Advanced Materials for Future Nuclear Plants

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Fission Energy Workshop: Opportunities for Fundamental Research and Breakthrough in Fission
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Outline

- Brief history of nuclear power
- Effects of neutron bombardment on structural materials
  - “Five scourges” of radiation
- Prospects for development of high-performance radiation-resistant materials
  - Crucial role of nanoscale architectures

Note: focus will be on metallic alloys; ceramic composites will be discussed in the talk by Akira Kohyama
The Launching of Nuclear Energy Largely Preceded the Development of Modern Materials Science

Fusion and Gen IV fission energy systems should take maximum advantage of current and emerging materials and computational science tools.
Radiation Damage can Produce Large Changes in Structural Materials

- Radiation hardening and embrittlement ($<0.4 \ T_M, >0.1 \ dpa$)

- Phase instabilities from radiation-induced precipitation ($0.3-0.6 \ T_M, >10 \ dpa$)

- Irradiation creep ($<0.45 \ T_M, >10 \ dpa$)

- Volumetric swelling from void formation ($0.3-0.6 \ T_M, >10 \ dpa$)

- High temperature He embrittlement ($>0.5 \ T_M, >10 \ dpa$)

Advanced nuclear energy systems impose harsh radiation damage conditions on structural materials

- 1 displacement per atom (dpa) corresponds to stable displacement from their lattice site of all atoms in the material during irradiation near absolute zero (no thermally-activated point defect diffusion)
  - Initial number of atoms knocked off their lattice site during fast reactor neutron irradiation is ~100 times the dpa value
  - Most of these originally displaced atoms hop onto another lattice site during “thermal spike” phase of the displacement cascade (~1 ps)

- Requirement for structural materials in advanced nuclear energy systems (~100 dpa exposure):
  - ~99.95% of “stable” displacement damage must recombine
  - ~99.9995% of initially dislodged atoms must recombine

- Two general strategies for radiation resistance can be envisioned:
  - Noncrystalline materials
  - Materials with a high density of nanoscale recombination centers

*after S.J. Zinkle, Phys. Plasmas 12 (2005) 058101*
Recent Molecular Dynamics simulations have provided key fundamental information on defect production

- Effect of knock-on atom energy and crystal structure on defect production
- Subcascade formation leads to asymptotic surviving defect fraction at high energies

Large vacancy clusters are not directly formed in BCC metal displacement cascades

Yu. N. Osetsky and R.E. Stoller

\[ \text{Vacancies} \quad \text{interstitials} \]

\[ \text{Cu} \]

\[ \text{Fe} \]

$25 \text{ keV cascades}$

Yu. N. Osetsky and R.E. Stoller

Comparison of Void Swelling Behavior in Neutron Irradiated Austenitic and Bainitic/ferritic/martensitic Steels

Gelles 1996; Garner & Toloczko 2000; Klueh & Harries 2001

![Graph showing comparison of void swelling behavior in neutron irradiated steels.](image)
Swelling Resistant Alloys can be developed by Controlling the He Cavity Trapping at Precipitates

Mansur & Lee

These nanoscale precipitates also typically provide improved thermal creep strength
Stress-Temperature Design Window for Nb-1Zr

- **Sm (1/3 UTS)**
- **St (10^5 h, 2/3 creep rupture)**
- **Desired operating temperature regime**
- **Low ductility regime**
  - (ϕt > 1x10^{20} n/cm^2)
- **Radiation embrittlement regime**
  - (ϕt > 1x10^{20} n/cm^2)

Can we break the shackles that limit conventional structural materials to \(~300^\circ\text{C}\) temperature window?

Structural Material Operating Temperature Windows: 10-50 dpa

\[ \eta_{\text{Carnot}} = 1 - \frac{T_{\text{reject}}}{T_{\text{high}}} \]

Additional considerations such as He embrittlement and chemical compatibility may impose further restrictions on operating window.

Comparison of Gen IV and Fusion Structural Materials Environments

S.J. Zinkle, OECD NEA Workshop on Structural Materials for Innovative Nuclear Energy Systems, Karlsruhe, Germany, June 2007, in press

All Gen IV and Fusion concepts pose severe materials challenges
New structural materials with temperature windows >300ºC are needed for efficient development of Gen IV concepts.

Structural Material Operating Temperature Windows: 10-50 dpa

S.J. Zinkle, OECD NEA Workshop on Structural Materials for Innovative Nuclear Energy Systems, Karlsruhe, Germany, June 2007, in press
Conventional Alloy Development is a Slow and Expensive Endeavor

• 55°C improvement in upper operating temperature limit after 40 years development!!

• Improvement in computational thermodynamics could accelerate development of new materials
Evolution of Improved Steels has Paralleled Improvements in Nuclear Reactor Designs

- Gen-IV reactors should not be based on Gen-I structural materials!

Steels:
- Gen-1: HT9, EM12
- Gen-II: 9Cr-1Mo, HCM12
- Gen-III: E911, NF616, HCM12A
- Gen-IV: SAVE12, NF12
Historical development of improved high-temperature steels has exhibited slow and steady progress.


The graph illustrates the progression of maximum use temperature over time for different generations of high-temperature steels. Each generation is marked with specific designations and a note indicating an annual increase of 2.5°C. The timeline spans from 1920 to 2020, with notable advancements in each subsequent generation.
Recent progress in developing high-strength steels that retain high-toughness has been remarkable

- Generally obtained by producing high density of nanoscale precipitates and elimination of coarse particles that serve as stress concentrator points.
Modern computational thermodynamics reveals pathway to improve precipitation hardened stainless steels

Both 15%Cr-7%Ni alloys are within allowable chemical composition for PH15-7 Mo precipitation hardened stainless steel (UNS S15700)

Fe–1.0Al–0.09C–15.0Cr–1.0Mn–2.5Mo–7.25Ni–1.0Si wt(%) 

Fe–1.0Al–0.09C–14.0Cr–1.0Mn–2.0Mo–7.5Ni–1.0Si wt(%) 

“average” Cr, Mo, Ni

UNS S15700: 14.0-16.0 Cr, 6.50-7.75 Ni, 2.0-3.0 Mo

• Within alloy specifications, large differences can be expected with standard heat treatment
• Computational thermodynamics calculations can lead to composition and heat treatment optimization

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U. S. DEPARTMENT OF ENERGY

J.M. Vitek
Microstructural Evolution In Irradiated Stainless Steels Provided the Key for Developing Improved High Temperature Alloys

- **Reactant Effects** (ie. Ti, V+Nb enhance MC formation)
- **Catalytic Effects** (ie. Si enhances Fe₂Mo or M₆C)
- **Inhibitor Effects** (ie. C, P or B retard the formation of Fe₂Mo or FeCr sigma phase during aging, G-phase during irradiation)
- **Interference Effects** (ie. N forms TiN instead of TiC; N does not form NbN instead of NbC; therefore C and N can be added with Nb, but not Ti)

Result of microstructural modification:
- Formation of stable nanoscale MC carbide dispersions to pin dislocations
- Resistance to creep cavitation and embrittling grain boundary phases (ie. sigma, Laves)
- Resistance to dislocation recovery/recrystallization
Technology Transfer of CF8C-Plus Cast Stainless Steel

- MetalTek International, Stainless Foundry & Engineering, and Wollaston Alloys received trial licenses in 2005 (18 months after project start)
- Over 350,000 lb of CF8C-Plus steel have been successfully cast to date
  - Now used on all heavy-duty truck diesel engines made by Caterpillar (since Jan. 2007)
  - Solar Turbines (end-cover, casings), Siemens-Westinghouse (large section tests for turbine casings), ORNL, and a global petrochemical company (tubes/piping).
  - Stainless Foundry has cast CF8C-Plus exhaust components for Waukesha Engine Dresser NG engines

6,700 lb CF8C-Plus end-cover cast by MetalTek for Solar Turbines Mercury 50 gas turbine

80 lb CF8C-Plus exhaust component cast by Stainless Foundry for Waukesha NG reciprocating engine

Caterpillar Regeneration System (CRS) Housing
Development of New Alumina-Forming, Creep Resistant Austenitic Stainless Steel

- Designed for 600-800°C structural use under aggressive oxidizing conditions
  - superior oxidation resistance to conventional chromia-forming alloys
- Comparable cost to current heat-resistant austenitic stainless steels

Computational thermodynamics can be used to identify new heat treatment conditions for modified Cr-Mo steels.

- Proper austenitization temperature (red arrow)
- Limits for tempering temperatures (blue arrow)
Creep Properties of New 3 Cr Steels have Advantages Over Existing 2 1/4Cr and 9-12Cr Steels

- Creep resistance improved over Japanese 2.25Cr (T23,T24) steels
- May not need to be tempered for high thermal creep strength; no postweld heat treatment?
- Properties better than HT9 and as good or better than modified 9Cr-1Mo steel
  - Long-term creep behavior (>5000 h) still needs to be determined
- Two 50 ton heats procured by industry are being tested to obtain ASME code approval
- Improved creep resistance is due to fine V-rich MC needles formed during 1100°C normalizing

New Thermomechanical treatment (TMT) Process Applied to Commercial 9-12%Cr Steels Yields Improved Microstructure

- Commercial 9Cr-1Mo and 12 Cr steels were processed
- TMT (hot rolling) on 25.4–mm plates
  - Several TMT conditions were investigated
- Precipitates formed on dislocations introduced by hot rolling
- Precipitate dispersion is much finer than observed in conventionally processed 9-12Cr steel

Large Increase in Rupture Life of Modified 9Cr-1Mo at 650°C

- Thermo-mechanical treatment (TMT) of modified 9Cr-1Mo produced steel with over an order-of-magnitude increase in rupture life

New 12YWT Nanocomposited Ferritic Steel has Superior Strength compared to conventional ODS steels

- Atom Probe reveals nanoscale clusters to be source of superior strength
  - Enriched in O (24 at%), Ti (20%), Y (9%)
  - Size: $r_g = 2.0 \pm 0.8$ nm
  - Number Density: $n_v = 1.4 \times 10^{24}/m^3$

- Original $Y_2O_3$ particles convert to thermally stable nanoscale (Ti, Y, Cr, O) particles during processing

- Thermal creep time to failure is increased by several orders of magnitude at 800°C compared to ferritic/martensitic steels
  - ~2% deformation after ~2 years at 800°C, 140MPa

- Potential for increasing the upper operating temperature of iron based alloys by ~200°C

- Acceptable fracture toughness near room temperature

Theory Has Shown That Vacancies Play a Pivotal Role in the Formation and Stability of Nanoclusters in ODS steel

The presence of Ti and vacancy has a drastic effect in lowering the binding energy of oxygen in Fe (C. L. Fu and M. Krcmar).
Conclusions

• Existing structural materials face Gen IV reactor design challenges due to limited operating temperature windows
  – May produce technically viable design, but not with desired optimal economic attractiveness

• Substantial improvement in the performance of structural materials can be achieved in a timely manner with a science-based approach

• Design of nanoscale features in structural materials confers improved mechanical strength and radiation resistance
  – Such nanoscale alloy tailoring is vital for development of radiation-resistant structural materials for advanced fission reactors

• Continued utilization of modern materials science techniques would be valuable to uncover new phenomena associated with localized corrosion, ultra-high toughness ceramic composites, ultra-high strength alloys, etc.
Comparison of Service Environments for Fusion and Gen IV Fission Reactors

Common themes: higher operating temperature (improved thermodynamic efficiency)

higher radiation damage levels (more compact design and longer design lifetime)
Effect on Neutron Irradiation on DBTT of Ferritic/martensitic Steels

![Graph showing the effect of neutron irradiation on DBTT of various steels.](image)

- Conventional alloys: MANET I, 12Cr-1MoV(HT9), 9Cr-1MoVNb
- F82H-IEA
- F82H
- Eurofer 97 (NRG data; replotted)

Reactor: HFR, HFIR
Irradiation: 300-400°C