Effect of ion irradiation of the metal on the oxidation rate of the M5\textsubscript{Framatome} alloy

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• Issue and Background

• Aim of the study

• Experimental results

• Discussion

• Conclusions
Comparison of $\text{M5}_{\text{Framatome}}$ and Zircaloy-4 performance in PWR

Reaction of oxidation:
\[ \text{Zr} + 2 \text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2 \text{H}_2 \]

$\text{M5}_{\text{Framatome}}$ : oxidation rate constant up to a high burn-up

[\text{Kaczorowski et al. ASTM STP1543 (2015)}]

\( \Rightarrow \) Working hypothesis : irradiation effect contribution to the « High Burn-Up »
good corrosion resistance of the $\text{M5}_{\text{Framatome}}$ alloy?

*$\text{M5}_{\text{Framatome}}$ is a trademark or a registered trademark of Framatome or its affiliates, in the USA or other countries
ISSUE AND BACKGROUND

Irradiation effect on the corrosion behavior of Zr-Nb type alloy: state of art

➢ neutron irradiation effect on the corrosion rate of the Zr-2.5%Nb alloy in moist air at 300°C
➔ decrease of the corrosion rate after irradiation

[Urbanic et al., AIEA (1990)]

➢ neutron irradiation effect on the corrosion rate of a pre-oxidized E110 alloy in PWR conditions at 350°C
➔ slight reduction of the corrosion rate after irradiation

[Markelov et al., ASTM STP1597 (2016)]

➢ ion irradiation effect of the oxide layer on the corrosion rate of the M5\textsubscript{Framatome} alloy in PWR conditions at 360°C
➔ significant decrease of the corrosion rate after irradiation

Focus on the change of the oxidation rate after irradiation of M5\textsubscript{Framatome} alloy
**ISSUE AND BACKGROUND**

**M5\textsuperscript{Framatome alloy}**

<table>
<thead>
<tr>
<th>wt. %</th>
<th>Fe</th>
<th>Cr</th>
<th>Sn</th>
<th>Ni</th>
<th>Nb</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>M5</td>
<td>&lt;0.1</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>1.03</td>
<td>0.13</td>
</tr>
</tbody>
</table>

[Zr(Fe,Nb)\textsubscript{2}SPP][1]

[\textsuperscript{[Doriot et al., ASTM STP1597 (2016)]}]

\beta-Nb precipitate

[\textsuperscript{[AIEA (1998)]}]
Neutron irradiation effect on the microstructure of the M5\textsubscript{Framatome} alloy

- the nucleation of dislocation loops

- growth of the initial \(\beta\)-Nb precipitates (same density)

- increase of \(\beta\)-Nb volume fraction (x2)

- Nb concentration decrease in the \(\beta\)-Nb particles

- radiation–enhanced precipitation of \(\beta\)-Nb needles

[1.Doriot et al., ASTM STP1467 (2005)]
[2.Doriot et al., ASTM STP1543 (2015)]
[3.Northwood et al., JNM 79 (1979)]

\[\text{metal hardening induced by neutron irradiation}\]
### AIM OF THE STUDY

**Irradiation effect on the corrosion behavior of Zr-Nb alloy**

**PWR**

- nucleation of dislocation loop
- growth the β-Nb precipitates
- increase of β-Nb volume fraction (x2)
- Nb concentration decrease in the β-Nb particles
- radiation–enhanced precipitation of β-Nb needles (ten nanometers)

**Ions**

- nuclear damage:
  - Frenkel pairs
  - dislocation loops
- radiation-induced precipitation of nanometric β-Nb needles
- metal hardening

**Aim** of the study: reproduce (if possible separately) each metallurgical change observed in-core using ion irradiation test in order to study their effect on the oxidation rate of M5Framatome alloy.

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**Zu et al., Philos. Mag 85 (2005)**

**H⁺/350°C**
EXPERIMENTAL APPROACH

- Oxidation: 50 days at 360°C, 18.7 MPa in H$_2^{16}$O with Li, B.

- Isotopic exposure H$_2^{18}$O / D$_2^{16}$O (20/80%)

SRIM Simulation

irradiation

Sample characterization
TEM

Oxidation kinetics
1. weight gain
2. isotopic exposure + SIMS analyses

post-oxidation characterization
TEM & XPS

Ion and energy choice
- defect distribution
- nuclear damage

JANNUS Orsay Facilities

Tecnai 300 kV Microscope

Tecnai 300 kV Microscope

1.5 µm
**Aim** of the irradiation test: corrosion monitoring up to 3 µm oxide thickness ➔ metal irradiated depth of around 2 µm (Pillig-Bedworth Ratio = 1.56)

Ion | Ion energy | Temperature (°C) | Fluence (ions/cm²) | Flux (ions/cm²/s) | dpa (on the plateau) | dose (dpa/s) | Target
---|-------------|------------------|-------------------|------------------|-------------------|-------------|---------
H⁺ | 300 keV | 350 °C | $10^{18}$ | $8.10^{13}$ | ~0.7 | $3.9 \times 10^{-4}$ | <a>-Dislocation loops + β-Nb-needles particles?
EXPERIMENTAL
METAL CHARACTERIZATION AFTER IRRADIATION TEST

- Oxidation: 50 days at 360°C, 18.7 MPa in H₂¹⁶O with Li, B.
- Isotopic exposure H₂¹⁸O / D₂¹⁶O (20/80%)

SRIM Simulation

irradiation

Sample characterization
TEM

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post-oxidation characterization
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Ion and energy choice
- Defect distribution
- Defect contents (dpa, Se)

JANNUS Orsay and Saclay Facilities

Tecnai 300 kV Microscope

Tecnai 300 kV Microscope

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TEM observations

**Particles:**
- length: 10-100 nm
- width: 2-20nm

- precipitation of long nanometric particles
  ➔ β-Nb needles found in neutron irradiated fuel cladding?
Long niobium-enriched precipitates looking like β-Nb needles
- Oxidation: 50 days at 360°C, 18.7 MPa in H$_2^{16}$O with Li, B.
- Isotopic exposure H$_2^{18}$O / D$_2^{16}$O (20/80%)

**EXPERIMENTAL OXIDATION KINETICS**

**Oxidation kinetics**
1. weight gain
2. isotopic exposure + SIMS analyses

**SRIM Simulation**
**irradiation**
**Sample characterization**
**TEM**

**Ion and energy choice**
- Defect distribution
- Defect contents (dpa, Se)

**JANNUS Orsay and Saclay Facilities**

**Tecnai 300 kV Microscope**

**post-oxidation characterization TEM & XPS**

**Tecnai 300 kV Microscope**
**strong effect** of the proton irradiation on the oxidation rate of the M5 Framatome alloy:

1. around 25% reduction of the corrosion rate up to 20 days: $R = 0.78$
strong effect of the proton irradiation on the oxidation rate of the M5_Framatome alloy:

1. around 25% reduction of the corrosion rate up to 20 days: \( R = 0.78 \)
2. around 95% reduction of the corrosion rate beyond 20 days: \( R = 0.05 \)

EXPERIMENTAL
OXIDATION KINETICS

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**EXPERIMENTAL OXYGEN DIFFUSION PROFILE**

**18O SIMS profiles after 24 hours of isotopic exposure in 18O enriched primary water**

![Graph showing 18O SIMS profiles](image)

- **unirradiated alloy**
- **proton irradiated specimen**

\[ R = \frac{\int_{0}^{x} I_{18O} \, dx}{\int_{0}^{x} I_{NI} \, dx} \]

- \( R = 0.75 \)
  - close to the parabolic constant ratio at the beginning of the oxidation process

- decrease of **18O surface concentration**
- **decrease** of the **18O amount** absorbed within the oxide layer after irradiation
  - consistent with the oxidation kinetics
- Oxidation: 50 days at 360°C, 18.7 MPa in H$_2^{16}$O with Li, B.

- Isotopic exposure: H$_2^{18}$O / D$_2^{16}$O (20/80%)

Ion and energy choice
- Defect distribution
- Defect contents (dpa, Se)

JANNUS Orsay Facilities

CAMECA X-rays Photoelectron Spectroscopy

EXPERIMENTAL OXIDE CHARACTERIZATION
XPS analyses: specimens with the same thicknesses as SIMS samples

- charge (or oxidation) state of niobium: +V
- measurement of the surface niobium concentration

<table>
<thead>
<tr>
<th>specimen</th>
<th>at. % of Nb at the surface</th>
<th>Niobium content ratio</th>
<th>$^{18}$O surface concentration ratio</th>
<th>oxygen diffusion flux ratio</th>
<th>parabolic constant ratio $(k_{p_{irr}}/k_{p_{unirr}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>unirradiated</td>
<td>4.3 (+/- 0.3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>proton irradiated</td>
<td>3 (+/- 0.3)</td>
<td>0.7</td>
<td>0.74</td>
<td>0.75</td>
<td>0.78</td>
</tr>
</tbody>
</table>

- reduction of the surface niobium content associated with:
- decrease of the $^{18}$O surface concentration and the oxygen diffusion flux
- oxidation rate reduction at the start of the corrosion process (~25%)
unirradiated material

proton irradiated material

dense and protective oxide layer

very damaged oxide with many cracks

Difference of the stress distribution within the oxide between reference and irradiated material due to metal hardening by irradiation?
Effect of irradiation on the **start** of the oxidation kinetics

- Precipitation of niobium rich particles (TEM)
- Reduction of niobium concentration in solid solution in the M5 alloy (needs to be confirmed)
- Decrease of surface niobium concentration (XPS)

**What’s going on beyond 20 days of oxidation time?**

- Decrease of $^{18}$O surface concentration and oxygen diffusion flux
1. **Diffusion model** taking into account an **electric field** (Fromhold equation):

\[ J_{OH} = -D_{OH} \left( \frac{\partial C_{OH}}{\partial x} \right) - \frac{F}{RT} C_{OH} \left( \frac{\partial \phi}{\partial x} \right) \]

- **Oxygen concentration gradient**
- **Electrical potential gradient**

→ Analytical solution for a constant and homogeneous electric field

2. **Diffusion model** considering the **Dollins** (D dependent on stress) and the **Stephenson** (stress gradient effect) effects on the oxygen diffusion flux:

\[ J_{O} = -D_{\sigma_0} \exp \left( \frac{V_A}{kT} \sigma_H \right) \left( \frac{\partial C_{O}}{\partial x} + \frac{\Omega N_A}{RT} \frac{\partial \sigma_H}{\partial x} \right) (C_{O}^A - C_{O}) \]

\[ \text{(Eq. 1)} \]

- **Oxygen concentration gradient**
- **Stress gradient**

[Zumpicchiat et al., Corr. Sci.(2015)]
Castem code:

\[ J_0 = -D_\sigma_0 \exp \left( \frac{V_A}{kT} \sigma_H \right) \left( \frac{\partial C_O}{\partial x} + \frac{\Omega N_A}{RT} \frac{\partial \sigma_H}{\partial x} \left( C_O^A - C_O \right) \right) \]

(Eq. 1)

\[ 10^{-13} \text{cm}^2\cdot\text{s}^{-1} \]

set stress gradient \[^2\]:

\[ \frac{\partial \sigma_H}{\partial x} = -0.6 \text{ GPa. } \mu\text{m}^{-1} \]

[1] Anisotropic strain tensor
\[ \rightarrow \] Parise et al., JNM 256 (1998)

\[ \rightarrow \] Godlewski et al. ASTM STP 1354 (2000)

\[ \rightarrow \text{ Good simulation of the kinetics of the irradiated material } \]

DISCUSSION
MECHANICAL EFFECT

[Graph showing oxide thickness vs. time with simulated curve and experimental data points]
CONCLUSIONS

• proton irradiation effect

➔ long niobium rich precipitates similar to β-Nb needles
➔ reduction of the niobium surface concentration associated with the decrease of the $^{18}$O surface concentration
➔ strong decrease of the oxidation rate

• interpretation of the irradiation effect on the corrosion behavior of M5$_{\text{Framatome}}$ alloy

➔ A chemical effect linked to the precipitation of the niobium rich particles
➔ a mechanical effect due to the matrix hardening induced by ion irradiation
Thank you for your attention

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