Contribution to the Study of Zr1Nb-O Phase Diagram and Numerical Modeling of Steam Oxidation of Zr1Nb Fuel Cladding

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Introduction

• modeling of Zr1Nb HT oxidation:

  • Zr1Nb-O ($C_{\alpha/\alpha+\beta}$ and $C_{\beta/\alpha+\beta}$) is of high importance (CALPHAD)

• experimental: new experimental procedure for assessment of Zr-alloy based on O concentration measurement inside cladding wall after HT oxidation

• assumption: equilibrium conditions are fulfilled at interfaces, redistribution upon quenching is negligible
Introduction

- first tests with Zry-4 with variable H content
  => validation of the procedure
  => influence of H can be treated

- tests with Zr1Nb – troubles

- comparison with CALPHAD agreement
  => new tests

- modeling of the (α+β) region
Main Goals

• determination of Zr rich Zr1Nb-O phase diagram (C\(\alpha\)/\(\alpha\)+\(\beta\) and C\(\beta\)/\(\alpha\)+\(\beta\)) based on O concentration measurements inside quenched Zr1Nb cladding wall after HT isothermal steam oxidation

• comparison of the experimentally determined Zr1Nb-O with CALPHAD calculations

• modeling of double-sided HT steam oxidation (\(\alpha+\beta\))-Zr region for T = 1,100°-1,300° C

• validation of the calculations
Material & Methods

- alloy: modified E110 (improved oxidation properties => lower H uptake!!!)
- 30 mm long tubes (outside diameter: 9.1 mm, wall thickness: 0.7 mm)
- as-received x corroded (non-irradiated) in steam (425 °C/10.7 MPa – 2 ppm H), 10 (~150 wppm H), or 20 µm (~600 wppm H)
- HT oxidation (double-sided) in steam
  - T measured by a thermocouple inside the tube
  - samples quenched in ice water
Material & Methods

- H content measured by vacuum extraction
- microstructure observation – LM & SEM
- microhardness & nanohardness measurements
- O concentration measurement:
  - WDS (Wavelength-Dispersive Spectrometry)
  - SIMS (Secondary Ion Mass Spectrometry)
  - TEA (Thermal Evolution Analysis)
O concentration $C_{\alpha/\alpha+\beta}$

determination of $\alpha/\alpha+\beta$ is not so obvious in some cases – O, Nb profiles, metallography

more measurements, substantial experimental data

O saturation – $\alpha/\alpha+\beta$, $\alpha+\beta/\beta$ solution
Nanohardness vs. O content

- Nanohardness depends strongly on O concentration.
- The relation is equal for both Zry-4 & Zr1Nb.
- Nanohardness and O concentration at the metal/oxide phase boundary (in the metal) are also involved.
- Nanohardness measurement followed with advantage of higher throughput.
O ceiling in $\beta$-Zr

- SIMS & TEA - determination of $C_{\beta/\alpha+\beta}$ (WDS only for higher T)
  - larger analyzed volume
- assumption: O solubility limit in $\beta$ is achieved and exceeded at certain exposure time upon HT oxidation approx. in whole at the same time
- HVM - determination of O saturation time
- SIMS & TEA results - satisfactory agreement with microhardness
- $C_{\beta/\alpha+\beta}$ can be then estimated
- LM confirm the conclusions
Zr1Nb-O

- CALPHAD - database „Zr_BASE“ (involving phases from publicly accessible sources without experiments)

- good agreement between the experimental results and calculated phase diagram

- comparison with other authors:
Numerical calculations - JKOX

2\textsuperscript{nd} Fick Law & mass balance equation, satisfied on each interface:

\[ \frac{\partial C(r,t)}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r J_r \right) \quad \quad J_r = -D(T) \frac{\partial C(r,t)}{\partial r} \]

- 1D finite difference method (implicit solution) - code predicts the double-sided oxidation \( \geq 1100 \, ^\circ\text{C} \)
- GB diffusion and diffusion of Nb are neglected
- \( \alpha\)-Zr(O) incursions are treated as an additional layer - \( (\alpha+\beta)\)-Zr
- O concentrations at phase boundaries in \( (\alpha+\beta)\)-Zr & O diffusivity are chosen based on experimental results
- Zr-O & Zr1Nb-O phase diagram are used
- diffusivities depend only on T:

\[ k = 1.987 \, \text{cal/mol/K} \]

\[ D_{\alpha} = \begin{cases} 0.127 \times e^{-35140/kT} & \text{if } \alpha-Zr(D) \\ D_{\alpha} & \text{if } (\alpha+\beta)-Zr, \text{ oxide, prior } \beta-Zr \end{cases} \]
Reaction layers development

- good agreement for all reaction layers - until O saturation
- measured oxide layers are slightly underestimated compared to predicted, mainly for higher thicknesses
- higher experimental scatter for α-Zr(O) & (α+β)-Zr
O pick-up in β-Zr

- satisfactory agreement
- code under-predicts experimental results
- possible explanations:
  - experimental results – O concentrations measured in prior β might be elevated by innermost α-Zr(O) incursions
  - no α-Zr(O) grains precipitation modeled (O saturation) - misfit for higher exposure times
Conclusions

• Zr1Nb-O was experimentally assessed employing O concentration measurements inside quenched cladding wall after HT steam oxidation.

• experimentally determined Zr1Nb-O was compared to CALPHAD calculations with a satisfactory agreement.

• proposed experimental procedure provides good estimation of the Zr1Nb-O phase diagram and can be used for higher H content.

• new diffusion model JKOX has been created using Zr1Nb high-temperature oxidation data, including O saturation.
Conclusions

• numerical calculations were compared to experimental results with satisfactory agreement

• estimated Zr1Nb-O phase diagram may be used for models predicting the oxidation behavior upon HT oxidation
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