Development of Alumina-Forming Austenitic Stainless Steels

=Multi-Phase High-Temperature Alloys=

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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

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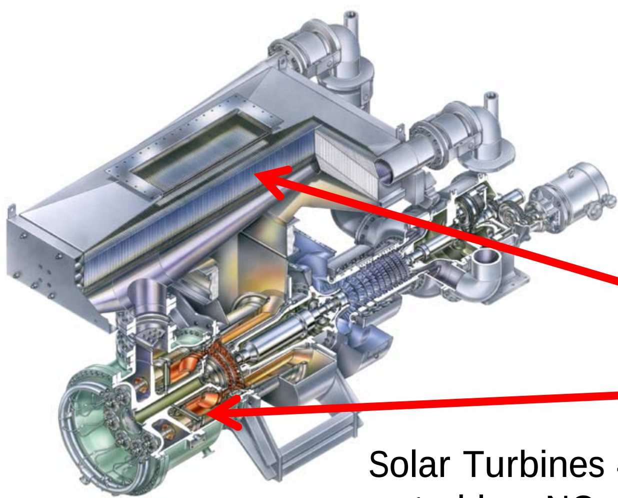
Development Effort for Low Cost, Creep and Oxidation-Resistant Structural Alloy for Use from ~600-900°C

- **Approach: Al_2O_3-forming austenitic stainless steels**
  -background and potential advantages
- Overview of alloy design strategy and initial results
- Current status and future research directions

Initial target(s)



Recuperator, Casing

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

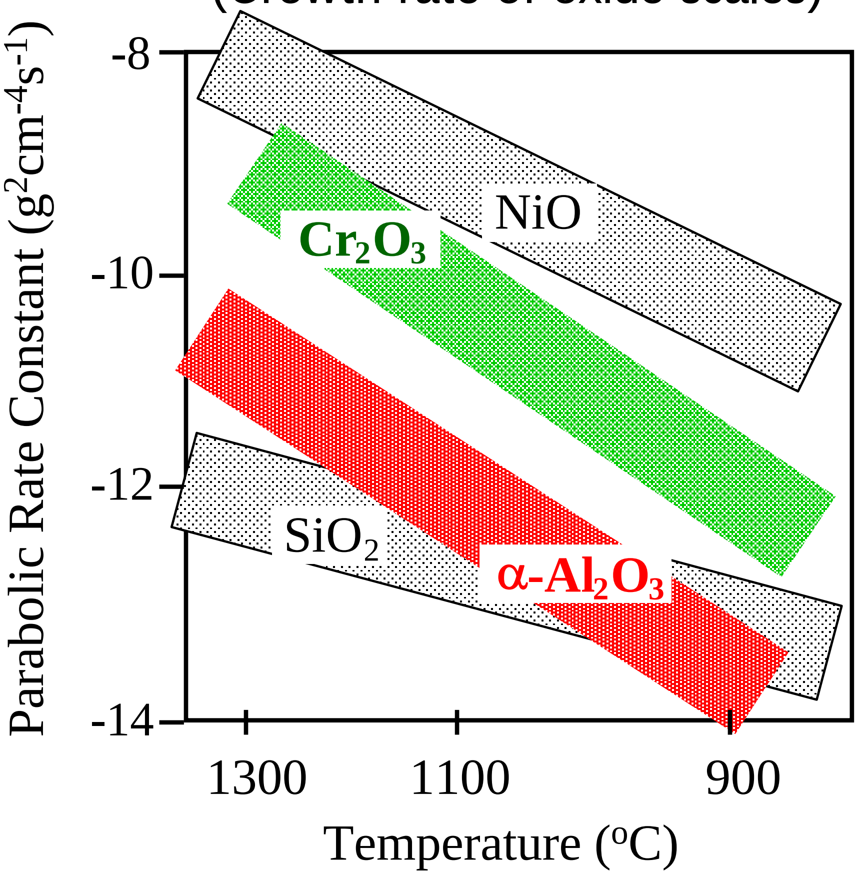
Fossil Power Steam Turbine, Boiler Tubing

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

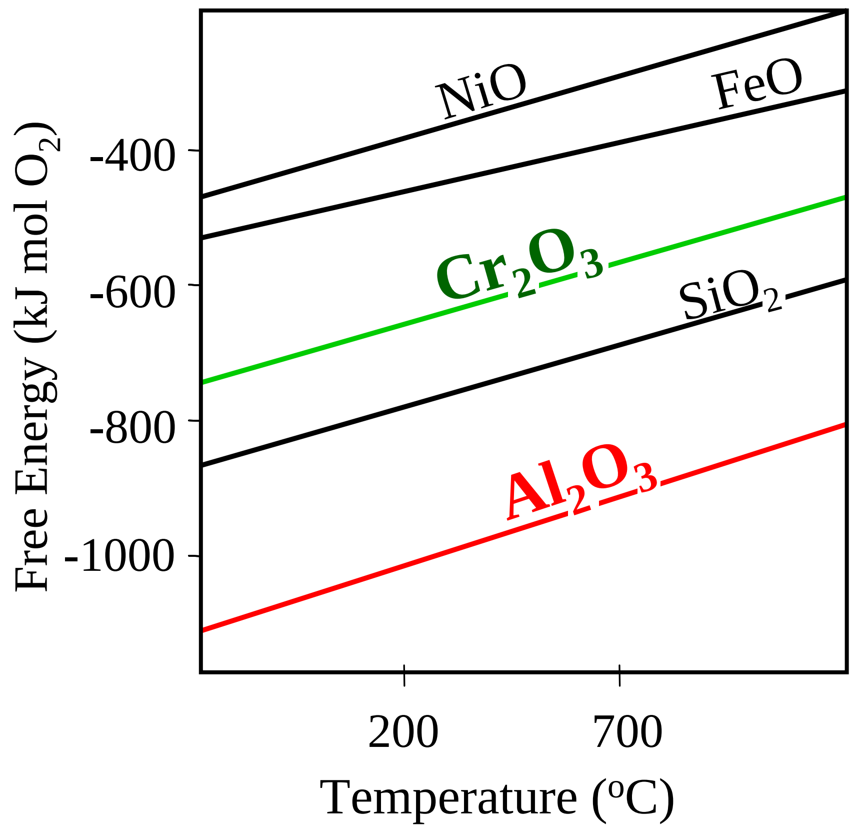
➢ Tubing in chemical/process industry, etc. also targeted.

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.

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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)

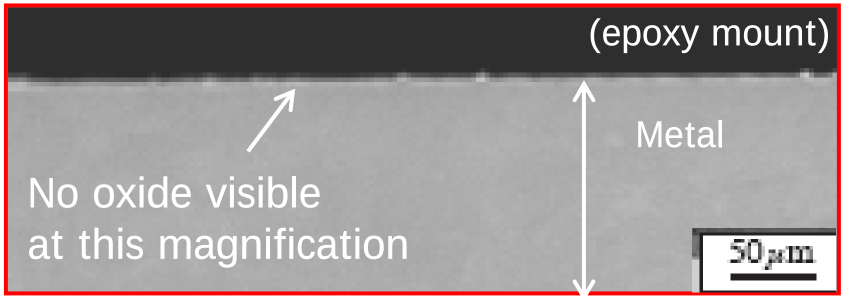
- Problem: Al additions are a major complication for strengthening
  - ➢ strong BCC stabilizer/delta-ferrite formation (weak)
  - ➢ interferes with N additions for strengthening

- 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

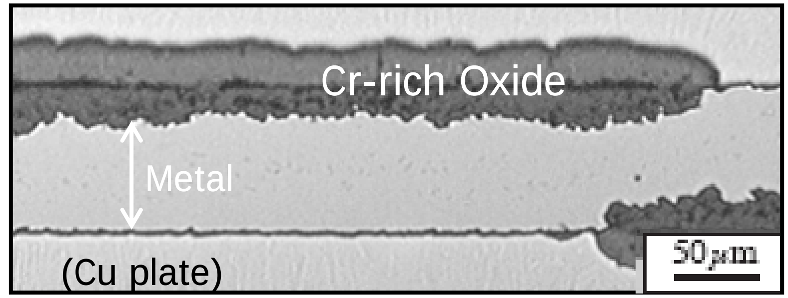
AFA Stainless Steel Alloys Successfully Developed

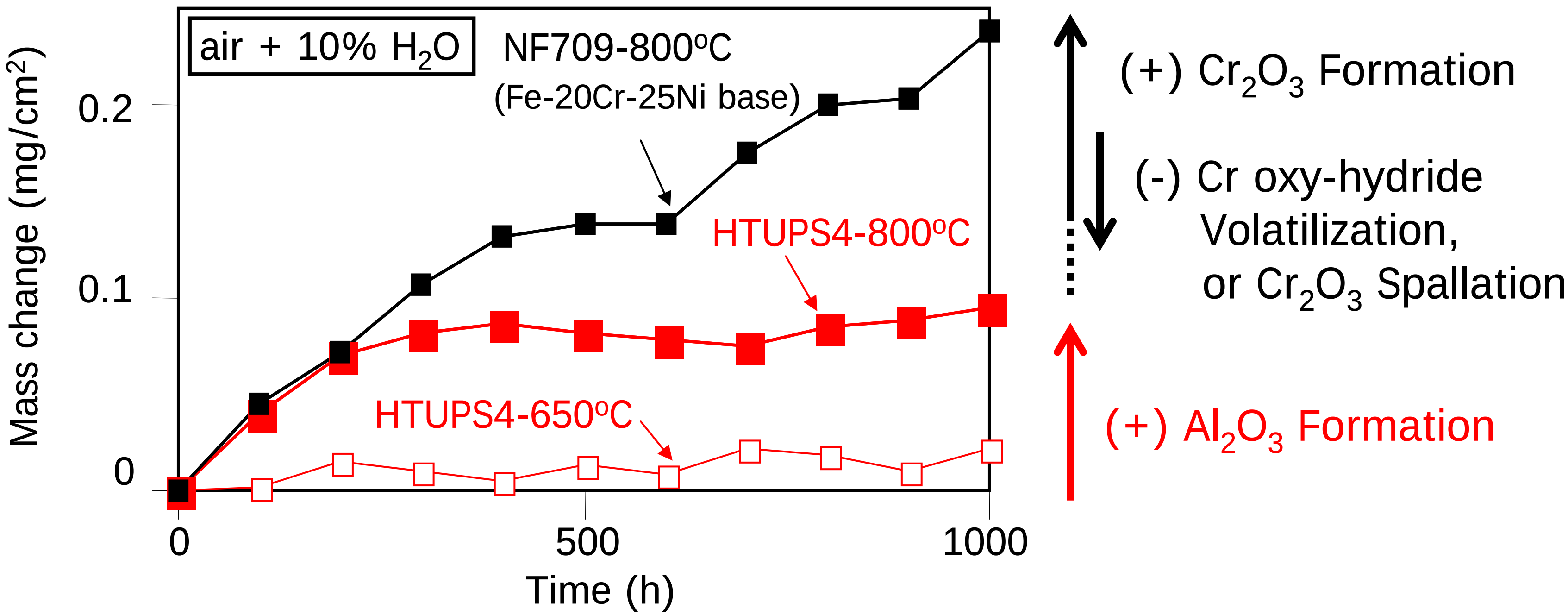
= 1000h, 800ºC in water vapor =

HTUPS4 (Fe-14Cr-20Ni-2.5Al-0.9Nb base)



347 foil (Fe-18Cr-12Ni base)





*Y. Yamamoto et al., *Science*, **316** (5823) (2007) pp.433-436.

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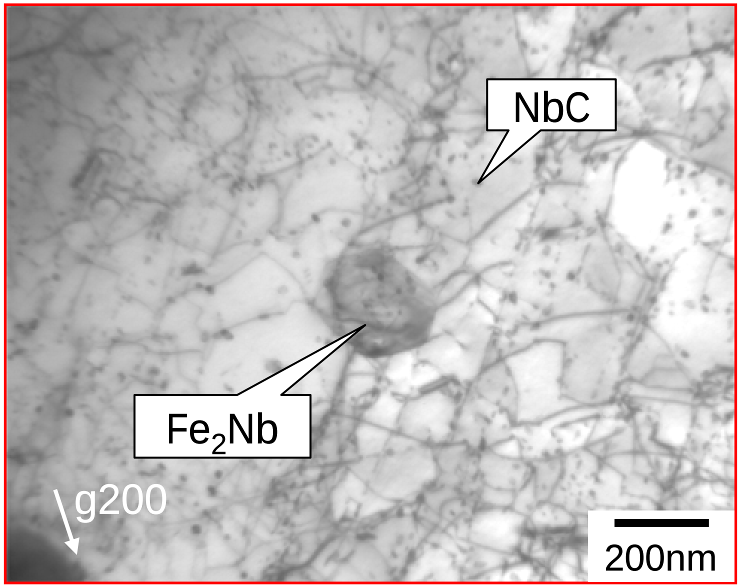
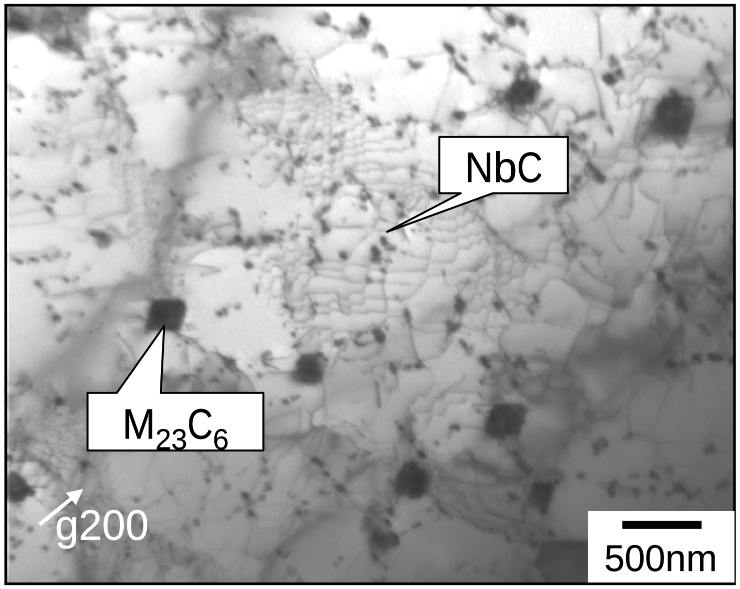
NbC Nano-Particles Pin Dislocations Effectively

TEM-BFI (after creep-rupture at 750^{o}C/100MPa)

HTUPS4 (Fe-14Cr-20Ni-2.5Al-0.9Nb base)

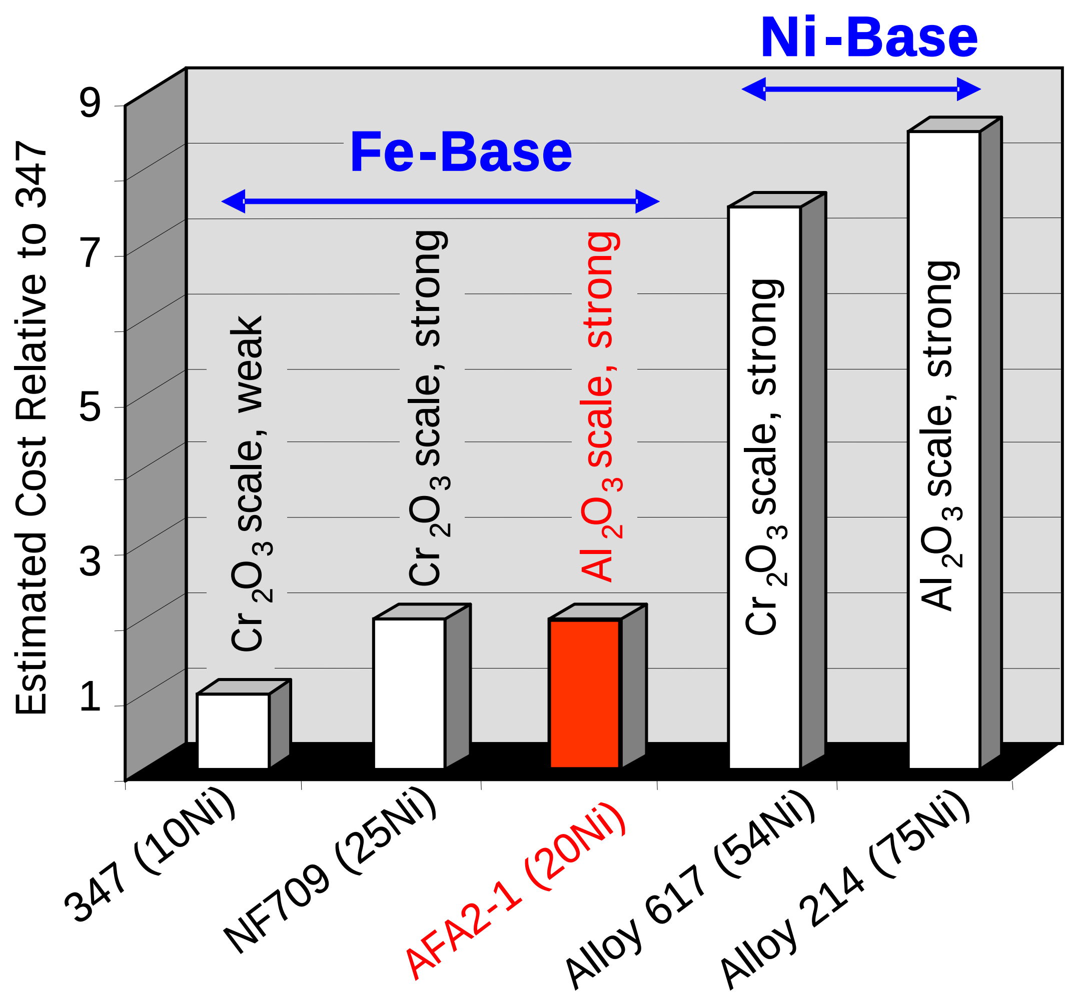


NF709 (Fe-20Cr-25Ni base)



- Dense dispersions of NbC become source of excellent creep resistance.

Estimated Comparable Raw Material Cost To Existing Advanced Austenitic Stainless Steels



- Significantly less expensive than Ni-base alloys with similar properties.

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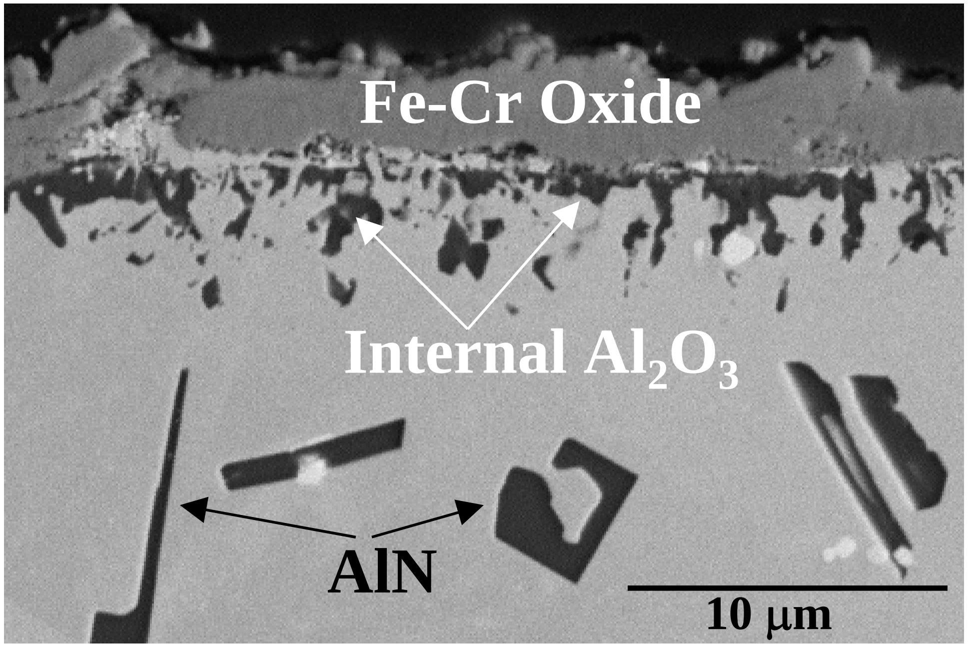
HTUPS 4 Loses the Ability to Form External, Protective Al_2O_3 at 900°C

SEM Cross-Section of HTUPS 4 (0.9Nb/2.5 Al wt.%) after 500 h at 900°C in air

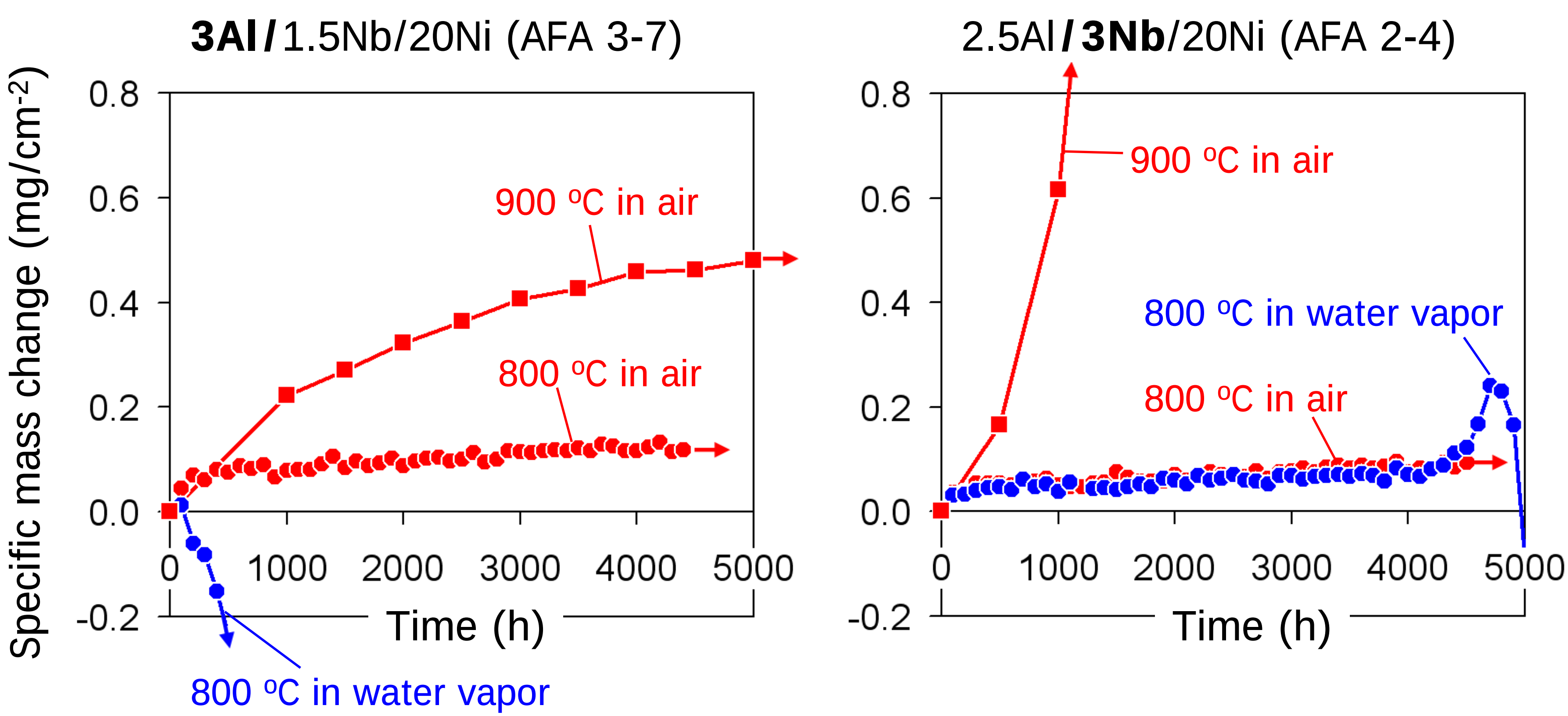


- Transition to internal oxidation/nitridation of Al between 800-900°C
- Reasons under investigation
  - suspect oxygen solubility trends with temperature is key

Alloys Studied (FY06~FY08)

Alloy Designation	Nominal Composition (wt%, Fe: balance)													
	Ni	Cr	Al	Nb	Ti	V	Mo	W	Cu	Mn	Si	C	B	P
Base alloy without Al addition														
HTUPS-1	20	14.3		0.15	0.3	0.5	2.5			2	0.15	0.08	0.01	0.04
2.5 wt% Al series														
AFA 2-1 (HTUPS4)	20	14.3	2.5	0.9			2.5			2	0.15	0.08	0.01	0.04
AFA 2-2	20	14.3	2.5	0.16	0.1	0.1	2.5			2	0.15	0.08	0.01	0.04
AFA 2-3	20	14.3	2.5	0.16			2.5			2	0.15	0.08	0.01	0.04
AFA 2-4	21	14	2.5	3		0.2	3.4					0.02	0.02	
AFA 2-5	21	14	2.5	3.3			3.4					0.08	0.08	
AFA 2-6	32	19	2.4	3.4										
3 wt% Al series														
AFA 3-1	20	14.3	3	0.4	0.1		2	1	0.5	2	0.15	0.08	0.01	0.04
AFA 3-2	20	14.3	3	0.6	0.1		2	1	0.5	2	0.15	0.1	0.01	0.04
AFA 3-3	26	14	3	0.6			1.25			0.2	0.2	0.04	0.01	0.02
AFA 3-4	20	14.3	3	1			2	1	0.5	2	0.15	0.1	0.01	0.02
AFA 3-5	20	14.3	3	1		0.2	2	1	0.5	2	0.15	0.1	0.01	0.02
AFA 3-7	20	14.3	3	1.5	0.1		2	1	0.5	2	0.15	0.1	0.01	0.04
AFA 3-8	20	14.3	3	2.5	0.1		2	1	0.5	2	0.15	0.1	0.01	0.04
4 wt% Al series														
AFA 4-1	20	12	4	0.6	0.1		2	1	0.5	2	0.15	0.1	0.01	0.04
AFA 4-2	20	12	4	1			2	1	0.5	2	0.15	0.1	0.01	0.02

Alumina-scale Formation in Aggressive Conditions (900°C in air / 800 °C in air + water vapor)



- High Al addition helps alumina-scale formation even at 900°C in air.
- High Nb addition improves oxidation resistance in water vapor containing environment.

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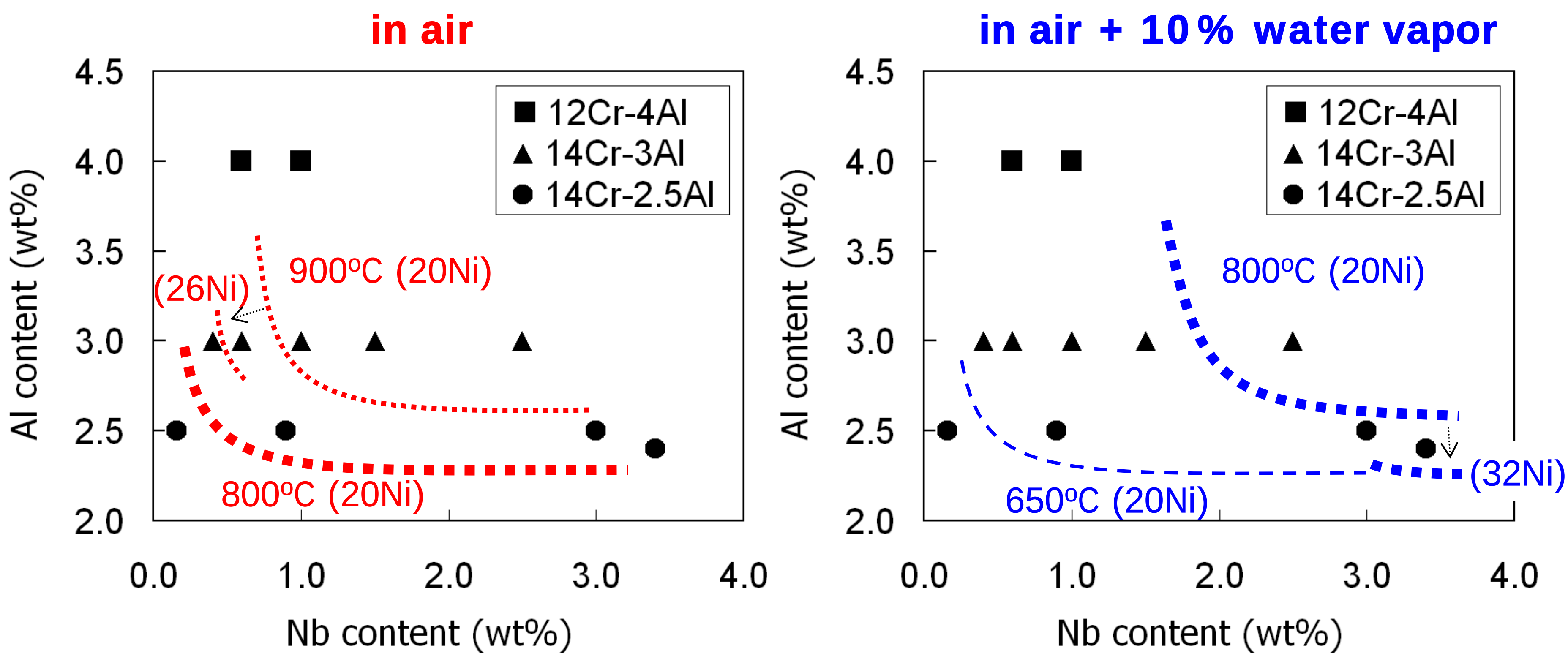
Higher Al, Nb, and Ni Levels Help Alumina-scale Formation

=Boundary for alumina-scale formation (~2000-5000 h exposure)=



- Ni additions also reduce the required amounts of Al/Nb additions to show protective alumina-scale formation.
- Preparation of the higher Al/Nb/Ni containing alloys is currently under progress.

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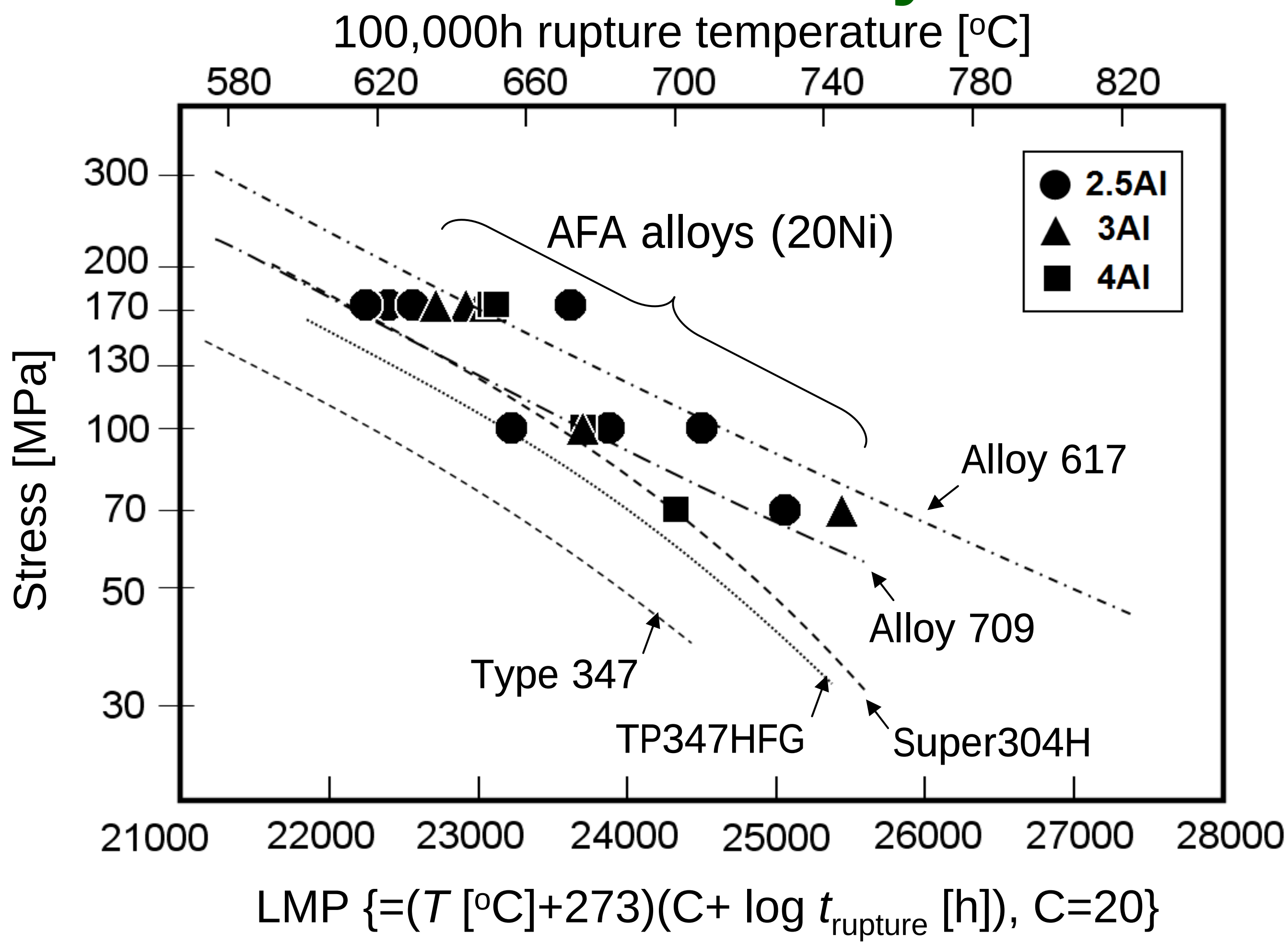
Comparable Creep Strength to Commercial Heat-Resistant Alloys



- AFA alloys (20Ni) are in the range between alloy 709 (Fe-20Cr-25Ni base) and alloy 617 (Ni-22Cr-12Co-9Mo base).

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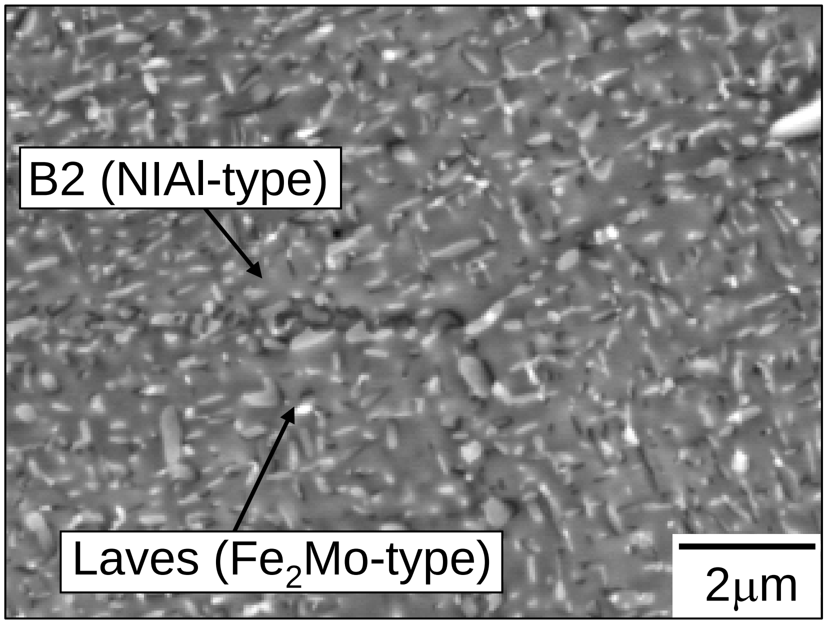
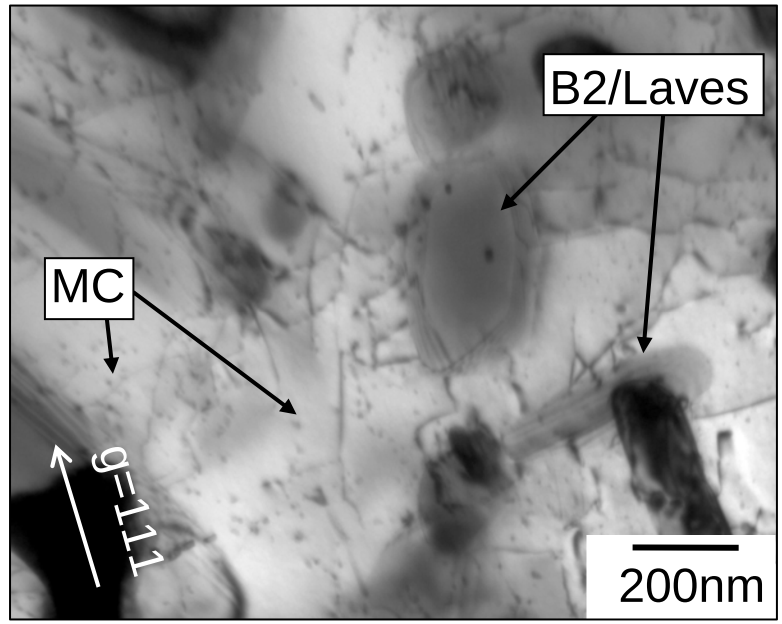
Multi Second-phase (Intermetallics/Carbides) Strengthening

3Al/0.6Nb/20Ni (AFA 3-3),
after creep-ruptured at 750^{o}C/170MPa

SEM-BSE

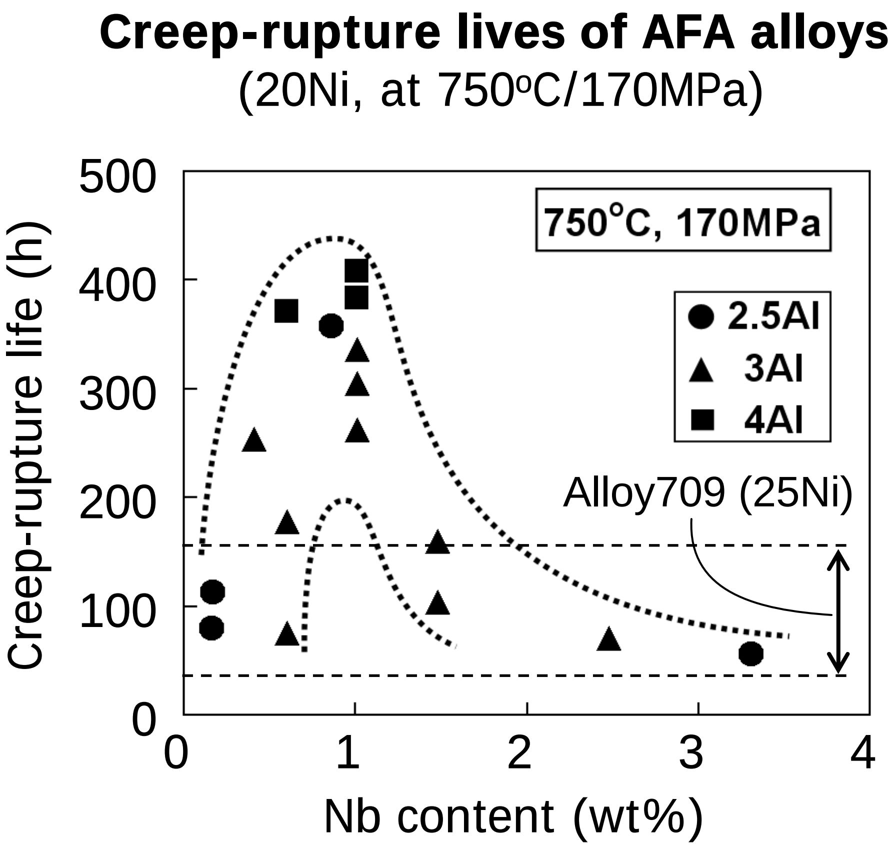


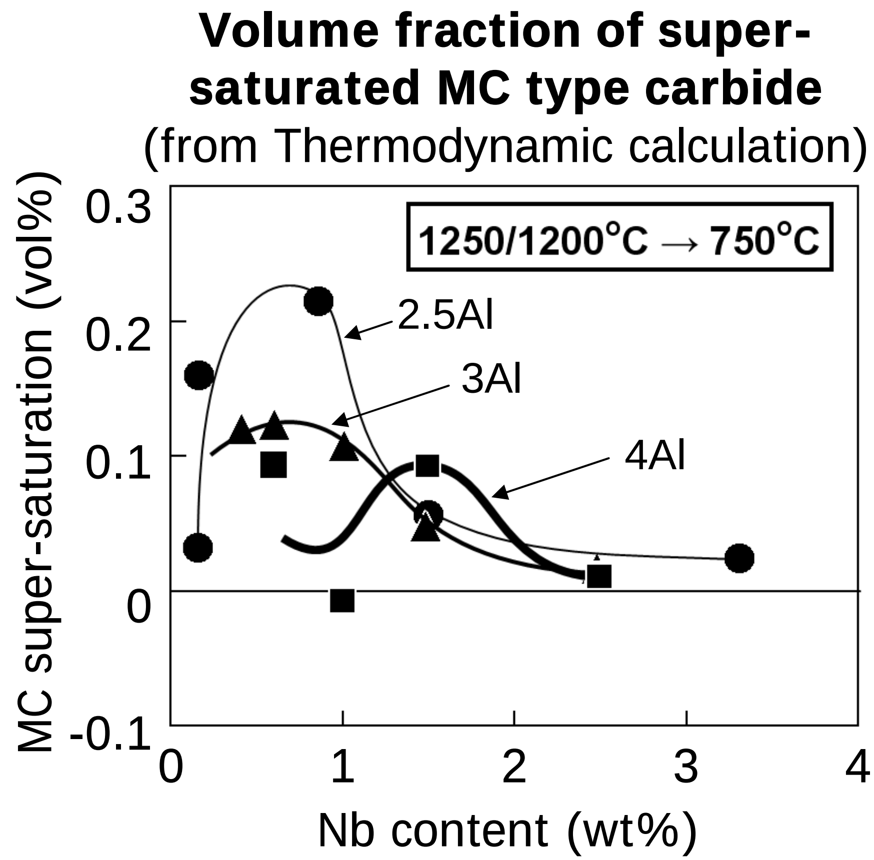
TEM-BFI



- B2 [(Ni,Fe)Al] and Laves [Fe_2(Mo,Nb)] precipitates form during creep
  - -may contribute to strengthening
  - -rupture elongation still good despite intermetallic precipitates

Optimal Creep Resistance at ~1 wt% Nb





- MC type carbide (M: mainly Nb) is the key of creep resistance.
- Predicted optimum Nb at 4Al is ~1.5 wt% Nb (maximum amount of NbC).
- Further optimization could be expected by controlling the alloying elements.

50 lb Trial Heat Made by Commercial Processes

- Vacuum melted and hot-rolled
- AFA4-1 Composition: Fe-20Ni-12Cr-4Al-0.6Nb base wt.%

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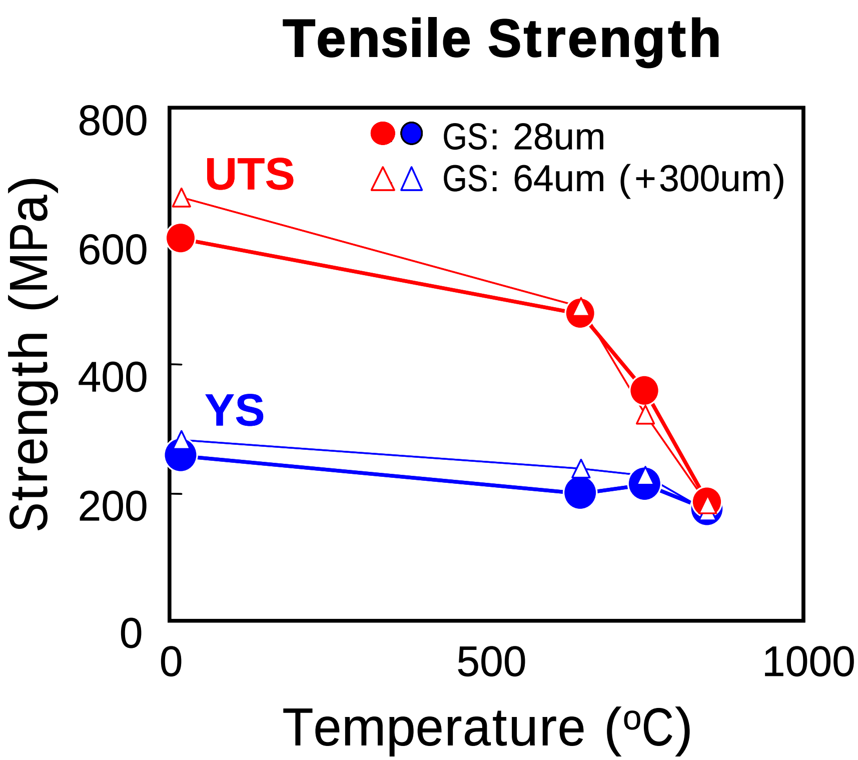
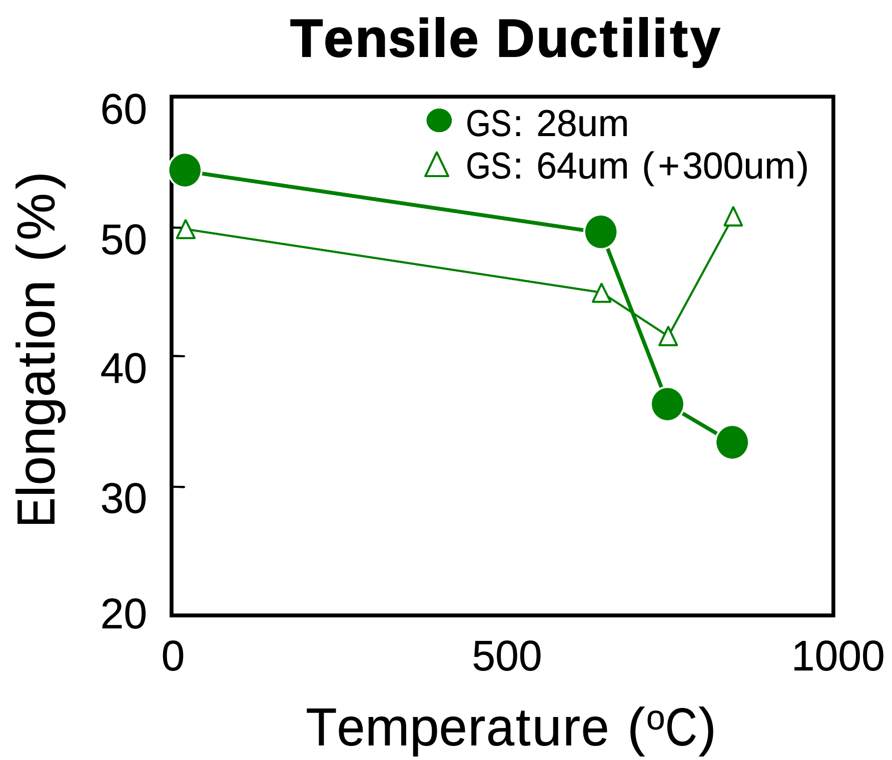
AFA 4-1 Trial Heat Exhibited Good Tensile Properties





(*GS = grain size)

- Decrease in elongation with increasing temperature likely related to precipitation of intermetallic B2 and Laves phase

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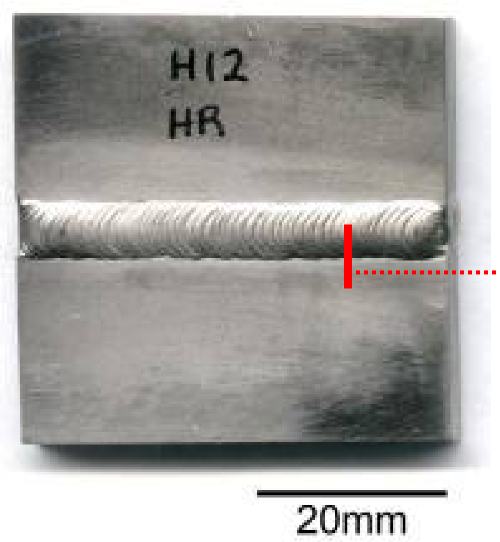
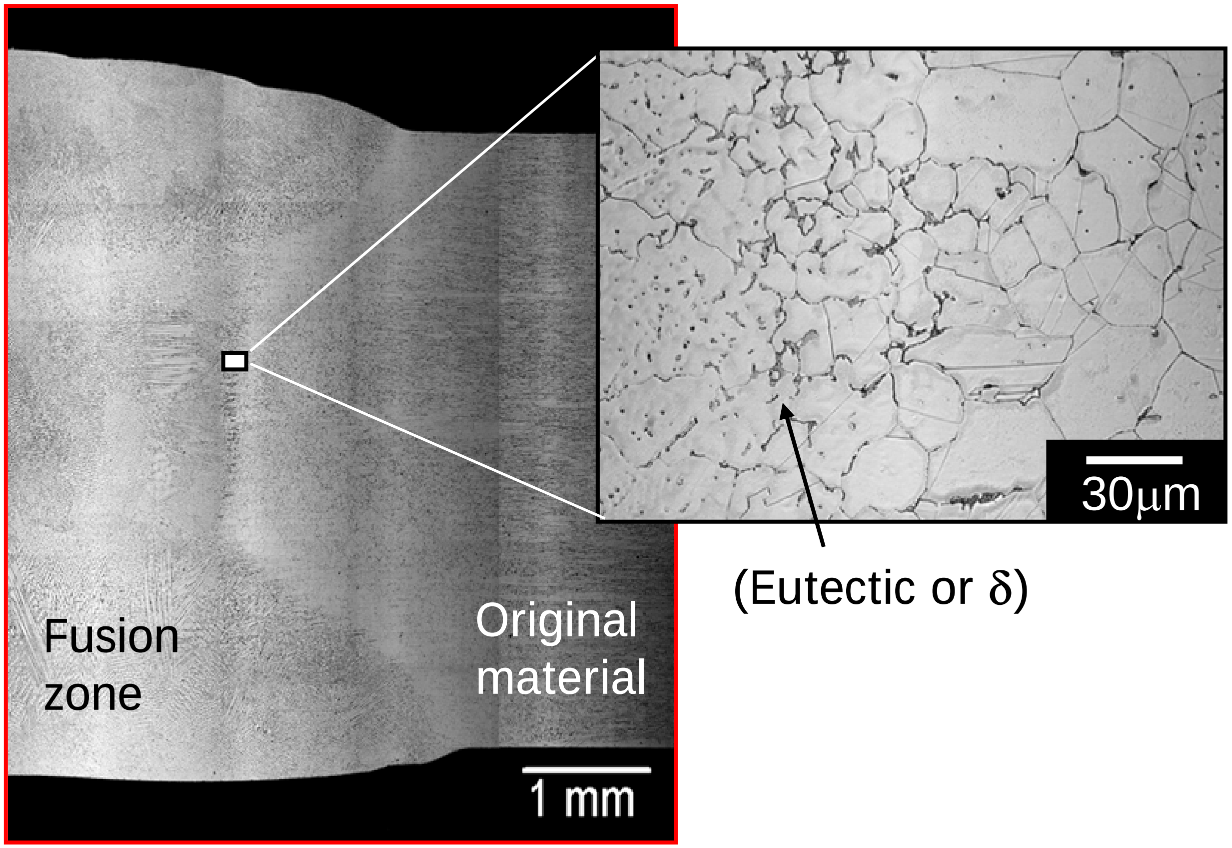
Trial Heat of AFA Alloy Readily Welded

Gas Tungsten Arc Weld

(used same alloy as a filler material)





- No crack appears at fusion/heat-affected zones

Future Work

Approach from both Engineering/Scientific aspects;

-Processing-

- Screen abilities of welding and brazing.

-Oxidation Resistance-

- Long-term oxidation test in aggressive conditions (cont'd).
- Effects of minor alloying additions: Y, Hf, etc.
- Atom probe analysis of oxygen solubility in AFA alloys.

-High Temperature Strength-

- Optimize alloy compositions by using computational thermodynamic tools.
- Long-term creep testing at lower stress.
- Tensile tests of long-time aged AFA alloys.
- In-situ SEM observation of creep deformation of AFA alloys.

Courtesy: C. Boehlert (Michigan State Univ.)

Summary

- A new class of Fe-base, Al_2O_3-forming, high creep strength austenitic stainless steel alloys has been developed.
- Al_2O_3 formation at low levels of Al (2.5-4 wt.%)
  - -current upper-temperature limit of 750-800^{o}C.
  - -higher Al, Nb, Ni levels may permit 800-900^{o}C (and higher).
- Creep resistance and strength of AFA alloys (20Ni) comparable to best available heat-resistant austenitic steel alloys in a temperature range of 750-850^{o}C.
- Comparable raw material costs to advanced heat-resistant steel alloys.

Summary (cont'd)

- 50 lb trial heat of AFA alloy was successfully hot-rolled by commercial processes.
- Preliminary screening tests suggest the AFA alloys are weldable.

Acknowledgments

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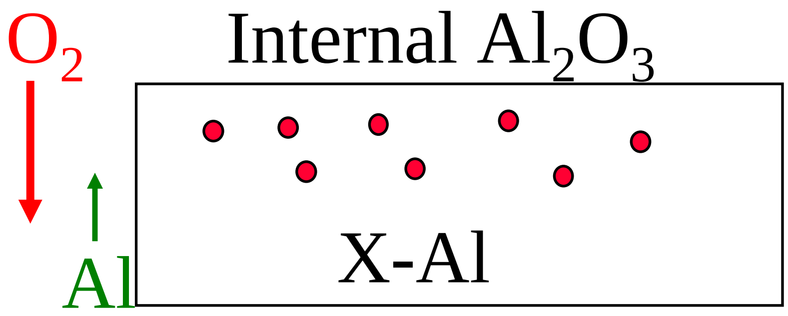
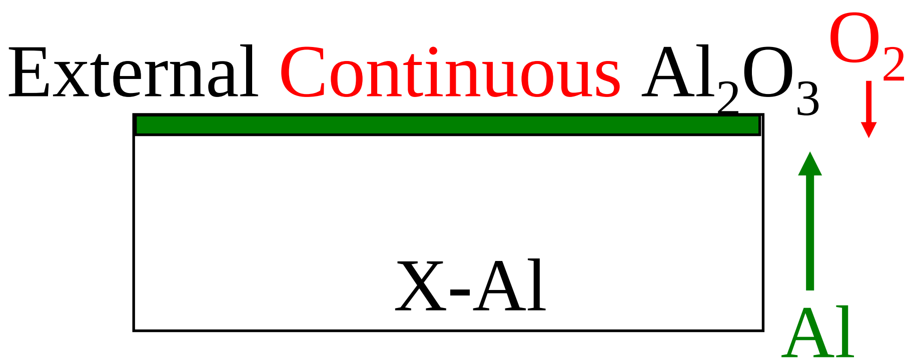
AFA2-1 (2.5Al/20Ni-0.9Nb), Solution Heat-treated

AFA2-1 (2.5Al/20Ni-0.9Nb), Aged for 72h@750ºC

Kinetics: Alloy Design From Flux Criteria (Classical Wagner Oxidation Theory)





$$\text{Minimum Al for Continuous } Al_2O_3 \propto \left[O_{\text{solubility}} * \frac{O_{\text{diffusivity}}}{Al_{\text{diffusivity}}} \right]^{1/2}$$

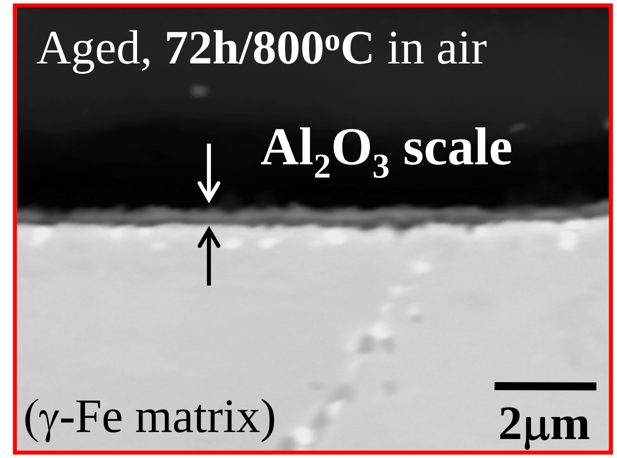
- Key is continuity: <u>**continuous = protective**</u>

- Continuous Al_2O_3 favored by alloy additions/reaction conditions that <u>decrease</u> Oxygen permeability or <u>increase</u> Al diffusivity

Protective Alumina Scale on Austenitic Steels at ~ 800°C

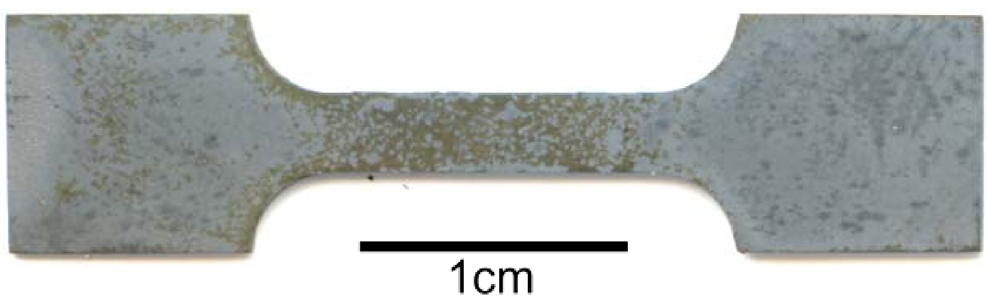
Al-modified (HTUPS4, Fe-14Cr-20Ni-**2.5Al**+x)

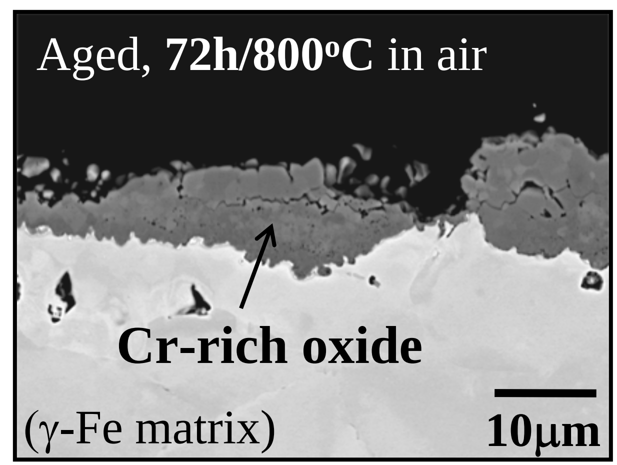
Creep-ruptured, **2192h/750°C**/100MPa in air



Base steel (HTUPS1, Fe-14Cr-20Ni base)

Creep-interrupted, **168h/750°C**/100MPa in air





Developmental Scheme of
"Alumina-forming, Creep Resistant Austenitic Stainless Steels"