The kinetic of α-Zr(O) layer in Zr1Nb alloy

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Introduction (1)

- Zr1Nb is used as a material for fabrication of fuel claddings

- operating conditions (VVER: 320 °C/16 Mpa) – claddings oxidation, oxygen and hydrogen absorption, etc. – influence on the mechanical properties

- LOCA (Loss of Coolant Accident) – additional claddings oxidation and oxygen and hydrogen absorption (even inside the cladding) upon the temperature ~ 1000 °C => phase transformation α-Zr → β-Zr – cooling down => lost of mechanical properties

- the reactor core integrity and cooling possibility, claddings’ thermal shock resistance and the consequential materials handling during transport from the reactor have to be maintained even after the LOCA

- many criteria have been set up so far – conventional oxidation criteria do not work for high hydrogen uptake

- an effort to create a universal criterion - it is necessary to know the oxygen distribution (microstructure evolution) inside the cladding’s wall during the transient – oxygen diffusion model
Introduction (2)

- The wall microstructure after the transient (high temperature oxidation) consists of three layers: oxide layer, oxygen stabilized α-Zr(O) layer and prior β-Zr layer.

- One has to known pseudobinary Zr1Nb-Oxygen phase diagram.
Introduction (3)

- The microstructure (α-Zr(O) morphology) depends on the chemical composition:
  - Zircaloys - alloy containing Sn (α-stabilizer) => the phase boundary between α-Zr(O) layer and prior β-Zr layer is quite uniform
  - Zr1Nb alloy - an additional mixture of α-Zr(O) and prior β-Zr, because of the β-stabilizing effect of niobium
Major goals

- $\alpha$-Zr(O) layer thickness determination
- determination of the nanohardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary depending on the temperature
- determination of the ceiling oxygen concentration in $\beta$-Zr depending on the temperature
- try to use the oxygen distribution in the cladding wall to pseudobinary Zr1Nb-Oxygen phase diagram construction
Experimental material

- Zr1Nb alloy

- Corrosion during operating conditions was simulated in autoclaves in water steam at 425 °C and 10.7 Mpa (~2 atm ~10 μm)

- High temperature oxidation: 800 - 1200 °C in water steam, atmospheric pressure

- Cooling down - quench in water with ice or slow cool down in the furnace

Sample 6212008 (1200 °C/9 min, 0μm)
Experimental methods

- layers measurement - LM NEOPHOT 21, image analyzer LUCIA G (UJP PRAGUE a.s.)
- micro-hardness measurement - micro-hardness tester OPL (KMAT FJFI ČVUT)
- nano-hardness measurement - nano-hardness tester XP (NTC ZČU)
- X-ray microanalyses - WD spectrometer INCA Wave 700 (ÚJV)
- SIMS - quadrupole SIMS Atomika 3000 (UJEP)
- TEA - LECO TC500C (UNIPETROL)
Layers' thickness measurement

- measurement on cross sections in 6 areas (after 60 min) at external and internal cladding's edge
The kinetic of the layer $\alpha$-Zr(O)

Results of the layer $\alpha$-Zr(O) have to satisfy the parabolic and Arrhenius laws:

$$L_\alpha^2 = K \times t$$

or

$$L_\alpha = k \times \sqrt{t}$$

$$K = A \times \exp\left(-\frac{Q}{RT}\right)$$

$$\ln K = \ln A - \frac{Q}{RT}$$
The kinetics

\[ L_\alpha = k \cdot \sqrt{t} \]

- \( \alpha \)-Zr(O) thickness: \( l_\alpha^2 = 0.231e^{-184928/RT}t \) for \( T = 800 - 1200 \) C

\( y = -22243x + 21.053 \)
\( R^2 = 0.966 \)

(\( \alpha + \beta \))-Zr area
Determination of nano-hardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary

\[ y = -0.0378x + 12.739 \]

\[ y = -0.0612x + 5.1729 \]
Determination of nano-hardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary

- Oxygen concentration and nano-hardness at $\alpha/\alpha+\beta$ phase boundary in the cladding of Zr1Nb are close to oxygen concentration and nano-hardness at $\alpha/\alpha+\beta$ phase boundary in the cladding of Zry-4 with ~2000 wppm hydrogen content.
Relation between nano-hardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary

- The relation between the nano-hardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary was specified.
- This relation is identical for both alloy.
- The oxygen concentration can now be estimated from the nano-hardness at $\alpha/\alpha+\beta$ phase boundary.

![Graph showing the relation between nano-hardness and oxygen concentration. The equation is $y = 0.9015x + 6.1876$ with $R^2 = 0.9893$.](image-url)
Oxygen saturation in $\beta$-Zr phase

- No $\alpha$-Zr grains in middle of prior $\beta$-Zr
- $\alpha$-Zr grains precipitation in $\beta$-Zr
Oxygen saturation in β-Zr phase

- very good agreement between both SIMS and TEA results
- the oxygen concentration in the prior β-Zr rises with rising exposure temperature and time
- the experimental scatter is mainly caused by various hydrogen content and various cooling rate
Oxygen saturation in $\beta$-Zr phase

- ceiling oxygen concentrations in $\beta$-Zr are close to ceiling oxygen concentrations in $\beta$-Zr at Zry-4 alloy.
Pseudo-binary Zr1Nb-O phase diagram

\[ \beta = 777.89e^{0.7208x} \]
\[ R^2 = 0.9569 \]

\[ \gamma = 722.49e^{0.1210x} \]
\[ R^2 = 0.9766 \]

other authors’ results (M5\textsuperscript{TM}) [4]
Conclusions

- $\alpha$-Zr(O) layer kinetic was set up in the cladding of Zr1Nb alloy – the kinetic is parabolic and slower in comparison with Zry-4.

- The oxygen concentration and the nano-hardness at $\alpha/\alpha+\beta$ phase boundary in the cladding of Zr1Nb are close to the oxygen concentration and the nano-hardness at $\alpha/\alpha+\beta$ phase boundary in the cladding of Zry-4 with ~ 2000 wppm hydrogen content.

- The relation between nano-hardness and oxygen concentration at $\alpha/\alpha+\beta$ phase boundary in the area of $\alpha$-Zr(O) was specified.

- Ceiling oxygen concentrations in $\beta$-Zr are close to ceiling oxygen concentrations in $\beta$-Zr at the Zry-4.

- The procedure of the pseudobinary phase diagram assessment was set up.

- On the base of results of nano-hardness measurement, WDS, micro-hardness measurements, SIMS and TEA analyses the Zr1Nb-O phase diagram was estimated in the 950-1200 °C temperature range and the 0.1 až 4.0 wt.% concentration range: $T_{\beta/\alpha+\beta} = 777.8e^{0.72C}$ a $T_{\alpha+\beta/\alpha} = 722.4e^{0.121C}$.
Thank you for your attention!
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References


