

# Hafnium Oxidation in Steam at High Temperature

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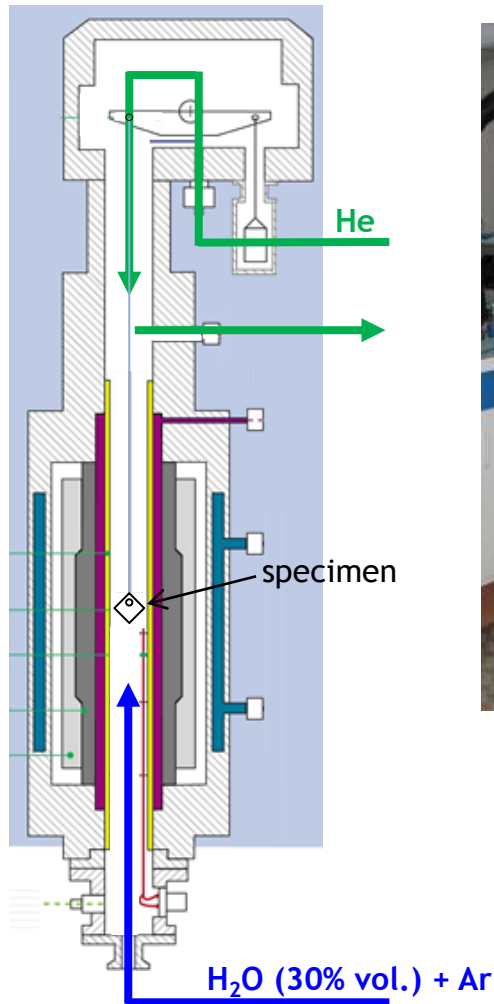
25<sup>th</sup> QUENCH Workshop, Karlsruhe, 22-24 Oct. 2019

# Contents

- Context
- Experimental devices
- Materials & Methods
- Experimental results
- Summary

- EDF plans to generalize the introduction of absorber rods of hafnium **not sheathed** in the 12 assemblies positioned in the core periphery in order to reduce the flux received by the vessel (900 MWe)
- $Hf + 2H_2O \rightarrow HfO_2 + 2H_2 : \Delta_r H^\circ (1500^\circ C) = -611 \text{ kJ/mol}$
- In SA, possible existence of a **runaway temperature** of the reaction between Hf and H<sub>2</sub>O ?
  - This runaway could lead to an early acceleration of the oxidation phenomena of the surrounding materials (and in particular the Zry-4) with increased hydrogen production and heat release.
- Hf/H<sub>2</sub>O interaction investigated in the past
  - Most studies at LT (< 700 °C)
  - Only one study in steam at 700-1200 °C by D'yachkov (2006)
  - Indicative of **better resistance** of Hf than Zr
- Hf/H<sub>2</sub>O interaction tests **at KIT and at IRSN**
  - KIT objective : to prepare the QUENCH-debris test
  - 600 °C to 1400 °C
  - Different materials (disc, rods and tube)

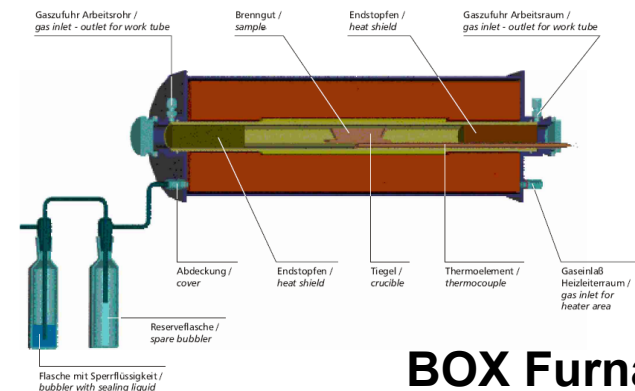
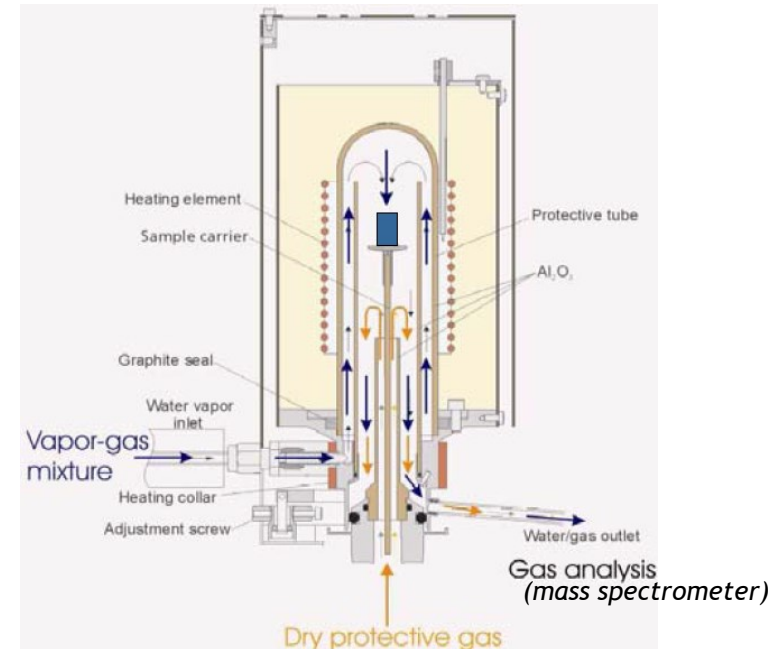
## SETARAM thermobalance



## HT Furnace



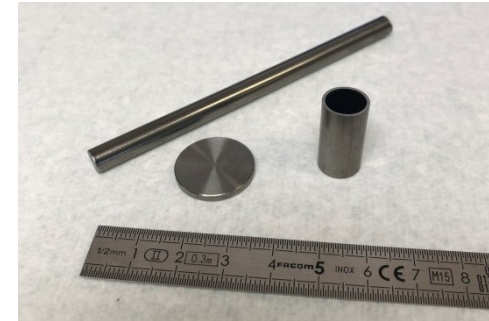
## NETZSCH STA 409 thermobalance



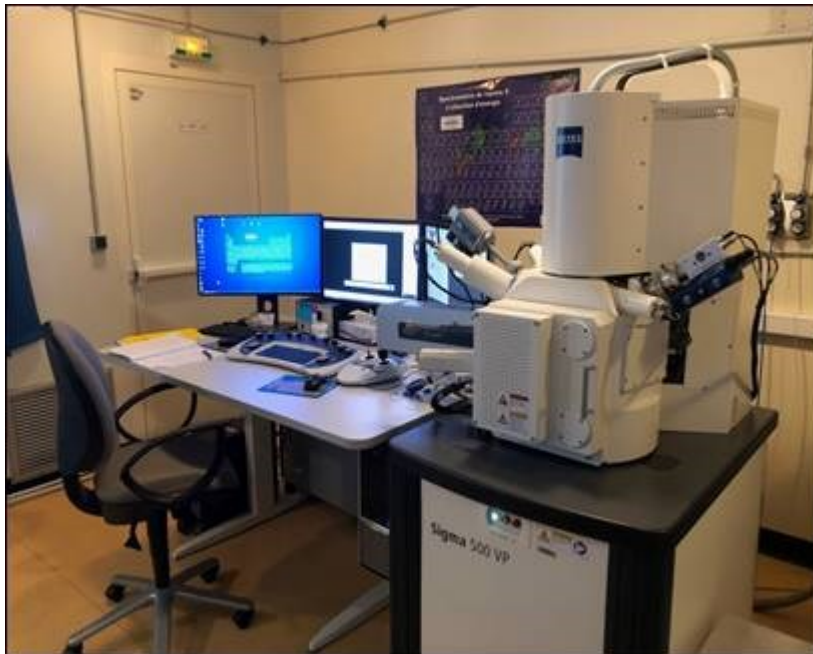
## BOX Furnace

Oxidation temperature range: 600-1400°C - Isothermal tests up to 60h

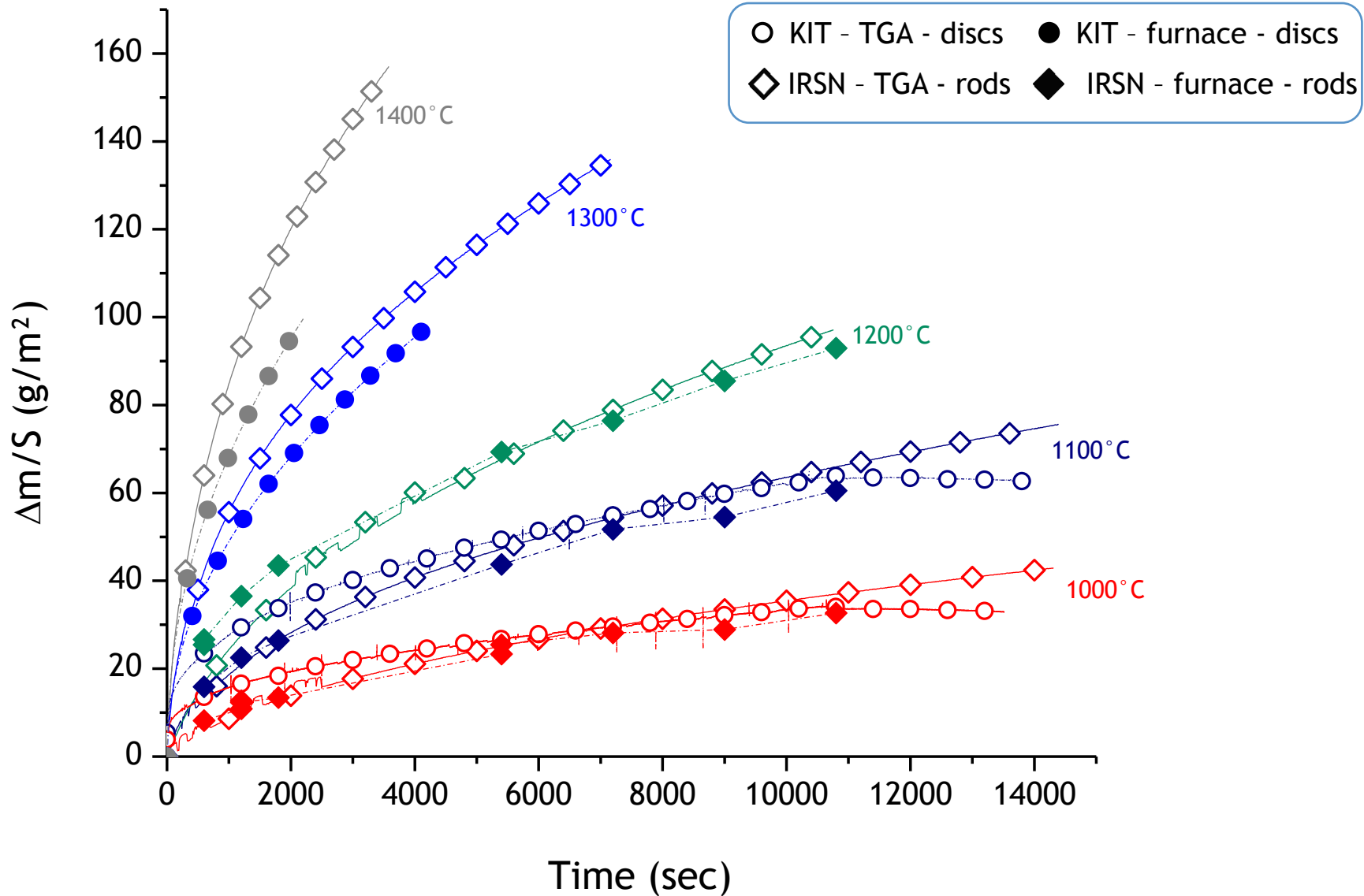
- Hafnium rods, discs and tubes



- Weight gain, metallography, EPMA, hydrogen measurements



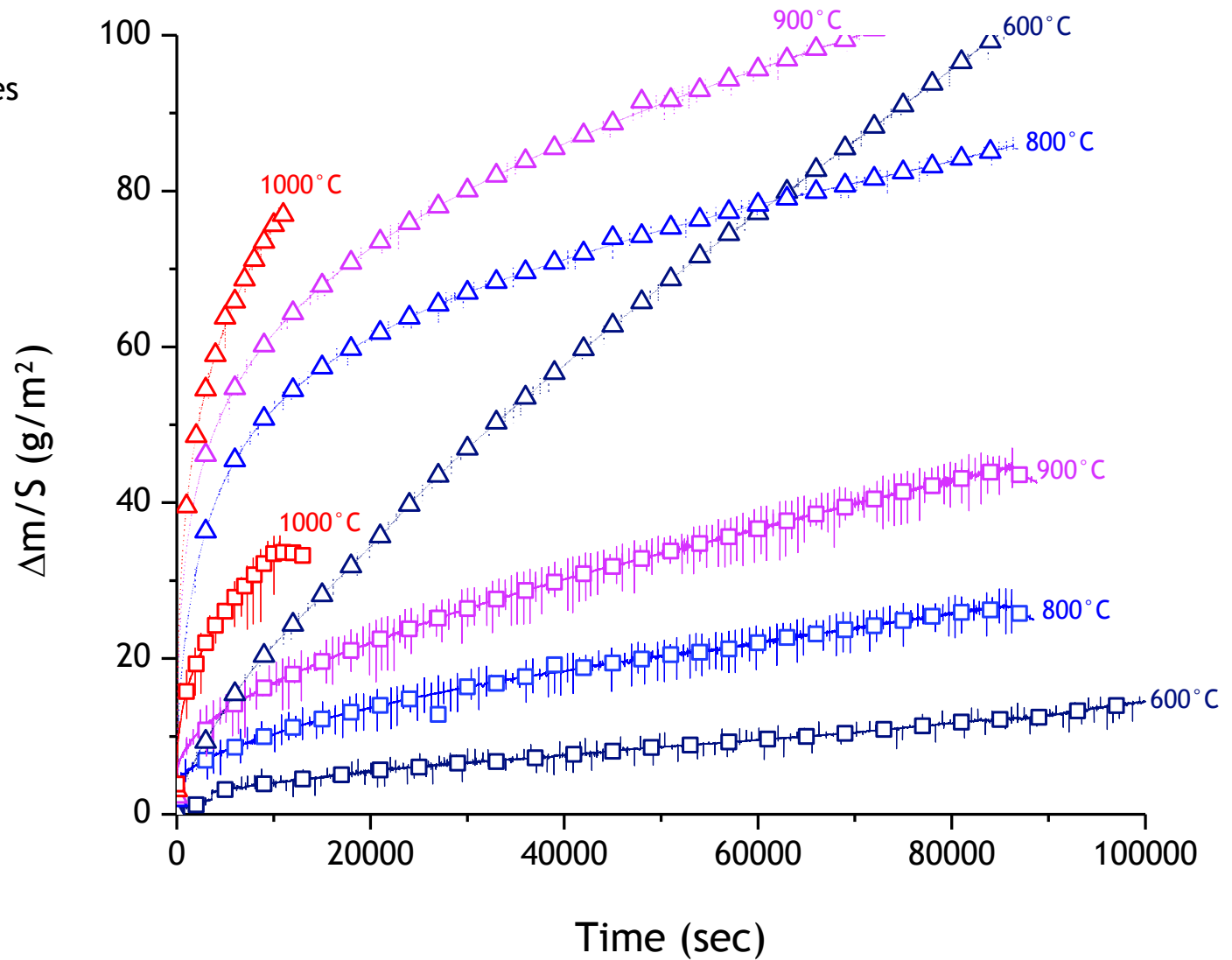
# Weight gain: comparison of furnace and TGA experiments



■ Good agreement between furnace and TGA experiments

# Weight gain : comparison of Hf rod and Hf tube results

□ Hf rods / △ Hf tubes



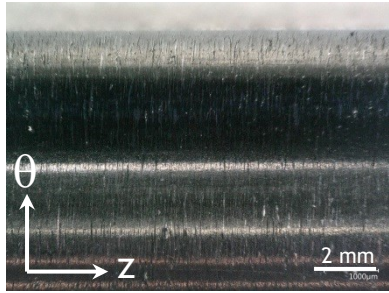
Large difference in oxidation kinetics between Hf rods and tubes....



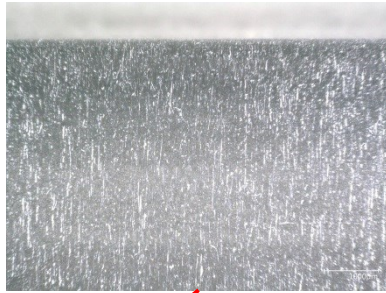
# Oxide microstructure: comparison of Hf rod and Hf tube's results

.....linked to a difference in oxide microstructure

as-received Hf rod



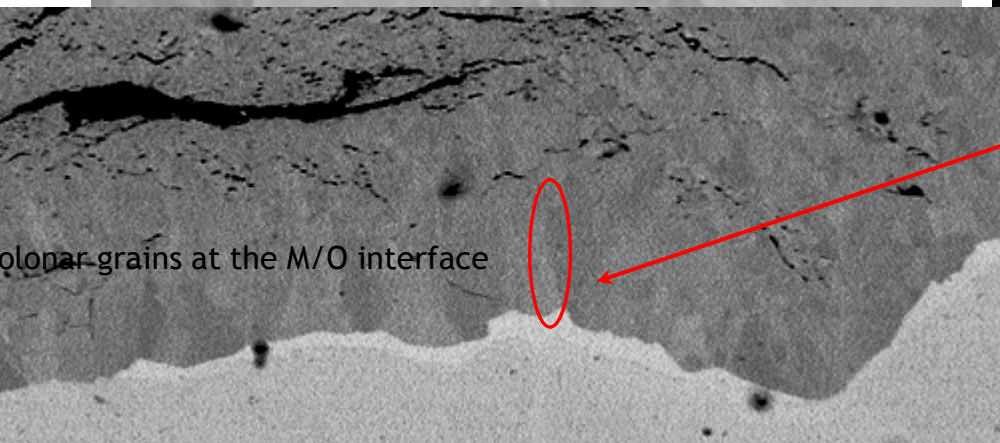
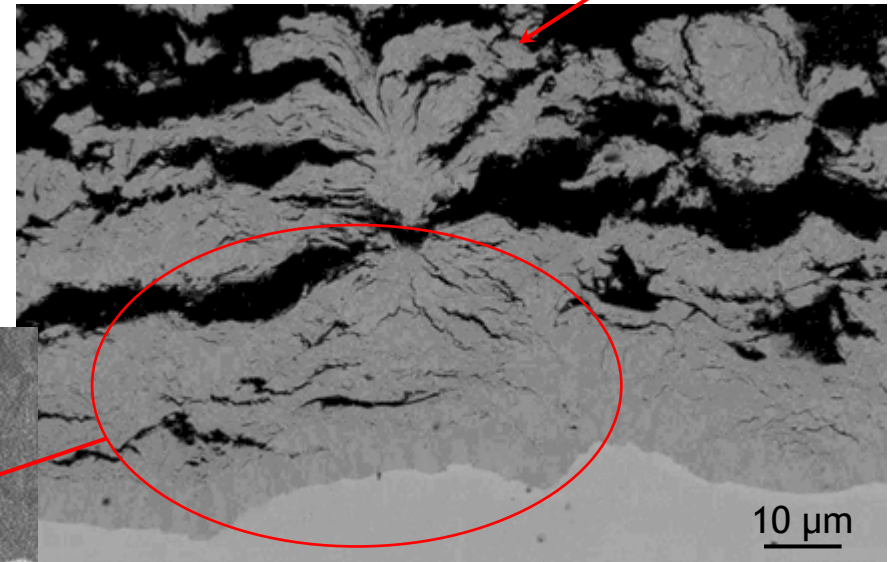
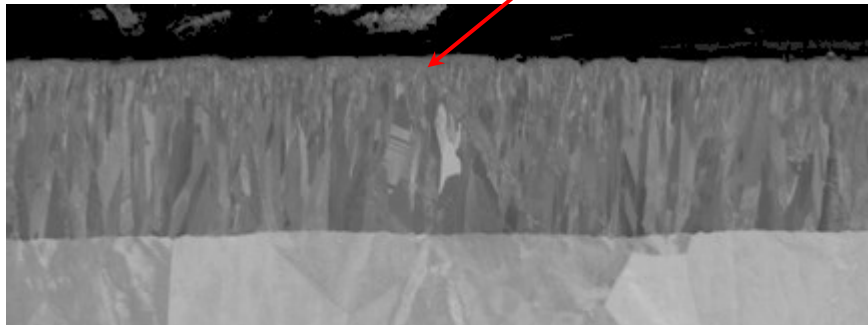
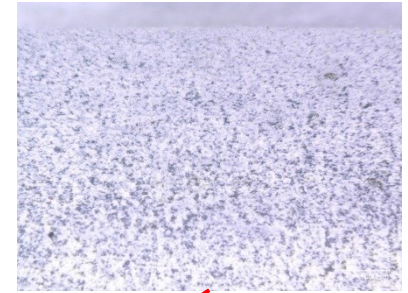
after ox900°C, 22h



as-received Hf tube

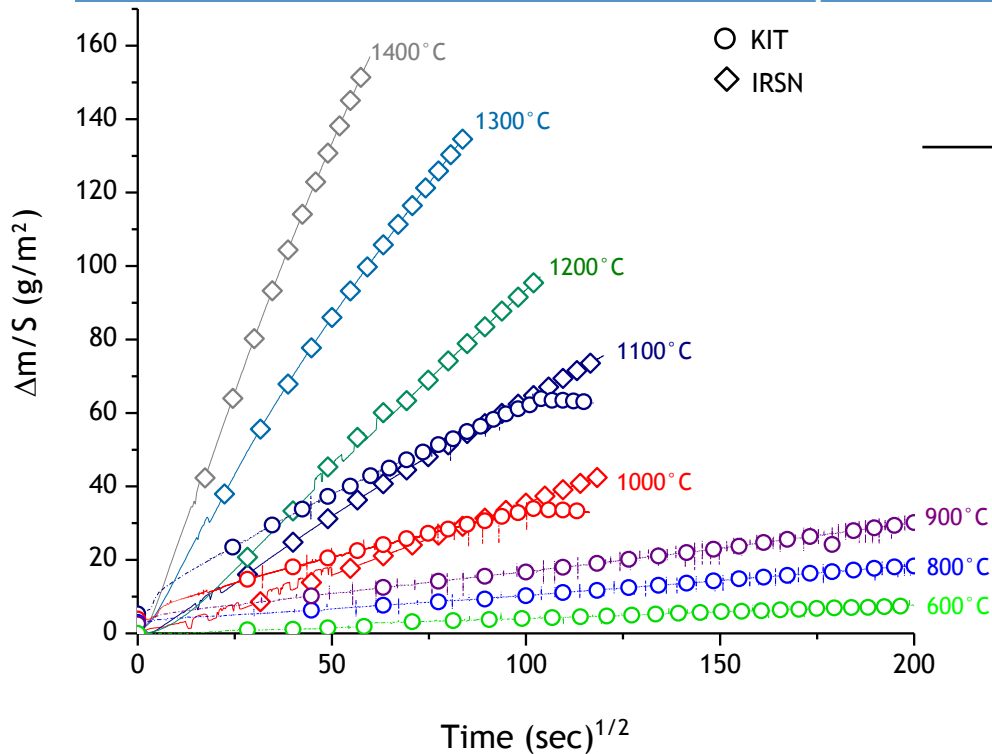


after ox900°C, 22h





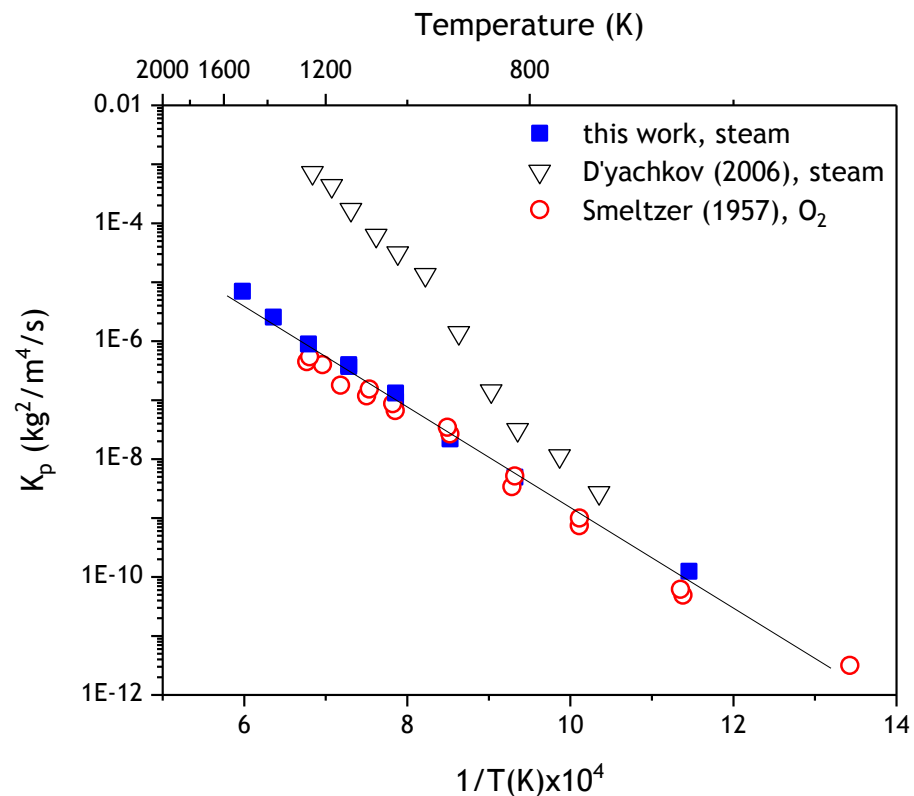
# Parabolic rate constant $K_p$



$$K_p = A \exp \frac{-E_a}{RT}$$

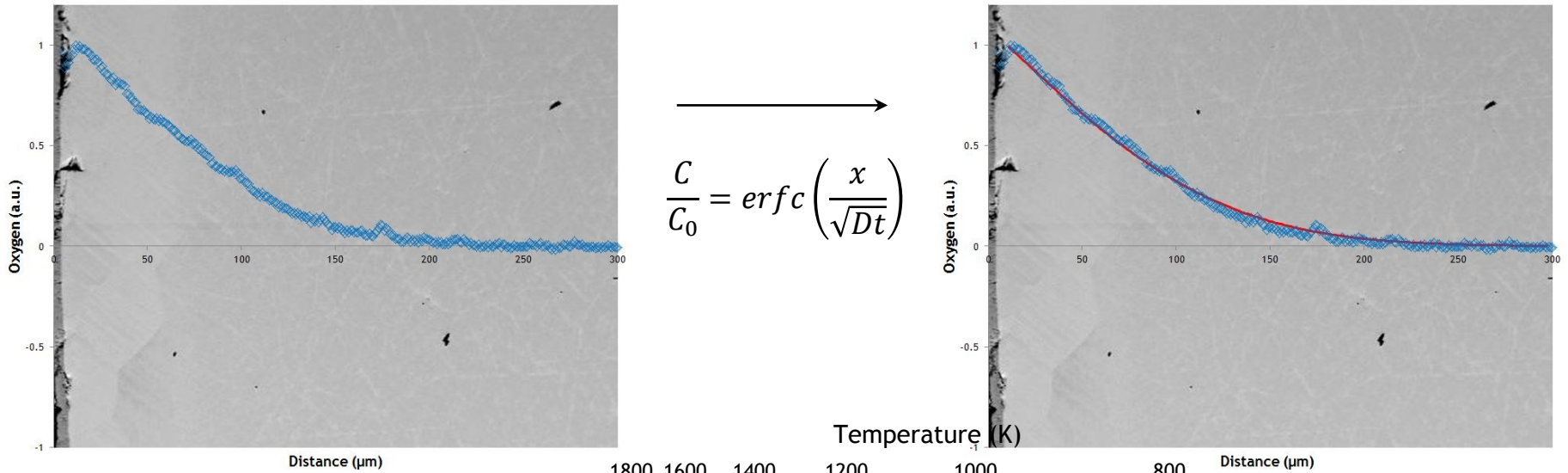
with  $E_a = 189,2 \text{ kJ.mol}^{-1}$

$$\left(\frac{\Delta m}{S}\right)^2 = K_p \times t$$



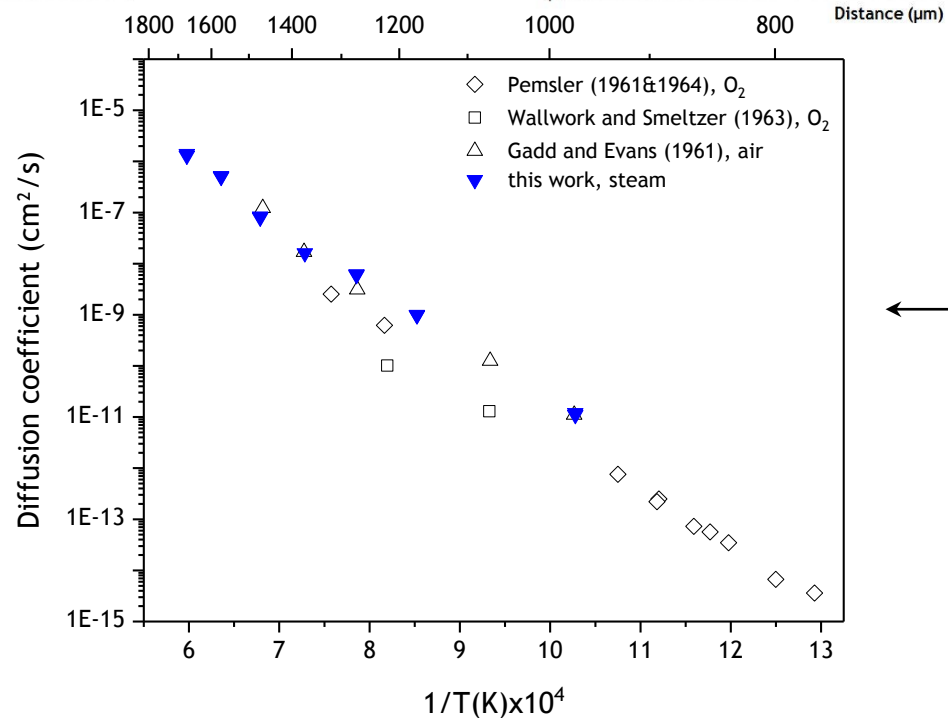
in good agreement with the activation energy obtained by Smelter and Pemsler

# Oxidation of Hafnium rods: oxygen diffusion in metal

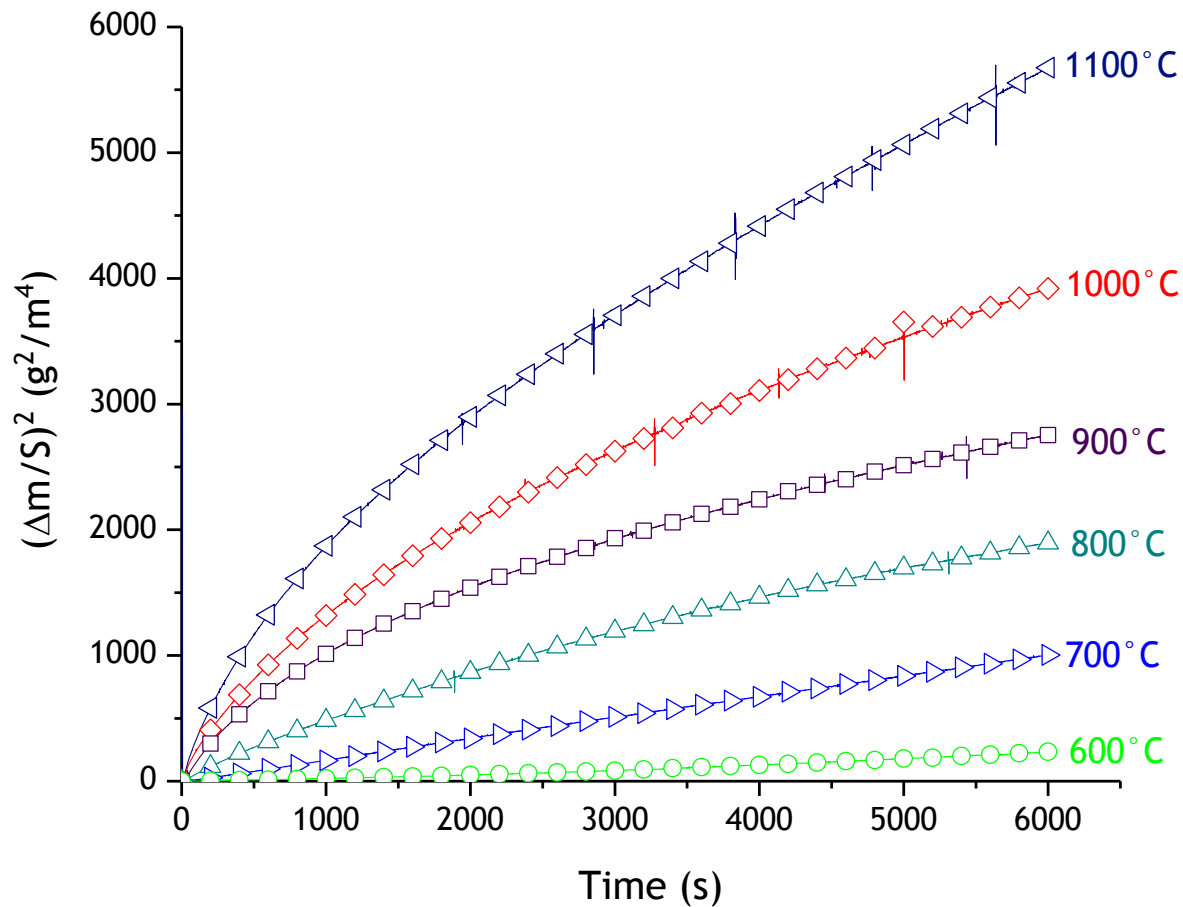


$$D = A \exp\left(\frac{-E_a}{RT}\right)$$

with  $E_a = 224,3 \text{ kJ.mol}^{-1}$

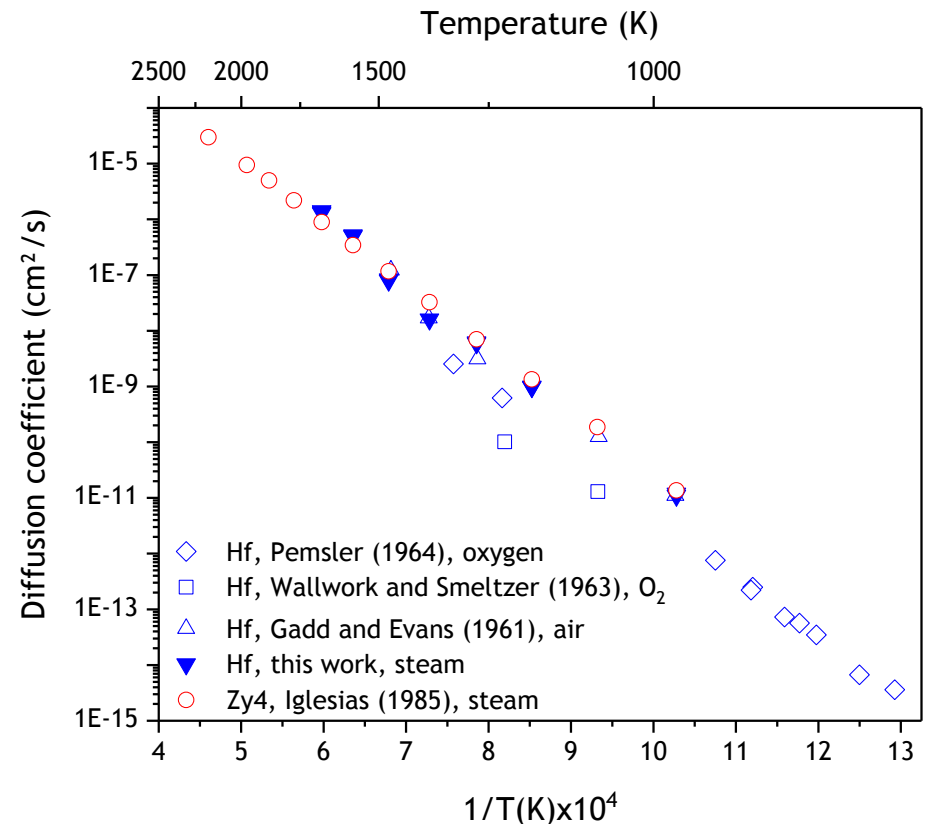
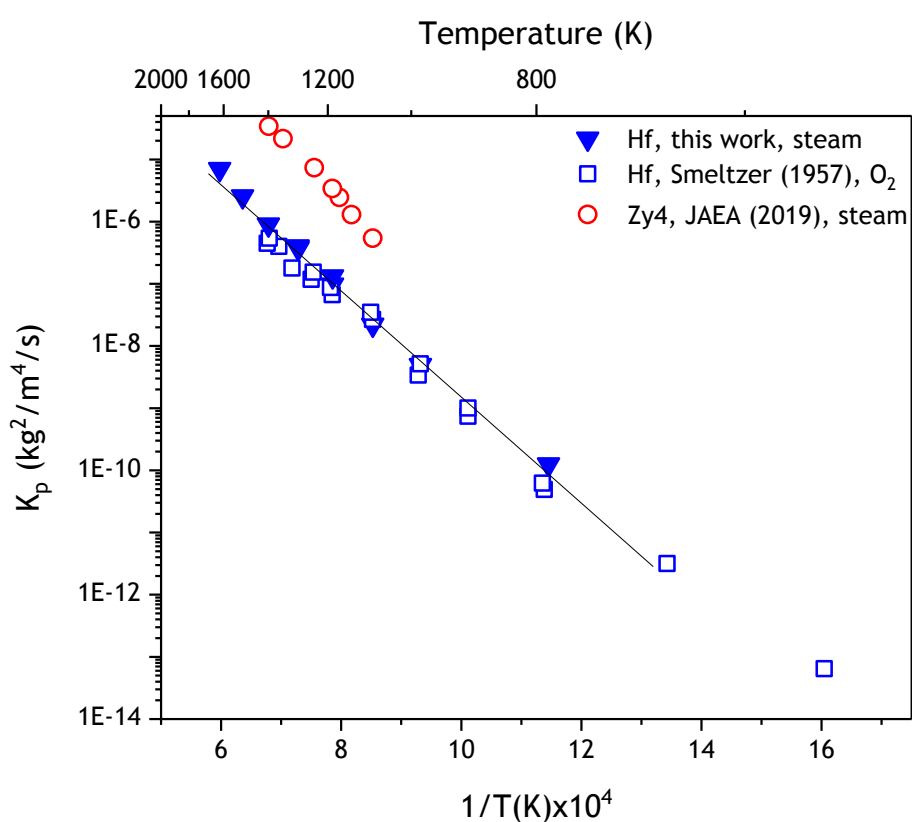


# Oxidation of Hafnium discs



- The oxidation rate is not parabolic above 700°C
- The higher oxidation rate seems to be associated to hydrogen pickup (>600 ppm after oxidation at 900°C for 22h)

# $K_p$ rate constant and oxygen diffusivity : Hf versus Zy4



■ The oxygen diffusivity in hafnium and in Zircaloy-4 is of the same order

■ However, the parabolic rate constant is much lower than in Zircaloy-4

- The oxidation rate of hafnium in steam was determined in the temperature range 600-1400 °C,
- The parabolic rate constant and the diffusion coefficient in the metal were estimated for hafnium rods/discs,
- Clearly, the oxidation rate depends on the surface conditions of the samples
- However, it remains well below the oxidation rate of Zircaloy-4
- First calculations show little impact on accident progression but, interactions between hafnium and core materials should be investigated to confirm this result.



Thank you for your attention !

# Comparison with Cr-coated Zy-4

