Intermetallic Strengthened Alumina-Forming Austenitic Steels for Coal-Fired Power Systems

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Outline

• Introduction
  – Motivation
  – Background

• Results and Discussion
  – Microstructural analysis
  – Thermo-mechanical treatments
  – SEM & TEM characterization
  – XRD analysis
  – Room temperature tensile tests
  – High 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)

www.siemens.com
Alumina-forming Austenitic (AFA) Stainless Steels

- Combination of good oxidation & 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.

BSE Image and EDS Results of DAFA29

- DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-0.1C-0.01B (wt.%) (as-hot-rolled)
  - Nb enrich precipitates and grain size ~40 μm

(a) BSE

(b) Nb, Fe

(c) Nb, Ti

(d) Matrix
BF&SAD of Precipitates in DAFA29

- DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-0.1C-0.01B (wt.%) (as-hot-rolled)
  - Fe$_2$Nb Laves phase precipitates + L1$_2$ precipitates in f.c.c. matrix
Thermo-mechanical Treatments (TMT) Procedures

DAFA29: Fe-14Cr-32Ni-3Nb-3Al-2Ti-0.3Zr-0.15Si-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 fine precipitates

Method#1
- Cold Rolling (90%)
- Anneal (800 °C)

Method#1 Control
- No Cold Rolling
- Anneal (800 °C)

Method#2
- Solutionizing Anneal (1200 °C)
- Cold Rolling (90%)
- Anneal (800 °C)

Method#2 Control
- Solutionizing Anneal (1200 °C)
- No Cold Rolling
- Anneal (800 °C)
The Effects of Cold Rolling on The Microstructures of TMT DAFA29

Method #1: Cold rolling + 800 °C
Method #2: 1200 °C + Cold rolling + 800 °C

Method #1 Control: 800 °C
Method #2 Control: 1200 °C + 800 °C
The Effects of Cold Rolling on The Microstructures of TMT DAFA29

Method #1
Cold rolling + 800 °C

Method #2
1200 °C + Cold rolling + 800 °C

Method #1 Control
800 °C

Method #2 Control
1200 °C + 800 °C
BF Images and SAD of DAFA29 after Thermo-mechanical Treatments

Method #1
Cold rolling + 800 °C

Method #2
1200 °C + Cold rolling + 800 °C

Method #1 Control
800 °C

Method #2 Control
1200 °C + 800 °C

2.4 h (100 nm)

2.4 h (200 nm)

2.4 h

2.4 h

24 h (270 nm)

24 h (450 nm)

24 h

24 h

240 h (1 µm)

240 h (2 µm)

240 h

240 h

500 nm

500 nm

500 nm

500 nm

100 nm

100 nm

100 nm

100 nm

N = 340
17.3 ± 3.7 nm

N = 389
27.6 ± 5.9 nm

N = 179
61.8 ± 14.2 nm

N = 126
71.0 ± 14.0 nm

N = 237
17.5 ± 2.5 nm

N = 188
36.0 ± 8.4 nm
BF TEM Image, EDS and CBED of Different Precipitates in TMT DAFA29

Laves-Fe$_2$Nb (4%)

B2-NiAl (2%)

L$_12$-Ni$_3$Al(Ti) (17%)

MC (M:Nb,Ti) (1%)
Synchrotron XRD Results

Lattice parameters

<table>
<thead>
<tr>
<th></th>
<th>Fe-f.c.c.</th>
<th>Fe₂Nb (a)</th>
<th>NiAl</th>
<th>Ni₃Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAFA29</td>
<td>3.611</td>
<td>4.820</td>
<td>2.888</td>
<td>3.604</td>
</tr>
<tr>
<td>Method #1: 2.4 h</td>
<td>3.599</td>
<td>4.812</td>
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<td>3.590</td>
</tr>
<tr>
<td>24 h</td>
<td>3.601</td>
<td>4.853</td>
<td>2.895</td>
<td>3.591</td>
</tr>
<tr>
<td>240 h</td>
<td>3.597</td>
<td>4.881</td>
<td>2.900</td>
<td>3.587</td>
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Lattice parameters

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<td>Method #2: 2.4 h</td>
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Lattice misfit of L₁₂ phase with f.c.c. matrix is calculated to be only ~0.28% for both treatments.

Method #1: Cold rolling + 800 °C
Method #2: 1200 °C + Cold rolling + 800 °C
Room Temperature Tensile Tests

**Method #1**
Cold rolling + 800 °C

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

DAFA29: YS: 560 MPa 22%

**Method #2**
1200 °C + Cold rolling + 800 °C

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

Method #1 Control
800 °C

- 2.4 h: YS: 747 MPa 20%
- 24 h: YS: 890 MPa 10%
- 240 h: YS: 760 MPa 8%

Method #2 Control
1200 °C + 800 °C

YS: ~660 MPa ~1%

DAFA29: YS: 560 MPa 22%
Hall-Petch Relationship for TMT DAFA29

Hall-Petch: $\sigma_{0.2} = \sigma_0 + KD^{-0.5}$,

where $\sigma_0 = 600$ MPa , $K = 230$ MPa$\cdot$µm$^{-0.5}$

$\sigma_0 = \sigma_{ppt} + \sigma_d + \sigma_{ss}$
**Cross-Sections and Fracture Surfaces for Samples Treated by TMT Methods**

<table>
<thead>
<tr>
<th>Method #1</th>
<th>Method #2</th>
<th>Method #1 Control</th>
<th>Method #2 Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold rolling + 800 °C</td>
<td>1200 °C + Cold rolling + 800 °C</td>
<td>800 °C</td>
<td>1200 °C + 800 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cross-Section</th>
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<tbody>
<tr>
<td><img src="image1" alt="Cross-Section" /></td>
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<td><img src="image4" alt="Cross-Section" /></td>
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<tr>
<th>Fracture surface</th>
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<tr>
<td><img src="image5" alt="Fracture surface" /></td>
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<tr>
<td>YS: 800 MPa</td>
<td>YS: 750 MPa</td>
<td>YS: 760 MPa</td>
<td>YS: 660 MPa</td>
</tr>
<tr>
<td>Elongation: 5.1 %</td>
<td>Elongation: 6.2 %</td>
<td>Elongation: 8.0 %</td>
<td>Elongation: 1.0 %</td>
</tr>
</tbody>
</table>
Tensile Tests at 700 °C

Method #1
Cold rolling + 800 °C

Method #2
1200 °C + Cold rolling + 800 °C

<table>
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<tr>
<th>Materials</th>
<th>Yield Strength (MPa)</th>
<th>Elongation (%)</th>
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<tr>
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<td>31</td>
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<tr>
<td>TMT 2.4h</td>
<td>384</td>
<td>35</td>
</tr>
<tr>
<td>TMT 24h</td>
<td>289</td>
<td>46</td>
</tr>
<tr>
<td>TMT 240h</td>
<td>218</td>
<td>59</td>
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<tr>
<td>TMT 240h</td>
<td>262</td>
<td>68</td>
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Strain Rate Jump Tests at 700 °C

\[ \sigma_y = C'(\dot{\varepsilon})^m \]

\[ m = \frac{\partial \ln \sigma(\varepsilon)}{\partial \ln \dot{\varepsilon}} \]

As-received DAFA29: \( m = 0.12 \)

TMT DAFA29: \( m = 0.19 \)
Dislocations in DAFA29 Tested in Different Strain Rates at 700 °C

5 x 10^{-2} \text{ S}^{-1} 

5 x 10^{-4} \text{ S}^{-1} 

5 x 10^{-6} \text{ S}^{-1}
Stacking Faults on Grain Boundaries
Laves Phase Precipitates

a) $5 \times 10^{-6} \text{ S}^{-1}$

b) 1100 1101 0001

1120 1100 1011
Stress Versus Temperature for as-received and TMT DAFA29
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 Laves phase, B2, and L1₂ precipitates

• Nanocrystalline steels processed through 90% cold rolling exhibit a dramatic increase in yield strength up to 1280 MPa at RT. The TMT alloys lose stress at 600 -700°C.

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

• The high temperature strength of both as-received and TMT DAFA29 are strain rate dependent at 700 °C
Future Work

• Continue high temperature tensile tests
  – Tests at different temperatures (600-800 °C)
  – Fracture behavior analysis

• Creep tests of TMT DAFA29
  – Study the creep mechanisms for as-received D29
  – Characterize the deformed creep samples
  – Determine dislocation/precipitate interactions
Strain Rate Jump Tests at 600 °C
Tensile Tests of D29 at Different Temperatures

![Graph showing tensile stress vs. tensile strain for different temperatures (600 C, 700 C, 800 C) with a strain rate of $5 \times 10^{-4} \text{ S}^{-1}$]