Development of Alumina-Forming Austenitic Stainless Steels

=Multi-Phase High-Temperature Alloys=

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“22nd Annual Conference on Fossil Energy Materials,” at Pittsburgh, PA
July 8-10, 2008
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:** $\text{Al}_2\text{O}_3$-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)**

- Fossil Power Steam Turbine, Boiler Tubing
- Recuperator, Casing

Solar Turbines 4.6 MW Mercury 50 recuperated low NO$_x$ gas turbine engine

➢ Tubing in chemical/process industry, etc. also targeted.
Al₂O₃ Scales Offer Superior Protection in Many Industrially-Relevant Environments

- Al₂O₃ exhibits a lower growth rate and is more thermodynamically stable in oxygen than Cr₂O₃.
- Highly stable in water vapor.

**Kinetics**
(Growth rate of oxide scales)

**Thermodynamics**
(Ellingham diagram)
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, 800°C in water vapor =

**HTUPS4** (Fe-14Cr-20Ni-2.5Al-0.9Nb base)  
347 foil (Fe-18Cr-12Ni base)

No oxide visible at this magnification

**NF709-800°C** (Fe-20Cr-25Ni base)

(-) Cr oxy-hydride
Volatilization, or Cr$_2$O$_3$ Spallation

(+) Al$_2$O$_3$ Formation

 NbC Nano-Particles Pin Dislocations Effectively

TEM-BFI (after creep-rupture at 750°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.
HTUPS 4 Loses the Ability to Form External, Protective Al$_2$O$_3$ 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)

<table>
<thead>
<tr>
<th>Alloy Designation</th>
<th>Nominal Composition (wt%, Fe: balance)</th>
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<tbody>
<tr>
<td></td>
<td>Ni</td>
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<tr>
<td>Base alloy without Al addition</td>
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<tr>
<td>HTUPS-1</td>
<td>20</td>
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<tr>
<td>2.5 wt% Al series</td>
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<tr>
<td>AFA 2-1 (HTUPS4)</td>
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<td>AFA 2-2</td>
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<tr>
<td>AFA 2-3</td>
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<td>AFA 2-6</td>
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<tr>
<td>3 wt% Al series</td>
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<td>AFA 3-1</td>
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<td>AFA 3-8</td>
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<tr>
<td>4 wt% Al series</td>
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<tr>
<td>AFA 4-1</td>
<td>20</td>
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<tr>
<td>AFA 4-2</td>
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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.
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.
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).
Multi Second-phase (Intermetallics/ Carbides) Strengthening

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

- B2 [(Ni,Fe)Al] and Laves [Fe₂(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.%
AFA 4-1 Trial Heat Exhibited Good Tensile Properties

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

• A new class of Fe-base, Al$_2$O$_3$-forming, high creep strength austenitic stainless steel alloys has been developed.

• Al$_2$O$_3$ formation at low levels of Al (2.5-4 wt.%)
  -current upper-temperature limit of 750-800°C.
  -higher Al, Nb, Ni levels may permit 800-900°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°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

AFA2-1 (2.5Al/ 20Ni-0.9Nb), Solution Heat-treated
AFA2-1 (2.5Al/ 20Ni-0.9Nb), Aged for 72h@750°C
Kinetics: Alloy Design From Flux Criteria (Classical Wagner Oxidation Theory)

Continuous $\text{Al}_2\text{O}_3$ favored by alloy additions/reaction conditions that decrease Oxygen permeability or increase Al diffusivity

Minimum Al for $\propto$ Continuous $\text{Al}_2\text{O}_3$

$$\left[ \text{O}_{\text{solubility}} \cdot \frac{\text{O}_{\text{diffusivity}}}{\text{Al}_{\text{diffusivity}}} \right]^{1/2}$$

• Key is continuity: continuous = protective

• Continuous $\text{Al}_2\text{O}_3$ favored by alloy additions/reaction conditions that decrease Oxygen permeability or increase 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”

- Protective $\text{Al}_2\text{O}_3$ scale formation

Addition of sufficient Al

- FCC matrix stabilization

$\text{Al, Cr}$

$\text{Ni, C, N, Mn, Cu}$

$\text{Nb, Ti, V, Mo, W}$

Stable Second Phase strengthening & Solution Hardening

High Temp. Strength