Thermodynamic properties of Fe-Zr-O system at high temperatures

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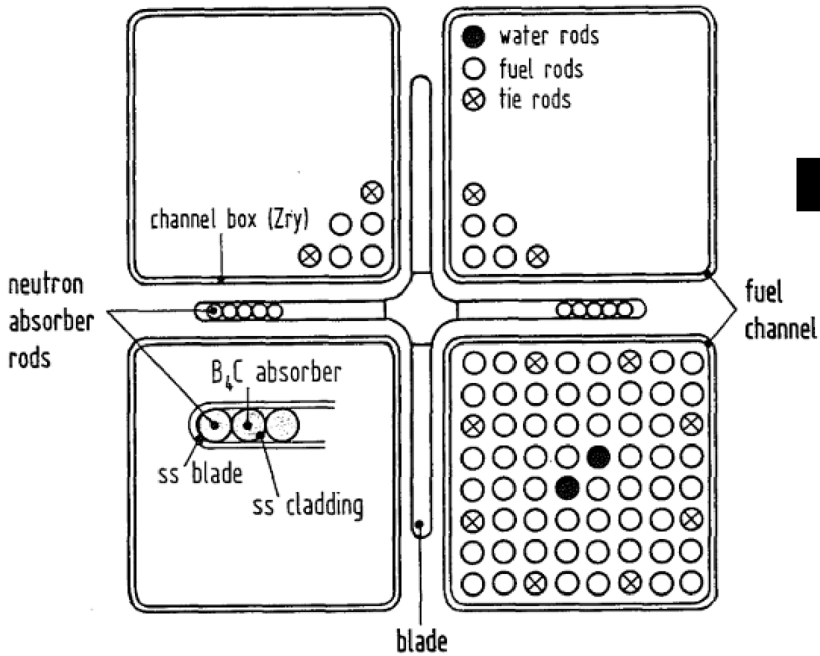
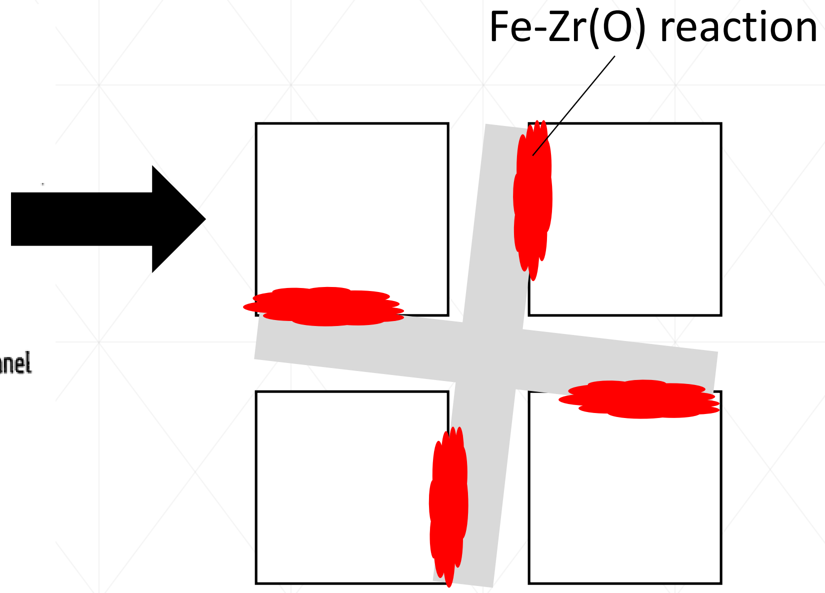
Background

From the point of view of FDNPP decommissioning (BWR type)

- Fe-Zr-O ternary system is important subsystem to understand the core degradation behavior on the severe accident conditions.
- Especially, the degradation of control blade is initiating process, which could involve the dissolution of Zry channel wall.



BWR cruciform control element [1]



Schematic image of deformation

[1] Hofmann, P., & Markiewicz, M. (1994). Chemical Interactions between as-received and pre-oxidized Zircaloy-4 and Stainless Steel at High Temperatures Kernforschungszentrum Karlsruhe. 81.

Objectives

Investigate thermodynamic properties of Fe-Zr-O system in low oxygen potential at high temperatures (1000 - 1500 ℃)

- The experimental data for Fe-Zr-O system is limited. There is still unknown behavior especially in the Zr(O) – Fe interaction region.
- Oxygen solubility in Fe-Zr liquid phase is crucial to predict the interaction of relocating metallic melt.
- Experimental assessment of phase formations for Zr(O) – Fe interaction is necessary to improve the accuracy of thermodynamics database.

Previous studies for Fe-Zr-O system

Effect of Zr on oxygen solubility in liquid iron

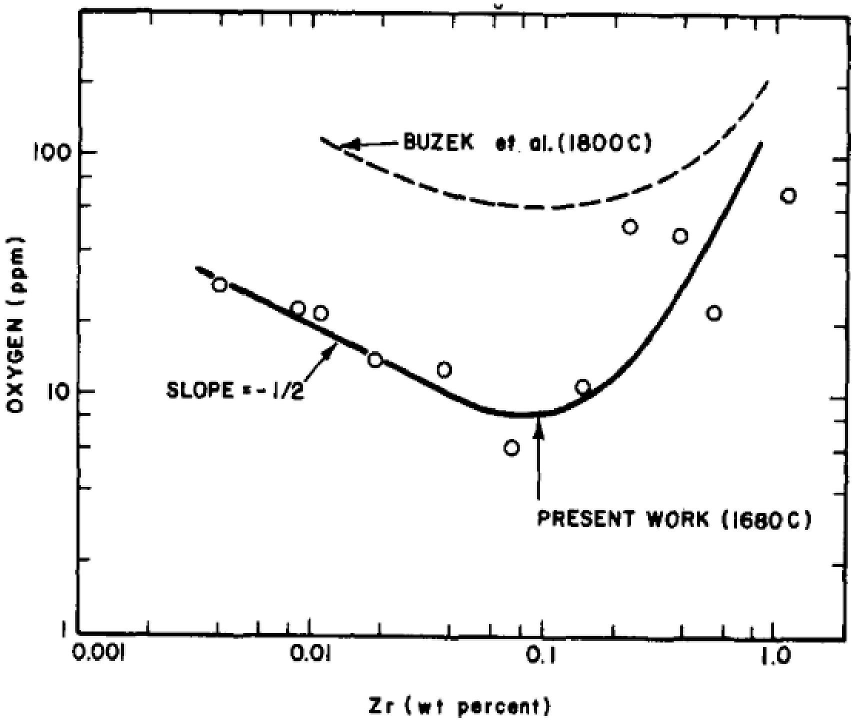
From steal smelting process

- The Fe-Zr alloys were melted in the ZrO_2 (calcia stabilized) crucible.
- The first-order interaction coefficient ε_O^{Zr} was experimentally obtained, which may be valid only for *the limiting case of infinite dilution*.

Experimental interaction coefficients [1]

Kitamura, Ban-ya and Fuwa (1969)	ε_O^{Zr}=-2.1	1610 – 1700℃
Buzek (1971)	ε_O^{Zr}=-0.44	1800℃
Yamamura and Fuwa (1973)	ε_O^{Zr}=-5.7	1600℃
Fruhen (1974)	ε_O^{Zr}=-3.0	1680℃
Janke and Fischer (1976)	ε_O^{Zr}=-0.5	1600℃

(Fruehan, 1974)



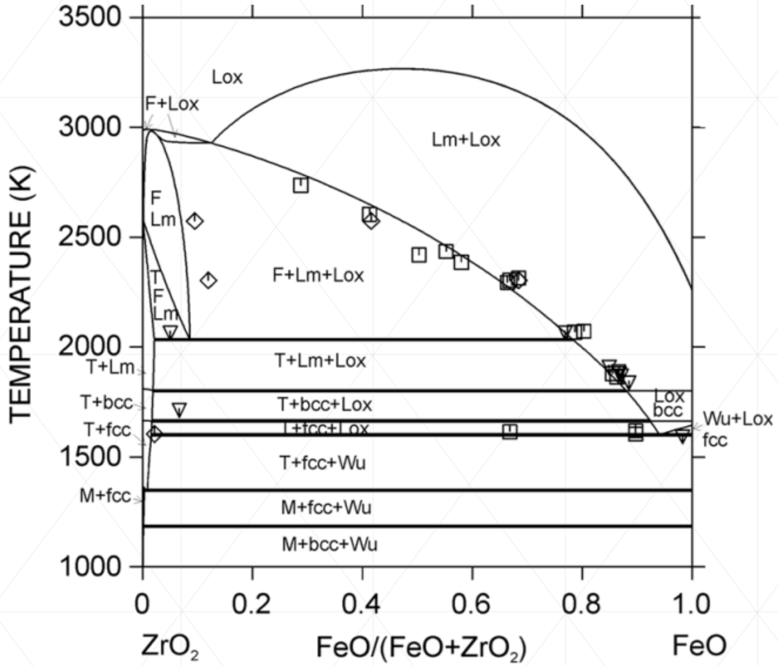
Fruehan, R. J. (1974). *The Effect of Zirconium , Cerium , and Lanthanum on the Solubility of Oxygen in Liquid Iron*. Metal. Trans. *5*(1974), 5–7.

[1] Recommended Values of Equilibrium Constants for the Reactions in Steelmaking, Japan Society for the Promotion of Science, 19th Committee, 1984

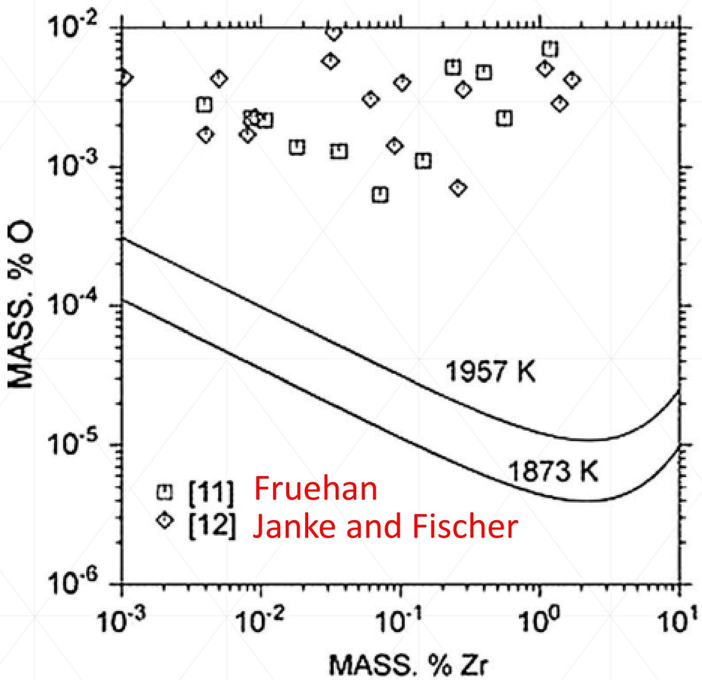
Database modeling of Fe-Zr-O system

From computation of phase diagram

- Fabrichnaya and Pacvlyuchkov proposed the thermodynamics model, which was assessed against oxides system (ZrO_2-FeO, ZrO_2-Fe_3O_4).
- *Oxygen solubility of liquid phase in equilibrium with ZrO_2 is underestimated* compared to experimental results by Fruehan, Janke and Fischer.



Calclated ZrO_2-FeO system with experimental points[1].



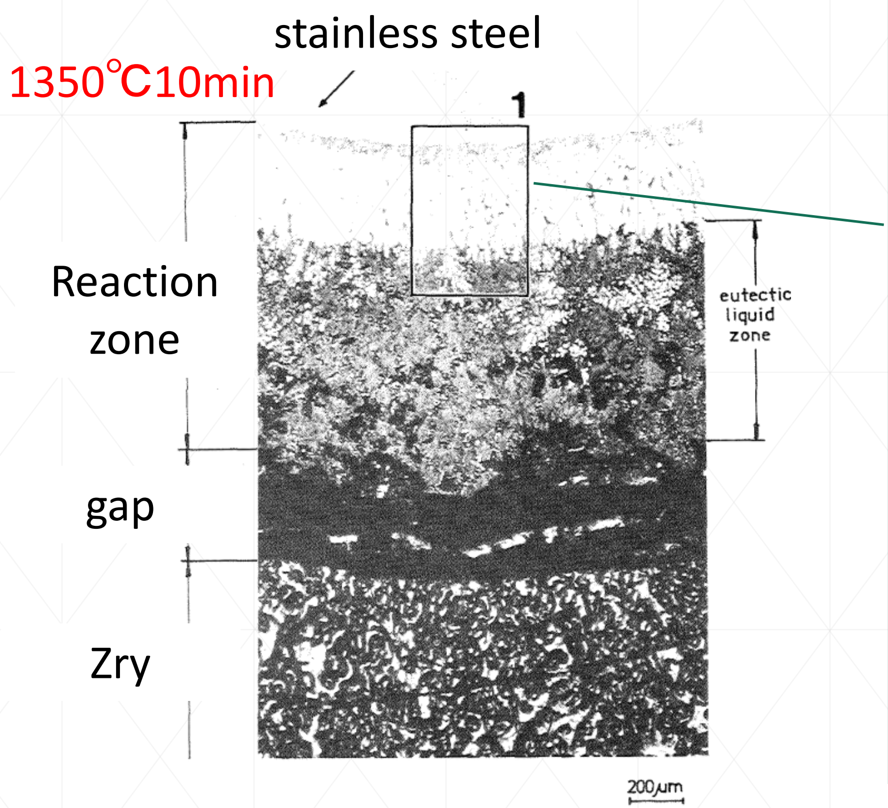
Calculated oxygen solubility in equilibrium between ZrO_2 and liquid [1].

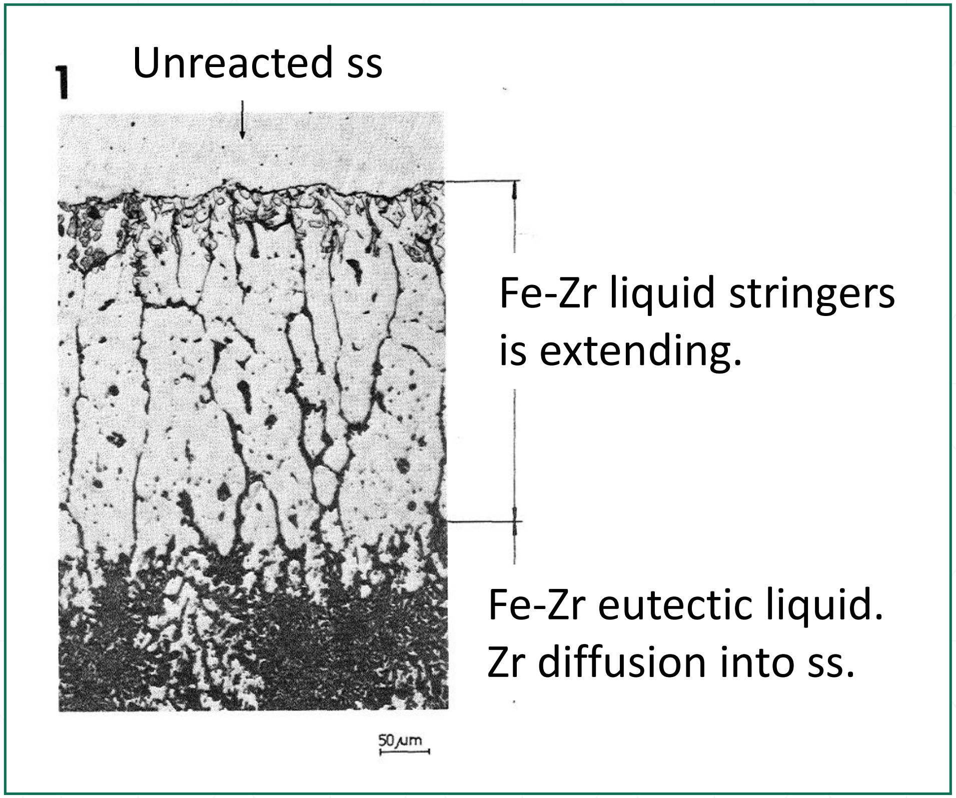
[1] Fabrichnaya, O., & Pavlyuchkov, D. (2016). Assessment of Experimental Data and Thermodynamic Modeling in the Zr-Fe-O System. Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science, 47(1), 152–159. https://doi.org/10.1007/s11661-015-2805-8

Chemical interaction between Zr(O) and SS

From reaction kinetics investigation under severe accident conditions

- Hofmann and Markiewicz investigated the reaction kinetics of stainless steel with oxygen-stabilized zircaloy-4, which shows *Fe-Zr liquid penetration into ss*.
- The chemical behavior of this study is explained by the phase relation investigated by Nevitt (next slide).





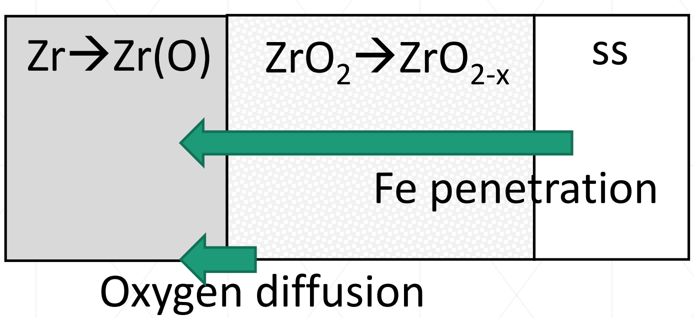
[1] Hofmann, P., & Markiewicz, M. (1994). Chemical Interactions between as-received and pre-oxidized Zircaloy-4 and Stainless Steel at High Temperatures Kernforschungszentrum Karlsruhe. 81. (KfK5106)

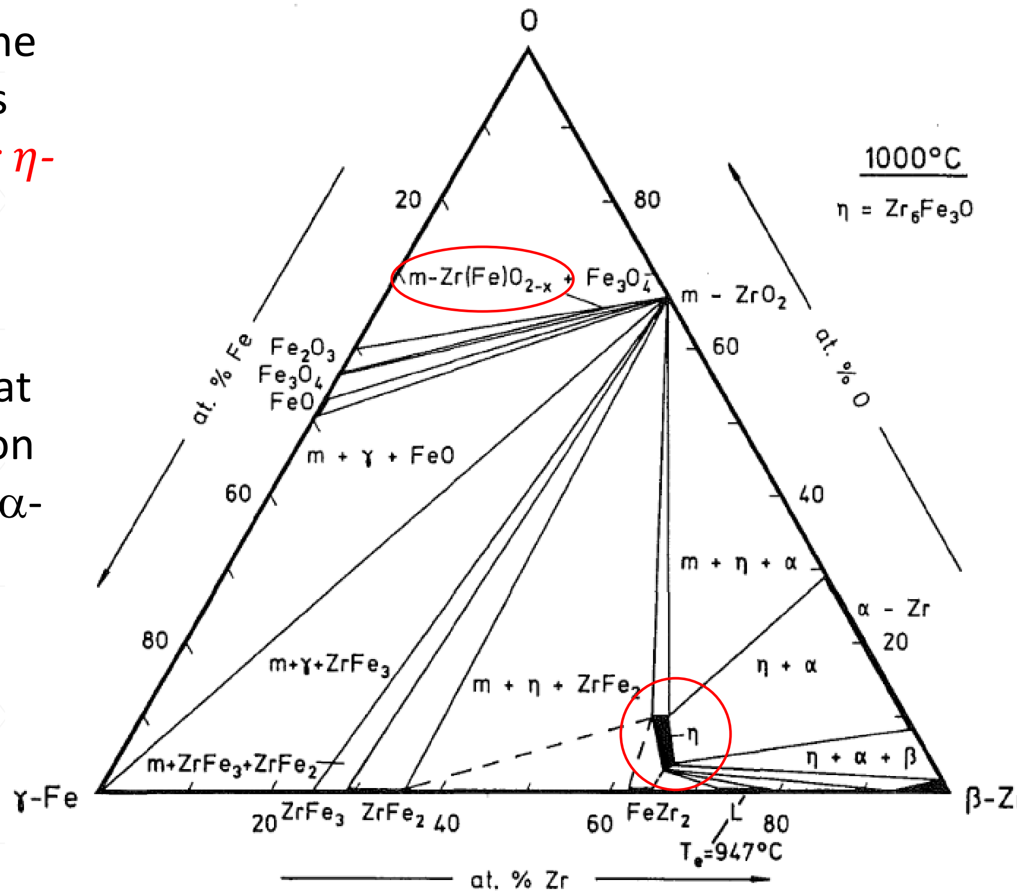
Phase relation study of Fe-Zr-O system

From the study of phase relation close to Fe-Zr region

- Nevitt et al. [1] investigated the Fe-Zr-O system with emphasis on *the oxygen stabilized cubic η-carbide type Zr_6Fe_3O phase*.

- *Substoichiometric ZrO_{2-x} can interact with Fe*, indicating that Fe can penetrate oxide layer on the Zry channel box reaching α-Zr(O).





Isothermal section of Fe-Zr-O system at 1000°C [2]

[1]M.V. Nevitt, J.W. Downey, R.A. Morris, Trans. Met. Soc. AIME 218 (1960) 1019-1023
[2]H.Kleykamp, R.Pejsa, Chemical and X-Ray diffraction analysis on selected samples from the TMI-2 reactor core. KfK 4872, May 1991.

Conclusion

1. Fe-Zr-O system is important subsystem to understand the core degradation process.

2. Previous experimental and modeling studies show
   - oxygen solubility in Fe-Zr liquid (limiting of Zr-diluted region)
   - ZrO_2-FeO_x oxides phase diagram is well modelled but still low oxygen potential region is missing experimental data to assess the model
   - oxygen-stabilized Zr_6Fe_3O phase at 1000℃ is predicted, which might be a hint to develop the phase stability near this composition region.
   - the kinetic study of Zr(O) – Fe reaction has been performed under SA conditions but it is linked only to the phase diagram at 1000℃.

3. We are planning the experimental works to investigate the oxygen solubility in Fe-Zr liquid phase and Zr(O) – Fe reaction. Preliminary result confirmed that Zr diffusion in the iron as a result of interaction reported in Hofmann's report.

Thank you for your attention

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