Microstructure and Mechanical Characteristics of Lanthana-Bearing Nanostructured Ferritic Steels

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Outline

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  - Oxide dispersion strengthened steels
  - Applications of ODS alloys as fuel cladding materials
  - Nanostructured ferritic steels

• **Objectives**
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  - Spark plasma sintering

• **Experimental**
  - Ball milling
  - Spark plasma sintering
  - Ion (Fe$^{+2}$) irradiation
  - Characterization

• **Results and Discussion**
  - Effect of milling time, SPS parameters and alloy composition
  - Microanalysis of oxide particles
  - Irradiation behavior

• **Conclusions**
Introduction
Oxide Dispersion Strengthened (ODS) Steels

- Excellent high temperature creep strength
- Good radiation damage tolerance
- Pioneering work by Fisher in 1982 (INCO): MA956/ MA957
- ODS steels developed for nuclear fission and fusion applications in the US, Japan and Europe

Conventional route for processing ODS alloys

Odette et al. (2008)
## Oxide Dispersion Strengthened Steels

<table>
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<tr>
<th>Alloy</th>
<th>Composition (wt %)</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Ti</th>
<th>Mo</th>
<th>W</th>
<th>C</th>
<th>Y₂O₃</th>
<th>Other</th>
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<td>MA956</td>
<td>bal.</td>
<td>20</td>
<td>4.5</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.05</td>
<td>0.5</td>
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<tr>
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<td>MA758</td>
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<td>3.4</td>
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<td>2.0Ta; 0.15Zr</td>
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<td>2.0</td>
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<td>1.1</td>
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<td></td>
<td>0.01</td>
<td>0.25</td>
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<td>2.0Ta; 0.15Zr</td>
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<td>1.5</td>
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<td></td>
<td>0.05</td>
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Special Metals Corporation
Plansee GmbH
Dour Metal S.A. (now Dour Metal s.r.o.)
**ODS Alloys for Nuclear Applications**

- **Fast reactors**: Significant challenges to materials selection (T > 700 °C and high neutron doses)
- **Limitations of some fuel cladding materials:**
  - Zirconium alloys: susceptibility to hydrogen embrittlement, allotropic changes at higher temperatures, poor creep properties
  - Austenitic stainless steels: swelling
  - SiC: low thermal conductivity, brittle
  - Ferritic-Martensitic (F-M) steels: susceptible to radiation hardening, embrittlement and relatively low strength at higher temperatures
- **Development of ODS ferritic steels for fast reactors:**
  - Dimensional stability
  - Thermal and radiation creep resistance
  - Helium traps (particle/matrix interface) and swelling resistance
  - Resistance to irradiation hardening/embrittlement
Nanostructured Ferritic Steels (NFSs)

- Strengthened by ultrafine Y-Ti-O-enriched nanofeatures:
  - Large numbers of stable nanometer-scale precipitates
  - Fine-scale bubbles
  - Reduced swelling
  - Stabilized grain boundaries
  - High creep strength

TEM micrograph and APT maps for MA957
Miller et al. (2004)
Objectives
Rare Earth Oxide Dispersions

- The most commonly used RE oxide: $\text{Y}_2\text{O}_3$
- Are there any potential alternative RE oxides?
- Meuller et al., (2000): Dispersion hardening effect of $\text{La}_2\text{O}_3$, $\text{Y}_2\text{O}_3$ and $\text{ZrO}_2$ in Mo-based ODS alloys demonstrated
  - Highest UTS and creep-rupture properties with $\text{La}_2\text{O}_3$

Free energy formation of oxides
Gupta et al. (2005)
Spark Plasma Sintering

- Sintering at lower temperatures, shorter dwell times and lower cost
- No texture or anisotropy
- Simultaneous uniaxial pressing and passing of electrical current
- Joule effect
- Local melting, evaporation of oxide layers, surface and volume diffusion enhance the neck formation

(a) Schematic of SPS and (b) densification mechanisms in SPS
Suárez et al., (2013)
Experimental
Experimental - Ball Milling

• The nominal composition (wt.%):
  o Fe-14Cr-1Ti-0.3Mo-0.5La$_2$O$_3$ (14LMT)
  o Fe-14Cr-1Ti-0.3Mo-0.3Y$_2$O$_3$ (14YMT)
  o Other compositions

• SPEX 8000M shaker mill:
  o Hardened steel balls (8 mm in diameter)
  o BPR of 10:1
  o Milling time for 0–20 h

• As-milled powder characterization:
  o XRD
  o SEM/EDS
  o Transmission electron microscopy (TEM) and atom probe tomography (APT) studies
Experimental - SPS

- Dr. Sinter SPS 515S with maximum current capacity of 1500 A and force of 30 kN
- Consolidating the milled powder via SPS at:
  - Temperature: 850-1050 °C
  - Time: 0-45 min
  - Pressure: 80 MPa
  - Heating rate: 100 °C/min
- Under vacuum (7×10^{-3} Torr)
- Tri-Gemini cylindrical graphite die (12.7 mm inner diameter)
Experimental - Characterization

- Density measurement
- Mechanical Properties
  - Vickers microhardness
  - Compression testing
- Microstructural Characterization
  - Sample preparation via electrojet-polishing and focused ion beam (FIB)
  - TEM (JEOL 2010 and FEI Tecnai TF30-FEG STEM)
  - APT (CAMECA LEAP 4000X HR)
Results & Discussion
The XRD pattern of 14LMT alloy as a function of milling time.
Effect of Milling Time on Milled Powder

Pasebani et al., Acta Materialia 61 (2013) 5605
Microstructure of Milled Powder

- Heavily deformed microstructure
- Very small crystallite size
- The nanoclusters (NCs) were Cr-, Ti-, La-, O- enriched: the mean radius 0.97 nm
- The nucleation of NCs that occurred during MA will be enhanced during SPS.
- Stable O-vacancy pairs enable nucleation of O-enriched NCs.

Pasebani et al., J. Nuclear Materials 434 (2013) 282
Effects of Milling Time on Kinetics

Volume diffusion

\[ \ln(YT \frac{dY}{dT}) = \ln\left(\frac{2.63\gamma\Omega D_v^0}{k\alpha^3 c}\right) - \frac{Q_v}{RT} \]

Grain boundary diffusion

\[ \ln(Y^2T \frac{dY}{dT}) = \ln\left(\frac{0.71\gamma b\Omega D_b^0}{k\alpha^4 c}\right) - \frac{Q_b}{RT} \]

• Activation energy for volume diffusion:
  o 247±6, 98±4 and 64±6 kJ/mol (0, 10 and 20 h)

• Activation energy for grain boundary diffusion:
  o 153±5, 164±4 and 144±15 kJ/mol (0, 10 and 20 h)
Effect of Milling Time on Sintered Microstructure

- Micron sized grains after sintering with no milling
- Nanograin after milling for 5 h and sintering
- A bimodal type of grain structure at longer milling times
- Such bimodal present in HIP or extrusion, too
- No strong texture
Effects of Milling Time on Microstructure (Contd.)

- No bimodal structure in unmilled/sintered 14LMT sample with average grain size 2.5 μm
- Bimodal grain size after 10 and 20 h
- Nanograins with high dislocation density and smaller particles
- Micron sized grains with low dislocation density and larger particles
Effect of SPS Parameters on Microstructure

(a) 14LMT alloy SPSed at 850 °C for 45 min

(b) 14LMT alloy SPSed at 950 °C for 45 min

(c) 14LMT alloy SPSed at 1050 °C for 45 min
Microanalysis of Oxide Particles

EFTEM elemental maps from raw data showing different elements in 14LMT alloy SPSed at 950 °C for 45 min

• Ti and La were mostly concentrated in the particles smaller than 10 nm.

STEM HAADF micrograph of particles

HRTEM micrograph of particle
Microanalysis of Nanoclusters

APT Analysis

- NCs - no. density $1.2 \times 10^{24}$ m$^{-3}$ with an average radius of $1.5 \pm 0.3$ nm

<table>
<thead>
<tr>
<th>Element</th>
<th>Bulk (at.%)</th>
<th>Matrix (at.%)</th>
<th>Cluster (at.%)</th>
<th>Matrix-corrected (at.%)</th>
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<tbody>
<tr>
<td>Cr</td>
<td>13.88±0.5</td>
<td>10.73±0.3</td>
<td>8.9±2.2</td>
<td>31.82±3.2</td>
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<tr>
<td>O</td>
<td>0.39±0.1</td>
<td>0.12±0.06</td>
<td>35.25±3.2</td>
<td>34.2±4.3</td>
</tr>
<tr>
<td>Ti</td>
<td>1.09±0.09</td>
<td>0.25±0.1</td>
<td>17.8±2.0</td>
<td>25.5±2.1</td>
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<tr>
<td>C</td>
<td>0.1±0.05</td>
<td>0.10±0.05</td>
<td>0.05±0.04</td>
<td>0.09±0.05</td>
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<tr>
<td>N</td>
<td>0.09±0.04</td>
<td>0.10±0.05</td>
<td>0.04±0.02</td>
<td>0.04±0.05</td>
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<tr>
<td>La</td>
<td>0.14±0.06</td>
<td>0.05±0.04</td>
<td>7.89±0.84</td>
<td>10.31±0.1</td>
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<tr>
<td>Mo</td>
<td>0.17±0.05</td>
<td>0.16±0.05</td>
<td>0.06±0.03</td>
<td>0.04±0.04</td>
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<tr>
<td>Fe</td>
<td>84.14±0.5</td>
<td>88.49±0.3</td>
<td>32.01±6.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>
The relative density values after SPS at 850, 950 and 1050 °C for 45 min were 94.3%, 97.8% and 98.3%, respectively.

Microhardness: 488, 561 and 324 HV, after SPS at 850, 950 and 1050 °C for 45 min, respectively.
Mechanical Properties

- Tensile test at room temperature: 0.2% YS - 836 MPa
- Strength is retained to a high level even at very high temperatures: Compression yield strength of 326 MPa at 800 °C

**Eng. Strain VS. Eng. Stress**

- Tensile test at strain rate of $10^{-3}$ s$^{-1}$
- Compression test at strain rate of $10^{-3}$ s$^{-1}$
Effect of Alloy Composition on Microstructure

(a) Fe-14Cr

(b) Fe-14Cr-0.5La$_2$O$_3$

(c) 14LMT

(d) 14YMT

Pasebani et al., J. Alloys & Compounds 599 (2013) 206
Effect of Alloy Composition on Mechanical Properties

Pasebani et al., J. Alloys & Compounds 599 (2013) 206
Effect of Alloy Composition on Oxide Particle Size

Pasebani et al., 2014
Ion Irradiation Experiments

- Texas A&M IMF Lab Accelerator (Dr. Lin Shao)
- Machine: IoneX 1.7 MV Tandetron accelerator
- Ion Source: SNICS sputter source
- At 30 and 500 °C for 10, 50, and 100 dpa
Microstructure of Irradiated 14LMT

Microstructure and dislocations:
- Un-irradiated

Microstructure and dislocations:
- Irradiated 500 °C for 100 dpa
Microstructure of Irradiated 14LMT

- Nanoparticles size and number density did not show any significant difference after irradiation

Nanoparticles: Un-irradiated

Nanoparticles: Irradiated 500 °C for 100 dpa

STEM HAADF from nanoparticles:
Irradiated 500 °C for 100 dpa
Conclusions (I)

- The nucleation of Cr-Ti-La-O nanoclusters during high energy milling was investigated.

- The role of ball milling was more complex than just the dissolution of the solute elements with a significant impact on the densification behavior.

- Adding La and Ti to Fe-14Cr matrix would significantly improve the mechanical behavior and microstructural stability.
Conclusions (II)

• Nano-oxide particles formed before and during the SPS, and hence the interaction of nanoparticles with dislocations and grain boundaries could be complex and impede further recrystallization.

• The APT analysis of the specimen sintered at 950 °C revealed high number density of $1.2 \times 10^{24} \text{ m}^{-3}$ of NCs with the average radius of 1.5 nm, enriched in Cr, Ti, La and O. At 1050 °C, the number density of NCs decreased to $0.66 \times 10^{24} \text{ m}^{-3}$ and the average radius increased slightly.

• High number of NCs along with the Hall-Petch mechanism, dislocation hardening and solid solution hardening led to a significant hardening in the sintered NFSs.
Acknowledgments

• This work was supported partly by the Laboratory Directed Research and Development Program of Idaho National Laboratory (INL), Contract DE-AC07-05ID14517, and partly by a grant of the Advanced Test Reactor National Scientific User Facility (ATR NSUF).

• Staff of the Microscopy and Characterization Suite (MaCS) facility at Center of Advanced Energy Studies (CAES).

• Dr. Kun Mo (University of Illinois / Argonne National Laboratory)