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DE RADIOPROTECTION
ET DE SÛRETÉ NUCLÉAIRE

SAFETY OF SOME FUEL CLADDING MATERIALS, ALTERNATIVE TO Zr ALLOYS

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Introduction

- In France, PWRs with large dry containment and H_2 recombiners to prevent detonation or deflagration-to-detonation-transition in case of severe accidents
- Fukushima Daiichi accident : Impact of hydrogen production on LWR core melt accident behavior
- New fuel cladding (& structural) materials under development by industry (presentation by EPRI during CSNI/WGFS meeting)
- Bibliographic study by IRSN

Method

Fuel cladding material behavior during LWR severe accident (cladding oxidation by steam) :

- **Number of H_2 moles produced per cladding length unit at thermochemical equilibrium**
- **Oxidation kinetics**
- **Heat of reaction**
- **Physico-chemical interactions between material or oxidation products and fuel**

Silicon carbide (SiC)

- **Number of CO + H_2 moles produced**
  - During SiC oxidation by steam, nearly 3 times more explosive gases (CO + H_2) moles produced per cladding length unit at thermochemical equilibrium
- **SiC oxidation kinetics below 1700°C (1)**
  - NASA, ORNL
  - Linear oxidation but protection by a thin vitreous SiO_2 layer :
    - Either volatilisation into $Si(OH)_4$ or $SiO(OH)_2$ (high steam flow rate)
    - Either devitrification into unprotective porous cristobalite layer (high steam pressure)
  - Importance of the steam pressure and flow rate

SiC oxidation kinetics below 1700°C (2)

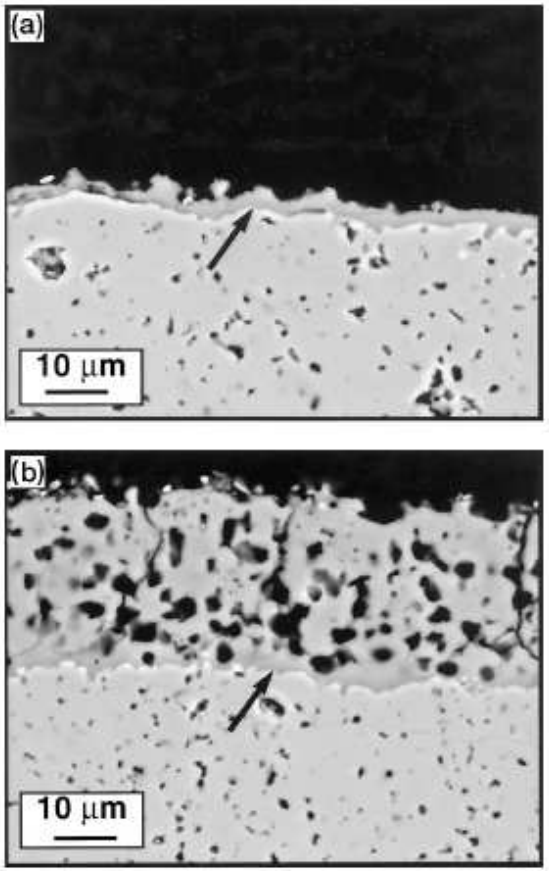


Fig. 2. Silica scale on sintered α-SiC after exposure at 1200°C for 100 h at 10 atm in (a) air only and (b) air+H_2O. Only a thin, dense silica layer formed when no H_2O was present.

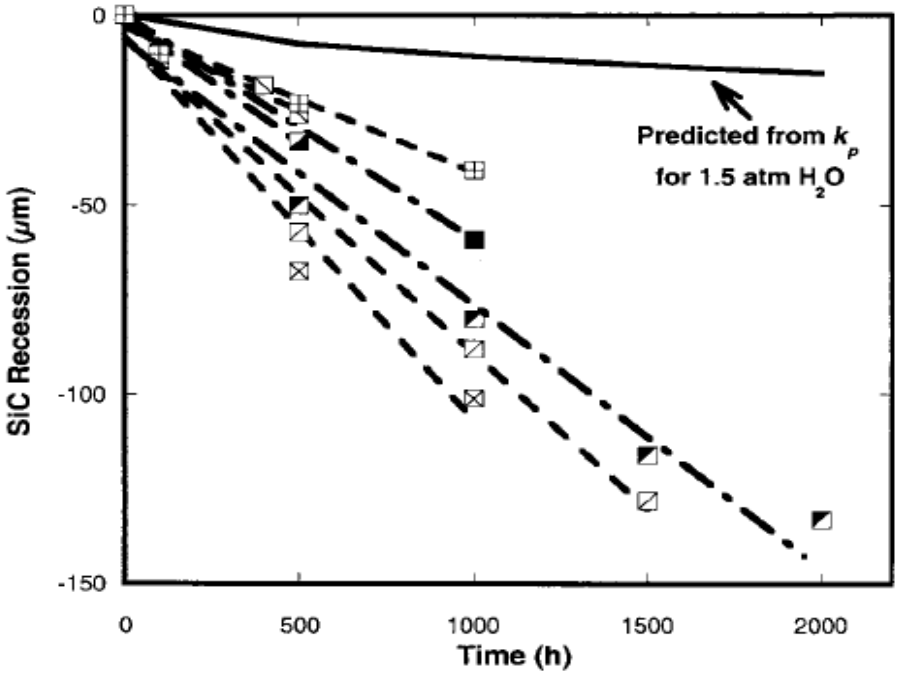


Fig. 8. SiC recession as a function of exposure time for air + 15% H_2O at 1200°C and 10 atm. Data points represent average recession and lines (black for CVD-SiC and gray for α-SiC) are best linear fits. CVD-SiC data represented by fully and partially shaded squares. Sintered α-SiC data shown as squares enclosing ×, +, /, or \. Upper solid curve (no data points) is based on recession controlled by parabolic oxidation kinetics with a k_p value calculated for this temperature and gas environment using the formulation of Opila.[8]

SiC oxidation kinetics below 1700°C (3)

- **Steam pressure during DBA :**
  - Large break LOCA : 5 bars (NRC Reactor Safety Course)
  - 3" LOCA : 35 bars (NRC LOCA PIRT)
- **MIT tests at atmospheric pressure and 1140-1200°C : weight loss two orders of magnitude less than Zry-4 weight gain**
- **ORNL tests at 3.4-10 bars and 800-1200°C : material recession much less than for Zrys**
- **Lack of tests at ~40 bars**

SiC oxidation kinetics below 1700°C (4)

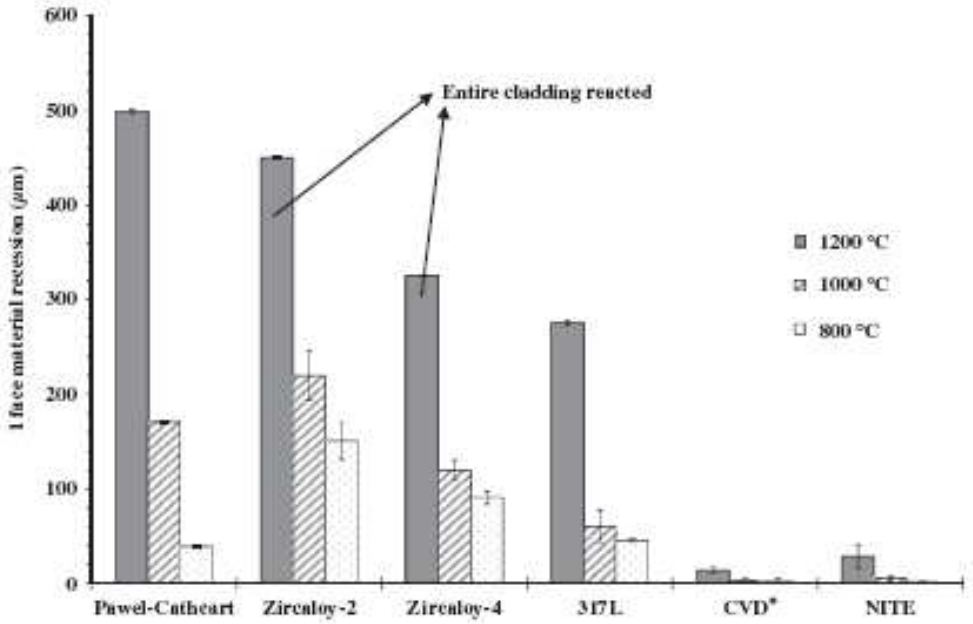


Fig. 1. Material recession of zirconium alloys, 317L steel and NITE SiC after 8 h exposure at 800 °C, 1000 °C and 1200 °C in 1 MPa steam. Materials loss of CVD SiC (labeled as CVD*) under that condition was approximated based on the results of CVD SiC specimens exposed in 0.34 MPa steam. Extent of zirconium alloy oxidation predicted by Pawel–Cathcart correlation [3] is provided for comparison. (Note that the materials loss values for the Zircaloys at 800 °C and 1000 °C do not include oxygen-stabilized α-Zr embrittled regions.)

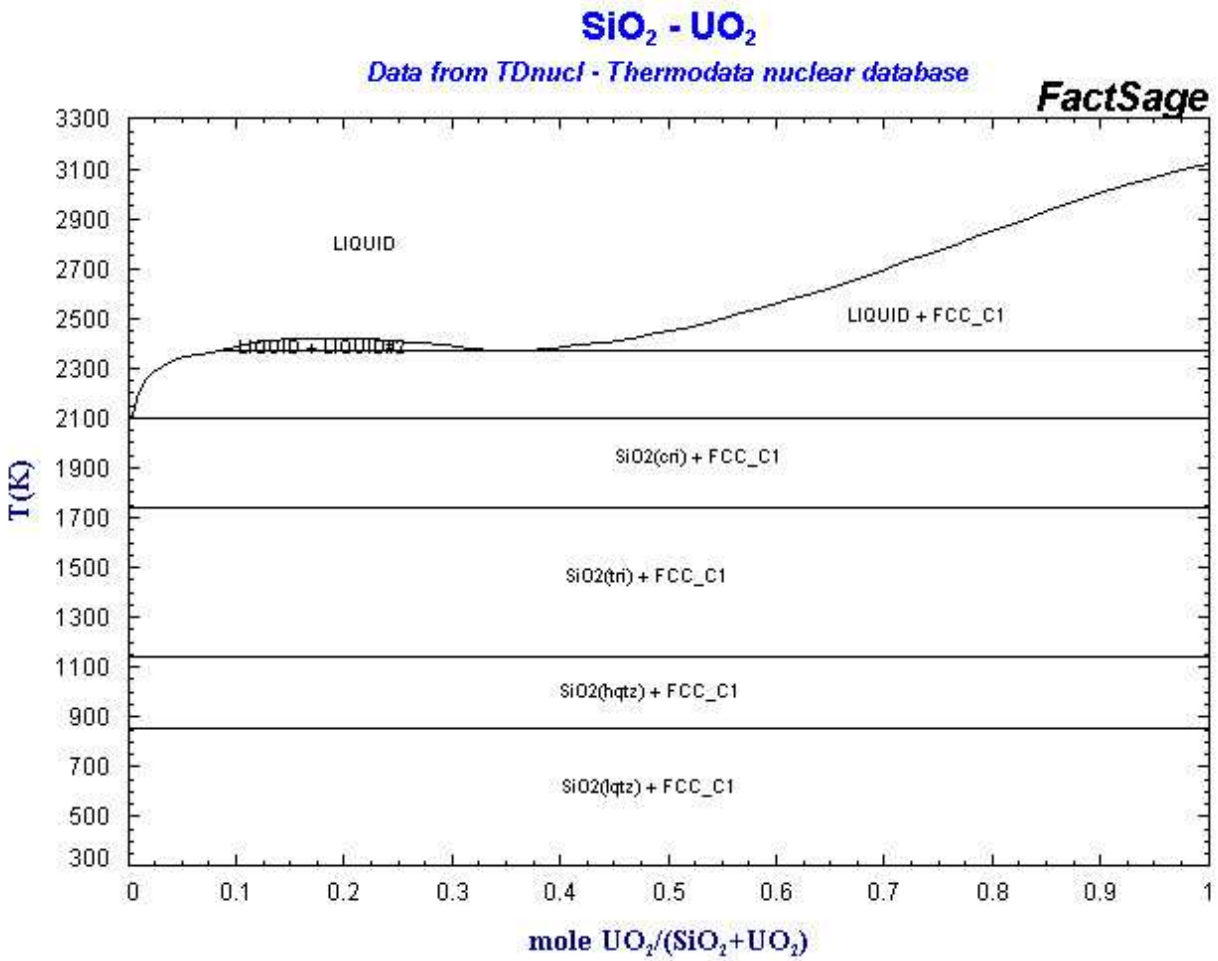
SiC oxidation kinetics above 1700°C

- Molten SiO_2 looses its protective effect
- « Catastrophic oxidation by molten oxides » (P. Kofstad)
- Cliff-edge effect
- Oxidation limited only by steam diffusion in gas phase (steam starvation, CO + H_2 blanketing)
- Saturation of recombiners, risk of CO + H_2 explosion in the containment (PWR)

SiC heat of reaction and physico-chemical interactions

- **Heat of reaction**
  - Nearly 2 times more heat of reaction produced per cladding length unit at thermochemical equilibrium
- **Physico-chemical interactions**
  - Molten SiO_2 will interact with UO_2 to form molten mixtures at temperatures well below UO_2 melting temperature

SiO_2/UO_2 interaction



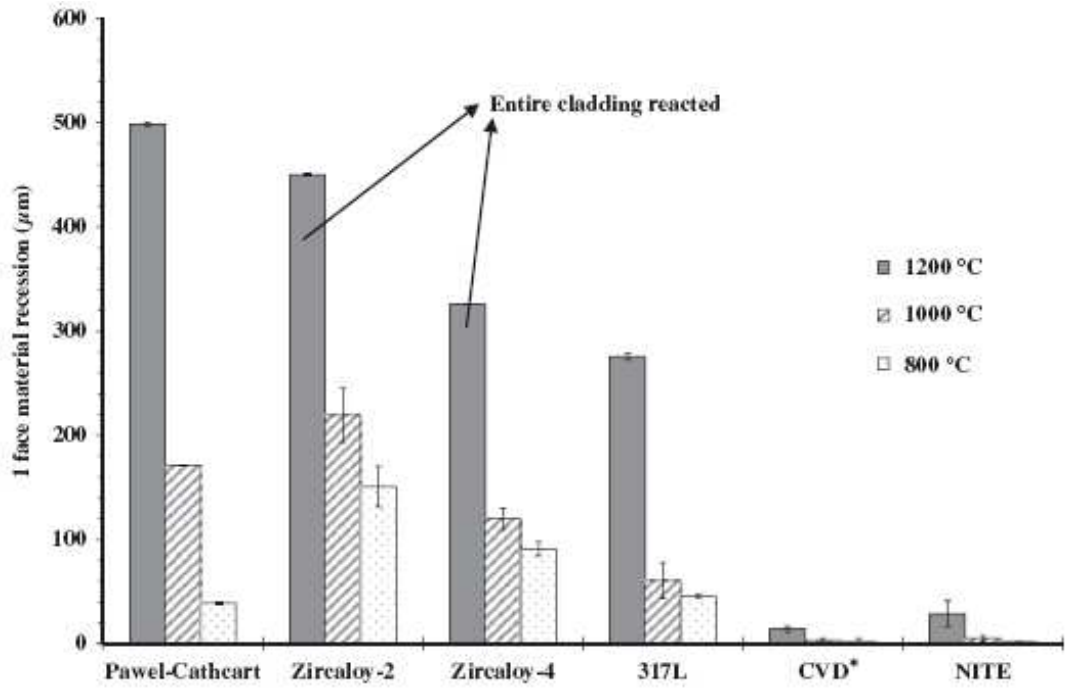
SiC MAAP calculations and conclusion

- **Calculations by Westinghouse & Fauske with MAAP (ICAPP-12)**
  - Assuming zero kinetics for SiC oxidation by steam and no physico-chemical interaction between SiO_2 and UO_2
  - Probable tolerance to DBAs and short duration severe accidents (TMI-2 like : 90 min between beginning of core uncovery and restart of a high pressure injection pump)
  - Intolerance to long duration severe accidents (extended station blackout), 1700°C may be reached 3 hours after beginning of core uncovery (Fukushima Daiichi-1 : 12-13 hours between beginning of core uncovery and start of water injection)
- **As a conclusion, despite probable tolerance to DBAs and short duration SAs, SiC seems to present essentially drawbacks compared to Zr alloys, under long duration Severe Accidents**

Stainless steels (SS)

- **Number of H_2 moles produced**
  - As Fe_2O_3 decomposes peritectically into Fe_3O_4 at 1457°C, we assume no Fe_2O_3 formation
  - Practically the same number of H_2 moles produced per cladding length unit at chemical equilibrium (Fe_3O_4)
- **SS oxidation kinetics below 1600°C (1)**
  - Depending on alloying elements, protection by a Cr_2O_3- or Al_2O_3-rich layer
  - Volatilization into $CrO_2(OH)_2$ or CrO_2OH or $Al(OH)_3$
  - 304L oxidizes faster than Zrys above 1150°C (CSNI SOAR)
  - 1.4970 steel is slightly better, due to Ti addition (FBR alloy)
  - 1.4914 ferritic steel is worse, due to lower Cr content (supercritical water reactor alloy)
  - New results by ORNL
  - Fe-25Cr or PM2000 (19 % Cr, 5 % Al) are comparable to SiC at 1200°C

SS oxidation kinetics below 1600°C (2)



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SS oxidation kinetics below 1600°C (3)

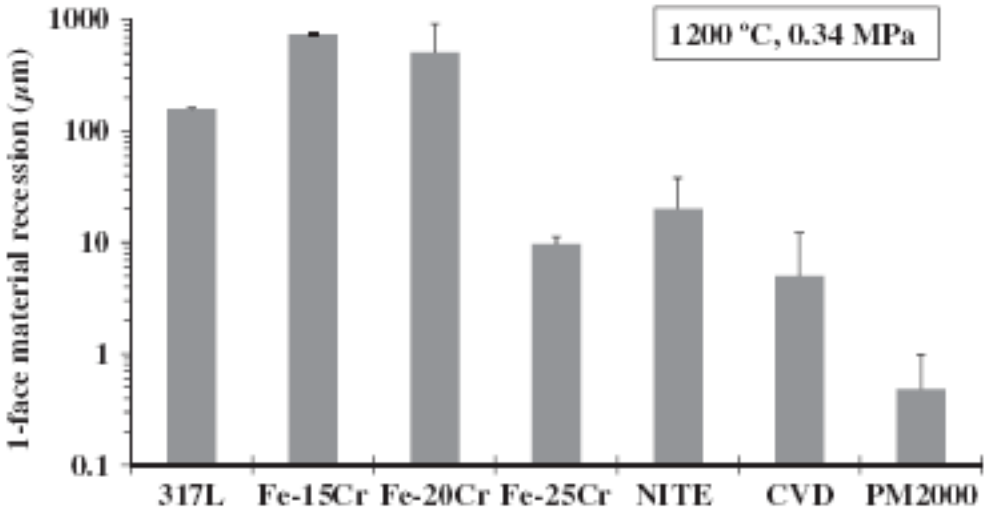

Fig. 5. Material recession of Fe–Cr, PM2000 alloys and NITE and CVD SiC after exposure for 8 h at 1200 °C in 0.34 MPa steam.

SS oxidation kinetics above 1600°C

- FeO_x is molten
- « Catastrophic oxidation by molten oxides » (P. Kofstad)
- Cliff-edge effect
- Oxidation limited only by steam diffusion in gas phase (steam starvation, H_2 blanketing)
- Saturation of recombiners, risk of H_2 explosion in the containment (PWR)

SS heat of reaction and physico-chemical interactions

Heat of reaction

- The main advantage of stainless steel is the lower heat of reaction produced per cladding length unit

Physico-chemical interactions

- However, molten FeO_x will interact with UO_2 to form molten mixtures at temperatures well below UO_2 melting temperature
- Possible intergranular attack leading to « wet sand » relocation (TMI-2)

FeO_x/UO_2 interaction

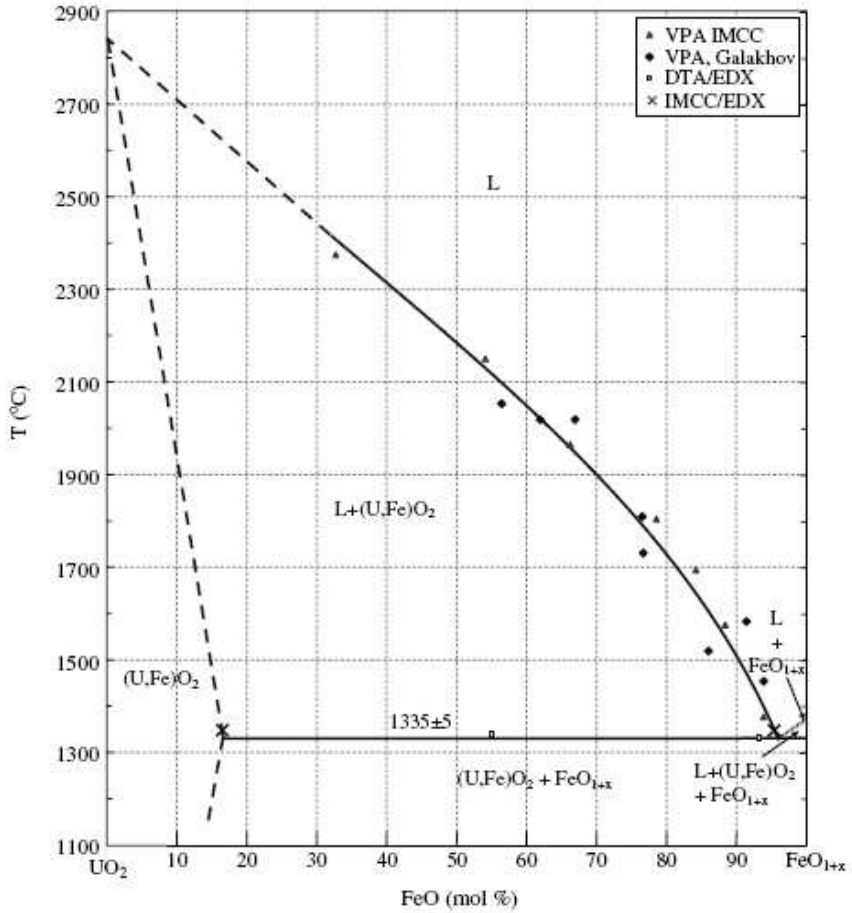

Fig. 5. Phase diagram of the UO_2–FeO_{1+x} system (inert atmosphere).

SS MAAP calculations and conclusion

- Necessity to perform calculations with system codes (ASTEC, MELCOR, MAAP…)
- None of the system codes (ASTEC, MELCOR, MAAP…) has models for catastrophic oxidation neither FeO_x/UO_2 interaction
- Calculations by Westinghouse & Fauske with MAAP (ICAPP-12) and 304L
  - Intolerance to long duration severe accidents (extended station blackout), temperature escalation delayed by 1 h but higher H_2 production
- Conclusion : even without fully adequate modelling, first calculations show no advantage for 304L during long duration severe accidents

Zr alloys reference

- **SS oxidation kinetics**
  - Parabolic oxidation
  - Faster kinetics when ZrO_2 is cubic, however ZrO_2 melts only at very high temperatures
- **Physico-chemical interaction**
  - Small reduction of the melting temperatures of the UO_2-ZrO_2 mixtures

ZrO_2/UO_2 interaction

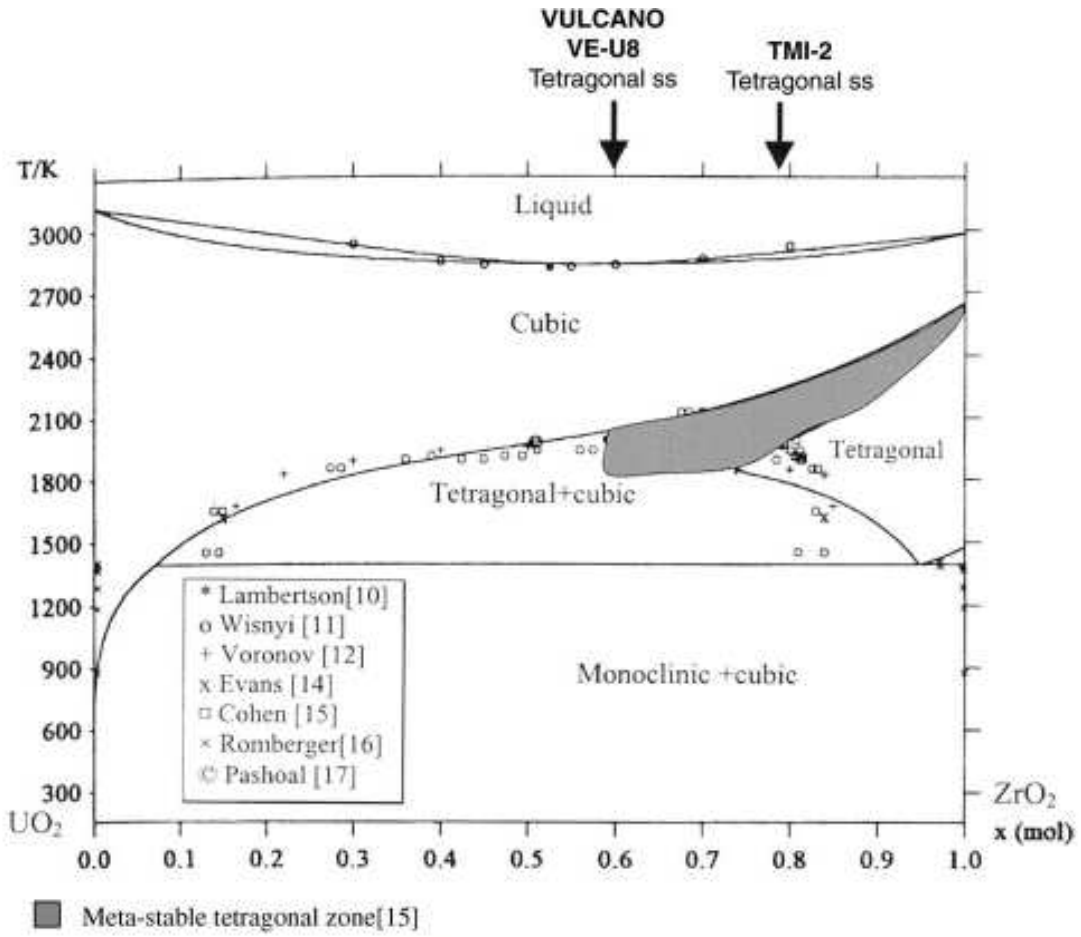

Fig. 2. UO_2–ZrO_2 phase diagram [3,22] and VULCANO VE-U8 and TMI-2 corium compositions.

Conclusion

- Despite probable tolerance to DBAs and short duration SAs, SiC seems to present essentially drawbacks compared to Zr alloys, under long duration Severe Accidents
- For 304L SS, even without fully adequate modelling, first calculations show no advantage for long duration severe accidents
- Zr alloys oxidation is more progressive, which helps to design H_2 recombiners