Overview of Alumina-Forming Austenitic (AFA) Stainless Steel Development

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Stainless Steels with Higher-Temperature Capability Needed

- Driver: Increased efficiencies with higher operating temperatures in power generation and chemical process 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).

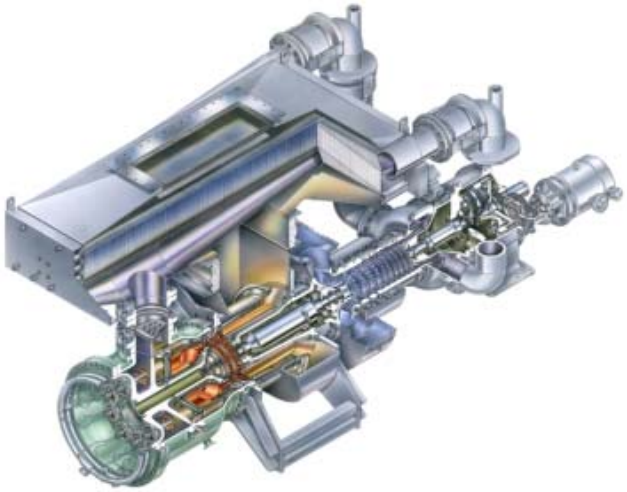
  - ➢Stainless steels rely on Cr_2O_3 scales for protection from high-temperature oxidation.
    -Limited in many industrial environments (water vapor, C, S)
    -Most frequent solution is coating: costly, not always feasible

Relevant to a Wide Range of Applications

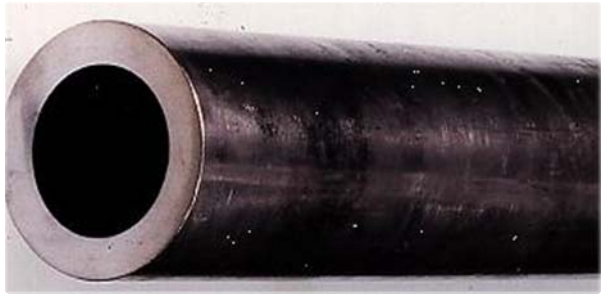
Gas Turbine Heat-Exchangers

Fossil-Fire Steam Turbine

Land-base Gas Turbine Engine



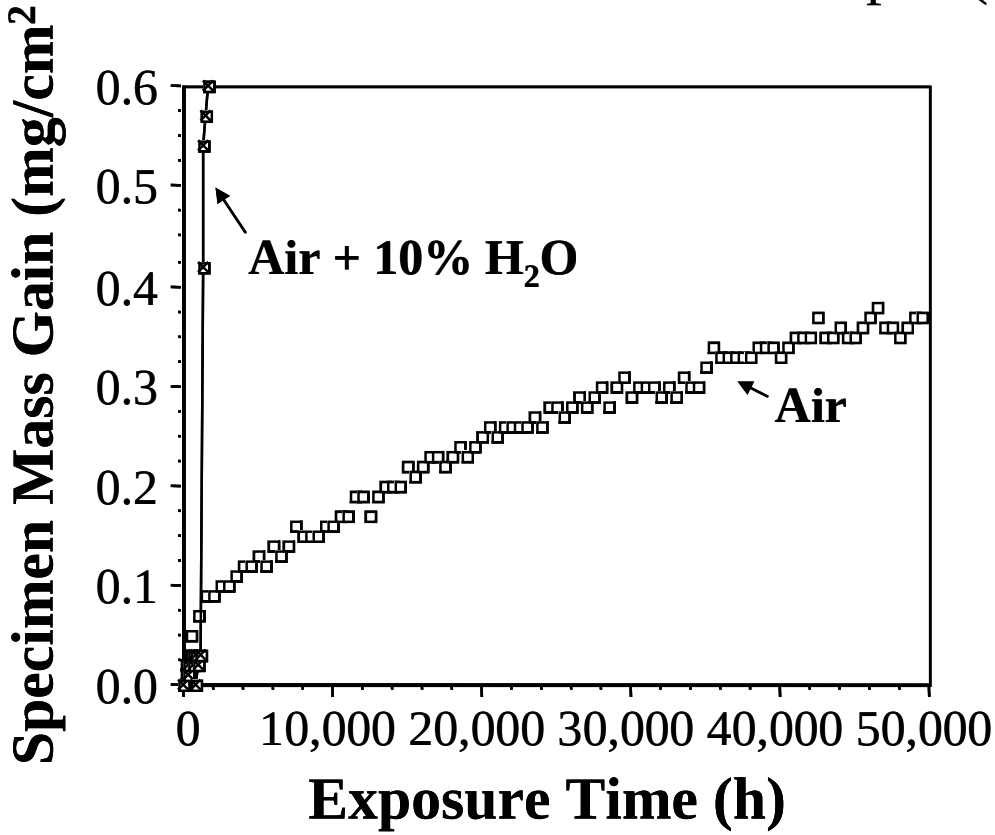
Chemical Process/ Steam Boiler Tubing



Materials Driver: A new structural material which increases efficiencies with higher operating temperatures and increased durability at 600-950°C temperature range

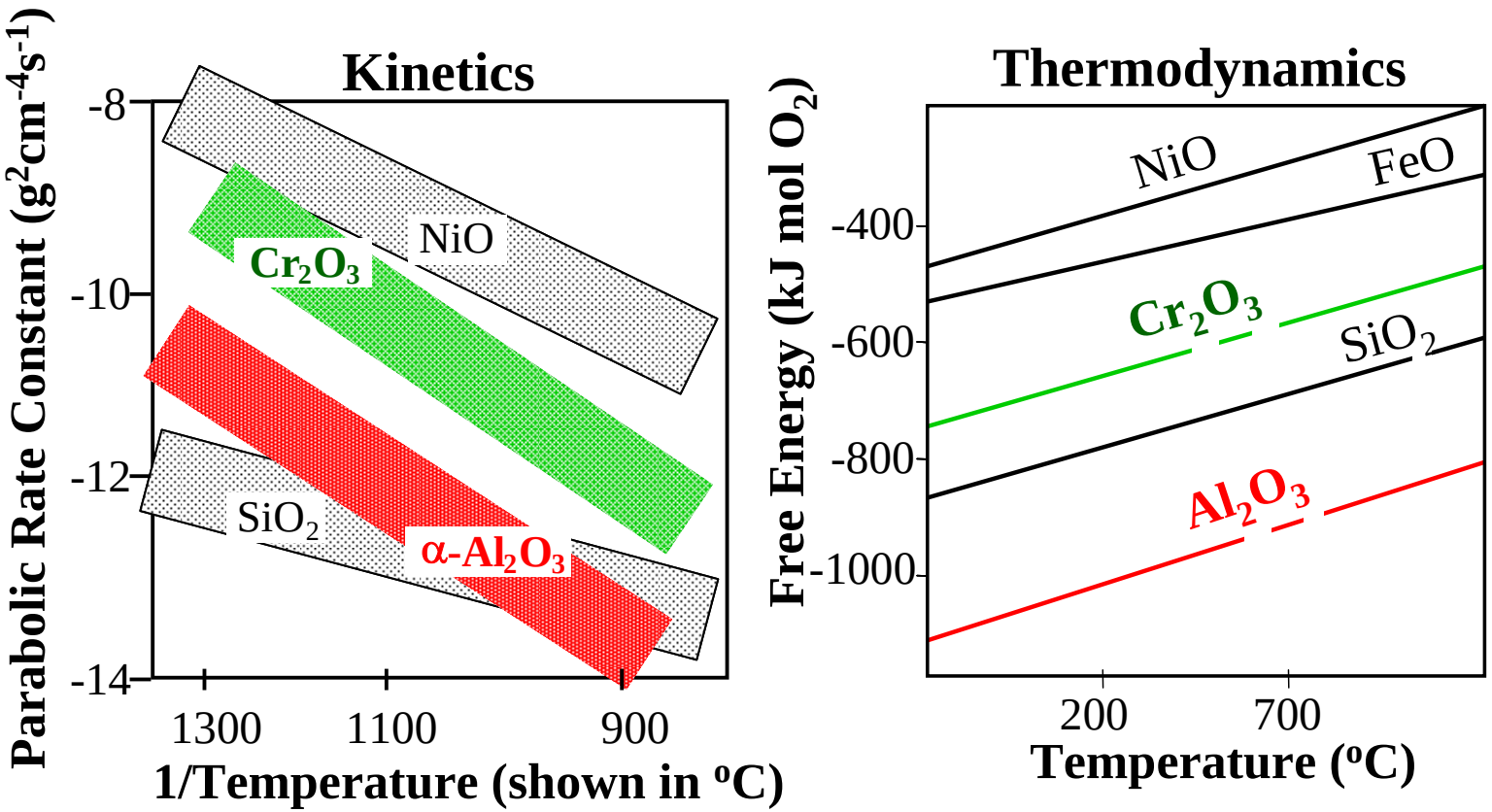
Cr_2O_3-Formers Suffer Accelerated Attack in Water-Vapor Environments

Oxidation Data for 347 Stainless Steel Foil (Fe-18Cr-11Ni base) at 650°C in Air and Air + 10% Water Vapor (Pint et al.)



- Susceptibility from Cr-oxide volatility in H_2O and enhanced internal oxidation
- Particularly important for thin components such as heat exchangers

Al_2O_3 Scales Offer Superior Protection in Many Industrially-Relevant Environments



- Al_2O_3 exhibits a lower growth rate and is more thermodynamically stable in oxygen than Cr_2O_3
- Al_2O_3 highly stable in water vapor
- Al_2O_3 generally better resistance to carburization and sulfidation

Few Available Options for Al_2O_3-Forming Alloys

- FeCrAl Alloys: Open body-centered cubic structure is weak
  - -Not suitable for most structural uses above ~500°C
- Ni-Base Alloys/Superalloys: too costly
  - -5 to 10 times greater cost than stainless steels
  - -limited to niche applications with ultrahigh performance needs
- Typically use Al_2O_3-forming coatings or surface treatments
  - -increases cost
  - -not feasible for many components/applications

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)

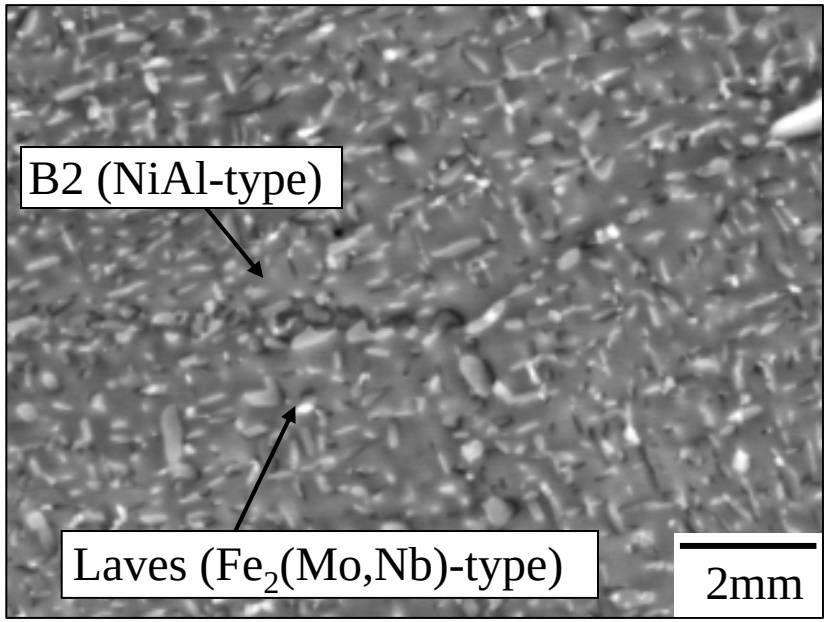
- Problem: Al additions are a major complication for strengthening
  - strong BCC stabilizer/delta-ferrite formation (weak)
  - interferes with N additions for strengthening

- 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

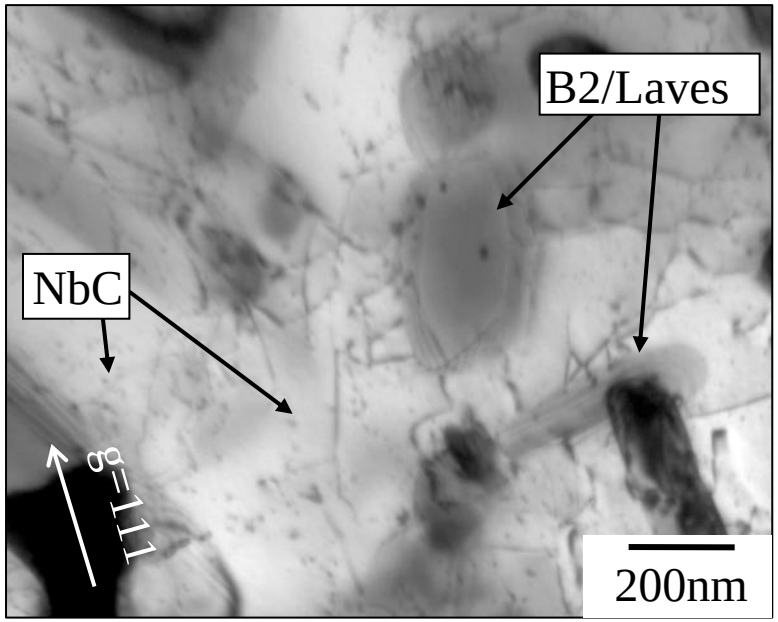
Composition and Microstructure Considerations for AFA Stainless Steels

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

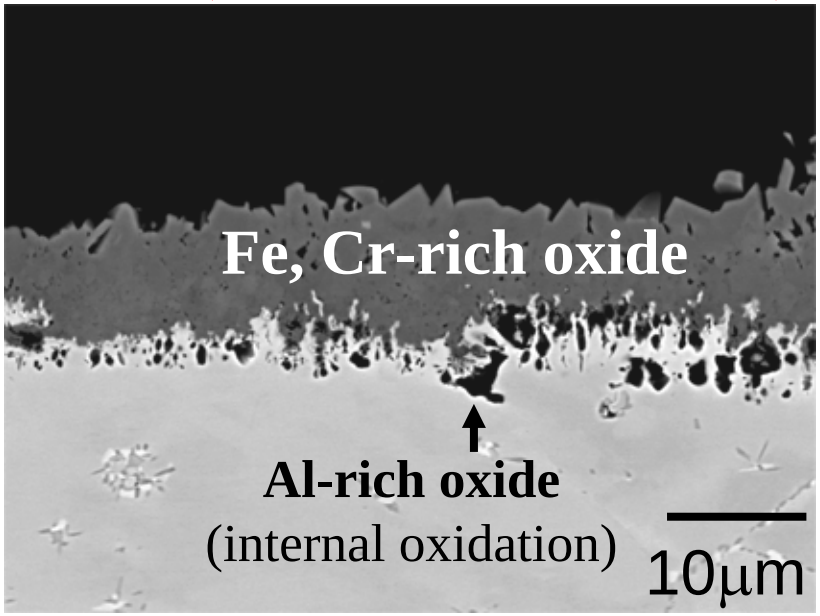


- Creep Strength
  - balance Al, Cr, Ni, to maintain single-phase FCC austenitic matrix
  - Nano NbC and submicron B2-NiAl + Fe_2Nb base Laves precipitates
- To form protective alumina:
  - Ti+V < 0.3 wt.%; Nb > (0.6-1) wt.%; N < 0.02 wt.%

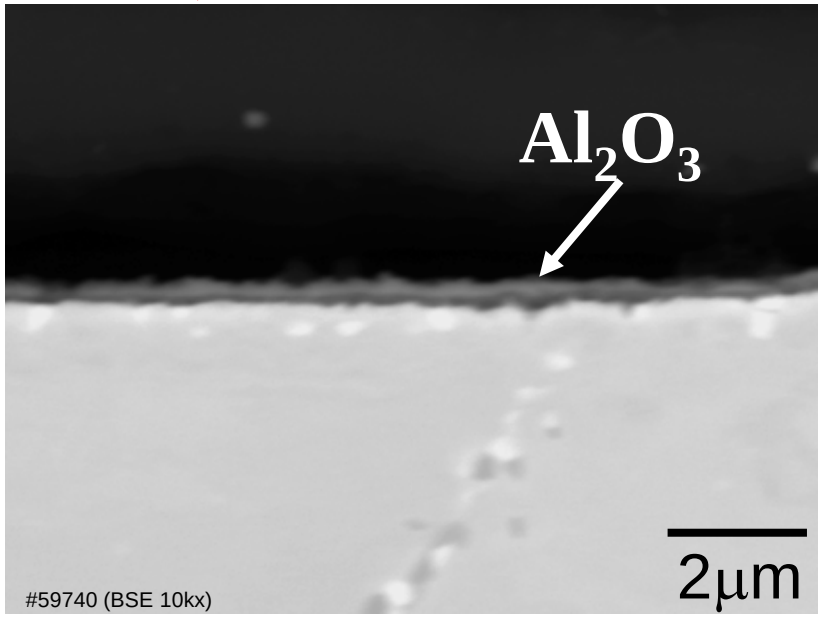
Replacing Ti and V with Nb Yields Al_2O_3 Scale Formation at only 2.5 wt.% Al

SEM Cross-Sections After 72 h at 800°C in Air

HTUPS2 (2.5Al/0.5V/0.3Ti wt.%)



HTUPS4 (2.5Al wt.%, 0.9Nb, 0Ti/V)



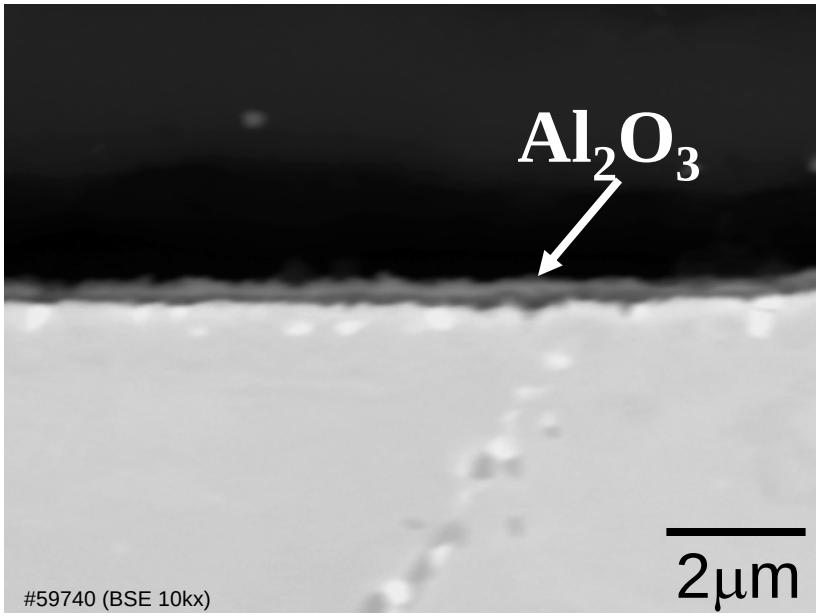
Note 5x Higher Magnification for HTUPS4

- Ti and V additions favor internal oxidation of Al
- HTUPS 4 relies on 0.9 wt.% Nb to form carbides

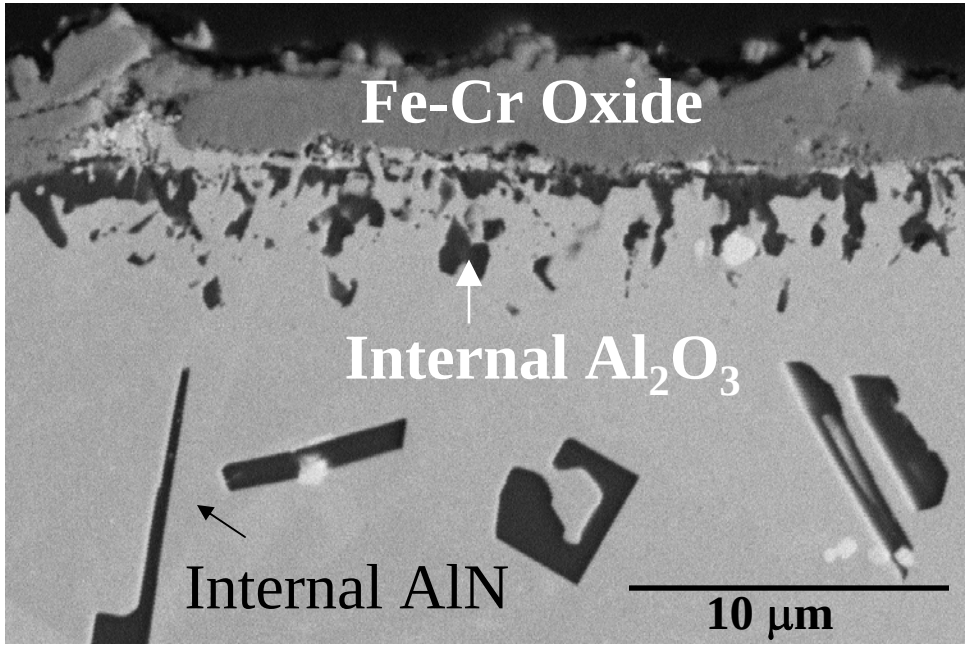
AFA Alloys Exhibit Critical Temperature Above which Protective Al_2O_3 Surface is not Formed

SEM Cross-Section of Oxidized Fe-20Ni-14Cr-2.5Al-1Nb

800°C in Air



900°C in Air



- Transition temperature complex function of Al, Cr, Nb, Ni content
- Consequence of need to balance mechanical properties with corrosion
- Best alloys to date protective to ~900-950°C

Three Classes of AFA Alloys Under Development

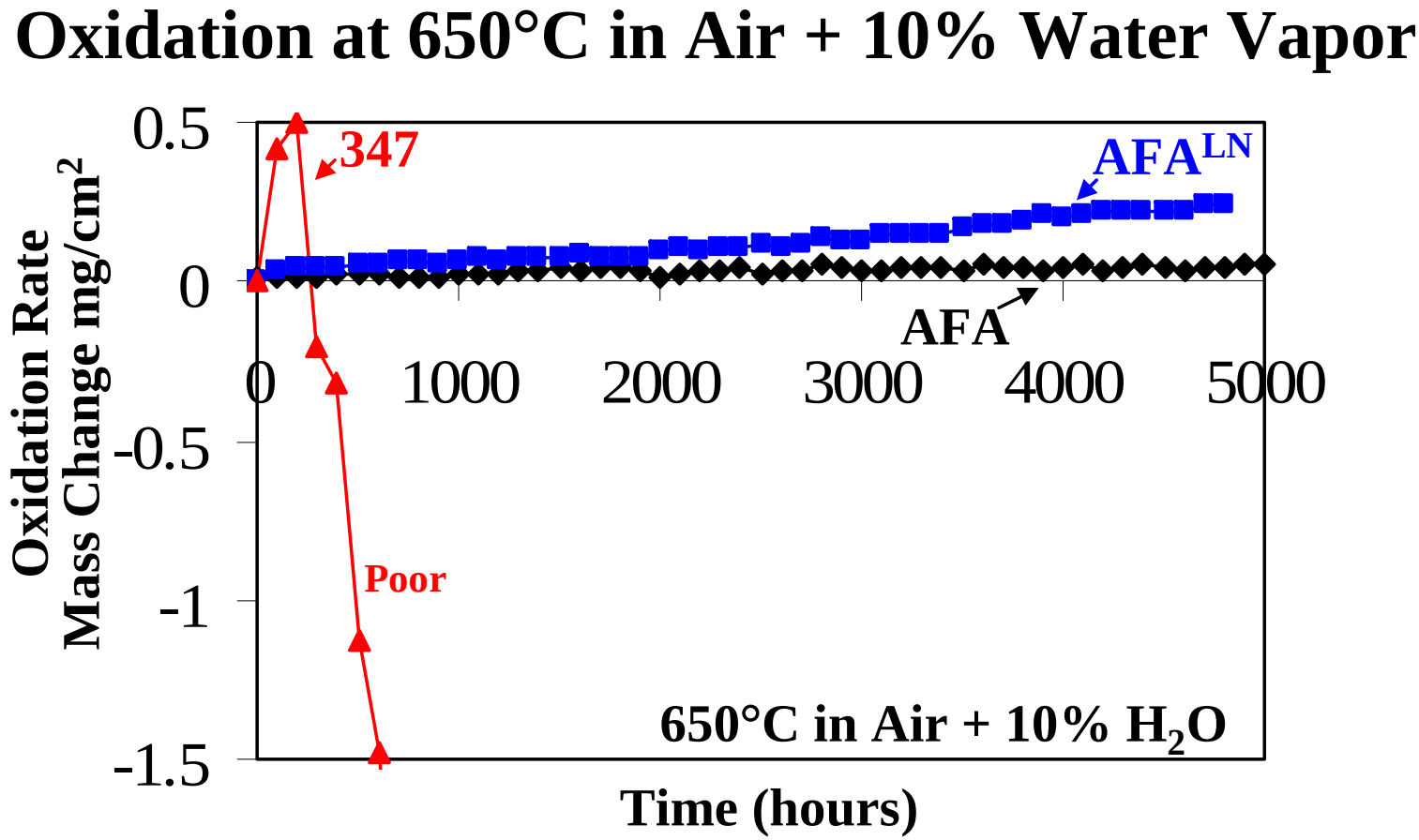
- **AFA Grade: Fe-(20-25)Ni-(14-15)Cr-(2.5-3.5)Al-(1-3)Nb wt.% base**
  - ~750-800°C temperature limit for Al_2O_3 formation
  - Trial heats with commercial alloy producer

- **High Performance AFA^{HP} Grade: Fe-(25-30)Ni-(14-15)Cr-(3.5-4.5)Al-(1-3)Nb + Hf/Y wt.% base**
  - ~850-950°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

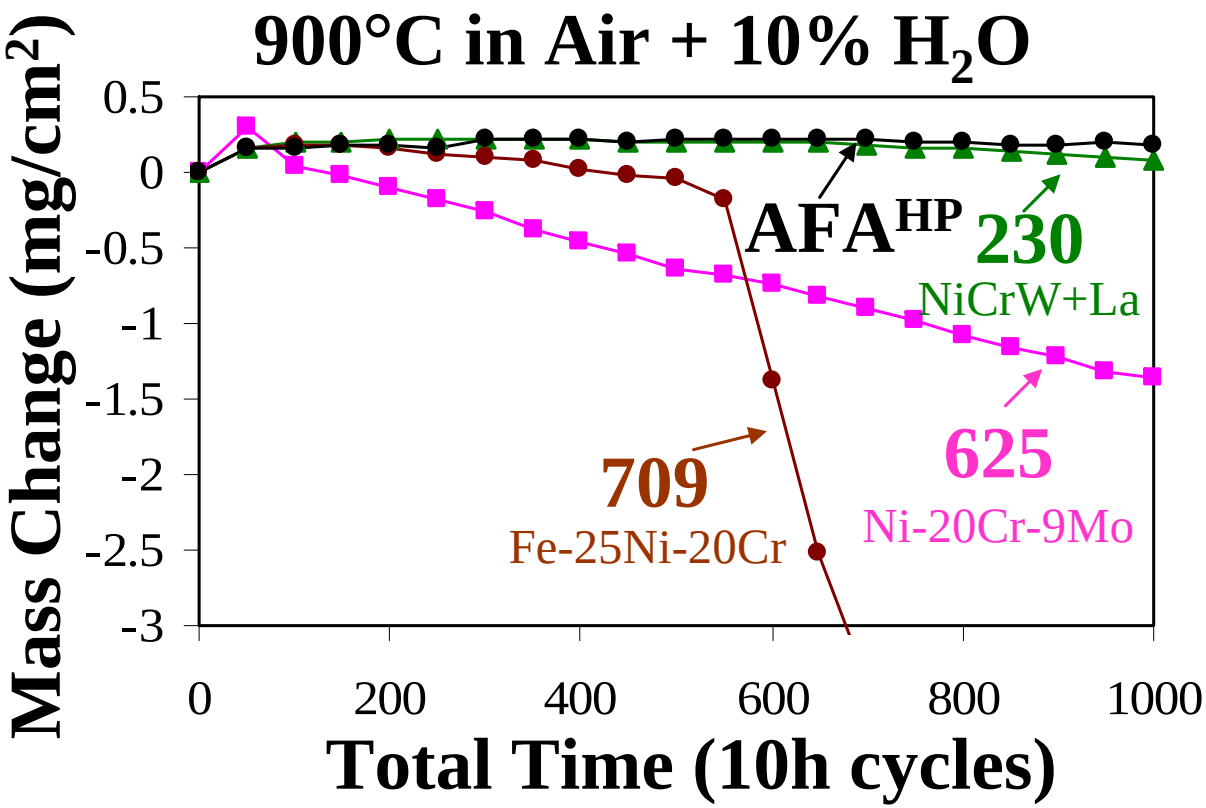
Temperature Limit Based on Oxidation in Air + 10% H_2O (~100°C Higher-Temperature Oxidation Limit in "Dry" Air

Excellent Oxidation Resistance at 650°C in Air + Water Vapor



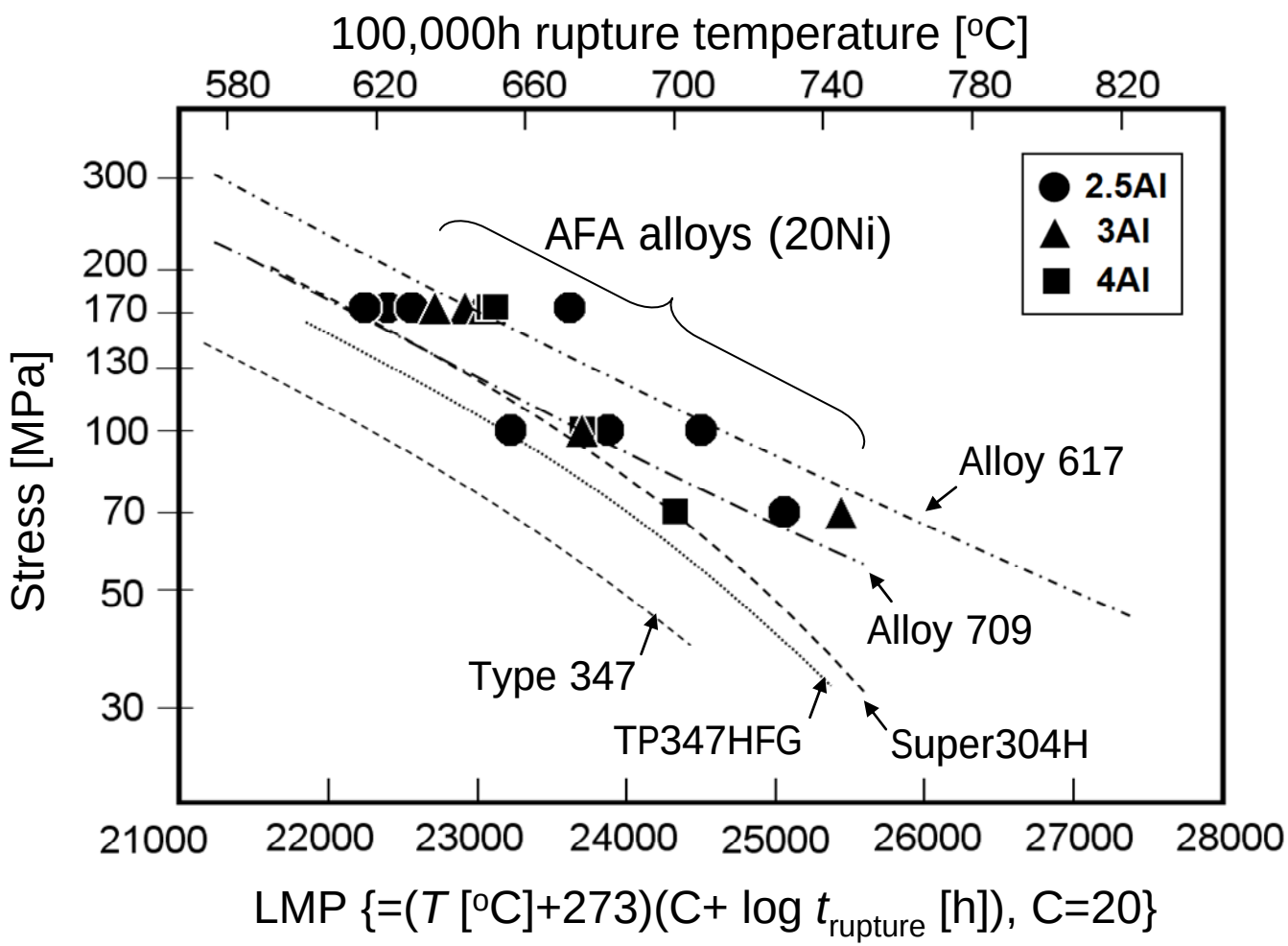
- AFA alloys now at 6000-8000 ongoing hours of exposure
  - -347 stainless steel shows Fe-oxide nodule formation followed by oxide scale spallation after a few hundred hours under these conditions

Fe-25Ni-15Cr-4Al-2.5Nb + Hf/Y AFA^{HP} Alloy Shows Promise to 900°C in Air + 10% H_2O



- Advanced austenitic alloy 709 and Ni-base alloy 625 suffer from oxide scale spallation and mass loss in this aggressive screening test
- Alloy 230 forms adherent Cr_2O_3 scale (small volatility driven mass loss)
- AFA^{HP} forms adherent protective Al_2O_3 for excellent corrosion resistance

AFA Creep Rupture Behavior in Range of Advanced Austenitics

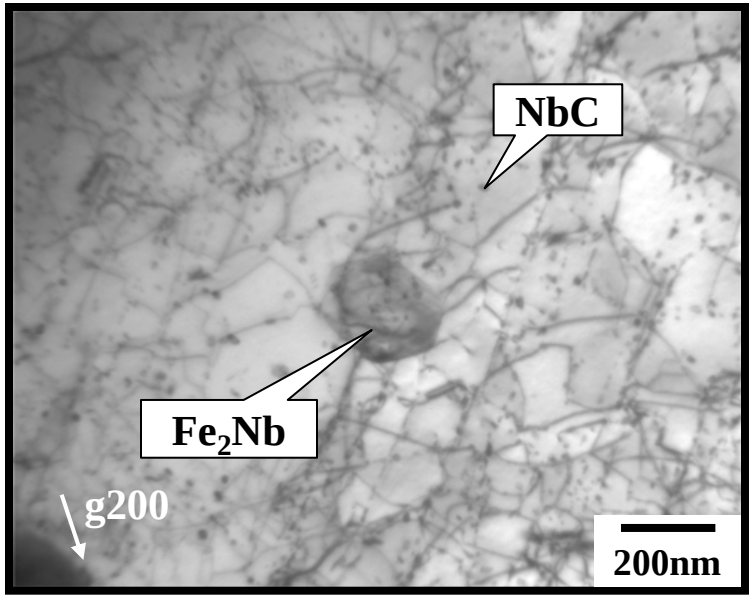


- Alloy 709 is an advanced austenitic: Fe-25Ni-20Cr base
- 617 is Ni-base alloy: Ni-20Cr-10Co-8Mo base

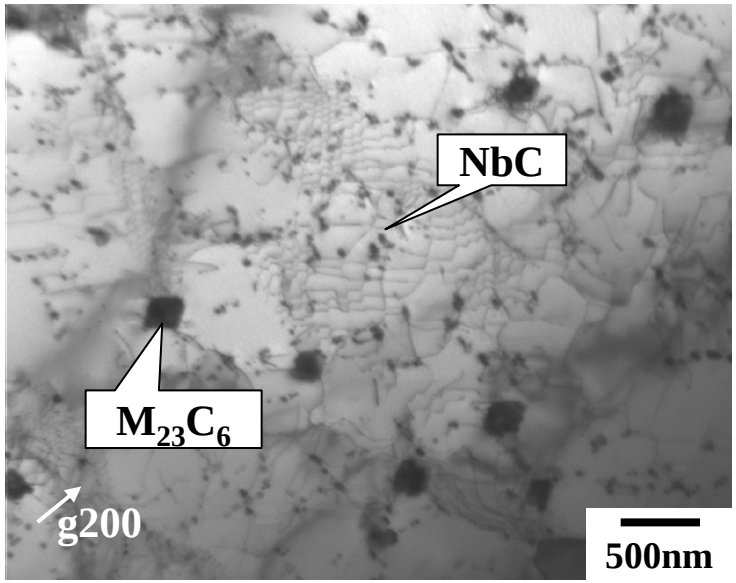
NbC Nano-Particles in AFA Alloys Pin Dislocations Effectively

TEM-BFI (after creep-rupture at 750°C/100MPa)

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



Alloy 709 (20Cr-25Ni base)

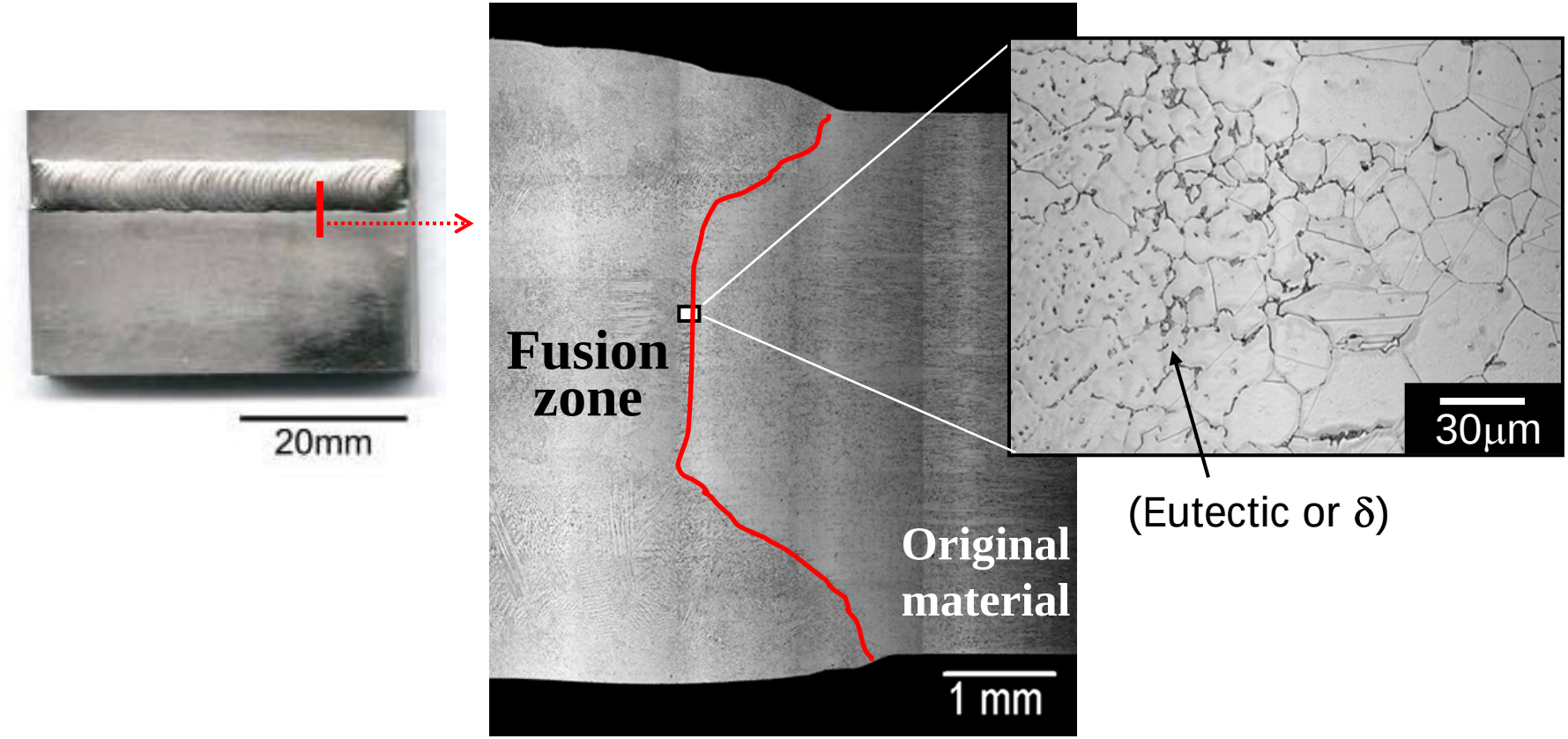


- NbC Source of excellent creep resistance

Preliminary Screening Suggests AFA Alloys Readily Welded

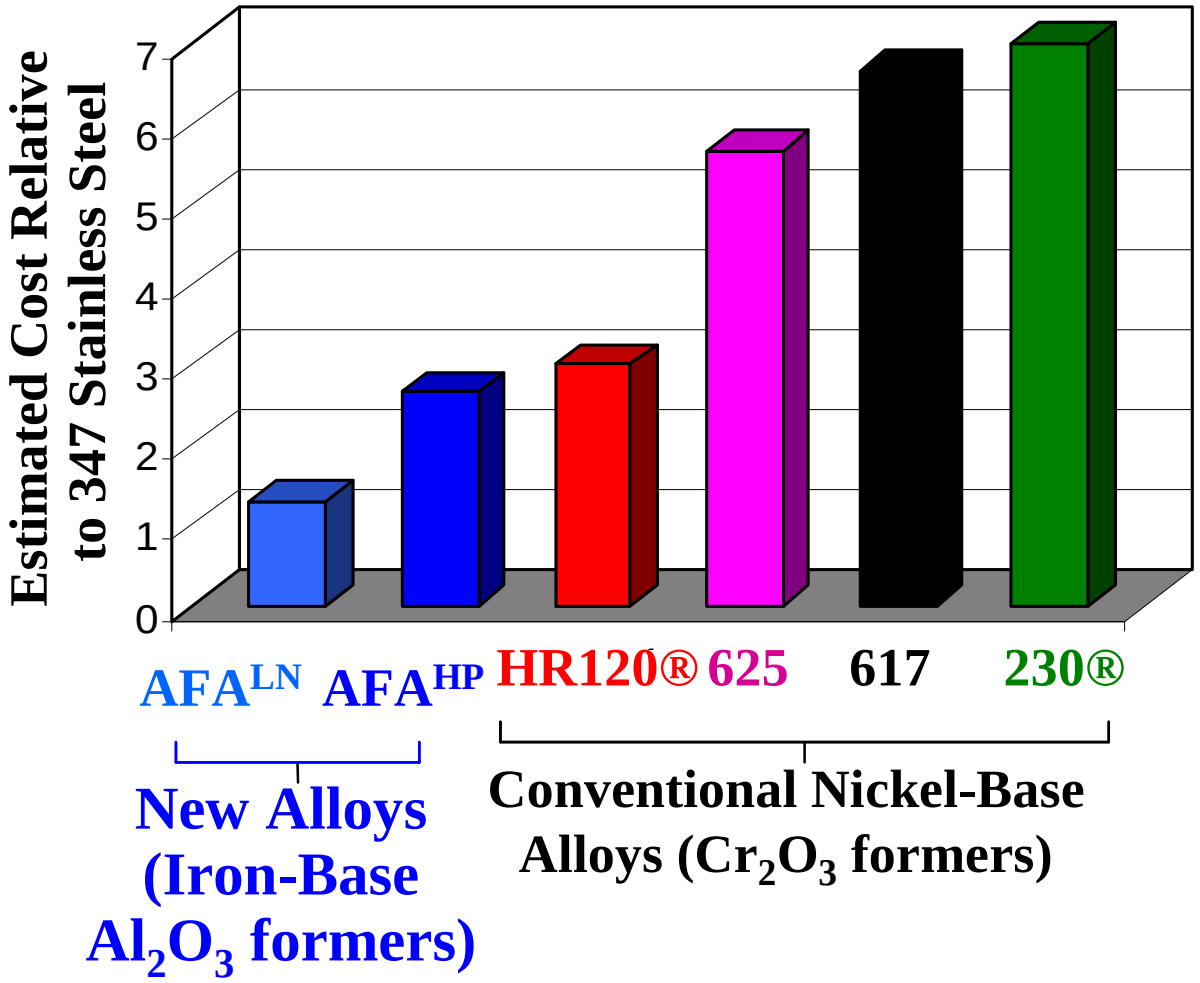
Gas Tungsten Arc Weld

(used same alloy as a filler material)



- No cracking at fusion/heat-affected zones (microstructure not yet analyzed)

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



Summary: Promising Initial Results for Development of AFA Alloys

- 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
  - ~650-950°C depending on composition
- Creep resistance comparable to best available austenitics
- Preliminary screening suggests the alloys are weldable