Intermetallic Strengthened Alumina-Forming Austenitic Steels for Energy Applications

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DOE grant DE-FE0008857
Acknowledgement

• Professors at Dartmouth College:
  – Erland M. Schulson, Ph.D.
  – Harold J. Frost, Ph.D.

• Dr. Charles Daghlian in EM Facility at Dartmouth College

• Dr. Yukinori Yamamoto, Dr. Michael Brady and Dr. Michael Miller at Oak Ridge National Laboratory

• Dr. Si Chen and Dr. Zhonghou Cai in Argonne National Laboratory

• Professors, colleagues and friends at Dartmouth College

• Funded by the U.S. Department of Energy NETL Award DEFG2612FE0008857
Outline

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  – Motivation
  – Background

• Results and Discussion
  – Microstructural analysis
  – Thermomechanical treatments
  – SEM & TEM characterization
  – XRD analysis
  – Room temperature tensile tests

• Summary
New Materials for High Temperature Applications

**Motivation:** Develop materials which can be used at higher temperature (>700 °C) and pressure (>100 MPa) to enhance efficiency (>50 %) and reduce CO₂ emissions in fossil fired boiler/steam turbine power plants

**Solutions:**
- Ni-Base Superalloys: too costly
- FeCrAl alloys: bcc structure, weak >500 °C
- Al₂O₃ coatings or surface treatments
- Alumina-Forming Austenitic Steels
  - Combination of creep and oxidation resistance
  - Lower cost (Lower nickel content)

Alumina-forming Austenitic (AFA) Stainless Steels

- Combination of good **oxidation resistance & creep resistance**
  - Oxidation resistance achieved by the formation of protective, external alumina scale. (~3 wt.% Al)
  - f.c.c. matrix with intermetallic strengthening (Ni$_3$Al etc.)

Fe-14Cr-20Ni-0.95Nb-2.5Al-2.5Mo wt. % base alloy (initial developed AFA)
BSE image after 72 hours of oxidation at 800°C in air

Fe-14Cr-32Ni-3Nb-3Al-2Ti wt.% base alloy (recent developed AFA)
TEM BF images of the alloys and SAD pattern

Oxidation Resistance and Creep Performance of AFA Steels

- Alumina formation in AFA alloys
  - Others: Ti content, C and B addition
- The best alloy has >7 times longer creep life than A286

32ZCB: Fe–14Cr–32Ni–3Nb–3Al–2Ti–0.27Zr–0.14Si (wt.%)  
41Z: Fe–14Cr–32Ni–3Nb–4Al–1Ti–0.27Zr–0.12Si (wt.%)  
A286: Fe–14Cr–25Ni–2Ti–0.15Al (wt.%)  

Iron-base superalloy

Cyclic oxidation test results at 800 °C in 10% water vapor  
creep-rupture curves at 750 °C and 100 MPa.

Composition of Recent Developed AFA Steels

- Arc-melted 600 g ingot by using pure element feedstock.
  - Drop cast into 1” x 1” x 3” bar shape die.
  - Soaked at 1100 °C for 2 h in Ar + 4% H₂ gas
  - Hot-rolled the ingot along longitudinal axis for up to 80 % thickness reduction (~15-20 % thickness reduction per pass)
  - Anneal the plate at 1100 °C for 30 min in Ar + 4% H₂ gas, followed by air cooling.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
<th>Si</th>
<th>Nb</th>
<th>Ti</th>
<th>Zr</th>
<th>C</th>
<th>B</th>
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<tbody>
<tr>
<td>DAFA26</td>
<td>45.55</td>
<td>14</td>
<td>32</td>
<td>3</td>
<td>0.15</td>
<td>3</td>
<td>2</td>
<td>0.3</td>
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<td></td>
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<tr>
<td>DAFA29</td>
<td>45.44</td>
<td>14</td>
<td>32</td>
<td>3</td>
<td>0.15</td>
<td>3</td>
<td>2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.01</td>
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<tr>
<td>A286</td>
<td>56.2</td>
<td>14.5</td>
<td>25</td>
<td>0.15</td>
<td>0.2</td>
<td>-</td>
<td>2.1</td>
<td>-</td>
<td>0.04</td>
<td>0.006</td>
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</table>

AFA alloys are supplied by Y. Yamamoto and M. P. Brady in Oak Ridge National Laboratory
SEM Analysis of DAFA26

- DAFA26: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si (wt.%) (as-hot-rolled)
  - Nb rich precipitates and grain size ~40 µm
BF and CBED of Laves Phase in DAFA26

- DAFA26: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si (wt.%) (as-hot-rolled)
  - Fe$_2$Nb Laves phase precipitates + L1$_2$ precipitates in f.c.c. matrix
APT Analysis of DAFA26 (as-hot-rolled)

- DAFA26: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si (wt.%)
Thermo-mechanical Treatments Procedure

DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-\textbf{0.1C-0.01B} (wt.%) (recent developed)

- Cold rolling 90% thickness reduction (~4.5% reduction per pass)
  - Enhance the creep properties
  - Introduce dislocations which will act as nucleation sites for precipitates and result in longer creep life
BSE Images of DAFA29 after Thermo-mechanical Treatment Method#1

Method#1: DAFA29 + Cold Rolling (90%) + 800 °C
BSE Images of DAFA29 after Thermo-mechanical Treatment Method#2

Method#2: DAFA29 + 1200 °C (50h) + Cold Rolling (90%) + 800 °C

a) As-hot-rolled alloy
b) After 50 h at 1200 °C
  Grain size ~250 μm
c) After cold rolling
d) 2.4 h at 800 °C
e) 24 h at 800 °C
f) 240 h at 800 °C
BF TEM Images and SAD of DAFA29 after Thermo-mechanical Treatment Method#1

Method#1: DAFA29 + Cold Rolling (90%) + 800 °C

- 2.4 h at 800 °C
  - Grain size: ~100 nm
- 24 h at 800 °C
  - Grain size: ~270 nm
- 240 h at 800 °C
  - Grain size: ~1 μm
BF TEM Images and SAD of DAFA29 after Thermo-mechanical Treatment Method#2

Method#2: DAFA29 + 1200 °C (50h) + Cold Rolling (90%) + 800 °C

Grain size: ~200 nm
Grain size: ~450 nm
Grain size: >1 μm
BF TEM image, EDS and CBED of a Laves Phase Precipitate in TMT DAFA29

- Fe$_2$Nb Laves phase precipitates
  - C14 structure, Fe:Nb = 2:1
BF TEM Image, EDS and CBED of a B2 Precipitate in TMT DAFA29

- NiAl precipitates
  - B2 structure
  - Predicted B2 phase fractions: 5% based on thermodynamic calculation
BF TEM Image, EDS and CBED of a L1₂ Precipitate in TMT DAFA29

- Ni₃Al(Ti) type L1₂ precipitates
  - L1₂ structure, Ni:Al(Ti) = 3:1
  - Predicted L1₂ phase fractions: 21 % based on thermodynamic calculation
SE Image and BF TEM Image of Ni$_3$Al(Ti) type L1$_2$ Precipitates

- Morphology of Ni$_3$Al(Ti)
  - Cold Rolling (90%) + 800 °C (240 h)
XRD and Synchrotron XRD Results

Method #1

Method #2

Lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>Fe-f.c.c.</th>
<th>Fe2Nb (a)</th>
<th>NiAl</th>
<th>Ni3Al</th>
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<tbody>
<tr>
<td>DAFA29</td>
<td>3.611</td>
<td>4.820</td>
<td>2.888</td>
<td>3.604</td>
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<td>Method #1</td>
<td>2.4 h</td>
<td>3.599</td>
<td>4.812</td>
<td>2.883</td>
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<td></td>
<td>24 h</td>
<td>3.601</td>
<td>4.853</td>
<td>2.895</td>
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<td></td>
<td>240 h</td>
<td>3.597</td>
<td>4.881</td>
<td>2.900</td>
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</tbody>
</table>

Lattice misfit of L1₂ phase with f.c.c. matrix is calculated to be only ~0.28% for both treatments.
Room Temperature Tensile Tests

Method #1
DAFA29 + Cold Rolling (90%) + 800 °C

- 2.4 h YS: 1280 MPa
- 24 h YS: 1070 MPa
- 240 h YS: 800 MPa

YS: 560 MPa 22%

Method #2
DAFA29 + 1200 °C (50h) + Cold Rolling (90%) + 800 °C

- 2.4 h YS: 1150 MPa
- 24 h YS: 1020 MPa
- 240 h YS: 750 MPa

YS: 560 MPa 22%

Hall-Petch: \( \sigma_{0.2} = \sigma_0 + KD^{0.5} \), where \( \sigma_0 = 600 \) MPa and \( K = 230 \text{ MPa} \cdot \mu \text{m}^{-0.5} \)

\[ \sigma_0 = \sigma_{\text{ppt}} + \sigma_d + \sigma_{\text{ss}} \]
Tensile Tests of Control Samples

Method #1 Control
DAFA29 + 800 °C

Method #2 Control
DAFA29 + 1200 °C (50h) + 800 °C

Without Cold Rolling
Without Cold Rolling

**YS:**
- 240 h: ~660 MPa ~1%
- 24 h: 890 MPa 10%
- 24 h: 747 MPa 20%
- 2.4 h: 560 MPa 22%
- 2.4 h: ~520 MPa 8%
- 240 h: 760 MPa 8%

**Without Cold Rolling**

**YS:** 560 MPa 22%
BSE Images of Grain and Grain Boundaries in Control Samples

Method #1 Control: DAFA29 + 800 °C

Method #2 Control: DAFA29 + 1200 °C (50h) + 800 °C
Ni₃Al Size Change after Method#1 Control
800 °C Treatment

- After 2.4 h: 17 ± 4 nm, N = 340
- After 24 h: 28 ± 6 nm, N = 389
- After 240 h: 62 ± 14 nm, N = 279
Ni$_3$Al Size Change after Method#2 Control
1200 °C (50h) + 800 °C Treatment

(a) 2.4 h

(b) 24 h

(c) 240 h

(d) 18 ± 2 nm  
N = 337

(e) 36 ± 8 nm  
N = 288

(f) 71 ± 14 nm  
N = 226
Summary

- A solutionizing anneal at 1200 °C followed by cold rolling and annealing at 800 °C can be used to generate a finer-scale and more uniform distribution of Laves phase precipitates.

- Cold rolling produces a high density of dislocations, which act as nucleation sites for Fe₂Nb Laves phase, B₂ NiAl, and Ni₃Al precipitate formation.

- Nanocrystalline steels processed through large strain cold rolling exhibit a dramatic increase in yield strength up to 1280 MPa. The yield strength decreases upon further annealing due to grain growth and precipitate coarsening.

- The yield strength of thermo-mechanically treated AFA steels exhibits a Hall-Petch relationship with a large value for \( \sigma_0 \) that likely arises from precipitate strengthening (\( \sigma_{ppt} \)).