Advanced Design Concepts for Steels and Alloys Tailored for High-Temperature Fossil Applications

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Presentation Outline

• Backgrounds/Motivation:
  – Concepts of “Advanced Alloy Design”

• Update on FY17/18
  – Development and optimization of “alumina-forming” high Cr FeCrAl ferritic alloys
  – Progress in “alumina-forming” austenitic stainless steels

• Summary and Future works
Project Goals and Objectives

**Goals:** To identify and apply breakthrough alloy design concepts and strategies for incorporating improved creep strength, environmental compatibility/resistance, and weldability into three classes of alloys (ferritic, austenitic, and Ni-base) intended for use as heat exchanger tubes in fossil-fueled power generation systems at higher temperatures than possible with currently available alloys.

**Objectives:** To develop and propose new creep-resistant, “alumina-forming”, cost-effective structural materials with guidance of computational thermodynamic tools.

- **Milestones (FY2018):**
  1. Prepare at least one hot-rolled plate of the second scale-up heat of “alumina-forming” high Cr FeCrAl ferritic alloy with high W content (December 2017, Met)
  2. Complete microstructural characterization and map hardness analysis of GTAW plate of the second scale-up heat (May 2018, in progress)
  3. Complete cross-weld Charpy impact test, fracture toughness test, and short-term creep test (up to 2,000h) of the second scale-up heat (August 2018, in progress)
  4. Complete alloy preparation and initial property screening including oxidation and ash-corrosion tests and fracture toughness test of proposed austenitic and Ni-based alloys (September 2018, in progress).
Propose New Alloy Design Concepts for Heat Resistant Steels and Alloys

- “Compositional guide” to form stable alumina-scale for surface protection in extreme environments
- High temperature strength through multiple second-phase precipitate strengthening

- Apply the design strategy to three different classes of fossil energy structural materials
  - **Ferritic (~600°C), Ferritic-Martensitic (~600-620°C)**
    - high Cr containing FeCrAl alloys
  - **Austenitic (up to 650°C)**
    - Alumina-Forming Austenitic stainless steels
  - **Ni-base (>700°C)**
    - Alumina-Forming Ni-base alloys

References:
Alumina-scale is Attractive for High-temperature Use with Water-vapor Containing Environments

**Oxidation Data for Chromia-forming 347 SS (18Cr-11Ni)**

(at 650°C in Air and Air + 10% Water Vapor)

![Graph showing Specimen Mass Gain vs. Exposure Time for Air and Air + 10% H₂O](Specimen Mass Gain (mg/cm²) vs. Exposure Time (h))

- **Air + 10% H₂O**
- **Air**

Data: B.A. Pint

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**Parabolic Rate Constant of Oxide Scales**

![Graph showing Log Parabolic Rate Constant vs. Temperature](Log Parabolic Rate Constant vs. Temperature)

- **Fe-oxides**: More Protective
- **Cr₂O₃**, **NiO**, **SiO₂**, **α-Al₂O₃**

- **x10 slower oxidation kinetics than chromia**

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Targets: Increase Service Temperature for Higher Efficiency

- Boiler
- Heat exchanger
- Header
- Superheater
- Reheater
- Boiler Tubing
- Steam Turbine
- Recuperator
- Casing

Alstom USC and AUSC Power Plants – J. Marion - NTPC/USAID Int. Conf. SC Plants - New Delhi, India, 22 Nov. 2013 – P 8

Solar Turbines 4.6 MW Mercury 50 recuperated low NO_x gas turbine engine
Currently Available Alumina-forming Alloys

• **Ni-base superalloys:**
  – Ni matrix (FCC) with intermetallic second-phase precipitate strengthening (e.g. coherent L1$_2$-Ni$_3$Al)
  – Attractive for high temperature use, but expensive

• **FeCrAl:**
  – Ferritic steels (BCC), mainly used as heating elements (e.g. Kanthal®)
  – Inexpensive, but weak at elevated temperature
  – PM-ODS approach improved high-temperature properties, but expensive

• **AFA (Alumina-Forming Austenitic) steels:**
  – Austenitic steels (FCC), developed as heat resistant steels at ORNL
  – Combined alumina-scale formability and multi second-phase strengthening
  – Fill the temperature gap between “Ferritic steels” and “Ni-base alloys”
Effect of Minor Alloying on Alumina-scale Formation (AFA)

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

Fe-14Cr-20Ni-2.5Al-0.5V-0.3Ti-0.1C

Fe, Cr-rich oxide

Metal

Al-rich oxide
(internal oxidation = bad) 10μm

Fe-14Cr-20Ni-2.5Al-0.9Nb-0.1C

Al2O3

Metal

#59740 (BSE 10kx)

2μm

Note: 5x Higher Magnification for Alloy with Nb

• Compositional guideline to form protective alumina:
  - Ti+V < 0.3 wt.%; Nb > (0.6-1) wt.%; N < 0.02 wt.%
### Positive/Negative Effects on Alumina-forming Alloys

<table>
<thead>
<tr>
<th>Key elements</th>
<th>Control elements</th>
<th>Detrimental</th>
</tr>
</thead>
</table>

#### Key Elements
- **Austenite stabilizer**
- **MC/Laves forming elements**
- **Solid-solution hardening**
- **Precipitate hardening**
- **N getter (for air-melt)**

#### Control Elements
- **Stable alumina-scale formation**
- **Degrade oxidation resistance (when combined)**
- **Improve fluidity**
- **May degrade weldability**

#### Detrimental Elements
- **Expensive**
- **Improve oxidation resistance**
- **Degrade oxidation resistance**

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### Periodic Table

<table>
<thead>
<tr>
<th>Li</th>
<th>Be</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
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<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
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</tbody>
</table>

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10  Advanced alloy design concepts for high temperature fossil applications.
Alumina-Forming Ferritic Steels
(High Cr containing FeCrAl alloys)
Design Corrosion/Oxidation/Creep Resistant Ferritic Steels

**Fe-30Cr-3Al** base alloys

- Fe-30Cr-3Al + Nb, Zr (Rolled at 300°C + Annealed at 1200°C) 500µm
- Fe-30Cr-3Al + W, Nb, Si (Aged at 700°C)

**Phase equilibrium** (JMatPro v.8)

- Fe-30Cr-3Al-0.2Si-1Nb

**Important design factors for creep:**
- Fraction of Laves phase at 700°C
- BCC solvus temperature

Yamamoto et al. TMS2017
Proposed Alloy Composition Ranges

**Model alloys:** Fe-30Cr-3Al-0.2Si-1Nb + (Nb, Ti, Mo, W, Zr), wt.%

**Engineering alloys:** Fe-30Cr-3Al-0.15Si-1Nb-6W-0.5Mo-0.3Ti-0.3Ni-0.4Mn-0.03C-0.05Y

Yamamoto et al. ASME-ETAM 2018 (to be published)
Min. Creep Rate / Creep-rupture Life Depend On Fraction of Laves Phase Precipitates

Min. creep-rate vs. Laves phase

Creep-rupture life vs. Min. creep-rate

Yamamoto et al., Crosscutting research program review meeting, 2017
Minimum Creep Rate Prediction
(Ferritic Fe-30Cr-3Al+Nb base, 700°C/50MPa)

*Used Bird-Mukherjee-Dorn (BMD) model

\[
\frac{\dot{\varepsilon}_m k T}{DEb} = A_{Dis} \left( \frac{\sigma_a - \sigma_{th}}{E} \right)^n
\]

\[
\sigma_{th} = \frac{Eb}{2\pi \lambda} \ln \frac{d_{ppt}}{b}
\]

2Nb model alloy
(crept at 700C/70MPa/1750h)

Slow Coarsening Kinetics in 2Nb and 1Nb-6W Alloys

X axis: particle diameter; Y axis: Cumulative Fraction, FCA = Fe-30Cr-3Al base, wt.% (model alloys)

FCA-1Nb

FCA-2Nb

FCA-1Nb-1Ti

FCA-1Nb-5W

FCA-1Nb-6W

Stable

FCA-1Nb-6W, 700°C/1000h

SEM-BSE

Kuo et al. TMS 2018
Creep Performance / Oxidation Resistance

Larson-Miller Parameter Plot
(tested at 650-800°C and 30-150MPa)

100h cycle exposure time, h

0 1000 2000 3000 4000 5000

Mass gain, mg/cm²

0 0.2 0.4 0.6 0.8 1

100h cycle exposure time, h

0 1000 2000 3000 4000 5000

Engineering alloys
- 30Cr-3Al-1Nb-6W-Mo-Ti-Mn-Si-C

Model alloys
- 25Cr-3Al-2Nb
- 30Cr-3Al-1Nb-0.5Ti
- 30Cr-3Al-1Nb-2W
- 30Cr-3Al-2Nb
- 30Cr-2.6Al-2Nb

Cyclic oxidation test
(100h cycle, at 800°C in 10% water vapor)

(3.3 mole % for 2Nb, and 7.1 mole% for 1Nb-6W-0.5Mo-0.3Ti)

Data: B.A. Pint

Yamamoto et al. Proceedings of ASME-ETAM 2018 (to be published)
High Surface Protection in Ash-Corrosive Environments

**Ash-Corrosion Test at 700°C, 500h Cycles**

<table>
<thead>
<tr>
<th>Ash</th>
<th>Al₂O₃ 16.9%, SiO₂ 22.6%, CaO 0.9%, Fe₂O₃ 7.8%, KOH 1%, TiO₂ 0.6%, MgO 0.2%, Fe₂(SO₄)₃ 19.8%, MgSO₄ 10.1%, K₂SO₄ 4.8%, Na₂SO₄ 15.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>N₂, CO₂, H₂O, O₂, SO₂</td>
</tr>
</tbody>
</table>

Data: B.A. Pint

Yamamoto et al. ASME-ETAM 2018 (to be published)
Potential Issues with Low Ductility at RT

1Nb-6W Engineering alloy, SS curves

- 23°C
- 23°C (repeated)
- 300°C
- 600°C
- 700°C
- 750°C
- 800°C

True stress, MPa

True strain, %

Transition, $10^{-3}$/s → $10^{-9}$/s

Cold/Warm deformation

Hot deformation

25.4mm

Advanced alloy design concepts for high temperature fossil applications
Process/Alloy Optimization for Grain Refinement in Progress

1Nb-6W-0.5Mo-0.3Ti (Base)

As processed*

After additional TMT**

1Nb-6W-0.5Mo-0Ti+Zr (Modified)

0Ti-0.1Zr

0Ti-0.3Zr
Alumina-Forming Austenitic Stainless Steels
Initiated Property Screening of Newly Proposed Advance AFA alloys

$M_{23}C_6 + MC$ strengthening (CA01 and CA02):
$Fe-14Cr-25Ni-4Al-Mn-Nb-C$ with $Cu$, $Hf$, $Y$

$Fe_2W + M_{23}C_6$ strengthening (CA03-CA05):
$Fe-14Cr-(16-25)Ni-(3-4)Al-Mn-Nb-C$ with $W$, $Cu$, $Hf$, $Y$

High Cr containing AFA (CA06 and CA07):
$Fe-18Cr-25Ni-4Al-Mn-Nb-C$ with $W$, $Cu$, $Hf$, $Y$

Reference AFA (OC4):
$Fe-14Cr-25Ni-3.5Al-2.5Nb-0.1C$ base
Summary

Successfully demonstrated “New Alloy Design Concepts for Creep-resistant, Alumina-forming Alloys for High-temperature Fossil Applications” through development of two different classes of Fe-base alloys:

**High Cr containing FeCrAl Ferritic alloy (Fe-30Cr-3Al-1Nb-6W base):**
- Designed with computational thermodynamic tools
- Promising high-temperature properties
  - Creep-rupture tests
  - Good surface protection in both steam containing environment and fire-side corrosive circumstances
- Optimization of processability/toughness is in progress
  - Searching for potential applications in various industries

**Alumina-forming Austenitic alloys (Fe-Cr-Ni-Al-Nb-C-W-Cu-Hf-Y):**
- Proposed three different alloy designs (by following compositional guideline)
- Property screening in progress
  - Creep-rupture test at 750/800°C
  - Oxidation at 800°C in 10% water vapor
Future Works

**High Cr containing FeCrAl alloys:**
- Cross-weld property evaluation:
  - A metal-core weld filler wire production was completed
- Seek potential applications:
  - Thin plate/sheet/foil products for heat exchangers
  - Cladding (weld overlay) for protective coating; additively manufactured production

**Alumina-Forming Austenitic Stainless Steels:**
- Continue property evaluation of new AFA alloys with various strengthening second-phases:
  - List potential candidate microstructural designs for near-future developmental efforts (e.g. EEM)
- Seek potential applications:
  - Various industries are interested in the AFA alloys; communications are in progress

**Alumina-Forming Ni-base alloys:**
- Leveraged with other DOE-funded projects for wrought alumina-forming Ni-base alloys:
  - Evaluation of coherent L12 strengthening high-temperature Ni-Fe base wrought alloy is in progress
Thanks
Tensile Properties Compared to F-M Steel (Grade 91)
History of “Heat-Resistant/Stainless Steel Development”

**Heat-resistant steels and alloys**
- **Carbon steels**: Steam locomotives, etc.
  - Quench and temper/annealing
  - Tempered martensite / pearlite transformation
- **Low alloy steels**: Supercritical (SC)
  - Normalization/quench and temper/annealing
  - Martensitic/bainitic transformation
- **High Cr (9-12) FM steels**: Ultra-supercritical (USC)
  - Normalization and temper
  - Introduction of MX (VN, NbC)
- **Advanced austenitic steels**: USC
  - Austenite (FCC) matrix, Fe-Ni base
  - Solution hardening/ carbide strengthening
- **Ni-base alloys**: Advanced USC (A-USC)
  - Austenite (FCC) matrix, Ni-base
  - Solution hardening/ carbide or intermetallic strengthening

**Stainless steels and alloys**
- **Fe-P**:
  - “non-rusting steel”, India, ~B.C. 400
- **Fe-Cr (ferritic stainless steel)**:
  - Monnartz, Germany, 1911
  - Dantsizen and Becket, USA, 1911-12
- **Fe-Cr-Ni (martensitic/austenitic stainless steels)**:
  - Struss and Maurer, “Nirosta”, Germany, 1912
  - Haynes, “Martensitic stainless steels”, USA, 1912
  - Brearley, “Martensitic stainless steels”, UK, 1912

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