Progress in TMSR Materials Research

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Outline

1. TMSR Materials Introduction

2. Research Progress of the UNS N10003 alloy
   - Fabrication, Corrosion & Mechanical Property Testing
   - Neutron and Ion Irradiation Activities

3. Research Progress of ultrafine-grain graphite
   - Property of Ultrafine-grain Graphite
   - Neutron and Ion Irradiation Activities

4. Next plan for TMSR materials research
Gen IV Fission Nuclear Reactors

- Sodium-Cooled Fast Reactor (SFR)
- Lead-Cooled Fast Reactor (LFR)
- Gas-Cooled Fast Reactor (GFR)
- Molten Salt Reactor (MSR)
- Supercritical-Water-Cooled Reactor (SCWR)
- Very-High-Temperature Reactor (VHTR)

Shanghai Institute of Applied Physics, Chinese Academy of Sciences

CAS "Strategic Priority Research Program" by SINAP-Thorium-based Molten-Salt Reactor Nuclear Energy System (TMSR)

- Research and development of molten salt reactors for thorium utilization as nuclear fuel, aimed for self-sustained Th/U fuel cycle.
- Research on multipurpose applications of high temperature nuclear energy.
Current Status of TMSR Program

Prototype Reactor
TMSR prototype reactor-SF0 (1:3)

Experimental Reactor
2MW TMSR-LF1

Demonstration Reactor
Design of TMSR Demonstration Reactor

2019.12
New Energy I Project

2020.12
New Energy II Project

New Energy III Project
Molten Salt Reactor - the Fourth Generation Fission Reactor

Service environments

- High temperature (650°C)
- High neutron doses (> 10 dpa)
- Corrosive coolant (FLiBe)

- MSR material is a specially developed high temperature corrosion resistant material

- Metal components in contact with molten salts can only be Nickel-based alloy
UNS N10003 alloy & Nuclear graphite

- The most promising structural materials for MSR: Hastelloy N alloy & GH3535 alloy (UNS N10003 alloy)

<table>
<thead>
<tr>
<th>Elem.</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>Nb</th>
<th>W</th>
<th>Ti</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy</td>
<td>7</td>
<td>16</td>
<td>5</td>
<td>-</td>
<td>Max 0.5</td>
<td>-</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Ni: high temperature, molten salt corrosion resistance
Mo: solution strength; Cr: oxidation resistance
Ti: irradiation embrittlement resistance

- Very good corrosion resistance in molten salt
- Operated successfully in MSRE for nearly five years
- Still the best choice for the MSR structural material

- Ultrafine-grain nuclear graphite used for MSR: NG-CT-50 & T-220

High purity: Boron equivalent < 2ppm
High density: > 1.7g/cm³
High Strength: Tensile > 20 MPa

Graphite properties used for MSR
- High isotropy: < 1.1
- Excellent High Temperature Chemical Stability (~3000 °C)
- Irradiation resistant materials (~30dpa)
- Micropore (<1m): Preventing molten salt infiltration
Research Progress of the UNS N10003 alloy

- Fabrication, Corrosion & Mechanical Property Testing
- Neutron and Ion Irradiation Activities
Nickel-based UNS N10003 alloy

- Technologies for the smelting, processing, and welding of a Nickel-based alloy, UNS N10003, China standard GH3535

GH3535: A nickel-based alloy with an outstanding corrosion resistance in molten salts

- Technologies for smelting (10 tons/ingot), processing & welding; performance comparable to Hastelloy N
- Deformation processing technologies for nickel-based alloys with high Mo, the largest UNS N10003 seamless pipes.

<table>
<thead>
<tr>
<th>Capability</th>
<th>China</th>
<th>US Haynes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipe Diameter</td>
<td>168mm</td>
<td>&lt;88.9mm</td>
</tr>
</tbody>
</table>

Seamless alloy pipes for the primary loop of MSR

Chinese Patent CN103966476A

Performance Test Report

Component (head)
Alloy corrosion control

- Solving the corrosion control in fluoride salt (GH3535 static corrosion rate < 2μm/y)

**Investigating Corrosion Mechanism**
- Salt impurities;
- Elements diffusion;
- Mass transfer;

**Developing Corrosion Control Technology**
- **Design Optimization**: Optimize the composition of alloy, degrade diffusion of Cr;
- **Salt Purification**: Modify purification technology, control the impurities content;
- **Surface modification**: FTD coating, improve the corrosion resistance;

**Comp. Optimization of Alloy (Cr)**

**Corrosion Depth (μm/y)**
- GH3535 exposed to impurity FLiNaK
- GH3535 exposed to high purity FLiNaK
- Without FTD Coating
- FTD Coating
A database of high-temp. mechanics of alloys has been established, the current data can support the operation of the experimental reactor for around 10 years.
Progress in Neutron Irradiation Test of TMSR Alloy

- Finish irradiation test on Hastelloy N @ T=650 °C, dose=2.5E19. PIE indicates that after irradiation the yield strength slightly increases, whereas the elongation keeps stable.

- Finish Irradiation test on Hastelloy N and GH3535 alloys (base metal & weld metal) @ T=40 °C, dose=2.5E19 & 1E20

- High Dose (3 -15 dpa) test on GH3535 alloys to be conducted in 2019 @PSI
Irradiation damage of UNS N10003 alloy

- ORNL report & FHR white paper: irradiation embrittlement

Considerations of Alloy N for Fluoride Salt-Cooled High-Temperature Reactor Applications

Weiju Ren, Govindarajan Muralicharan, Dane F. Wilson and David E. Holcomb

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Paper No. PVP2011-57029, pp. 725-736; 12 pages
doi:10.1115/PVP2011-57029

Fluoride-Salt-Cooled High Temperature Reactor (FHR)
Materials, Fuels and Components White Paper

Integrated Research Project Workshop 3

- Hardening embrittlement: displacement cascade damage
- Non-hardening embrittlement: He embrittlement (grain boundary segregation of helium bubbles)
Ion irradiation experiment (GH3535 alloy)

<table>
<thead>
<tr>
<th>Materials</th>
<th>GH3535 Weld</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of ions</td>
<td>8MeV Ni⁺</td>
</tr>
<tr>
<td>Ion dose (ions/cm²)</td>
<td>5×10¹⁴, 2×10¹⁵, 1.2×10¹⁶</td>
</tr>
<tr>
<td>Irradiation damage (dpa)</td>
<td>0.5, 2, 12</td>
</tr>
<tr>
<td>Temperature</td>
<td>RT &amp; 600 ºC</td>
</tr>
</tbody>
</table>

- An 1/5-power law dependence of the hardness increment on dpa is obtained.

\[ \Delta \sigma_p = \alpha \cdot M \cdot \mu \cdot b \cdot \sqrt{N \cdot D} \]

- The presence of defects is the main reason for irradiation hardening.
- Temperature effect of irradiation hardening.

Ion irradiation experiment (Hastelloy N alloy)

Irradiation damage peak region
(a) $1 \times 10^{17}$ion/cm$^2$ (b) $3 \times 10^{17}$ion/cm$^2$

AFM: Irradiation swelling of 2.67%
($3 \times 10^{17}$ion/cm$^2$)

- Helium bubbles formation under high temperature irradiation
- Helium bubbles cause the irradiation swelling and also the hardening / embrittlement

3 Research Progress of ultrafine-grain graphite

- Property of Ultrafine-grain Graphite
- Neutron and Ion Irradiation Activities
Fabrication of Ultrafine grain graphite

- Development of the ultrafine grain nuclear graphite for TMSR, involved in the establishment of ASME code of MSR nuclear graphite.

Nuclear graphite: moderator/ reflector

- Industrial production technologies of Chinese ultrafine-grain nuclear graphite
- Pore diameter < 1μm, ensured better infiltration resistance than existed nuclear graphite
- Establishing database of its performance & deep involvement in Intl. Std. for MSR nuclear graphite
Properties evaluation of ultrafine-grain graphite

- **Conventional properties of graphite**
  - Properties of thermal, mechanical, and physical, etc. (Already completed)

- **High-temperature properties of graphite materials**
  - High-temperature modulus of elasticity (In progress)
  - High-temperature thermology (thermal conductivity, coefficient of thermal expansion) (Already completed)

- **Non-conventional properties of graphite**
  - Fracture properties: Effect of cracks (dimension, morphology) on mechanical properties of graphite (In progress)
  - Fatigue properties: (S-N curve, Goodman curve, Sinosteel AMC) (In progress)

- **Performances of graphite materials in molten Li₂BeF₄ (FLiBe) salt**
  - Compatibility of molten FLiBe salt with graphite (Already completed)
  - Mechanical properties for salt-impregnated graphite (tensile strength, compressive strength, flexural strength) (Already completed)
## Conventional property data of ultrafine-grain graphite

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ultrafine-grained Graphite (1#)</th>
<th>Data Source</th>
<th>Ultrafine-grained Graphite (2#)</th>
<th>Data Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density(g/cm$^3$)</td>
<td>1.87±0.01</td>
<td>SINAP</td>
<td>1.79±0.01</td>
<td>SINAP</td>
</tr>
<tr>
<td>Specific Heat Capacity(J/g·K)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Thermal Conductivity(W/m·K)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Open Porosity(%)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Expansion Coefficient</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Boron Equivalent of Graphite Impurity(ppm)</td>
<td></td>
<td>Sinosteel AMC</td>
<td>Chengdu Carbon Co., Ltd</td>
<td></td>
</tr>
<tr>
<td>Pore Size(μm)</td>
<td>0.95</td>
<td>SINAP</td>
<td>0.83</td>
<td>SINAP</td>
</tr>
<tr>
<td>Young's modulus(GPa)</td>
<td></td>
<td>Sinosteel AMC</td>
<td>Chengdu Carbon Co., Ltd</td>
<td></td>
</tr>
<tr>
<td>Anisotropy Coefficient</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Two-parameter Weibull Distribution for Tensile Strength (MPa)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Tensile Strength(MPa)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Flexural Strength(MPa)</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
<tr>
<td>Fracture Toughness (K$_{IC}$) MPa.m$^{1/2}$</td>
<td></td>
<td>SINAP</td>
<td></td>
<td>SINAP</td>
</tr>
</tbody>
</table>

Conventional property data of ultrafine-grain graphite
Infiltration behavior of graphite exposed to molten FLiBe salt under different pressures

The higher the pressure, the greater the weight gain ratio

The threshold pressure for FLiBe salt infiltration for two grades of ultrafine-grain graphite are between 6 and 7 atm.
Neutron irradiation test of Chinese Graphite

- Over 300 samples were irradiated in HFETR at 650 °C to a dose of 0.4 dpa.
- Based on primary results, Chinese ultrafine-grain graphite shows very good stability in dimension and a great enhance in strength after irradiation.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>environment</th>
<th>Temperature</th>
<th>Fluence</th>
<th>PIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFETR (NPIC)</td>
<td>Inert gas</td>
<td>650 ±50 °C</td>
<td>5E20 n/cm² (E &gt;0.1MeV)</td>
<td>Dimension, weight, strength, modulus</td>
</tr>
</tbody>
</table>
Equivalence of ion and neutron irradiation effects

Irradiation induced anisotropic swelling of graphite crystal

- Neutron data
- Ion data

An first increase then decrease of graphite modulus induced by irradiation

- Neutron irradiation
- Xe ion irradiation

Ar ion irradiation induced anisotropic dimensional change

Micron-scale

- Ar ion irradiation induced anisotropic dimensional change

Macro-scale

- Low-dose proton-irradiation induced modulus increase

Pore structure evolution during irradiation

- After irradiation to 21dpa at 600 °C, much more contracted pores (71%) than expanded pores (12%) were found.
- Pore size distribution don’t show obvious changes after irradiation, indicating that irradiation won’t facilitate salt intrusion into graphite.

Red: shrinkage; Blue: expansion; Black: unchanged
Compatibility of irradiated graphite and FLiBe salt

- Graphite was irradiated with Xe ions to ~4.5 dpa and then tested in molten flibe salt.
- Testing in molten flibe salt did not have obvious effects on graphite’s surface morphology and Raman peaks, indicating that irradiated graphite has a great structural stability in molten flibe salt.

Characteristics of long-life nuclear graphite

- Neutron irradiation data of many nuclear graphites were collected and evaluated

Density's influence on irradiation life of nuclear graphite
Characteristics of long-life nuclear graphite

- Graphitization degree's influence on irradiation life of nuclear graphite
- Coke type's influence on irradiation life of nuclear graphite

- Moderate density (1.75 - 1.85 g/cm³)
- High degree of graphitization (high thermal conductivity)
- Petroleum coke seems better than pitch coke

✓ Extensive cooperation with the company to develop the new graphite, and achieve the irradiation performance modification.
Next plan for TMSR materials research
Main issues for the TMSR materials research

- Development of high-temperature (>800 °C) molten salt corrosion resistant Alloy;
- Te embrittlement modification of nickel-based alloys;
- Development of nuclear graphite with long irradiation life-time;
- Establishment of irradiation performance evaluation method for nuclear graphite using ion beam;
- Completion and upgrading of the current material database for molten salt reactor;
Thank you for your attention!