Modelling of zircaloy-4 cladding degradation in nitrogen-oxygen mixtures at 850°C

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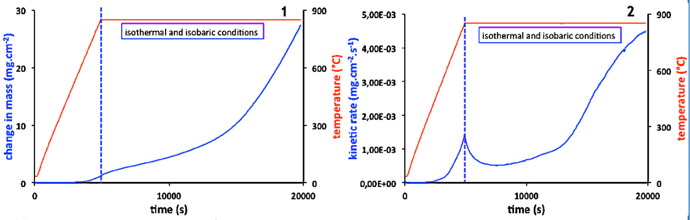
INTRODUCTION

Zy4 cladding, providing the first containment of UO_2 fuel, could be **exposed to air** in case of severe accident in nuclear power plant (PWR: pressurized water reactor).

Kinetic analysis is made to understand the corrosion mechanism of Zy4 plates at 850°C in nitrogen and oxygen mixtures during **post-transition stage** :

-does the corrosion proceed in a steady-state ?
-is the assumption of a rate-determining step confirmed?
-what is the influence of oxygen and nitrogen partial pressures on the kinetic rate and how could it be explained?



Thermogravimetric test at 850°C in 20% O_2 - 80%N_2 mixture; **1** change in mass as a function of time and **2** derivation versus time of the change in mass (kinetic rate)

EXPERIMENTS

Thermogravimetric tests

Symmetrical balance Setaram TAG-24
Plates of recrystallized Zy4 (10mm x 10mm) : 1.32-1.35 wt.% Sn
Experimental conditions :

- $O_2 - N_2$ – He or Ar flowing mixtures (10 $L.h^{-1}$)
- heat-up ramp to 850°C : 10°$C.min^{-1}$
- total pressure: 1 atm

KINETICS TESTS

Steady-state and rate-determining step assumptions validation[1]:

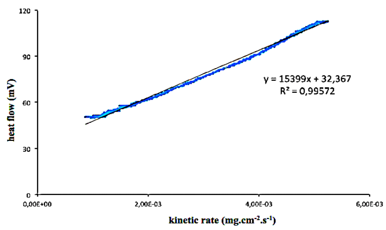
$$\frac{d\left(\frac{\Delta m}{S}\right)}{dt} = \frac{n_0 . M(O_2)}{S} . \frac{d\alpha}{dt} = \frac{n_0 . M(O_2)}{S} . \Phi . Sm(t)$$

1) Steady-state approximation:

Heat flow (dQ/dt) versus mass gain rate (dΔm/dt)
→ **test validated if the kinetic rates measured by the two methods are proportional**

$$\frac{d\Delta m}{dt} = -\frac{\sum_G (M_G . \nu_G)}{\Delta H} . \frac{dQ}{dt}$$

- ΔH: enthalpy of reaction
- M_G: molar mass of gas
- n_G: stoichiometric number of gas



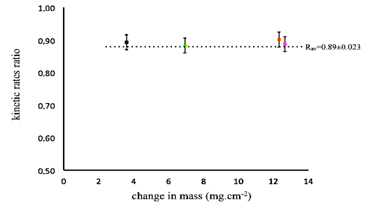
Steady-state test in 20% O_2 - 80%N_2 mixture

2) Rate-limiting step assumption: ΦSm test jumps method

Jumps from temperature T_1 to temperature T_2 for experiments conducted up to various change in mass (t_a, t_b, etc.)
→ determination of **the ratio of kinetic rates after and before the jump**

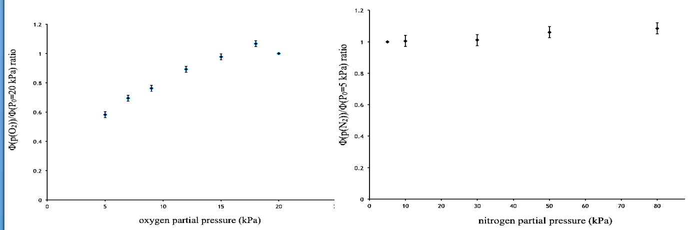
$$R = \frac{\left(\frac{d\left(\frac{\Delta m}{S}\right)}{dt}\right)_2}{\left(\frac{d\left(\frac{\Delta m}{S}\right)}{dt}\right)_1} = \frac{B_0 . \Phi(T=830) . \cancel{Sm(t_a)}}{B_0 . \Phi(T=850) . \cancel{Sm(t_a)}} = \frac{B_0 . \Phi(T=830) . \cancel{Sm(t_b)}}{B_0 . \Phi(T=850) . \cancel{Sm(t_b)}} = \frac{\Phi(T=830)}{\Phi(T=850)}$$

ΦSm test in 20% O_2- 80%N_2 mixture with temperature jumps from 850°C to 830°C. Kinetic rates ratio obtained for various change in mass is constant: R = 0.89 → **a rate determining step controls the growth process**



3) Pressure jumps : study of Φ(p(O_2)) and Φ(p(N_2))

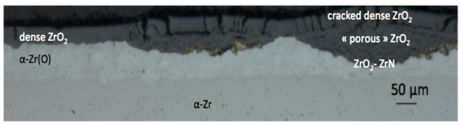
Pressure jumps at 8$mg.cm^{-2}$:p(N_2) or p(O_2) changes



p(O_2) =20 kPa and p(N_2)= 80 kPa
➔ **Φ(p(O_2)) variable**

p(O_2) =20 kPa, p(N_2)= 5 kPa and p(He)= 75 kPa
➔ **Φ(p(N_2)) = constant**

4) Zy-4 post-transition sample



"Porosity" of the oxide layer due to:
→ cracks during ZrN creation
→ cracks in dense zirconia during oxidation of ZrN

MODELLING - CONCLUSION

Optical micrography + SEM → 3 reactions

❑ **oxidation of ZrN precipitates** $PBR_{ZrO2/ZrN}$=1,47
$$O_2 + ZrN = ZrO_2 + N^*$$

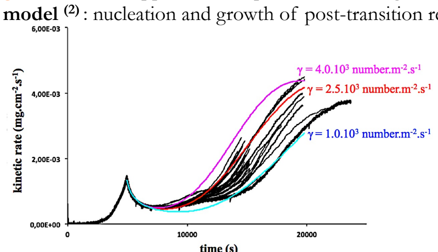
❑ **nitridation of metal** $PBR_{ZrN/Zr}$ =1,03
$$N^* + ZrO_x = ZrN + x\,O^*$$

❑ **oxidation of metal** $PBR_{ZrO2/Zr}$ =1,51
$$(2-x)O^* + ZrO_x = ZrO_2$$

Steady-state and rate-determining step assumptions have been validated.

-**Φ modelling**: kinetic rate strongly dependant of p(O_2)
→ controlled by **interfacial reaction** step of ZrN oxidation

-**Sm modelling**: non uniform appearance of post-transition regions → nucleation
→ **Mampel's model** [2] : nucleation and growth of post-transition regions



Comparison of the model with experimental results
Conditions : flow rate = 10 L/h, p(O2) = 20 kPa, p(N2) = 80 kPa, T = 850°C

References
(1) M. Pijolat & al., *Thermochim. Acta* 478, 34 (2008)
(2) B. Delmon, *"Introduction à la cinétique hétérogène"*,Technip Editions, Paris (1969)