On the Cu/P and Mn/Ni Interactions During Irradiation of A533B Reactor Pressure Vessel Steels

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Objectives and Motivation

- Long term operation
- Available databases
  - Multiple–variable experiments
  - Difficulty to determine the effect of a single variable but also combined effects
- Selection of key elements Cu, P, Ni and Mn
- Cu/P and Ni/Mn synergies
  - RADAMO-13 irradiation program
  - Systematic single–variable experiments with Cu/P and Ni/Mn
  - Irradiation hardening and microstructure
Experimental Conditions

- Irradiation space optimization
  - Transition temperature determination requires a higher number of specimens
  - Tensile tests: miniature specimens (triplicated)
  - At least a factor of 4 in space gain

- Excluding non-hardening embrittlement (often the case)
  - Proportionality between irradiation hardening and embrittlement
  - Load diagram illustration

- Chemically-tailored composition
  - Reference: A533B Cl.1
  - Targeted elements: **Cu, P, Ni** and (Mn) (→ Cu/P and Ni/Mn interaction)
    - Experimental evidence
    - Artificial Neural Networks
Consistency between the various properties

- Flow properties: strain rate and temperature dependence
- Characteristic loads – SFA
- Crack arrest → NDT
- Micro-cleavage fracture stress
- $T_1 - T_0$ master curve correlation

⇒ **Simple tensile tests** can provide important information when baseline condition is well characterized
Dominant Elements

736 data points; $\Phi_{\text{ref}} = 2.5 \times 10^{19} \text{ n/cm}^2$

72 data points; $\Phi_{\text{ref}} = 11.4 \times 10^{19} \text{ n/cm}^2$

Major influence $\Rightarrow$ Cu and Ni

Major influence $\Rightarrow$ Cu, Ni and P

Key elements: Cu, Ni and P (confirmed by ANN: see JNM 408 (2011) 30-39).
<table>
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<tr>
<th>n°</th>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Mn</th>
<th>Ni</th>
<th>Cu</th>
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**Ni/Mn Effects : 9 steels**

<table>
<thead>
<tr>
<th>Ni</th>
<th>Mn</th>
<th>Cu</th>
<th>P</th>
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<td>~0.8</td>
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<tr>
<td>high</td>
<td>~1.7</td>
<td>~1.8</td>
<td>0.05</td>
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**Cu/P Effects : 12 steels**

<table>
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<th>P</th>
<th>Ni</th>
<th>Mn</th>
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<td>~0.010</td>
<td>0.7</td>
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<tr>
<td>low</td>
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<td>~0.020</td>
<td>1.50</td>
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<tr>
<td>medium</td>
<td>~0.14</td>
<td>~0.030</td>
<td>0.7</td>
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<tr>
<td>high</td>
<td>~0.30</td>
<td>~0.51</td>
<td>1.50</td>
</tr>
</tbody>
</table>

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**Materials**

- Cu/P Effects : 12 steels
- Ni/Mn Effects : 9 steels

- all ‘low’
- all ‘high’
→ Same heat treatments for all steels
Unirradiated μstructure (Ø8.5 mm)

Irradiated tensile (Ø4.5 mm)

n° 6 + 8 + 10: medium low fluence
n° 31 + 33 + 35: low fluence
n° 15 + 17 + 19: medium high fluence
n° 22 + 24 + 26: high fluence
Cu/P Effects
Role of Cu/P in Irradiation Hardening and Embrittlement

Question: how does Cu interact with P?
Combined Cu/P Effect on Irradiation Hardening

The effect of Cu-content significantly larger than P-content effect

\[ \Delta \sigma_{y_0} \] before irradiation

13 – 40 MPa
Cu/P-Effects on Irradiation Hardening

Constant slope at all Cu-levels $\Rightarrow$ No synergy between P and Cu (at 290°C PWR-relevant) [! Might not hold for other $T_{irrad}$]
Ni/Mn Effects
Objective and Motivation

- The role of Mn was reported by many authors to significantly affect irradiation hardening and embrittlement in particular in presence of high Ni-content (e.g. Ringhals welds)
- Modeling supported by microstructural data suggest also that Mn should play some role as it is found in the solute clusters
- Experimental data on model alloys were also suggesting an important effect of Mn (Yabuuchi data)

- Objective: how Ni and Mn interact
  - Individual effect of Ni versus individual effect of Mn-content
  - Interaction Ni/Mn
  - Does the amount of Mn affects directly or indirectly irradiation hardening
Motivation: Mn effect

Model alloys

![Tensile Stress vs Tensile Strain graph](image)

From K. Yabuuchi, JNM 414 (2011) 498–502

Commercial alloys

![Mn-effect graph](image)


![Adjusted yield strength increase graph](image)

From LONGLIFE, R-5089 (2010)

adjusted to account for Cu, P and Ni differences

---

<table>
<thead>
<tr>
<th>Mn Content (at.%)</th>
<th>Fe-Mn binary alloy (0.09 dpa)</th>
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<tbody>
<tr>
<td>0.69% Mn</td>
<td><img src="image" alt="Graph" /></td>
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<tr>
<td>0.82% Mn</td>
<td><img src="image" alt="Graph" /></td>
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<tr>
<td>1.40% Mn</td>
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</tr>
<tr>
<td>2.10% Mn</td>
<td><img src="image" alt="Graph" /></td>
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</table>

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0.69%Mn  
0.82%Mn  
1.40%Mn  
2.10%Mn  

adjusted yield strength increase $\Delta \sigma_y$ (MPa)

$\Delta \sigma_y$ vs neutron fluence ($10^{19}$ n/cm², E>1MeV)
No Effect of Mn-content on Low Ni Steels

$\Delta \sigma_{y_0}$ before irradiation 17 – 33 MPa
No Effect of Mn-content on Medium Ni Steels

\[ \Delta \sigma_y^0 \text{ before irradiation} = 10 - 47 \text{ MPa} \]
Significant Effect of High Mn-content of High Ni Steels

$\Delta \sigma_y$ before irradiation

22 – 41 MPa

yield strength increase, $\Delta \sigma_y$ (MPa)

neutron fluence ($10^{19}$ n/cm$^2$, $E>1$MeV)

0.01%Mn
0.80%Mn
1.78%Mn

Ni/Mn-Synergistic Effects
Cu=0.05%
P=0.010%
Ni=1.70%

±25 MPa

Ni/Mn-Synergistic Effects
Cu=0.05%
P=0.010%
Ni=1.70%

$\pm 25 \text{MPa}$

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Clear Mn-content Effect at High Mn-content (~1.7%)

Ni/Mn Effects
Cu=0.05% ; P=0.010% ;
irradiated condition
$\Phi_{\text{average}} \approx 5.6 \times 10^{19} \text{ n/cm}^2$, $E>1\text{MeV}$ ($\pm 1$)
Effect of Ni– and Mn– Content on the Initial Tensile Properties

<table>
<thead>
<tr>
<th>Ni%</th>
<th>Mn%</th>
<th>Σi(Fe)</th>
<th>σy</th>
<th>σu</th>
<th>σu−σy</th>
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<td>392</td>
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<td>121</td>
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<td>542</td>
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<td>1.78</td>
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<td>492</td>
<td>792</td>
<td>300</td>
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</tbody>
</table>

*all other alloying (excl. Ni and Mn) and trace elements <~1%

⇒ The high Ni/high Mn steel has definitely another behavior than other steels including RPV materials in both unirradiated and irradiated conditions.
Effect of Ni/Mn on the Flow Curve

- Distinct strain hardening behavior of the high Ni/High Mn steel
Unirradiated Condition  TEM Examination

Enriched phase: 3.4 Mn / 2.6 Ni (wt%)  
Complex structure (mainly bcc)

Bainite: 1.7 Mn / 1.8 Ni (wt%),  
with (Fe,Mn)$_3$C and Mo$_2$C carbides

Before deformation:  
Enriched phase is partially twinned  
from martensite transformation

After deformation (~12%):  
Progressive martensite tranformation  
(→ cfr. TRIP steel)

Before deformation :
Before deformation :

1 μm

100 nm

Before deformation :

After deformation (~12%):

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Progressive martensite tranformation  
(→ cfr. TRIP steel)
**Irradiated Condition**

**TEM Examination**

**Undeformed**
- Similar phases as in unirradiated
- No visible radiation damage

**Deformed (~11%)**
- No progressive martensite transformation

*Work in progress …*
Pre-straining + Annealing removes deformation-induced martensitic transformation of the high Ni/high Mn steel
Conclusions

Within the limits of the present experimental data (composition variables, irradiation conditions)

- On the Cu/P effects
  - Cu is clearly and by far the most radiation-sensitive element
  - The effect of P is relatively small
  - No synergy between these Cu and P (at this $T_{\text{irrad}}$)

- On the Ni/Mn effects
  - Ni and Mn effects are significantly lower in comparison to Cu-effect
  - No synergy between Ni and Mn is observed except for the high Ni/high Mn steel (1.7%Ni/1.8%Mn)
  - TEM examination revealed the presence of a second phase (NiMn-rich phase)
  - 1.7%Ni/1.8%Mn steel significantly higher work hardening capacity
  - Behavior attributed to martensitic transformation during deformation (twins)
Closing Remarks

- The conclusions on Cu/P synergistic effects drawn from this work should be confirmed
  - at lower irradiation temperature (260°C or lower) where P-contribution is expected to significantly increase
  - eventually new batch of steel with higher P-content (>0.05%)
- The conclusions on Ni/Mn synergistic effects drawn from this work should be confirmed
  - at higher fluence levels (> $1 \times 10^{20}$ n/cm$^2$)
  - at lower irradiation temperature (260°C or lower)
  - Performing experiments on a new batch of 1.7%Ni/1.8%Mn with adapted heat treatment avoiding the formation of the unwanted secondary phase and leading to moderate work hardening (long term)
- TEM examination (in progress) + additional microstructural analysis (APT)