Development of thermokinetic tools for phase transformation studies of Zr alloys in service and LOCA conditions

As nuclear fuel cladding materials, Zr alloys are subjected to numerous solicitations both in:

<table>
<thead>
<tr>
<th>service conditions</th>
<th>LOCA conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurized water: 155 bars</td>
<td>Internal pressure: up to &gt; 100 bars inducing creep/ballooning and burst</td>
</tr>
<tr>
<td>Water temperature: 320-360°C</td>
<td>Max (Peak Cladding) Temperature : 1200 °C</td>
</tr>
<tr>
<td>Neutron irradiation</td>
<td>Steam environment inducing High Temperature Oxidation and potential secondary hydriding</td>
</tr>
<tr>
<td>Oxidation / hydriding</td>
<td></td>
</tr>
</tbody>
</table>

Considering the influence of microstructure on mechanical properties:

The development of thermokinetic tools enables the determination of:

- phase transformation temperatures
- phases chemical compositions
- phases volume fractions
- precipitation of more or less brittle phases
- new alloy compositions
- ...
New thermodynamic database for Zr alloys

Systematic use of Density Functional Theory (DFT) and Special Quasirandom Structure (SQS) calculations

Phase diagram and thermodynamic data calculations
Extended to Cr containing alloys for Cr-coated Zr EATF R&D

Numerical code Ekinox-Zr

Linked with Open Calphad/OCASI and thermodynamic database

Simulation of O concentration profiles and thickness evolution of the different phases appearing/developing during a LOCA transient
THERMODYNAMIC TOOL
NEW THERMODYNAMIC DATABASE:
Zr-Cr-Fe-Nb-Sn SYSTEM

10 binary systems:

- Cr-Nb
- Cr-Sn
- Cr-Zr
- Cr-Fe
- Fe-Sn

10 ternary systems:

- Cr-Fe-Nb
- Cr-Fe-Zr
- Cr-Nb-Zr
- Cr-Fe-Sn
- Cr-Sn-Zr

- Nb-Sn
- Nb-Zr
- Sn-Zr
- Fe-Zr
- Fe-Nb

- Sn-Nb-Zr
- Nb-Fe-Zr
- Fe-Sn-Zr
- Fe-Nb-Sn
- Cr-Nb-Sn

Binary and ternary models are combined into a quinary database.
**THERMODYNAMIC MODELLING USING THE CALPHAD METHOD**

**Calphad method**

- **Solution (ex: A−B)**
  
  $srf G_\phi = x_A G_\phi (A) + x_B G_\phi (B)$

- **cnf $G_\phi = -T \cdot cnf S_\phi = -RT(x_A \ln x_A + x_B \ln x_B)$**

- **ex $G_\phi = x_A x_B L_{AB},$ où $L_{AB} = \sum_{i=0}^{\infty} L_{\phi}^{A,B} (x_A - x_B)^i$**

**Stoichiometric compound (AB₂)**

$G (AB₂) = G_{SER} (A) + 2G_{SER} (B) + a + b \cdot T + ...$

**Non-Stoichiometric compound**

Sublattice model

**DFT-SQS calculations of $\Delta H_m$**

**DFT calculation of $\Delta H_f$**

**Thermodynamic database**

**Phase equilibria**

**Crystallography**

**Thermodynamic parameters**
WHY SYSTEMATIC USE OF DFT AND SQS CALCULATIONS? ⇒ SUBLATTICE MODEL

Structure | Intermetallic compound | Wyckoff position | Space group
--- | --- | --- | ---
C15 | ZrFe₂ | 8a (Zr) 16d (Fe) | Fd-3m (227)

End-members ΔHf calculated by DFT

$2^2 = 4$ end-members for a binary system

$3^2 = 9$ end-members for a ternary system
The calculated ground-state confirms the stability of Fe$_2$Nb (C14) and Fe$_7$Nb$_6$ (μ) phases.
New assessment of the FeNb system

Validation of the optimisation by comparison with exp. data:

- Fe activity at 1600°C
- Mixing enthalpy of the liquid phase at 1762°C
Mixing binary systems enables extrapolation towards ternary systems.

EXTRAPOLATION TO THE Fe-Nb-Zr TERNARY SYSTEM
EXISTENCE OF THE Fe$_2$(Nb,Zr) (C36 LAVES PHASE) INTERMETALLIC PHASE?

Experimental verification:

Alloy fabrication Fe$_2$Nb$_{0.5}$Zr$_{0.5}$ → 3 weeks annealing at 800°C →

Analysis by:
- X-ray diffraction
- EPMA

2 experimentally observed phases: Fe$_2$Nb (C14) and Fe$_2$Zr (C15)

Non existence of the Fe$_2$(Nb,Zr) (C36) confirmed by DFT calculations
Good agreement between experimental and calculated data

The whole database has been created applying the same methodology
APPLICATION ON INDUSTRIAL ALLOYS

Zr-0.7% Nb-0.3% Sn-0.35% Fe-0.25% Cr

annealing at 675 °C

EDS analysis → quaternary equilibria: α-Zr + β-Zr + LAVES + LAVES

Zr

<table>
<thead>
<tr>
<th>Zr0.7Nb0.3Sn0.35Fe0.25Cr</th>
<th>Zr</th>
<th>Nb</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr(Nb,Fe,Cr)₂</td>
<td>33.8</td>
<td>20.2</td>
<td>29.2</td>
<td>16.8</td>
</tr>
<tr>
<td>Zr(Fe,Cr)₂</td>
<td>33.0</td>
<td>4.6</td>
<td>29.5</td>
<td>32.9</td>
</tr>
</tbody>
</table>

Zircobase

• α-Zr + β-Zr + LAVES

• Modification of the nominal composition
  α-Zr + β-Zr + C14 + C14

Our database

• α-Zr + β-Zr + C14 + C15

<table>
<thead>
<tr>
<th>Zr</th>
<th>Nb</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>C14</td>
<td>34.2</td>
<td>24.6</td>
<td>38.4</td>
</tr>
<tr>
<td>C15</td>
<td>32.0</td>
<td>3.8</td>
<td>33.0</td>
</tr>
</tbody>
</table>

*Barberis et al., 17th Int. Symp. Zr Nucl. Indust, STP1543, Hyderabad, India, 2015
KINETIC TOOL
CONTEXT: MICROSTRUCTURAL EVOLUTIONS DURING LOCA ⇒ HIGH INFLUENCE ON THE MECHANICAL PROPERTIES: BALLONING & BURST, WATER QUENCHING AND POST-QUENCHING RESISTANCE/DUCTILITY…)

Loss Of Coolant Accident (LOCA)

Temperature of the cladding at a given axial position (°C)

Zr + 2H₂O → 2H₂ + ZrO₂

Prior-βZr

βZr

αZr

( mono.)

βZr

( cc)

ZrO₂

O

Ex.: Single-side oxidation

Example of Large Break LOCA transient

Steam

JAEA, A 3-1

CEA

ANL, ICL#2

Time

Distance from the outer surface

Oxygen content

ZrO₂

~25 wt.%

~66 at.%

2-7 wt.%

10-29 at.%

0.14-0.9 wt.%

1-5 at.%

ZrO₂

αZr(O)

βZr

αZr

( + H)

βZr

( hcp)

βZrO₂

( tetra.)

αZrO₂

( mono.)

Steam

19th International Symposium on Zr in the Nuclear Industry, May 20-23 2019, Manchester, UK | PAGE 15
CONSEQUENCES OF HIGH TEMPERATURE OXIDATION ON POST-QUENCH MECHANICAL BEHAVIOR OF THE CLADDING

At Room-Temperature (RT):

Remaining ductility at RT only in the prior-βZr layer for [O] < 0.4wt%
Otherwise ductile → brittle

Create a tool able to forecast thicknesses of brittle and ductile phases, O diffusion profiles (and weight gains) as a function of HT steam oxidation time and temperature (and able to take into account the additional effect of hydrogen)

J.-C. Brachet et al. Journal of ASTM international, 5, n°5 (2008), Paper ID JAI101116
Initially developed for Ni base alloys

- **Chemical species and atomic defects transport**
  - via atomic solid diffusion

- **Interface reaction**
  - local thermodynamic equilibrium

- **Intermediate scale**
  - system is described by "slabs" of constant concentration:
    - [O] in the metal layers
    - \([V_0]\) in the oxide phase
  - 1st and 2nd Fick’s law

- **Moving boundaries algorithm for interfaces motion**

- **Numerical time integration**

- **growth kinetics**
  - Diffusion of chemical species and vacancies **concentration profiles**
    - in the oxide scale
    - in the metal

**Numerical code EKINOX-Zr**

(ESTIMATION KINETICS OXIDATION MODEL FOR ZR-BASED ALLOYS)

- Initially developed for Ni base alloys
NUMERICAL CODE EKINOX-ZR
(ESTIMATION KINETICS OXIDATION MODEL FOR ZR-BASED ALLOYS)

Surface interne

[O]↑

β_{Zr}

α_{Zr}(O)

ZrO₂

Surface externe

[O]↓

[O]↓

[H]

[O]

C_{β/α}

C_{α/β}

C_{α/ox}

V₀_{ox/α}

V₀_{ox/gaz}

EKINOX numerical resolution of diffusion equations

Interface

OCASI

C_{α/β}, C_{β/α}

OPENCALPHAD + Zircobase (thermodynamic calculations)
Ekinox-Zr has already demonstrated its ability at:

- Simulating O diffusion profiles in $\alpha_{\text{Zr}(O)}$ and $\beta_{\text{Zr}}$ [1]
- Taking into account the influence of H [2]
- Taking into account the effect of a pre-oxide layer on the O concentration profile [3]

During isothermal HT oxidation (1100 < T < 1250°C)

New development: simulation of anisothermal (HT oxidation) transients

Comparison between calculated and experimental (TGA) anisothermal weight gain variation of Zircaloy-4 upon heating under \(O_2+He\) environment at 2°C/min and 20°C/min.
Calculated O concentration profiles in Zircaloy-4 alloy for anisothermal oxidation at two different heating rates (2 and 20°C/min) at \( \Delta t = 200s \)

Similar ECR can be reached by different LOCA type anisothermal transients: the resulting O concentration profiles can potentially be very different.
CONCLUSIONS

- Development of a **new thermodynamic database for Zr** alloys including systematic and massive use of DFT and SQS calculations

- Consistency of the database: very good agreement of thermodynamic computations with experimental data

- Improvement of the **Ekinox-Zr numerical** code: enabling anisothermal calculations of the HT **phase thicknesses** and associated **oxygen concentration profiles** induced by HT steam oxidation typical of LOCA

FURTHER WORK

- Include **H** and **O** in the thermodynamic database: « work in progress! »

- **Ekinox-Zr** :
  - Extend anisothermal calculations from room temperature to high temperature
  - Adaptation of the code for the simulation of HT oxidation of Cr-coated EATF claddings
This work is funded by the project GAINE from the French Nuclear tripartite Institute CEA – EDF - FRAMATOME
WHY SYSTEMATIC USE OF DFT AND SQS CALCULATIONS? → SUBLATTICE MODEL

\(2^2 = 4\) end-members for a binary system

\(3^2 = 9\) end-members for a ternary system

<table>
<thead>
<tr>
<th>Structure</th>
<th>Intermetallic compound</th>
<th>Wyckoff position</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15</td>
<td>ZrFe(_2)</td>
<td>8(a) (Zr)</td>
<td>Fd-3m (227)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16(d) (Fe)</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>Groupe d'espace</td>
<td>Wyckoff (CN)</td>
<td>Configurations</td>
</tr>
<tr>
<td>-------</td>
<td>----------------</td>
<td>-------------</td>
<td>----------------</td>
</tr>
<tr>
<td>C15</td>
<td>Fd-3m (227)</td>
<td>8a (16); 16d (12)</td>
<td>25</td>
</tr>
<tr>
<td>C14</td>
<td>P6$_3$/mmc (194)</td>
<td>2a (12); 4f (16); 6h (12)</td>
<td>125</td>
</tr>
<tr>
<td>C36</td>
<td>P6$_3$/mmc (194)</td>
<td>4e (16); 4f (16); 4f (12); 6g (12); 6h (12)</td>
<td>125</td>
</tr>
</tbody>
</table>
## MODÈLE EN SOUS-RÉSEAUX

<table>
<thead>
<tr>
<th>Phase</th>
<th>Groupe d'espace</th>
<th>Wyckoff (CN)</th>
<th>Prototype</th>
<th>Système</th>
<th>Nbre de sous-réseaux</th>
<th>Modèle en sous-réseaux</th>
</tr>
</thead>
<tbody>
<tr>
<td>C15</td>
<td>Fd-3m (227)</td>
<td>8a (16); 16d (12)</td>
<td>MgCu₂</td>
<td>Système quinaire</td>
<td>2</td>
<td>(Cr,Nb,Fe,Sn,Zr)₁, (Cr,Nb,Fe,Sn,Zr)₂</td>
</tr>
<tr>
<td>C14</td>
<td>P₆₃/mmc (194)</td>
<td>2a (12); 4f (16); 6h (12)</td>
<td>MgZn₂</td>
<td>Système quinaire</td>
<td>3</td>
<td>(Cr,Nb,Fe,Sn,Zr)₄, (Cr,Nb,Fe,Sn,Zr)₂, (Cr,Nb,Fe,Sn,Zr)₆</td>
</tr>
<tr>
<td>C36</td>
<td>P₆₃/mmc (194)</td>
<td>4e (16); 4f (16); 4f (12); 6g (12); 6h (12)</td>
<td>MgNi₂</td>
<td>Système quinaire</td>
<td>3</td>
<td>(Cr,Nb,Fe,Sn,Zr)₄, (Cr,Nb,Fe,Sn,Zr)₄, (Cr,Nb,Fe,Sn,Zr)₁₆</td>
</tr>
<tr>
<td>μ*</td>
<td>R-3m (166)</td>
<td>3a (12); 6c (15); 6c (16); 6c (14); 18h (12)</td>
<td>W₆Fe₇</td>
<td>Cr-Fe-Nb</td>
<td>4</td>
<td>(Cr,Fe,Nb)₁, (Nb)₄, (Cr,Fe,Nb)₂, (Cr,Fe,Nb)₆</td>
</tr>
<tr>
<td>σ*</td>
<td>P₄₂/mnm (136)</td>
<td>2a (12); 8i (12); 4f (15); 8i (14); 8j (14)</td>
<td>Crₐ₀.₄⁹Fe₀.₅₁</td>
<td>Cr-Fe-Nb</td>
<td>2</td>
<td>(Cr,Fe,Nb)₁, (Cr,Fe,Nb)₂</td>
</tr>
</tbody>
</table>

Calculs DFT des $\Delta H_f$

$C_{15}$

Calculs DFT-SQS des $\Delta H_m$

Consistance de la description !

Solutions solides peu étendues
Interfaces conditions:

\[ C_{ox}(n, t) = C_{ox/vap} \]
\[ C_{ox}(i, t) = C_{ox/\alpha} \]
\[ C_{\alpha}(i, t) = C_{\alpha/ox} \]
\[ C_{\beta}(j, t) = C_{\beta/\alpha} \]
\[ C_{\beta}(1, t) = C_{0} \]

1st and 2nd Fick’s law:

\[ J = -D \frac{\partial c}{\partial x} \]
\[ \frac{\partial J}{\partial x} = -\frac{\partial c}{\partial t} \]

\[ \left( C_{\alpha/\beta} - C_{\beta/\alpha} \right) \frac{\partial x_j}{\partial t} = D_{\alpha} \frac{\partial c_{\alpha}}{\partial x} \bigg|_j - D_{\beta} \frac{\partial c_{\beta}}{\partial x} \bigg|_j \]

\[ \left( C_{ox/\alpha} - C_{\alpha/ox} \right) \frac{\partial x_i}{\partial t} = D_{ox} \frac{\partial c_{ox}}{\partial x} \bigg|_i - D_{\alpha} \frac{\partial c_{\alpha}}{\partial x} \bigg|_i \]

OpenCalphad / OCASI + Zircobase
Zy4 + [H] = 150 ppm mass. –oxydation – 1200°C – 190s

EPMA profil

EKINOX-Zr profil
Le paramètres optimisés de ce système sont résumés dans le tableau 6

<table>
<thead>
<tr>
<th>Phase</th>
<th>Paramètres (J/mol)</th>
</tr>
</thead>
</table>
| Liquide | \[ \begin{align*}
L_{Fe,Nb} &= - 74858 + 99.7^*T - 10^*T^*\ln(T) \\
L_{Fe,Nb} &= 17624 - 10.8^*T
\end{align*} \] |
| fcc     | \[ L_{Fe,Nb} = - 9123 \]                                                            |
| bcc     | \[ \begin{align*}
L_{Fe,Nb} &= - 13127 + 11.8^*T \\
L_{Fe,Nb} &= 6812 - 7.26^*T
\end{align*} \] |

Tableau 6: Paramètres optimisés du système Fe-Nb.

| C14 \((Fe,Nb)_4(Fe,Nb)_2(Fe,Nb)_6\) | G_{Fe:Fe:Fe} = 148839 + 12\*GHSERFE \[ G_{Fe,Nb:Fe} = 209136 + 10\*GHSERFE + 2\*GHSERNB \[ G_{Nb:Fe:Fe} = - 237991 + 38.8^*T + 8*GHSERFE + 4*GHSERNB \[ G_{Fe:Fe:Nb} = 492692 + 6*GHSERFE + 6*GHSERNB \[ G_{Nb:Nb:Fe} = - 63529 + 6*GHSERFE + 6*GHSERNB \[ G_{Fe,Nb:Nb} = 682920 + 4*GHSERFE + 8*GHSERNB \[ G_{Nb,Nb:Nb} = 120679 + 2*GHSERFE + 10*GHSERNB \[ L_{Fe,Nb:Fe,Fe} = + 77437 - 40.57^*T \[ L_{Nb,Nb,Fe,Nb} = + 77437 - 40.57^*T
| (Fe,Nb)_1(Nb)_4(Fe,Nb)_2(Fe,Nb)_6 | G_{Fe:Fe:Fe} = - 100230 + 9*GHSERFE + 4*GHSERNB \[ G_{Nb:Nb:Fe} = - 27430 + 8*GHSERFE + 5*GHSERNB \[ G_{Fe,Nb:Fe} = - 266116 + 50^*T + 7*GHSERFE + 6*GHSERNB \[ G_{Nb,Nb,Nb} = - 131400 + 6*GHSERFE + 7*GHSERNB \[ G_{Fe:Fe:Nb} = 426530 + 3*GHSERFE + 10*GHSERNB \[ G_{Nb,Nb:Fe} = 499200 + 2*GHSERFE + 11*GHSERNB \[ G_{Fe,Nb:Nb} = 176020 + GHSERFE + 12*GHSERNB \[ G_{Nb,Nb,Nb} = 227500 + 13*GHSERNB \[ L_{Fe,Nb:Nb,Nb:Fe,Nb} = - 759678 + 513.7^*T

\[ L_{Fe,Nb:Nb,Nb:Fe,Nb} = - 759678 + 513.7^*T \]