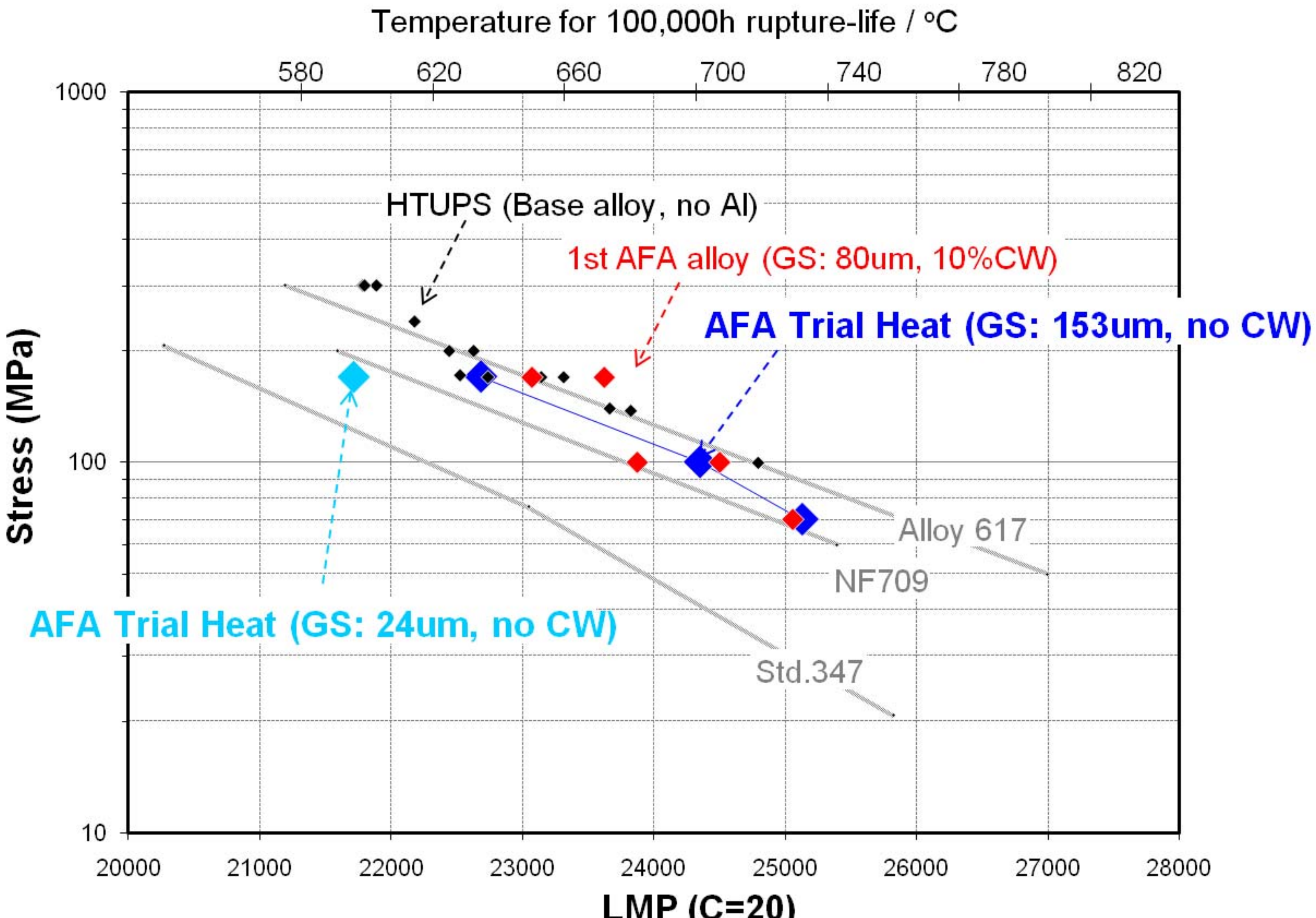
50 lb AFA Trial Heat Made by Conventional Vacuum Melting and Hot Rolling Processes

- Fe-20Ni-12Cr-4Al-0.6Nb-0.1C base wt.% composition
- Material used for rigorous creep evaluation with standard specimen design, solution treated condition (no cold work)

(collaboration w/J.P. Shingledecker)

Comparable Creep Strength to that Obtained in Screening Studies

(Hot-rolled + Solution heat-treated, no cold-work applied)



Ductile Creep Rupture at Failure

(Most of the gage portions showed just tinted color even after >6000h testing)

(750ºC/170MPa)
150h /55%

* Almost no damage on the surface, because of relatively shorter testing time.

(750ºC/100MPa)
6382h/7.5 %

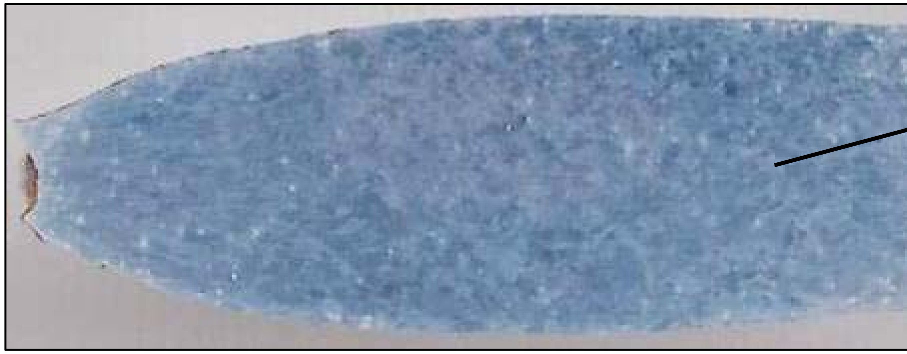
* Heavily oxidized only at necking regions.

(800ºC/70MPa)
2634h/28%

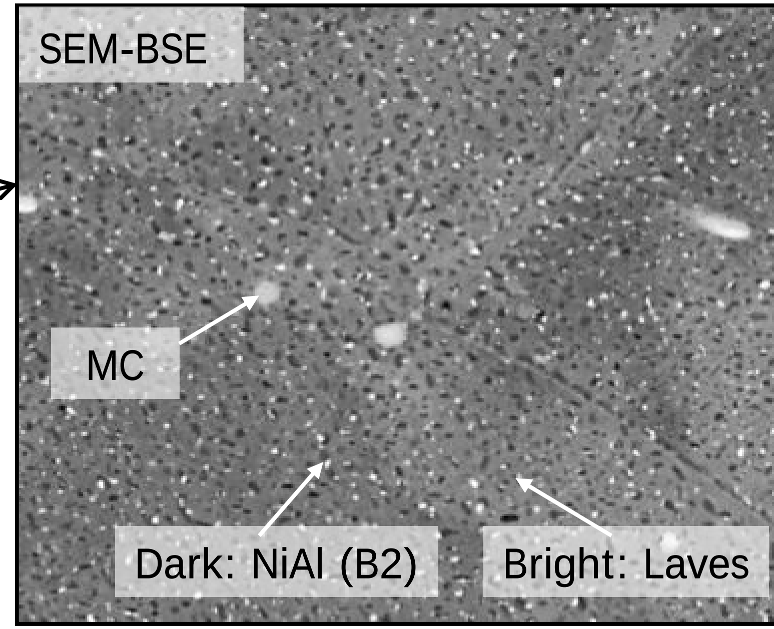
20mm

Intermetallics Appeared in Early Stage of Creep-testing

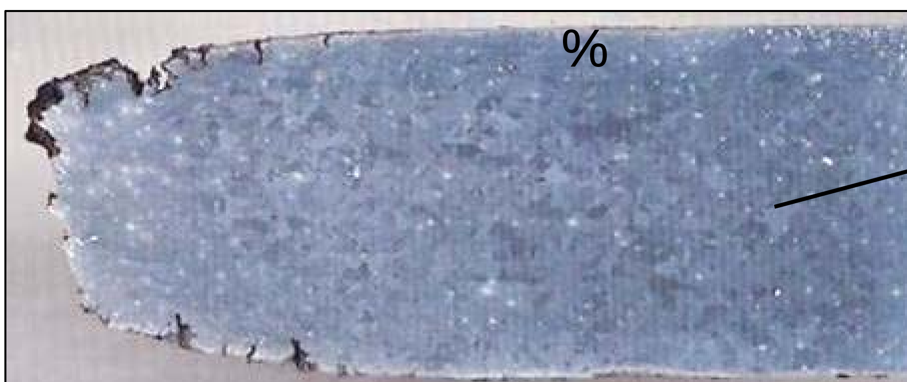
(750^{o}C/170MPa) **150h** /55%



5mm



(750^{o}C/100MPa) **6382h**/7.5 %



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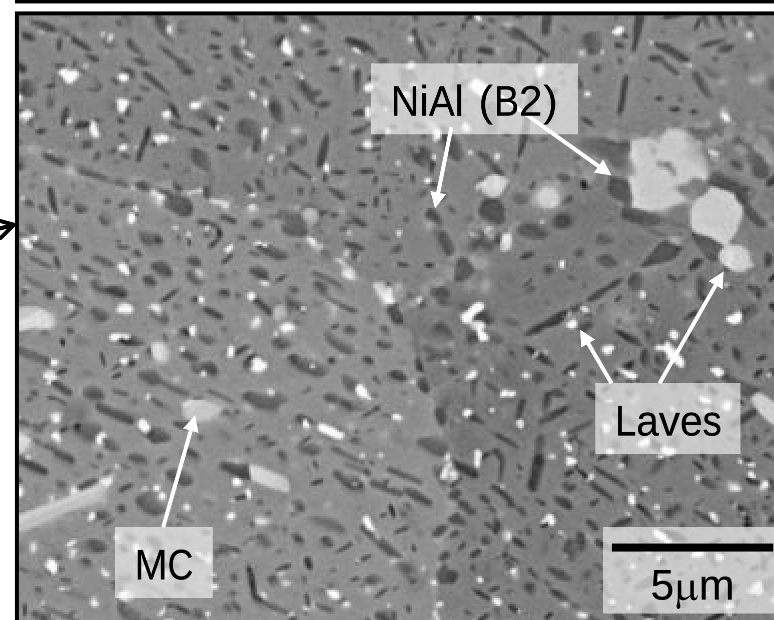
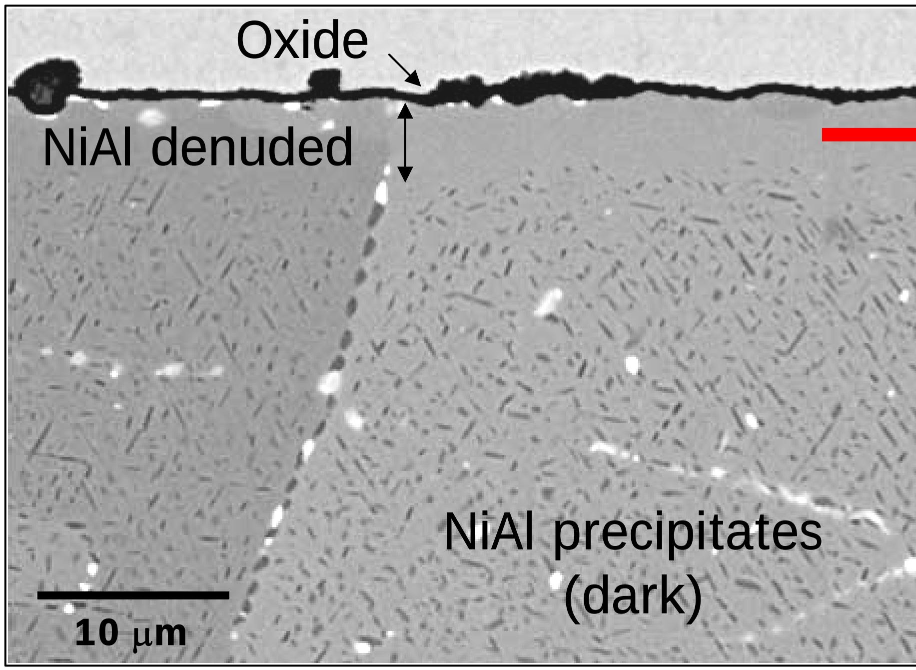
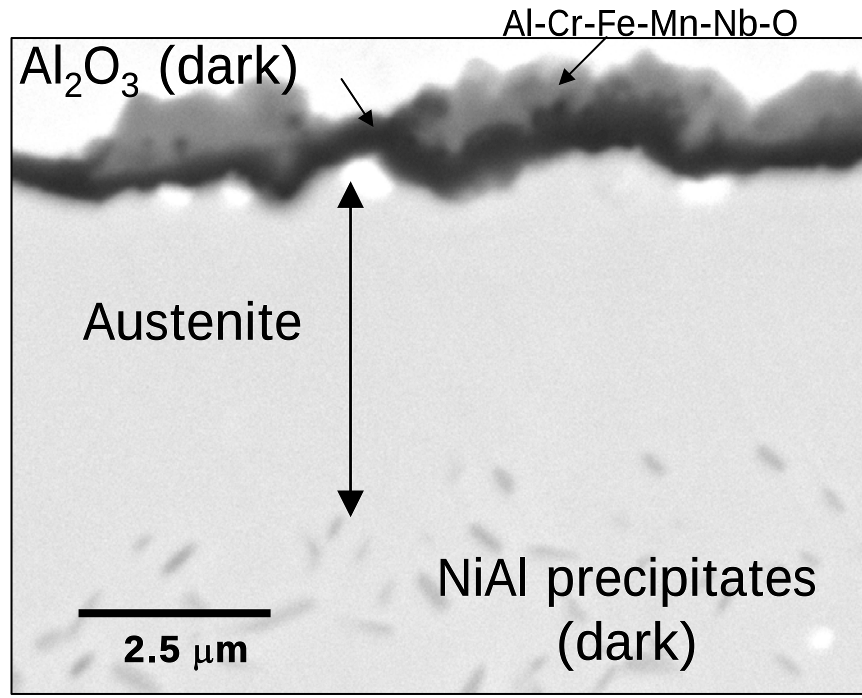


Austenite Matrix and NiAl Precipitates Key to Establishing and Maintaining Alumina

SEM-BSE Images of Typical Oxidized Cross-Section for a 4 Al wt.% AFA Alloy (900ºC/100h/in air)

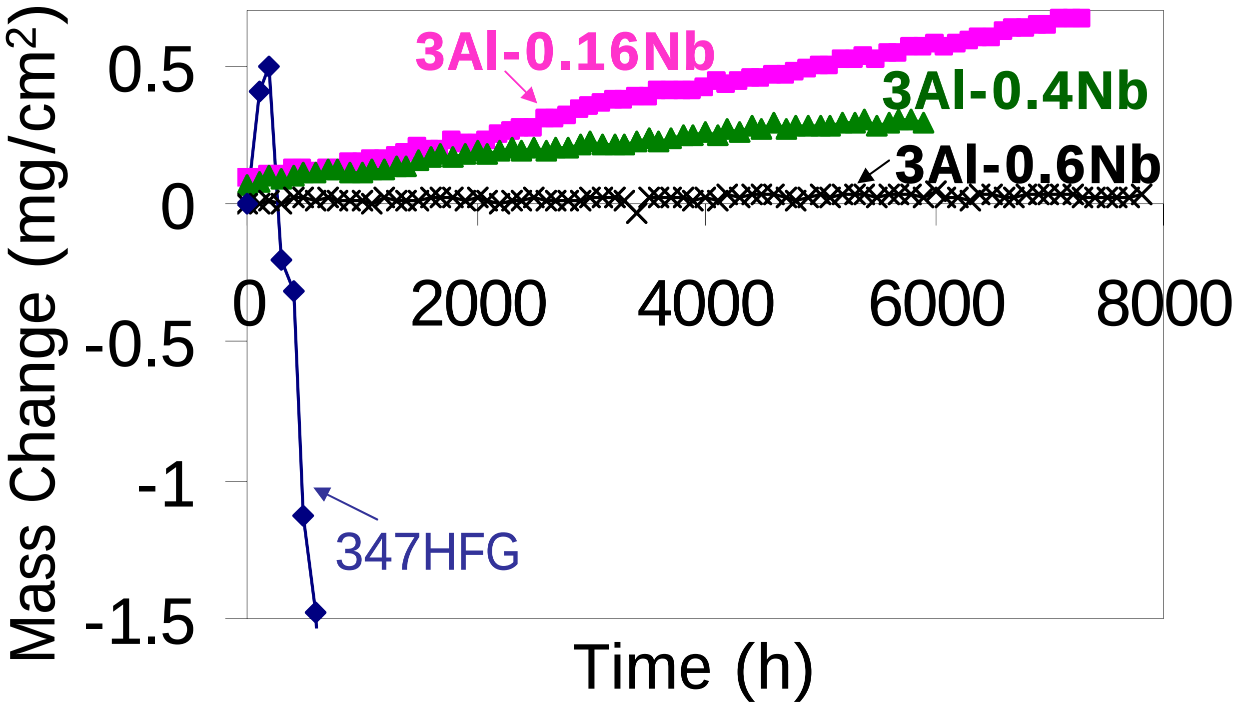




- Austenite matrix composition key to forming alumina
- NiAl precipitates act as Al reservoir to maintain alumina

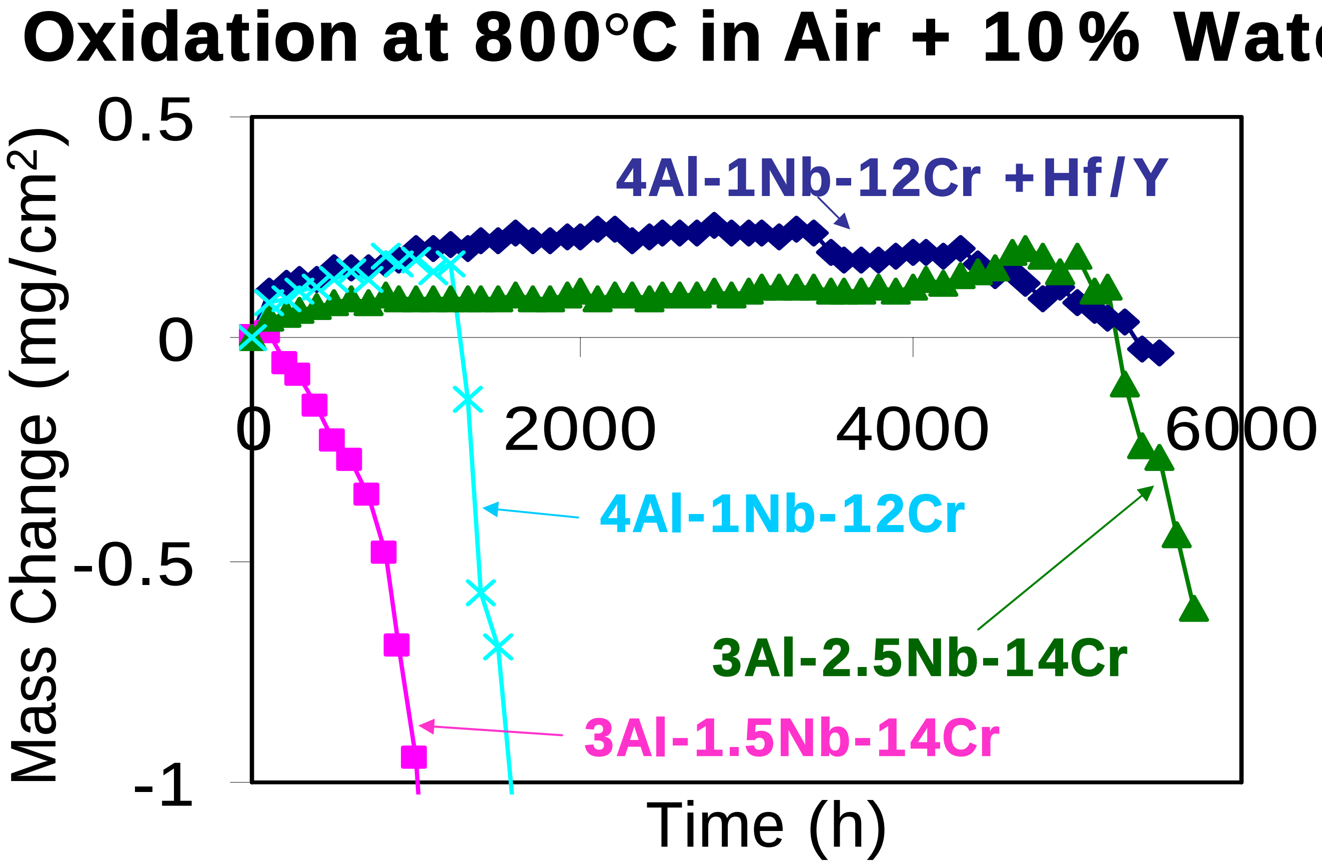
Higher Nb in Alloy Favors Better Oxidation Resistance in Air + Water Vapor

Oxidation at 650°C in Air + 10% Water Vapor



- Excellent resistance out to ~8000 h of ongoing exposure
  - -347 stainless steel shows accelerated attack after a few hundred hours under these conditions

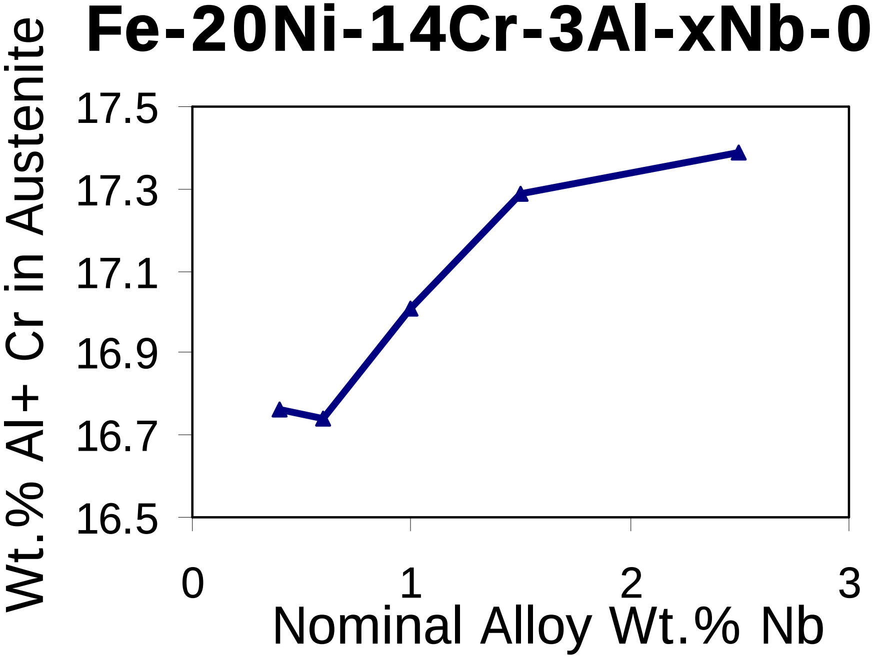
Increased Nb or Hf/Y Additions Aide Al_2O_3 Formation at 800°C in Air + Water Vapor

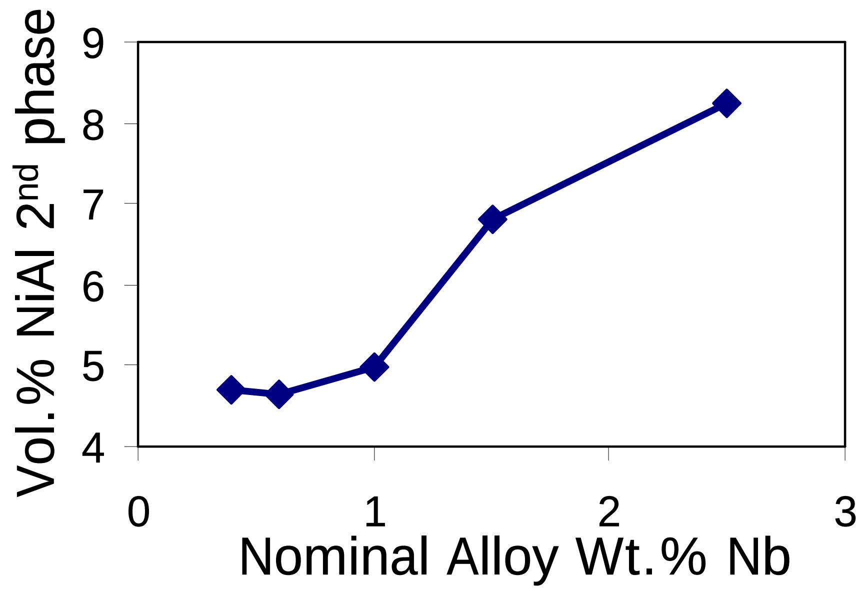


- Best alloys still showed transition to Fe oxide nodule formation and mass loss
  - upper temperature limit 700°C< t< 800°C in H_2O for these alloys

Hypothesized Microstructural Benefits of Nb for Improved Oxidation Resistance

Computational Thermodyamic Predictions for Fe-20Ni-14Cr-3Al-xNb-0.1C wt.% Base (750°C data)

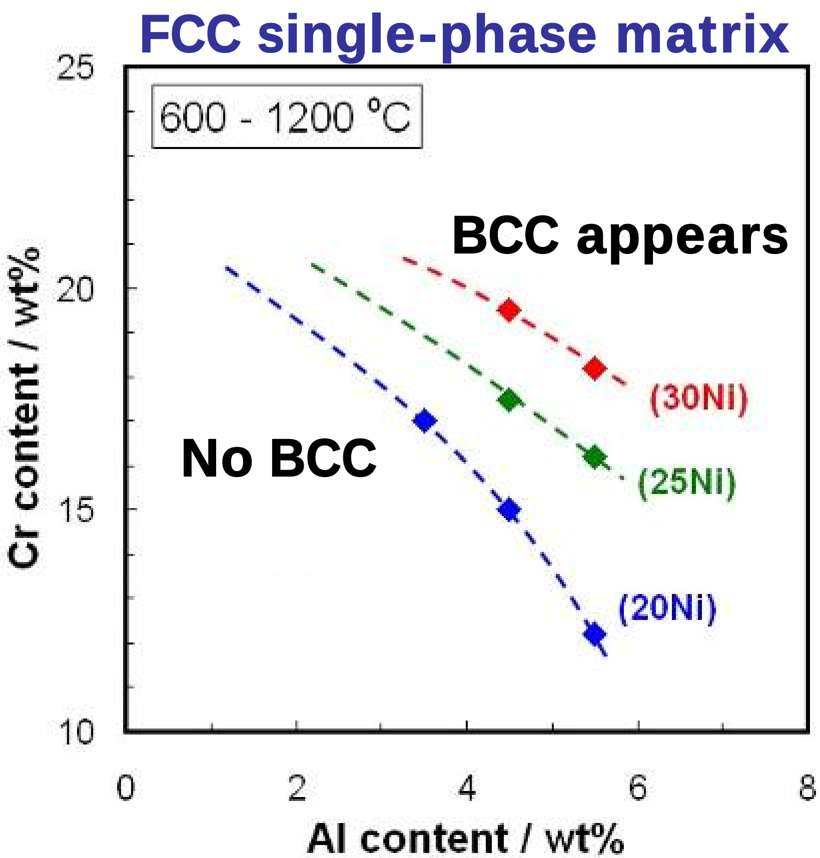


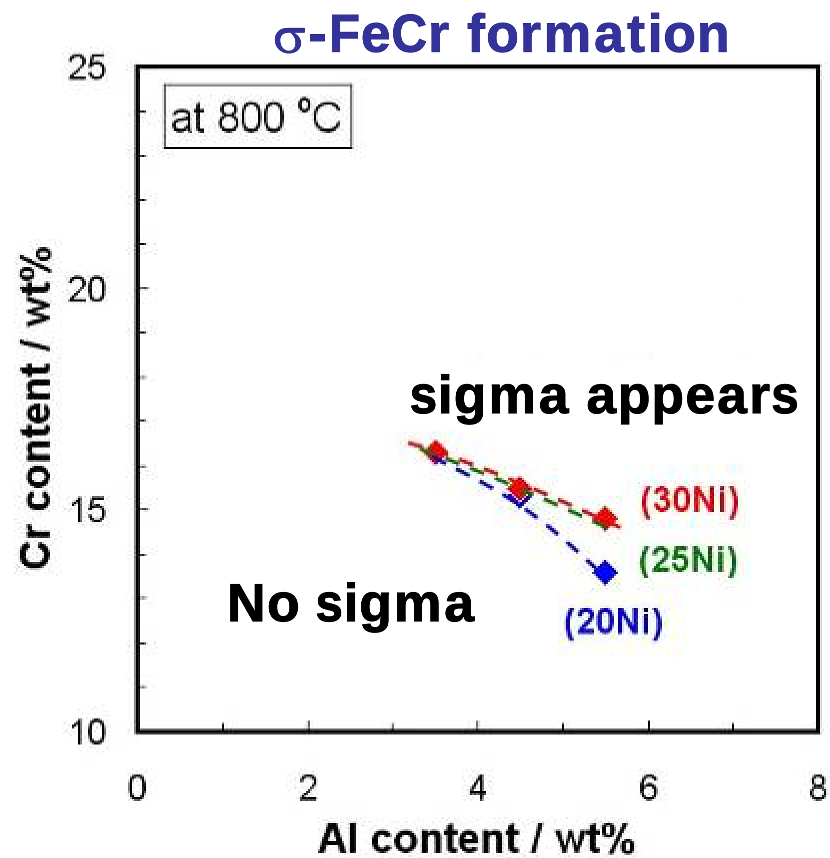


- Nb increases relative Cr + Al levels in austenitic matrix to help form Al_2O_3
    - -Cr aides formation of alumina via third-element effect
- Nb increases B2-NiAl precipitate volume fraction (Al reservoir for Al_2O_3 scale)
- Insights used to design next iteration of AFA for higher service temperature

Thermodynamic Calculations Predict Al-Cr-Ni Balance for Austenite and σ

Fe-Cr-Ni-Al-1Nb-2Mo-0.1C (wt%)

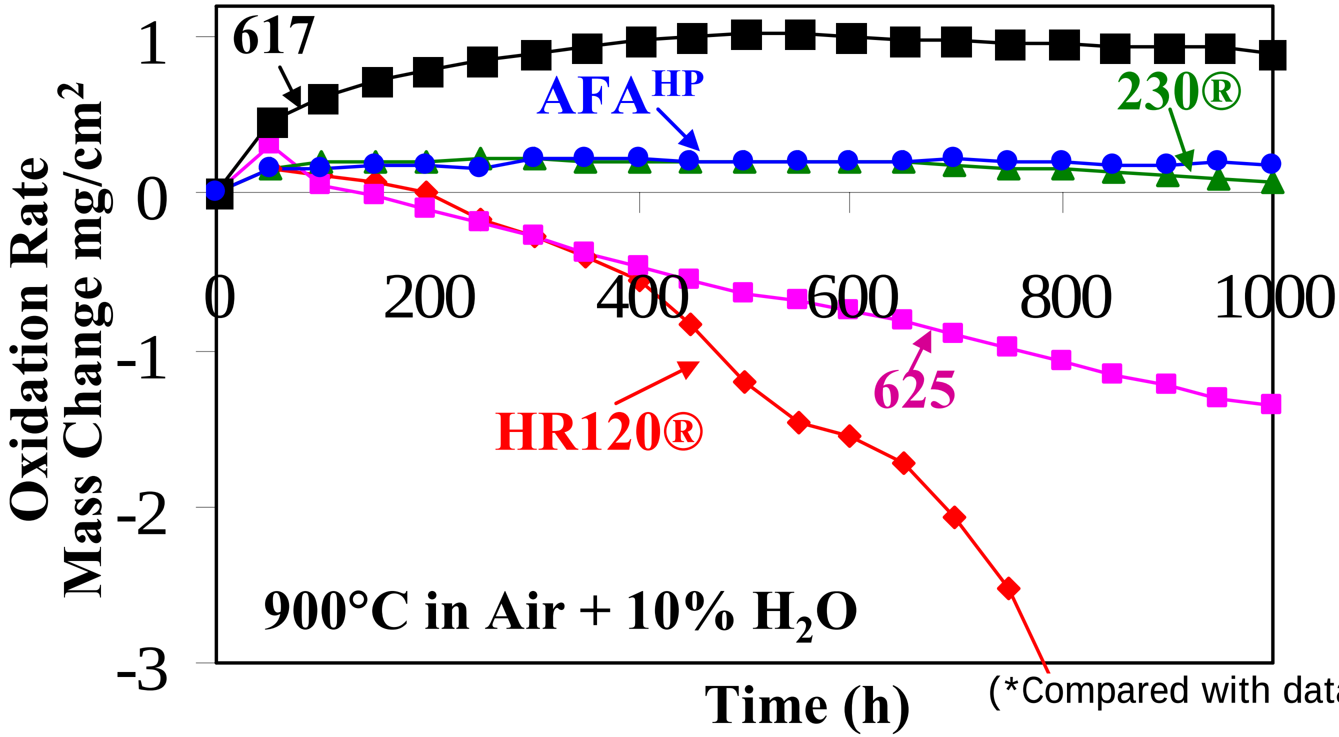




- Higher Cr levels possible at 4 Al and 25 Ni than early 4Al-12Cr alloy series
- Increased sigma risk w/decreasing temperature below 800°C
    - -counter balance with lower Mo, Nb, and W

Recent High Al and Cr AFA^{HP} Alloys Show Promise to 900°C in Air + 10% H_2O

Cyclic Oxidation (10 h cycles) at 900°C in air + 10% H_2O

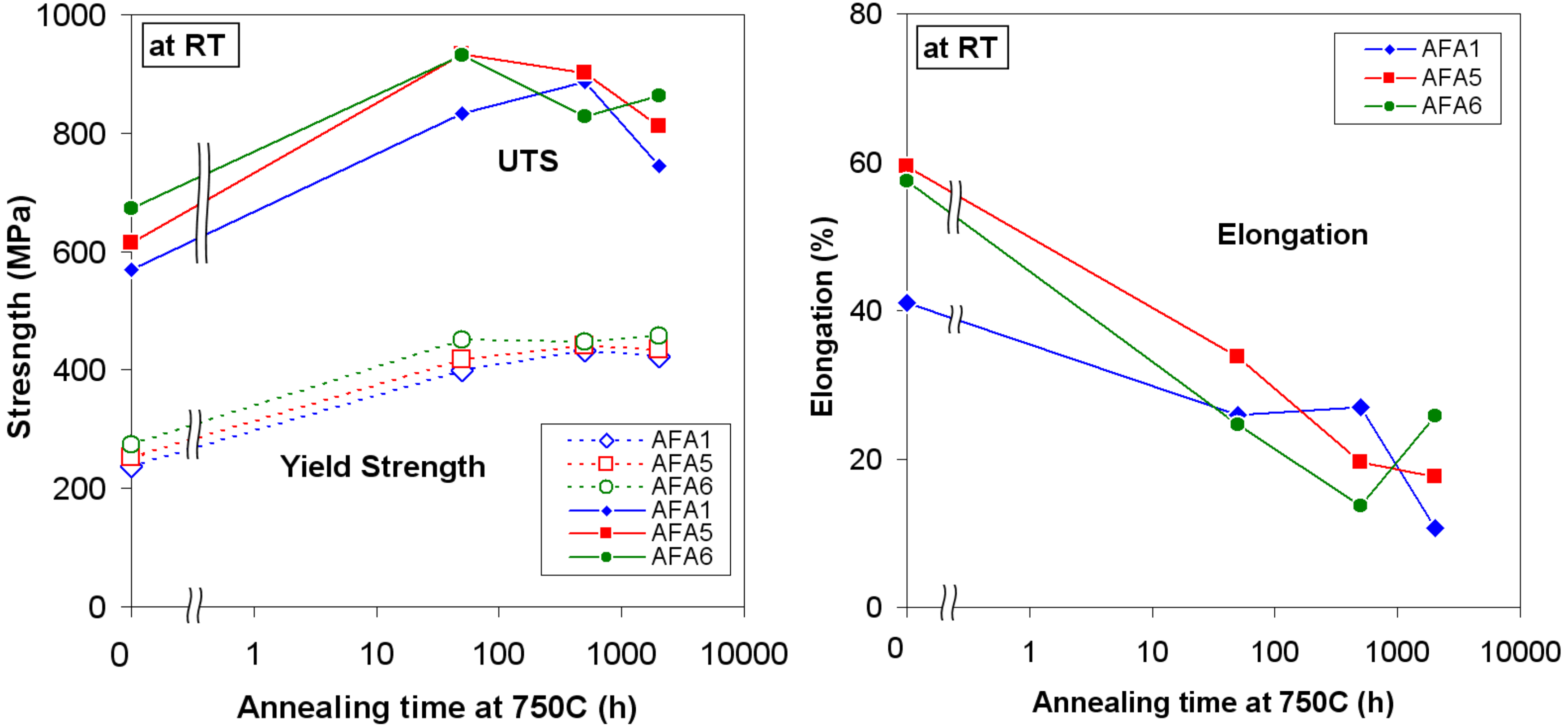


(*Compared with data from B.A. Pint)

- AFA^{HP}: Fe-25Ni-(14-15)Cr-4Al-2.5Nb-Hf/Y wt.% base
  - -Good 900°C behavior also observed at 3-3.5Al wt.% and no Hf/Y addition
- Better resistance than more expensive HR120 (~Fe-35Ni-25Cr) and Ni-base alloys 625 and 617 under this test condition

Room-Temperature Tensile Evaluation as a Function of 750°C Ageing Time

Fe-(20-25)Ni-(3-4)Al-1Nb base wt.% Alloys Evaluated at Room Temperature After Ageing at 750°C

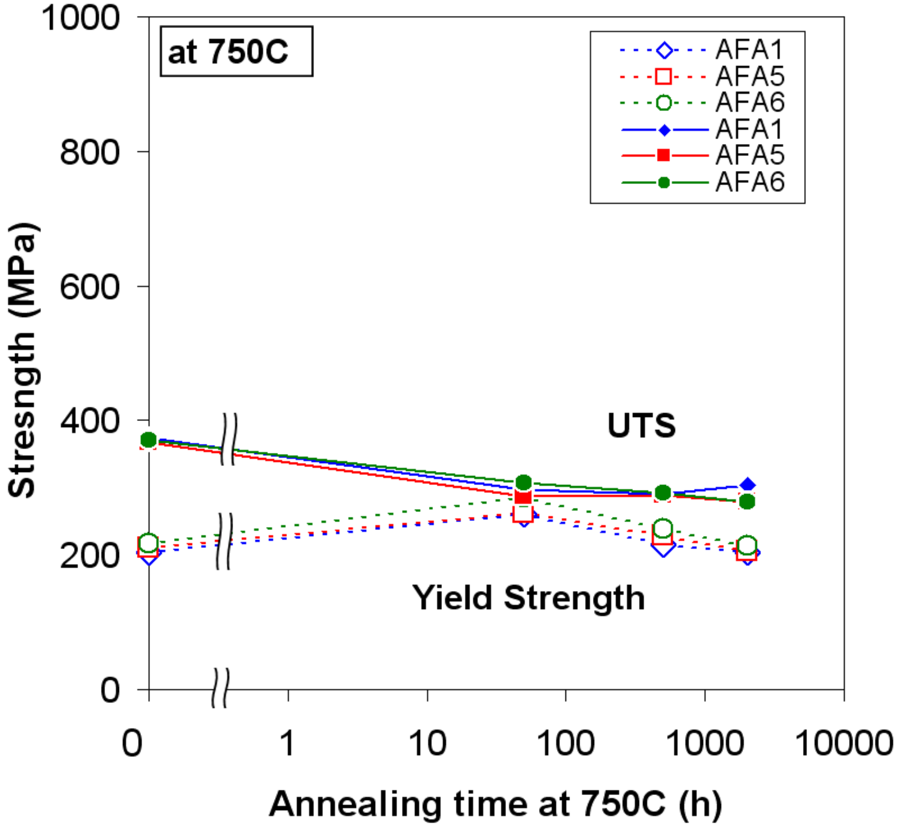


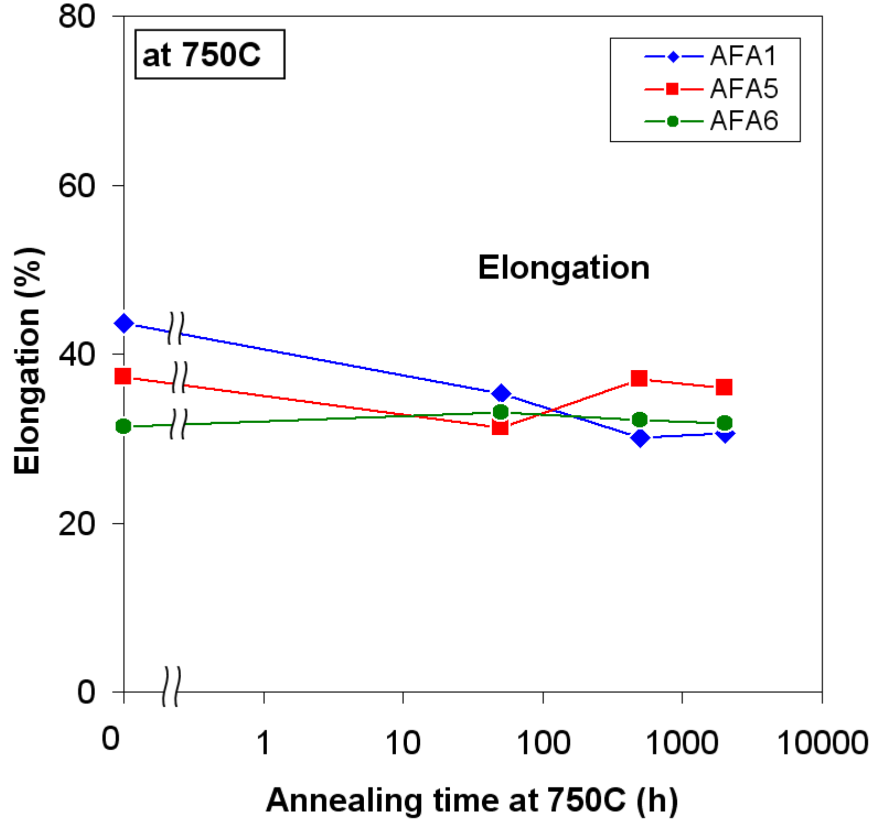
At room temperature:

•Yield strengths reach maximum after ageing ~ 50 hour at 750°C

• Elongation to fracture decreases with ageing: ~10-20% elongation retained

Little Effect of 750°C Ageing on Tensile Behavior at 750°C





- Lower yield/ultimate strength at 750°C than at room temperature
- Elongation unaffected by ageing

Summary

- A new class of Fe(Ni)-base, Al_2O_3-forming, high creep strength austenitic stainless steel alloys is under development

- Excellent oxidation resistance observed in air + H_2O

  -All AFA alloys have upper-temperature limit for Al_2O_3 formation (consequence of low Al + Cr to also achieve mechanical properties)

  - ~650-900°C in air + H_2O depending on alloy composition

- Promising mechanical properties

  -Creep resistance comparable to best available austenitics

  -High tensile elongation in solution treated condition

  -10-20% ambient tensile elongation retained on ageing

  -trial heats show good properties comparable to lab scale castings

Future Work

•Spin-off demonstration project under EERE for AFA foil in turbine recuperator applications (3 CRADAs signed)

•Continued AFA development under Fossil (funding permitting)

-linked experimental and modeling efforts directed toward improved understanding of AFA microstructure, oxidation, and creep to provide basis for further alloy development

-long-term studies of creep and oxidation to provide basis for transition to industry

-expand and evolve AFA concept towards development of alumina-forming, Fe-base superalloys

Acknowledgments

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Three Grades of AFA Alloys Identified Thus Far

- **AFA Grade: Fe-(20-25)Ni-(14-15)Cr-(2.5-3.5)Al-(1-3)Nb wt.% base**
  - ~750-800°C temperature limit for Al_2O_3 formation
  - Trial heats with commercial alloy producer

- **High Performance AFA^{HP} Grade: Fe-(25-30)Ni-(14-15)Cr-(3.5-4.5)Al-(1-3)Nb + Hf/Y wt.% base**
  - ~850-900°C temperature limit for Al_2O_3 formation

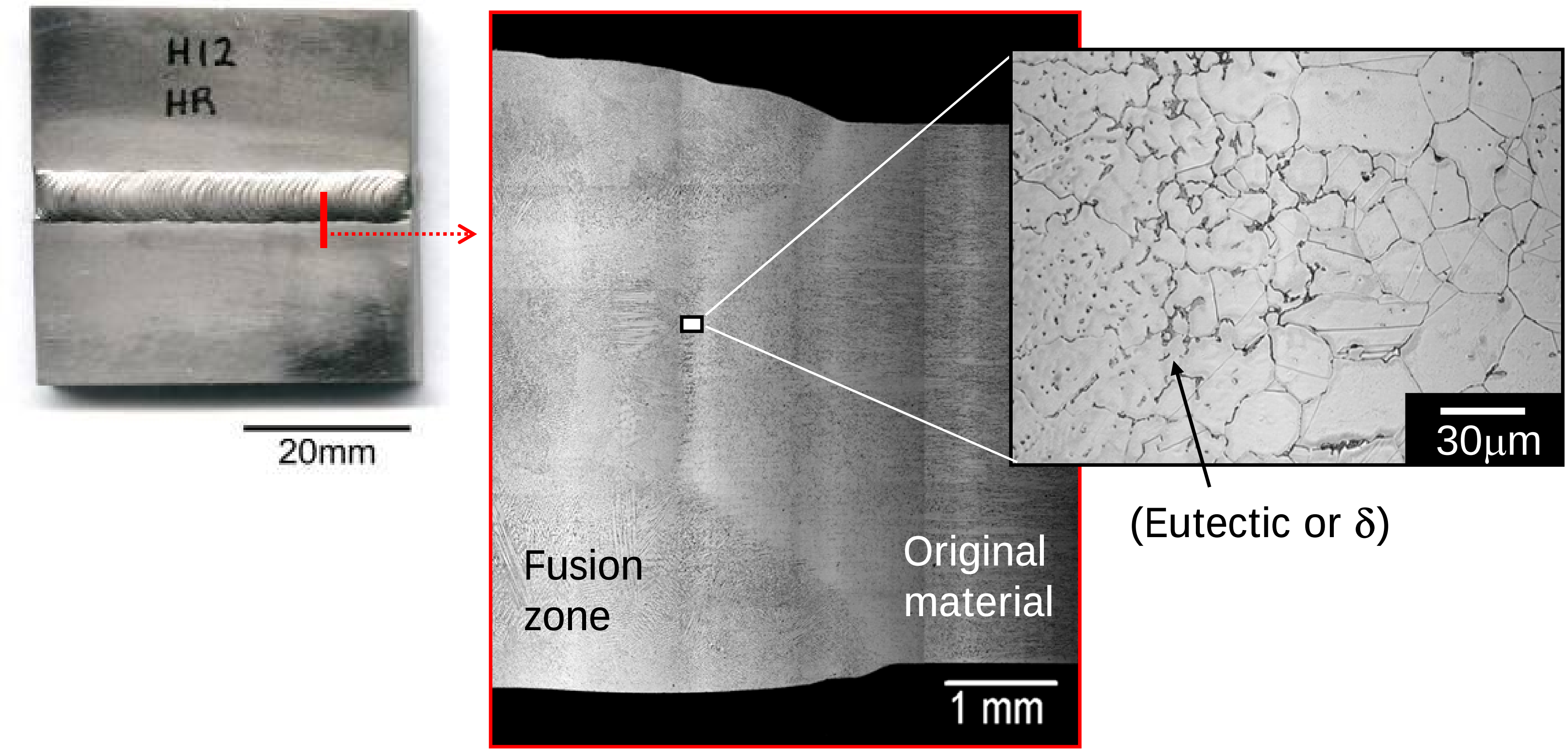
- **Low Nickel AFA^{LN} Grade : Fe-12Ni-14Cr-2.5Al-0.6Nb-5Mn-3Cu wt.% base**
  - ~650°C temperature limit for Al_2O_3 formation

Temperature Limit Based on Oxidation in Air + 10% H_2O (~100°C)
Higher-Temperature Oxidation Limit in “Dry” Air

Trial Heat of AFA Alloy Readily Welded

Gas Tungsten Arc Weld

(used same alloy as a filler material)



- No crack appears at fusion/heat-affected zones

Thermodynamic Calculation Results (750^{o}C)

Alloy	750^{o}C composition in austenite phase					750^{o}C Calculated Phase Vol.%		
	Cr	Al	Ni	Nb	C	MC	Fe_2Nb	NiAl
2-0.2	13.67	2.23	20.28	0.008	0.0618	0.07	1.66	1.49
2-0.9	14.52	2.11	19.64	0.012	0.0179	0.66	2.14	2.7
3-0.4	14.55	2.21	19.24	0.005	0.0384	0.4	2.24	4.71
3-0.6	14.53	2.21	19.21	0.006	0.0337	0.59	2.29	4.65
3-1	14.86	2.15	19.10	0.008	0.0199	0.76	2.53	4.97
3-1.5	15.38	1.91	18.42	0.026	0.0065	0.79	3.09	6.82
3-2.5	15.72	1.67	18.29	0.064	0.003	0.78	4.58	8.25
4-1 ^{LNi}	12.91	2.20	16.60	0.005	0.0188	0.64	2.4	10.68

Nb in the alloys (wt%)

← **0.4**

← **0.6**

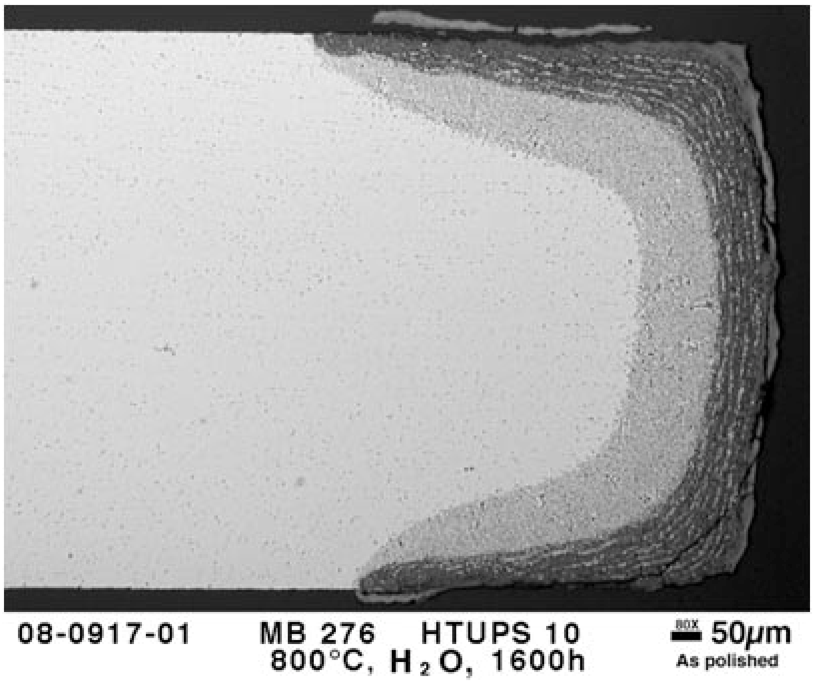
← **1.0**

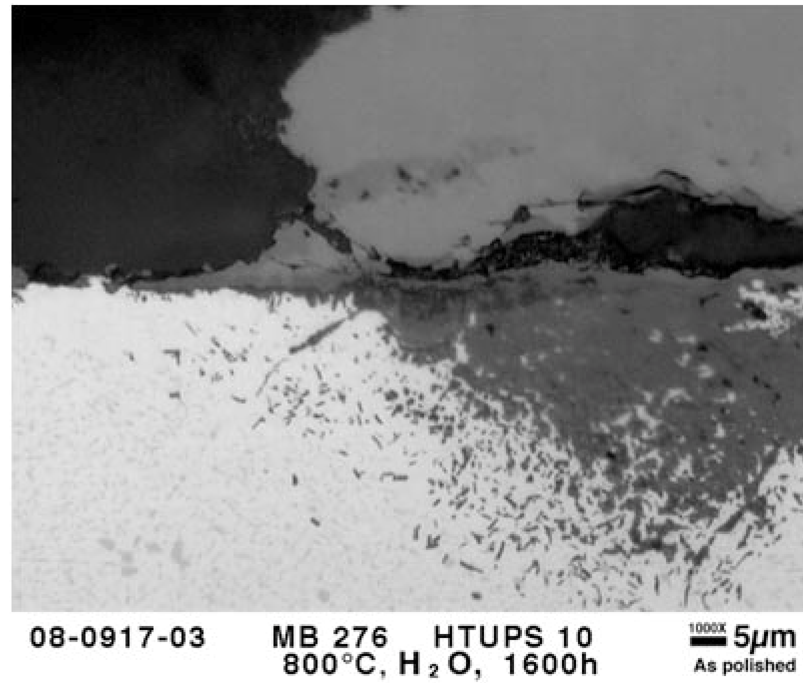
← **1.5**

← **2.5**

Fe-Rich Oxide Nodules + Extensive Internal Attack of Al When AFA Alloys Go “Bad” in Air + H_2O

Optical Cross-Section of Fe-20Ni-14Cr-3Al-1.5Nb wt.% base after 1600 h at 800°C in Air + 10% Water Vapor

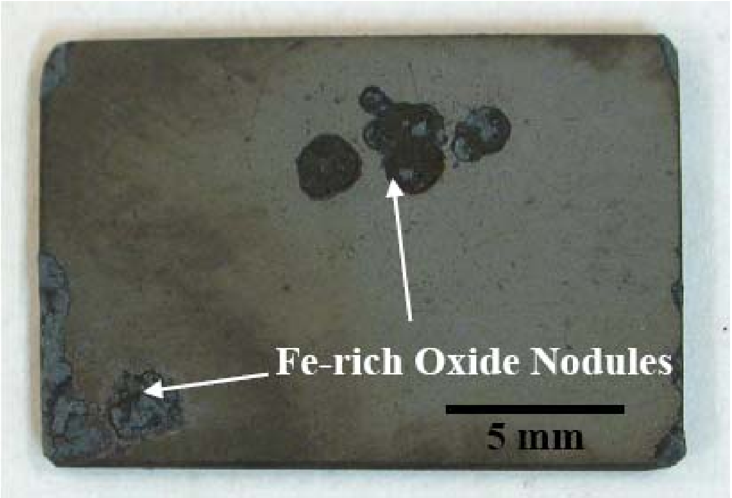




- Raising temperature/adding water vapor favors transition to internal attack (transition temperature varies with composition)
- AFA alloys near borderline for Al_2O_3 formation to co-optimize mechanical properties

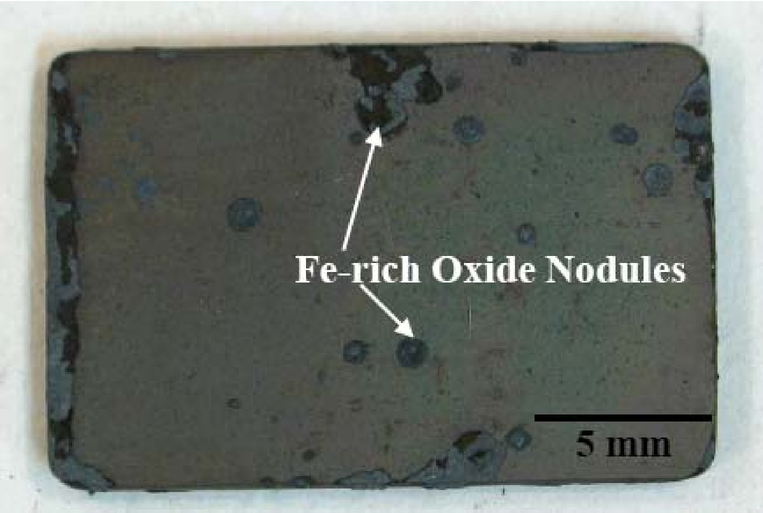
After Cyclic Oxidation at 800ºC in Air + H_2O

3Al-1.5Nb-14Cr



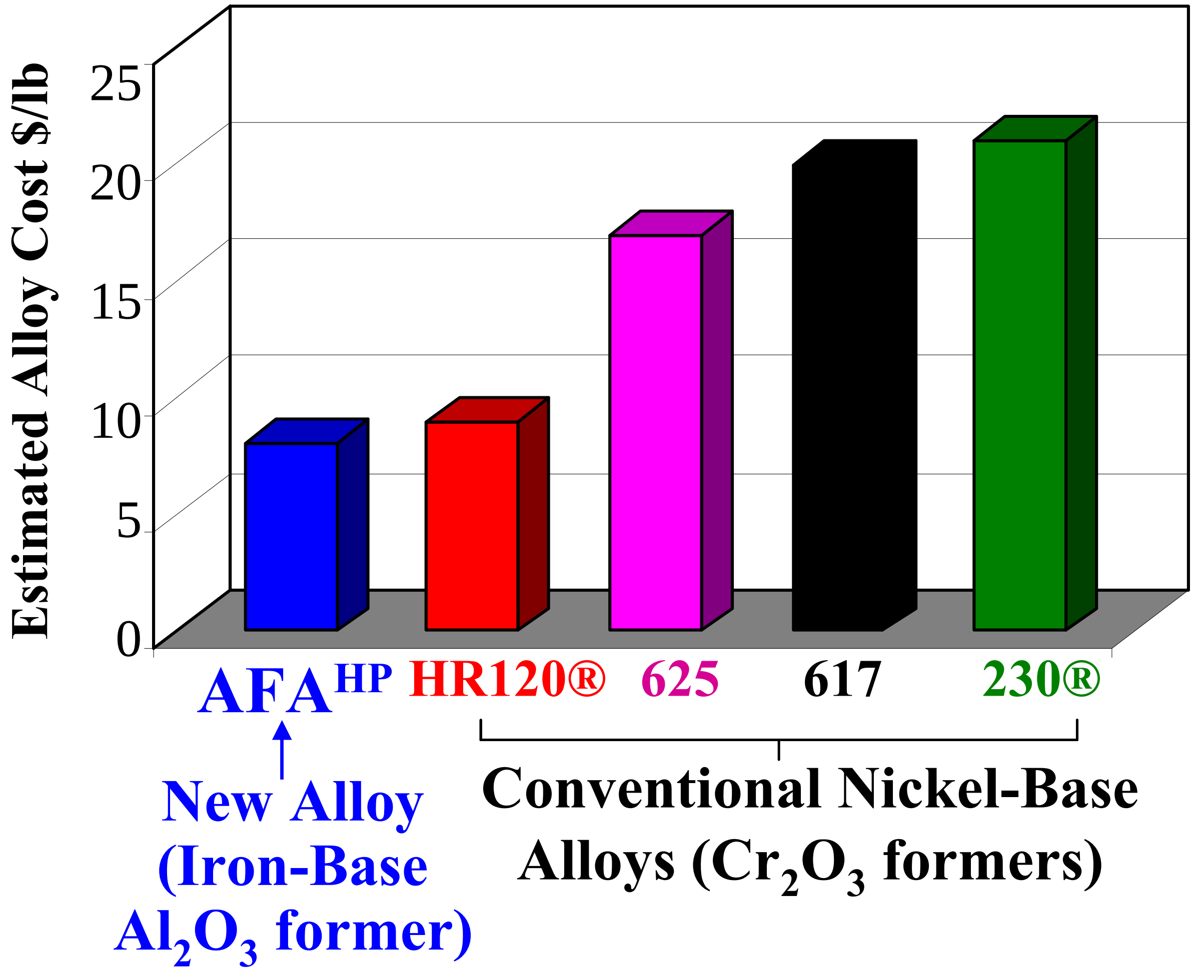
(1600h)

3Al-2.5Nb-14Cr



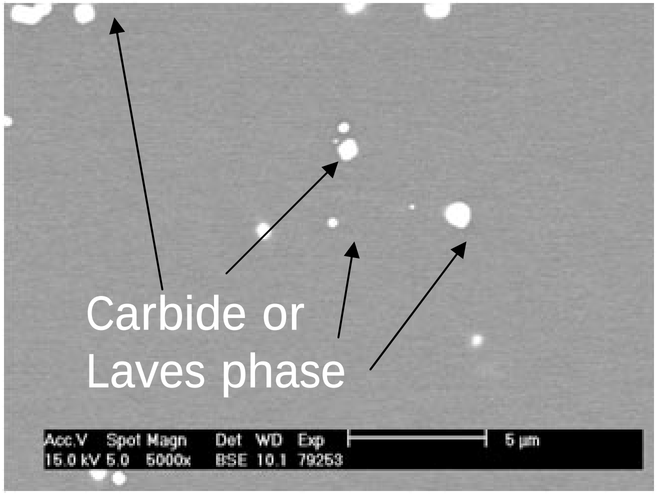
(5700h)

AFA^{HP} Significantly Lower Raw Material Cost to High-Ni Austenitics / Ni-Base Alloys

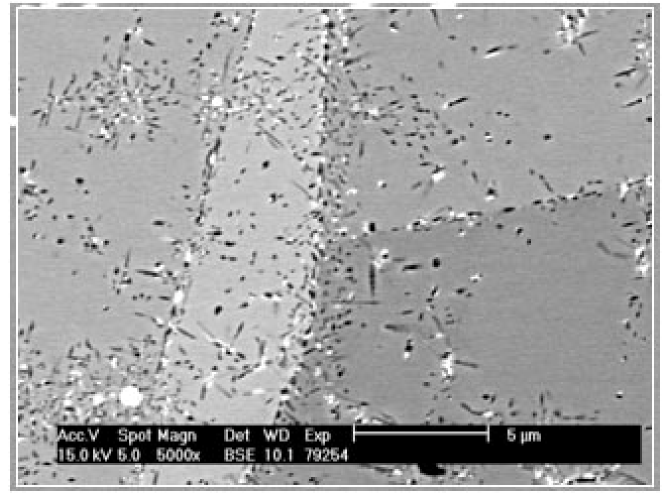


- AFA^{HP} grade estimated comparable raw material cost to state-of-art austenitics such as alloy 709 (Fe-25Ni-20Cr base)

B2 NiAl Precipitation on Ageing AFA 5 (Fe-20Ni-12Cr-4Al-1Nb wt.% base)

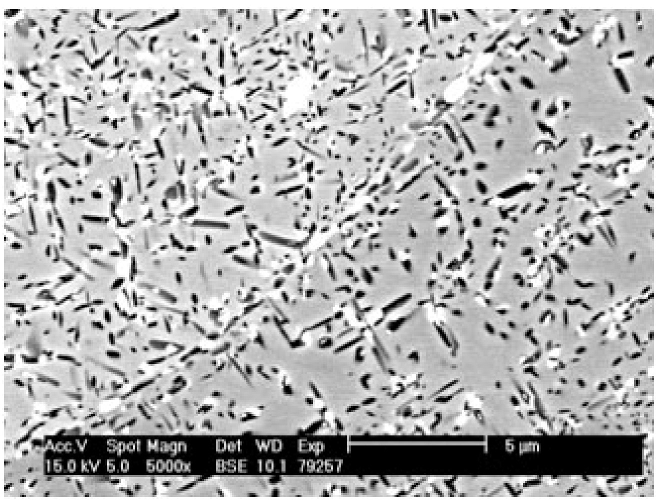


Before ageing

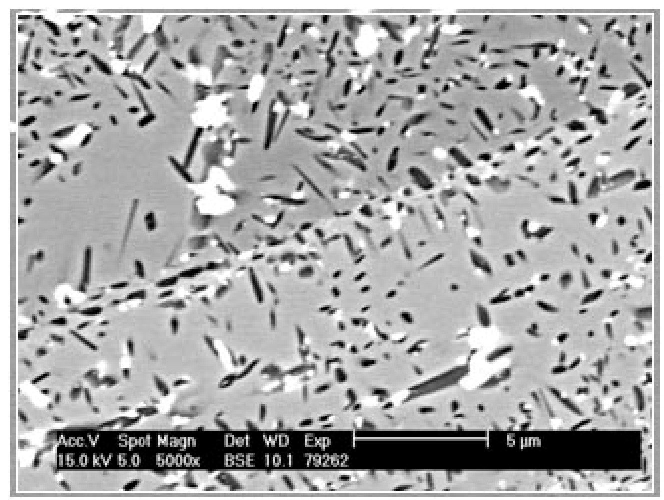


Ageing 50h

Black needle-like NiAl precipitates



ageing 500h

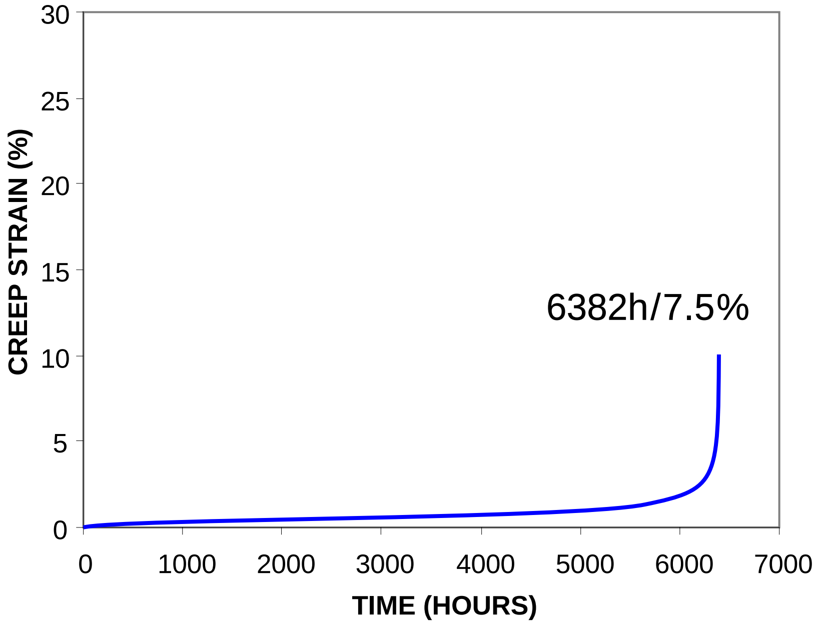


Ageing 2012 h

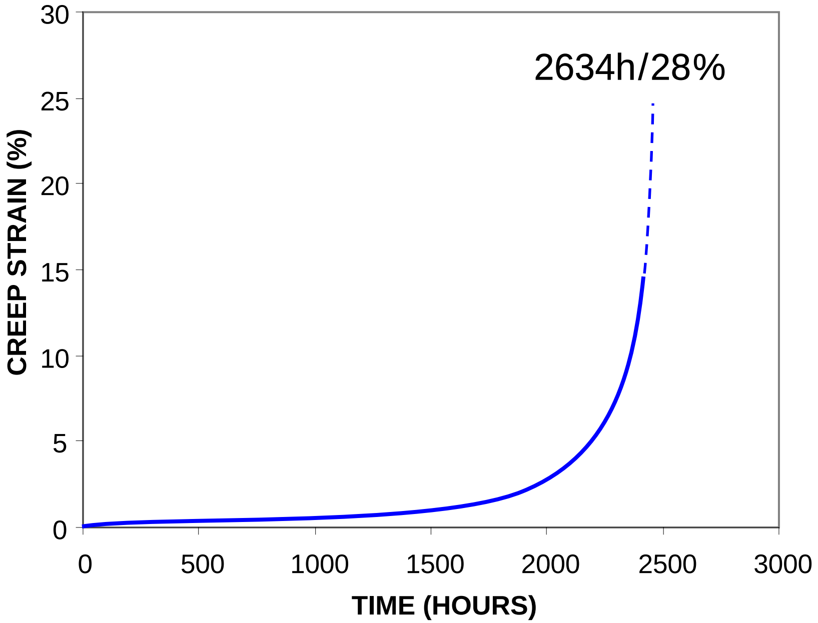
- NiAl precipitation after 50 h at 750°C
- Coarsening of NiAl reached mostly completed after ~500 h at 750°C

Creep Curves Also Showed Necking Instability

(750ºC/100MPa)



(800ºC/70MPa)



- Acceleration creep started after only ~3% creep-deformation.
- Necking instability causes accelerating stress concentration.