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Materials for Nuclear Energy
Irradiation Embrittlement of
Pressure Vessel Steels (Ferritic)

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Most slides taken from a lecture by Berquist & Burke on “Pressure Vessel Steels”
Outline

1. Radiation Damage Event
2. Atom Displacement
3. Damage Cascade
4. Point Defect Formation & Diffusion
5. Loss of, Sinks for Point Defects
6. Radiation Induced Segregation
7. Radiation Induced Dislocations
8. Radiation Induced Voids, Bubbles
9. Radiation Effects on Phase Stability
10. Ion Bombardment, Implantation
11. Surrogates for Neutron Irradiation
12. Radiation Effects on Hardening, Deformation
13. **Radiation Effects on Fracture Toughness, Embrittlement**
14. Radiation Effects on Creep and Growth
15. Radiation Effects on Corrosion: emphasis on Stress Corrosion Cracking (SCC)
The Charpy test uses a square bar with a small notch in it. The further the pendulum swings after breaking the specimen, the less energy was absorbed in the impact, and *vice versa*. Higher toughness results in higher energy absorbed. The test is effectively a dynamic test because the strain rates are much higher than in a fracture toughness test. Brittle materials exhibit low toughness; conversely, ductile materials exhibit high toughness.
Fractography

- These micrographs contrast the appearance of *ductile* and *brittle* fractures at the microstructural scale.

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*Figure 8.35* Cleavage fracture surface (left) in a 49Co-49Fe-2V alloy, and dimpled rupture (right) in a low-alloy steel. (Photos courtesy of A. Madeyski, Westinghouse Science and Technology Ctr., Pittsburgh, PA.)
**Toughness vs. Temperature**

- Most metals are ductile at high temperature and brittle at low temperature. The transition in toughness is, as we shall see, quite sharp so we can define a *Ductile-to-Brittle Transition Temperature*, DBTT.
- FCC metals are the exception because they do not exhibit a DBTT but (typically) maintain high toughness down to cryogenic temperatures.
- BCC metals all exhibit a DBTT, which for Fe is around room temperature. This means that one must be careful with alloying to avoid having a too high DBTT.

This WW-2 era “Liberty” ship, with a welded steel hull, failed by brittle propagation of a crack while moored in dock! The fracture toughness of the steel was too low for the design.
**General Points**

- Along with hardening, irradiation of metals results in losses of ductility and decreases in fracture toughness.

- The most serious issue of all is the increase in the Ductile-to-Brittle Transition Temperature or DBTT in (ferritic) pressure vessel steels, which is determined at 41 J (slightly higher in Russia). Note the shift to the right (higher T) and decrease in upper shelf energy in the graph.

- This is a serious issue because, to first order, the increase in temperature is linear in the dose (dpa). Operating a pressure vessel at a temperature where the fracture toughness is low implies that a catastrophic burst is at least potentially possible.

- This issue was also addressed in the NATO conference article by Odette.

- As will be addressed by Fyfitch, stainless steels and nickel alloys also experience loss of ductility, especially once swelling has started.
Radiation Effects

• Focus on metals (steel)

• Effects include:
  – Hardening
    • Increase in yield stress & UTS
  – Embrittlement & Fracture
    • Reduced plastic or creep deformation/reduced ductility
    • Brittle fracture with rapid crack growth
  – Void Swelling
    • Interstitial loops cause expansion; if vacancies agglomerate into voids, then no contraction corollary
    • Requires sufficient thermal activation (energy) for agglomeration; not so important for recombination
  – Irradiation Creep
    • Can be “irradiation enhanced” or “irradiation induced”

• Effects depend on level of irradiation & material temperature
Summary of Effects

Integrated fast neutron* flux refers to fission reactor neutron spectrum but can be related to high energy fusion neutrons too.

Important for fission fuel & cladding, and for fusion first wall and blanket.

*See Supplemental slides
Summary of Effects

Thermal & epithermal neutrons → more prevalent in reactor structure
Fig. 18.15  Effect of fast-neutron irradiation on the tensile properties of reactor steels. (a) Face-centered cubic structure. (b) Body-centered cubic structure.
Pressurized Thermal Shock (PTS)

- During normal operation, embrittlement of the vessel wall occurs by fast neutron damage, which results in reduction of $K_{lc}$, or alternatively, an increase in the ductile-to-brittle transition temperature ($\Delta T$) as measured in Charpy tests.
- Brittle fracture is not a problem during normal operation because the temperature is high (~300°C) and the main stress on the vessel is due only to residual stresses and the membrane (hoop) stress due to the internal pressure in the vessel.
- If cold water from the emergency core cooling system (ECCS) should be injected into the system (because of a LOCA= Loss of Coolant Accident) near the end of the vessel lifetime when $K_{lc}$ is lowest due to irradiation embrittlement, brittle failure is possible.
- The rapid reduction in the inner wall temperature during ECCS creates tensile thermal stresses which add to existing tensile stresses (from the pressurization).
- Small flaws (cracks) on the inner wall of the vessel may have grown throughout the reactor lifetime due to fatigue during shutdown and startups.
- If the increased crack size and the corresponding increase in the applied stress intensity factor ($K_I$) exceeds $K_{lc}$, the crack will grow rapidly.
- The crack may not penetrate the entire vessel wall because temperature, stress and irradiation dose change through the wall thickness. The crack will stop when the applied $K_I$ reaches the crack arrest toughness $K_{ia}$. [Wirth]
Remedies for PTS Problem

• [from Wirth notes]
• For new pressure vessels, minimize the Cu content of the steel in particular, also avoid high Ni and Mn contents.
• Russian reactor vessel codes were more concerned with Cu and P.
• For old, existing pressure vessels, take following actions:
  - anneal critical components
  - manage the position of high burn-up versus new fuel elements
  - use reflector parts that can handle neutron irradiation such as tungsten
  - heat make up water (not practicable?!)
Microstructural evolution: ferritic steels

- Here we discuss the response of ferritic steels, such as those used for pressure vessels
- For $T<\sim 350 \, ^\circ C$
  - Depleted zones & vacancy clusters are stable “black dots”, which are clusters of solute atoms (esp. Cu, Mn, Si, Ni) too small to resolve in a transmission electron microscope
  - Increased neutron fluence $\rightarrow$ increased “black dot” density
- For $T>\sim 350 \, ^\circ C$
  - Microstructure is completely different!
  - Point defects mobile
  - Dislocation loops & voids form
Materials Properties of Ferritic Steels
Key Embrittlement Property: Toughness

Ductile-to-Brittle Transition Temperature or DBTT is determined at 41 J
Mechanical Properties of Pressure Vessel Steels

- Impact properties of a standard sized Charpy Test
- Key parameter is Energy Absorbed during fracture
- Perform tests over a range of temperatures – plot provides a standard curve
  - Sigmoidal shape
  - Upper Shelf Energy
  - Lower Shelf Energy
  - 30 ft-lb “Ductile to Brittle Transition Temperature”

Table 3-1. Typical PWR pressure vessel steels with their chemical composition and mechanical properties (from the EPRI Reactor Pressure Vessel Materials Database).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Plant</th>
<th>Cu</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>YS (ksi)</th>
<th>RT\textsubscript{NDT} (°F)</th>
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<tbody>
<tr>
<td>SA302B</td>
<td>Point Beach-1</td>
<td>0.16</td>
<td>—</td>
<td>0.013</td>
<td>0.020</td>
<td>62.9</td>
<td>—</td>
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<td></td>
<td>(2 heats)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SA302B</td>
<td>Palisades</td>
<td>0.23</td>
<td>0.49</td>
<td>0.014</td>
<td>0.021</td>
<td>63.8</td>
<td>14</td>
</tr>
<tr>
<td>modified</td>
<td>(4 heats)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SA533B-1</td>
<td>Diablo Canyon-1</td>
<td>0.12</td>
<td>0.52</td>
<td>0.011</td>
<td>0.014</td>
<td>65.4</td>
<td>5</td>
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<tr>
<td></td>
<td>(5 heats)</td>
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<td></td>
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<tr>
<td>SA533B-1</td>
<td>Vogtle-1</td>
<td>0.07</td>
<td>0.60</td>
<td>0.007</td>
<td>0.014</td>
<td>66.6</td>
<td>19</td>
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<tr>
<td>low Cu/P</td>
<td>(4 heats)</td>
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<tr>
<td>SA508-2</td>
<td>North Anna-1</td>
<td>0.15</td>
<td>0.79</td>
<td>0.013</td>
<td>0.014</td>
<td>73.4</td>
<td>28</td>
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<tr>
<td></td>
<td>(3 heats)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>SA508-3</td>
<td>Braidwood-1</td>
<td>0.04</td>
<td>0.72</td>
<td>0.008</td>
<td>0.007</td>
<td>64.1</td>
<td>-15</td>
</tr>
<tr>
<td></td>
<td>(3 heats)</td>
<td></td>
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Ferritic RPV Steels: Effects of Irradiation/Service Degradation

• Long term degradation of RPV Steels has been observed – shift in ductile to brittle transition and reduction of upper shelf energy
• Degradation occurs by “hardening and embrittlement”
• Hardening is due to
  – irradiation induced crystal damage/defects (e.g. vacancies, interstitials, dislocation loops and debris, )
  – formation of nanoscale clusters enriched in solute
  – Current thinking points to Mn-Si-Ni precipitates that only form at low temperatures with kinetics enhanced by irradiation
• Hardening of the material matrix will enhance any existing susceptibility to embrittlement.
Irradiation Hardening of Low Alloy Steels
Microstructural Features

• All features are on sufficiently fine scale that….
• High resolution microscopy and microanalysis are required to observe defects
• Multiple techniques are required to separate out size and chemistry effects
• Heavily dislocated structures obscure observation of other features
• Field Ion Microscopy (FIM) results have identified “solute enriched clusters” rather that “copper precipitates” as solute hardening
• Voids and dislocation structures observed by Transmission Electron Microscopy (TEM)
• Advanced Analytical Electron Microscopy (AEM) can now be used to resolve local chemistry variations
• The Atom Probe*, combined with atomistic modeling, has been particularly useful for understanding the generation of solute clusters in steels.

* 3DAP, successor to the field ion microscope, where atoms are removed from the tip of a sharp needle-shaped specimen one at a time, sometimes with the aid of laser light, and analyzed in a mass spectrometer
Microstructures of Irradiated Pressure Vessel Steels – Solute Clustering

Fig. 1. 3DAP atom maps of the solute distributions in RPV surveillance test specimens of Doel-2. (a) $0.83 \times 10^{19}$ n/cm², (b) $5.1 \times 10^{19}$ n/cm².
Effect of Irradiation and Annealing on Hardness of A533 Gr 4 (3.5Ni) RPV Steel
(M.G. Burke et al., in “Effects of Radiation on Materials” ASTM STP-1447, 2002))

Solute cluster related hardening cannot be annealed out, unlike vacancy related hardening.
**Solute clusters**

- Why is Cu a problem? Odette [1984 *Scripta*] points out that the solubility of Cu at 290° C is about 0.0002%, which is far less than the typical level of 0.01% encountered. The ratio is 50 which implies a large driving force for precipitation. He further notes that the cleavage stress (seen at low temperatures in the *lower shelf*) is unlikely to be sensitive to irradiation because it is controlled by carbides that are too coarse to be affected by irradiation. Intergranular embrittlement is also absent in this class of steels. Therefore it is increases in strength that lead to increases in the DBTT.

- Modern analysis clearly points to fine precipitates of Mn-Ni-Si as being the culprits for hardening [2014 *Acta* Wells *et al.*].
Atom probe reconstructions

Fig. 2. Atom maps for the highest-Ni content, Cu-free (top), and high-Ni–Cu content (bottom) alloys irradiated to high fluence.
Toughness : Impact Testing

- Impact properties of a standard sized Charpy Test
- Key parameter is Energy Absorbed during fracture
- Perform tests over a range of temperatures – plot provides a standard curve
  - Sigmoidal shape
  - Upper Shelf Energy
  - Lower Shelf Energy
  - 30 ft-lb “Ductile to Brittle Transition Temperature” (DBTT)
- Differences in Materials
  - Change in Upper Shelf Energy (USE)
  - Shift in DBTT

Figure 3-2. Charpy V-notch surveillance data, showing radiation embrittlement effects.
*Change in Toughness vs. Hardening*

- The upper figure is a Davidenkov diagram, showing the effect of hardening on embrittlement.
- The second fig. shows the remarkably (near-)linear relationship between the fractional decrease in the upper shelf energy, plotted versus the hardening increment.
Effect of Cu

An A-302B steel was made with various levels of Cu and Ni. See the ref. for full details.

Note that the low copper steel, upper panel, shows a much smaller increase in DBTT compared to the high Cu+Ni steel, lower panel.

Recall that European PWRs+BWRs generally have lower Cu contents in their PV steels.
- In the same paper, the effect of post-irradiation heat treatments was investigated.
- In this case, the DBTT was significantly reduced, although not completely back to the un-irradiated state.
- The latter point is the same as that noted on slide no. 16
Summary

- Irradiation brings about increases in hardness and yield stress in structural materials used in reactors.
- Reactor Pressure Vessel (RPV) Steels are ferritic and exposed to moderate irradiation at mildly elevated temperatures – the concern is the steady increase in hardness and consequent decrease in Upper Shelf Energy (USE) and increase in the Ductile-to-Brittle-Transition Temperature (DBTT). The key scenario is a Loss-of-Coolant accident (LOCA) coupled with Pressurized Thermal Shock, leading to catastrophic crack propagation.
- The magnitude of hardening depends on the composition: Cu in steel (a tramp element, generally) strongly increases the radiation hardening.
- The main contributors to hardening are voids, dislocation loops, bubbles and network dislocations. However, clustering of solutes also appears to contribute to hardening (but is hard to quantify).
- The hardening dependence on dose rate is often sub-linear.
Supplemental Slides
Neutron energy distribution ranges

- Moderated and other, non-thermal neutron energy distributions or ranges are listed in the table below:
- Fast neutrons have an energy greater than 1 eV, 0.1 MeV or approximately 1 MeV, depending on the definition.
- Slow neutrons have an energy less than or equal 0.4 eV.
- Epithermal neutrons have an energy from 1 eV to 10 keV.
- Hot neutrons have an energy of about 0.2 eV.
- Thermal neutrons have an energy of about 0.025 eV.
- Cold neutrons have an energy from $5 \times 10^{-5}$ eV to 0.025 eV.
- Very cold neutrons have an energy from $3 \times 10^{-7}$ eV to $5 \times 10^{-5}$ eV.
- Ultra cold neutrons have an energy less than $3 \times 10^{-7}$ eV.
- Continuum region neutrons have an energy from 0.01 MeV to 25 MeV.
- Resonance region neutrons have an energy from 1 eV to 0.01 MeV.
- Low energy region neutrons have an energy less than 1 eV.
Effects on Mechanical Properties

- Defects produced by neutron irradiation (coupled with time and temperature in some cases):
  1. Point defects
  2. Impurity atoms
  3. Vacancy clusters (depleted zones)
  4. Dislocation loops
  5. Dislocation lines
  6. Cavities (voids & He bubbles)
  7. Precipitates (e.g. carbides)

- 1,2 do not (directly) cause hardening; 3-7 do

- Two strengthening mechanisms:
  - Source hardening (increased stress required to initiate dislocation motion)
  - Friction hardening (moving dislocations impeded by obstacles that are close to or in the slip plane)