Ultra low tin quaternary alloys PWR performance – Impact of tin content on corrosion and mechanical resistance

V. Chabretou¹, P.B. Hoffmann², S. Trapp-Pritsching², G. Garner³, P. Barberis⁴, V. Rebeyrolle⁴, J.J. Vermoyal¹

¹ AREVA NP SAS, ² AREVA NP GmbH, ³ AREVA NP Inc, ⁴ CEZUS Research Centre

16th International Symposium on Zirconium in the Nuclear Industry
2010, May 09 - 13, Chengdu, Sichuan Province, China
Introduction

- Extensive R&D program in order to assess the performance of ultra low tin quaternary alloys Zr1NbSnFe

- Evolutionary development of M5™ obtained by the addition of small amounts of tin and iron
  - Tin addition: improvement of the irradiation creep strength
  - Iron addition: beneficial for corrosion behavior

- This presentation will focus on the following results
  - Classical out-of-pile characterizations
  - In-pile irradiations on demo fuel rods
  - First hot cell measurements
Zr1NbSnFe alloys within the range of Sn 0-0.65% and Fe 0.03-0.35%

- alloys derived from M5™ (1% Nb, and controlled sulfur and oxygen additions), with low tin and iron additions
- from laboratory scale to industrial size ingots
- transformed into tubes
  - with the same manufacturing route as M5™
  - 0.4 to 0.7 mm of final thickness

Typical studied compositions
- Zr1%Nb0.1%Fe
- Zr1%Nb0.3%Sn0.1%Fe
- Zr1%Nb0.3%Sn0.2%Fe
- Zr1%Nb0.5%Sn0.1%Fe
- Zr1%Nb0.5%Sn0.35%Sn
OUT-OF-PILE RESULTS
Out-of-pile characterization
Microstructure, texture

- Fully recrystallised microstructure with fine equiaxed grains and uniformly distributed precipitates

*Optical micrographies on Zr1Nb0.3Sn0.1Fe tubes*

- Texture representative of a recrystallised state, annealed at low temperature

*TEM examination*
Out-of-pile characterization
Mechanical properties

- Tensile properties
  - the tin and iron contents do not significantly impact the yield and ultimate tensile strength and the elongation

- Creep
  - the tin content decreases the creep rate
  - the iron content slightly degrades the thermal creep strength

---

**Normalized UTS at RT**

- Tin content (%)
- Normalized UTS

**Creep strains after 240h at 400°C and 160 MPa (internal pressure)**

- Tin content (%)
- Diametral strain (UA)
Corrosion tests

- at 360°C in water
  - the tin content is detrimental for the oxidation rate and the iron has no significant effect
  - tin has a detrimental impact on hydriding whereas iron slightly improves the resistance

**Oxide thickness after 1080 days at 360°C in water**

<table>
<thead>
<tr>
<th>Tin content (%)</th>
<th>Oxide thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 Sn</td>
<td>16</td>
</tr>
<tr>
<td>0.1 Fe</td>
<td>12</td>
</tr>
<tr>
<td>0.2 Fe</td>
<td>12</td>
</tr>
<tr>
<td>0.35 Fe</td>
<td>14</td>
</tr>
<tr>
<td>0.3% Sn</td>
<td>12</td>
</tr>
<tr>
<td>0.5% Sn</td>
<td>14</td>
</tr>
</tbody>
</table>

**HPUF (%)**

- 0 Sn: 15 ± 2
- 0.3% Sn: 18 ± 2
- 0.5% Sn: 20 ± 2
IN-PILE RESULTS
In-pile results - FR irradiation

- Demo fuel rods have been irradiated in two European reactors operating with different fuel management strategies
  - Five annual cycles have been achieved in a German plant with a maximum fuel rod average burn up of 56 GWd/tU.
  - In France, the fuel assembly burn up is about 55 GWd/tU after three 18-month cycles. A fourth cycle has just been achieved.

- On site visual inspections and measurements to follow oxide thickness, fuel rod length and diameter have been performed
The visual appearance of the material variants with tin addition varies from grey to white, whereas M5™ is mostly grey and Zr1Nb0.1Fe is dark. Variants with 0.3% Sn show brighter appearance, and fuel rod cladding with 0.5% Sn is white.
In-pile results - FR irradiation
Diameter measurements

FR diameter was measured from cycle 1 to 5 in a German PWR and after 2 cycles in a French PWR

- The cladding creep resistance is improved with increasing tin content
- No significant effect of iron is observed

---

**Fuel rod diameter changes before pellet-cladding contact**

*(relative to M5™)*

![Graph showing diameter changes](image)

0%Sn  0.5%Sn  0.3%Sn  0.3%Sn

0.1%Fe  0.2%Fe

G for German PWR
F for French PWR
FR length was measured from cycle 1 to 5 in a German PWR and after 2 and 3 cycles in a French PWR.

- The addition of tin induces a reduction of fuel rod length changes.
- There is no significant impact of iron content.
After 2 and 3 cycles in a French PWR

At the currently achieved burn up of 55 GWd/tU, with 0.3% of tin the corrosion behavior is almost unchanged compared to M5™, whereas an addition of 0.5% of tin leads to a more significant increase of the oxidation rate.

No significant impact of iron is detected.
After 2 to 5 cycles in a German PWR

- A strong degradation of the oxidation resistance of the alloy with 0.5% tin is observed: the oxide thickness reaches 90 µm at 55 GWd/tU, while a maximum around 30 µm is measured on the alloys with 0.3% Sn
- An addition of iron is slightly beneficial for oxidation resistance
It seems that there is a break-away for an oxide thickness of around 15-20 µm on the 0.5% Sn containing alloy.
Hot-cell characterizations

- Hydrogen content was measured on 2-cycle FR with 0.3% Sn and irradiated in a French PWR (BU ~ 36 GWd/tU)
  - An average value of 68 ppm and 84 ppm has been obtained on the FR with 0.1% Fe and 0.2% Fe, respectively. The hydrogen pick up fraction is low, around 10-12%, and close to that obtained for M5™.

- Oxide thickness and hydrogen content was measured on 5-cycle material specimen inserted in a guide tube with a two face waterside corrosion, with 0.5% Sn (BU ~ 90 GWd/tU)
  - low oxide thickness : < 10 µm
  - hydrogen content around 230 ppm

- These first results seem to show that for cladding tubes tin has no impact on hydrogen uptake up to 0.3%. This needs to be confirmed by additional measurements.
  - Scheduled measurements on 3- and 5-cycle FR irradiated in a French and a German PWR, and on 5-cycle material specimens
Discussion on the oxidation

- Acceleration of the oxidation rate for Zr1%Nb0.5%Sn0.1%Fe material for oxide thickness of about 15-20 µm
  - could be correlated to a higher metal/oxide interface temperature in the German PWR, due to a higher linear heat generation rate during the first two cycles: the break-away is reached for a lower burn up in this irradiation condition
  - highly probable that the microstructural evolutions under irradiation are also involved in the oxidation break-away mechanism. Some hypotheses are:
    - Hydride precipitation and accumulation at the metal oxide interface
    - Dissolution of the SPP (with the Fe depletion of the SPP and subsequently Fe enrichment in the Zr matrix) and diffusion of iron in the matrix
    - Impact of tin content on the oxidation break-away

Future metallographic characterizations and TEM investigations will bring further information
Conclusion

▶ Under irradiation, recrystallised ultra low tin Zr1%NbSnFe alloys within the range of Sn 0-0.65% and Fe 0.03-0.35% show improved creep performances correlated to the addition of tin. No significant impact of Fe is observed.

▶ On the other hand, an addition of tin higher than 0.3% induces a degradation of oxidation kinetics strongly dependant on irradiation conditions. For a tin content of 0.5%:
  - a significant degradation of the oxidation behavior of fuel rods is observed when irradiated in high duty conditions, with a break-away that occurs at a low burn up of 25 GWd/tU and for an oxide thickness of around 20 µm.
  - a low oxidation is observed on material specimen inserted in a guide tube at a burn up around 90 GWd/tU

▶ First results on hydrogen content indicate a low hydrogen uptake for alloys containing 0.3% of tin when used for cladding tubes
Thank you for your attention
Out-of-pile characterization

**Texture**

- The (0002) pole figure shows two poles in the (radial, tangential) plane, orientated at about 30° from the radial direction.
- The (0110) pole figure exhibits poles at about 20° from the axial directions.
- These features are representative of a recrystallised state, annealed at low temperature: the recrystallisation is completed, while the grains could not grow significantly.

**Typical Kearns factor**

- fN 0.6, fL 0.08, fT 0.32

Pole figures for Zr1%Nb0.2%Sn0.1%Fe
Stress free Zr1%Nb0.3%Sn0.1%Fe and M5™ have been simultaneously irradiated during five cycles in a PWR. Low free growth elongation is measured on the Zr1%Nb0.3%Sn0.1%Fe alloy, with very similar elongations to M5™ until fluence of 14 E+25 n/m². At higher fluences, elongations on the Zr1%Nb0.3%Sn0.1%Fe alloy are a bit lower than those measured on M5™.