Advancing mechanism of oxide/matrix interface for the internal oxidation of austenitic stainless steel in liquid LBE

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31 August, 2023, St. Petersburg, Russia
Min WANG

◆ Associate Researcher of the Institute of Metal Research, CAS

◆ Specializing in austenitic structural nuclear materials R&D
  • Austenitic stainless steels (316Ti, 15-15Ti) for the cladding tubes of lead-cooled fast reactors;
  • Fe-Ni-based heat resistant steel (800H) for gas-cooled small reactors;
  • Alloy 690 for the steam generator tubes of pressurized water reactors.

◆ Doctor Degree in Materials Science and Engineering

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Founded in 1953 to serve the iron and steel industry

Structural Materials
- Super-alloys
- Ti alloys
- Nuclear alloys
- Composite
- Mg alloys
- Al alloys
- Steels

Functional Materials
- Ceramic
- Nanomater.
- Amorphous
- Carbon
- Magnetic
- Biomater.
- Energy mater.
- Absorb mater.
• More than 100 cooperation agreements with many foreign enterprises, research institutes and universities in the US, UK, Japan and Australia.

• Organizing the Lee Hsun Lecture Series in Materials Science.

• 300 foreign scholars visit the institute annually.

For more information, please visit: https://english.imr.cas.cn/
Nuclear Energy Development
Roadmap of China

PWR
Control rods
Pressuriser
Steam generator
Steam
Water
Fuel elements
Reinforced concrete containment and shield

LFR

GFR

SFR

MSR

Fusion reactor

Generation II+/III
(2000 2015)

Generation IV
(2020 2025 2030)

Future
Lead-Bismuth Eutectic (LBE)

- Small neutron absorption cross section
- Low melting and high boiling point
- Atmospheric pressure operation
- High heat-carrying/natural circulation capacity and chemical stability

SMR design friendly
- Natural coolant circulation
- Simple reactor core structure
- High core power density

Key role of assemblies:
- Containment of fuel
- Export of heat
- First barrier to leakage

!! Highly corrosive to metallic materials !!
### Parameters of Pb/Pb-Bi fast reactors in several countries and post-selected materials for key components

<table>
<thead>
<tr>
<th>Reactor type[2]</th>
<th>Power $M_W$</th>
<th>Core inlet temperature °C</th>
<th>core outlet temperature °C</th>
<th>cladding tube temperature °C</th>
<th>Cladding tube material</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid lead cooling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BREST 300</td>
<td>300</td>
<td>420</td>
<td>540</td>
<td>650</td>
<td>EP823</td>
</tr>
<tr>
<td>ELFR</td>
<td>600</td>
<td>400</td>
<td>480</td>
<td>550</td>
<td>T91-($\text{Al}_2\text{O}_3$)</td>
</tr>
<tr>
<td>ALFRED</td>
<td>125</td>
<td>400</td>
<td>480</td>
<td>500</td>
<td>15-15Ti- ($\text{Al}_2\text{O}_3$)</td>
</tr>
<tr>
<td><strong>Liquid LBE Cooling</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SVBR-100</td>
<td>75-100</td>
<td>320</td>
<td>480</td>
<td>600</td>
<td>EP823</td>
</tr>
<tr>
<td>CLEAR- I</td>
<td>10</td>
<td>300</td>
<td>385</td>
<td>450-507</td>
<td>F/M Steels</td>
</tr>
<tr>
<td>PBWFR</td>
<td>310</td>
<td>460</td>
<td>620</td>
<td>620</td>
<td>9Cr-ODS</td>
</tr>
</tbody>
</table>
LFR cladding materials

<table>
<thead>
<tr>
<th></th>
<th>Corrosion resistance</th>
<th>Radiation resistance</th>
<th>Embrittlement tendency</th>
<th>Stability</th>
<th>High temperature Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenitic stainless steel</strong></td>
<td>Prone to elemental dissolution</td>
<td>Ordinary</td>
<td>Barely</td>
<td>Good</td>
<td>Up to 650~700°C</td>
</tr>
<tr>
<td><strong>Ferritic/Martensitic stainless steel</strong></td>
<td>Thick oxide layer</td>
<td>Excellent</td>
<td>Easily</td>
<td>LAVES phase coarsening</td>
<td>Up to 550~600°C</td>
</tr>
</tbody>
</table>

**O concentration is controlled at 10^{-4}-10^{-6} wt.%**

<table>
<thead>
<tr>
<th>Temperature/ °C</th>
<th>&lt;500</th>
<th>500-550</th>
<th>550-600</th>
<th>600-650</th>
<th>&gt;650</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenitic SS.</strong></td>
<td>316L, 15-15Ti</td>
<td>+Si</td>
<td>15-15Ti+coating</td>
<td>Alumina Forming ASS</td>
<td></td>
</tr>
<tr>
<td><strong>F/M SS.</strong></td>
<td>T91, P122</td>
<td>(1) +Si :EP823, 05Cr18Si2; (2) T91+coating</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ODS</strong></td>
<td>-</td>
<td>-</td>
<td>9-12Cr-ODS</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**F/M steels --- popular choice of current LFR constructions and designs**

**Austenitic steel --- more suitable for SMR with higher core temperature**
LBE Corrosion of ASS.

Current status of research on corrosion behavior of austenitic stainless steel in LBE

**Oxide-layers formation**

Double-layer structure
Magnetite (Fe$_3$O$_4$) + Spinel (FeCr$_2$O$_4$)

**Beneficial effects of elements**

Si addition
reduced oxide thickness

**Influence of microstructure**

Grain boundaries, O in-diffusion
Twin boundaries, LBE penetration
Bulk Ni-riched zones in the inner oxide layer

- **Bright white areas** in the inner layer;
- Commonly found at grain boundaries;
- Enriched with Ni, poor in Cr;
- Selective oxidation elements: Cr, Si, Fe;
- Thought to be matrix remnants;

Hosemann-2013-Transmission electron microscopy

Charalampopoulos-2019-Transmission electron microscopy
New!

Ni enrichment in unoxidized matrix

Matrix oxidation remnants → Already formed before oxidation

Why didn’t we find them before?
**Ni-rich area distribution**

**Locations:** unoxidized matrix, O/M interface, internal oxidation area, original surface

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Mechanical polishing

- 2000h
- 6000h

Chemical etching

Layer-by-layer grinding

**Effects?**

**What?**

**How?**
Effects of Ni-rich areas

Deviating the diffusing path of oxygen

- Grain boundary---the short-circuit diffusion path of oxygen;
- Cr, Si and O react and form oxides on the grain boundaries;
- Ni-rich areas deviate the growing direction of intergranular oxides.

15-15Ti, \( T = 550 \, ^\circ\text{C}, t = 2000 \, \text{h} \)

Longitudinal section

Layer-by-layer grinding
Ni-riched structure and composition

<table>
<thead>
<tr>
<th>point</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
<th>Nb</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.97</td>
<td>4.35</td>
<td>0.48</td>
<td>0.09</td>
<td>3.46</td>
<td>0.64</td>
<td>16.13</td>
<td>73.62</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4.18</td>
<td>5.53</td>
<td>0.26</td>
<td>0.03</td>
<td>3.05</td>
<td>0.38</td>
<td>18.3</td>
<td>68.09</td>
<td>0.19</td>
<td></td>
</tr>
</tbody>
</table>

- Same crystal structure as austenite
- Similar lattice constants
- Ni content up to 70 wt.%
Ni-rich areas
Orientation and Composition

➢ Same orientation as the matrix
➢ Inducing grain boundary migration and serration
➢ Sharp composition interface
➢ Nucleating driven by Cr depletion and vacancies
➢ Growing to release more Cr supplying oxide growth
➢ Low O-affinity, delaying O intrusion

15-15Ti, $T = 550 \, ^{\circ}\text{C}$, $t = 2000 \, \text{h}$
➢ Materials problem is still a tough task for the development of lead-cooled SMR
➢ For high core temperature SMR, austenitic stainless steel is a choice
➢ Ni-rich areas formed on the O/M interface and the matrix nearby
➢ Inducing GB serration and delaying the intrusion pace of oxygen
➢ Releasing Cr and Si promoting the formation of GB oxides
Thanks for listening

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