

Technical Basis for New Alloy Definition from PQD Testing Perspective

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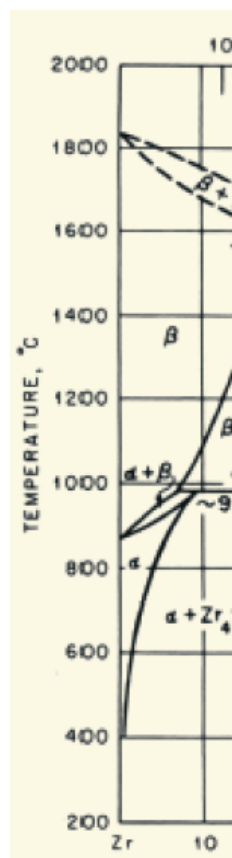
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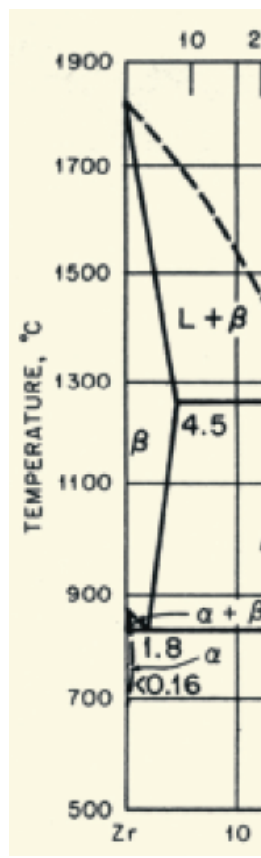
Zirconium Based Alloy Metallurgy

- Commercial zirconium based alloys are > 97 wt% Zr
- Alloys are typically used in the α -phase
 - Low alloying element solubility
- The material transforms into the β -phase at $\sim 850^{\circ}\text{C}$
 - High alloying element solubility, $\geq 1.9\%$ for all commonly used alloying elements
- Controlled thermal-mechanical processing typically starts with a β -phase quench ($\sim 1000^{\circ}\text{C}$) in the manufacturing process
 - Homogenizes the alloying/impurity elements in solution
 - Eliminates any prior thermal-mechanical processing history

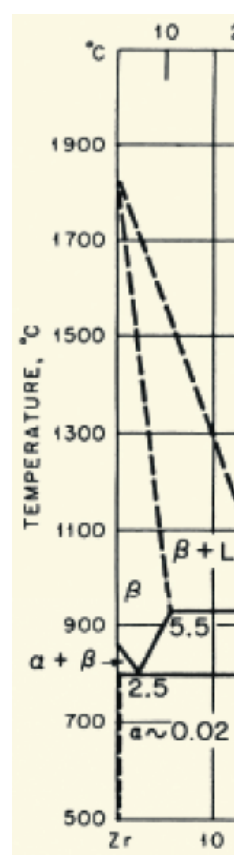
Zirconium-X Binary Phase Diagrams



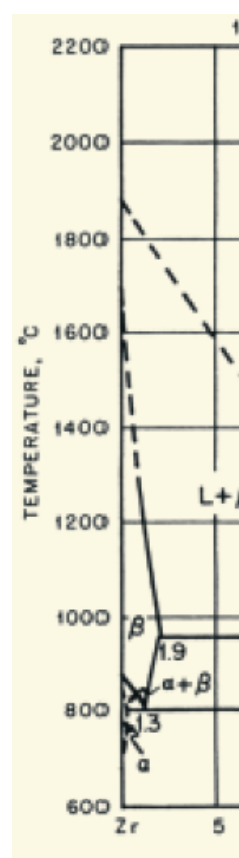
Zr-Sn



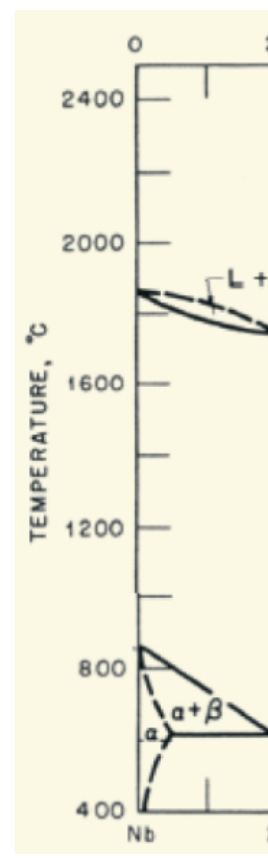
Zr-Cr



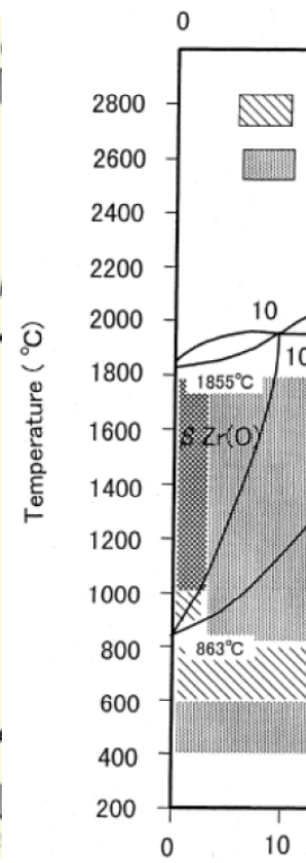
Zr-Fe



Zr-Ni



Zr-Nb



Zr-O

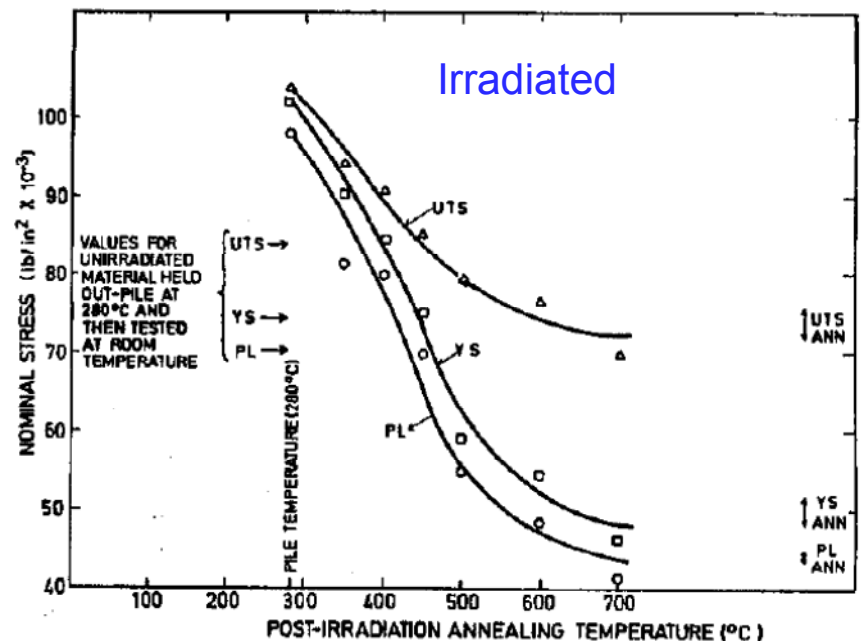
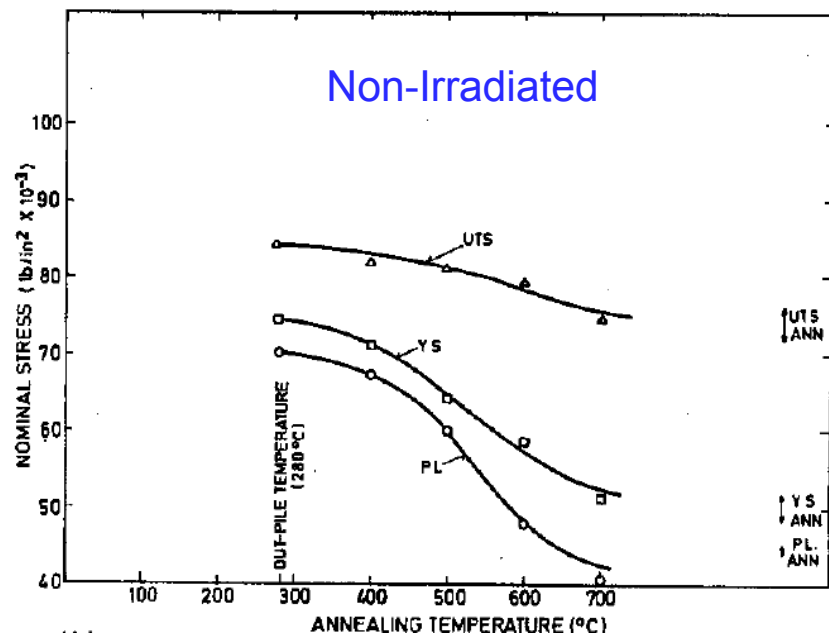
Solubility of alloying elements in the beta phase is high relative to alloying element concentrations – No new phase forms within expected concentration range

Changes to Material During Irradiation

- Irradiation damage
 - Point and dislocation defects generation
- Fission fragments embedding near the inner diameter surface
- Alloying element re-distribution
- Alloying element transmutation

Changes to Material During a LOCA 1/3

- Zircaloy-2 irradiation damage (point defects and dislocation) recovery



Irradiation damage recovery is completed below 700 $^{\circ}\text{C}$

Changes to Material During a LOCA 2/3

- Embedded fission fragments
 - Mostly embedded in the ID oxide, not relevant to the base cladding material
 - Existing test data do not show they form any “unacceptable phase” with other alloying/impurity element detrimental to post LOCA ductility
- Alloy element re-distribution
 - No impact since homogenization takes place in β -phase above $\sim 850^{\circ}\text{C}$

Changes to Material During a LOCA 3/3

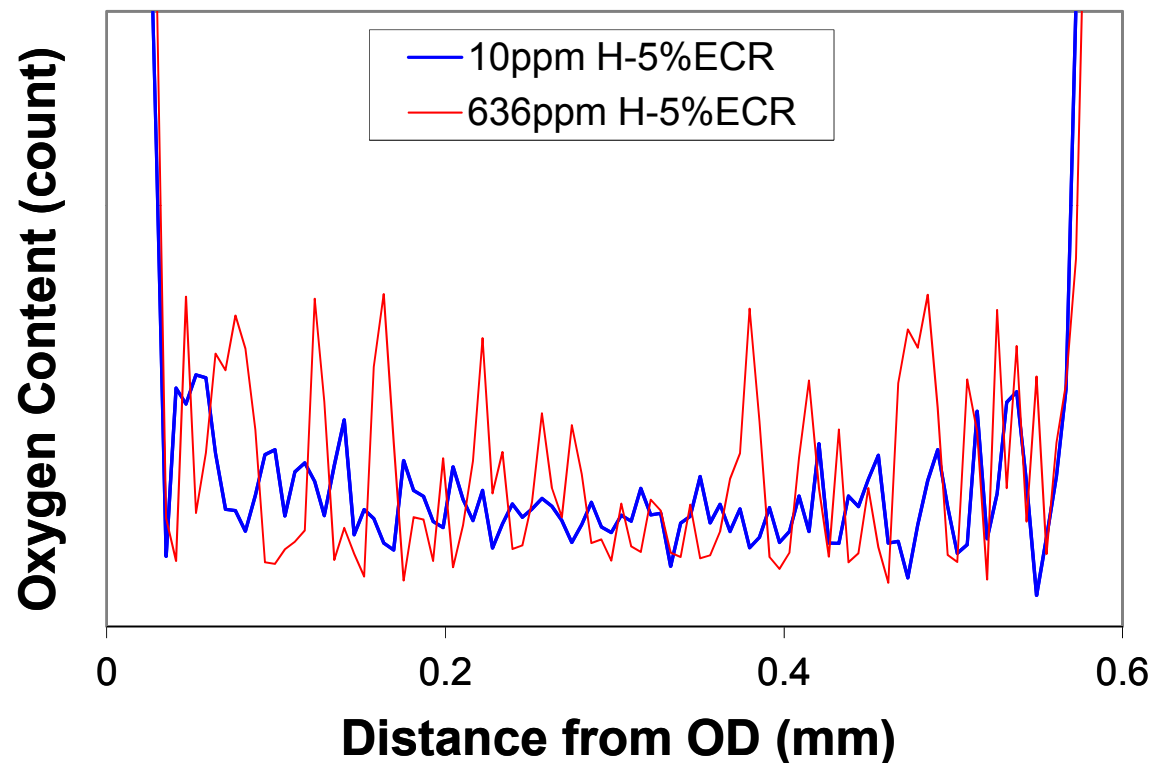
- Transmutation of alloying elements is the only irradiation induced changes not erased during LOCA temperature exposure
- Transmuted elements could be accounted for in one of two ways
 - Testing of irradiated cladding near end of life
 - Testing of the alloy with addition of expected transmutation elements

Ductility Degradation During a LOCA

- Generally accepted oxygen ingress into the beta phase leads to ductility degradation
- Hydrogen accelerates degradation
 - ANL concluded hydrogen increases oxygen diffusion
 - Evidence showing oxygen concentration is not enhanced with hydrogen
 - Hydrogen by itself without oxygen diffusion can reduce cladding ductility

Effect of Hydrogen on Oxygen Concentration

- Wavelength Dispersive X-ray (WDX) analysis of ANL samples

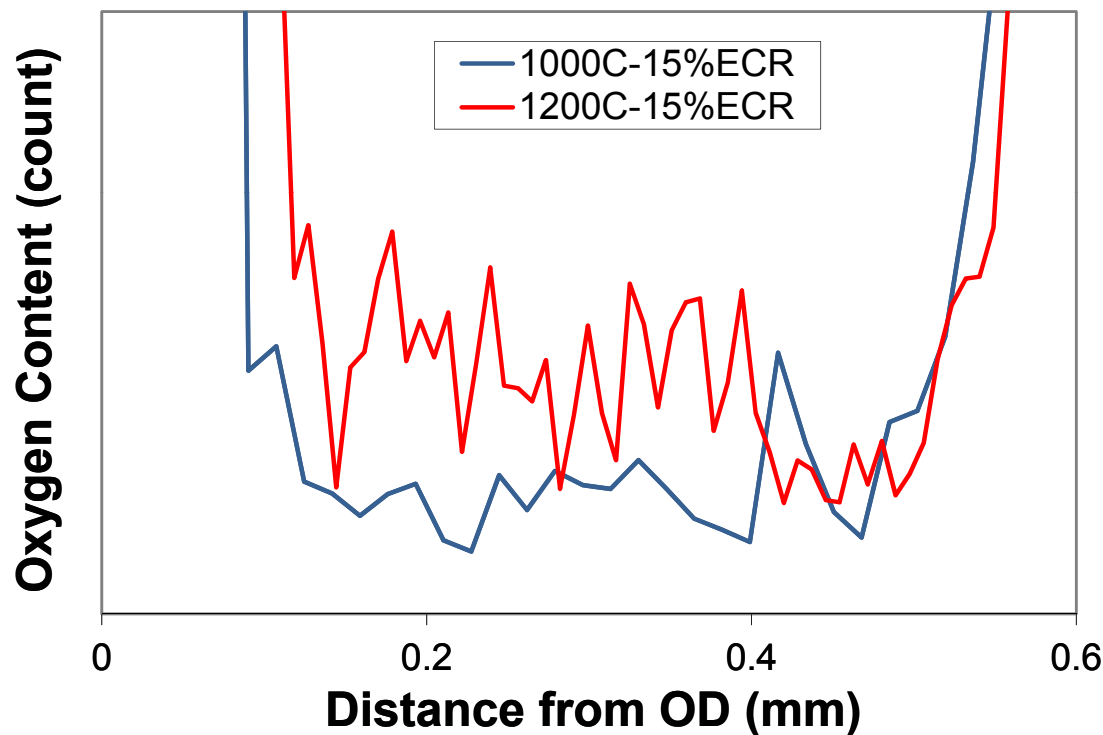


- No significant increase in oxygen concentration from hydrogen
- Hydrogen contributes to localization of oxygen during cooling

Hydrogen does not appear to significantly enhance oxygen diffusion

Oxidation Temperature Effect

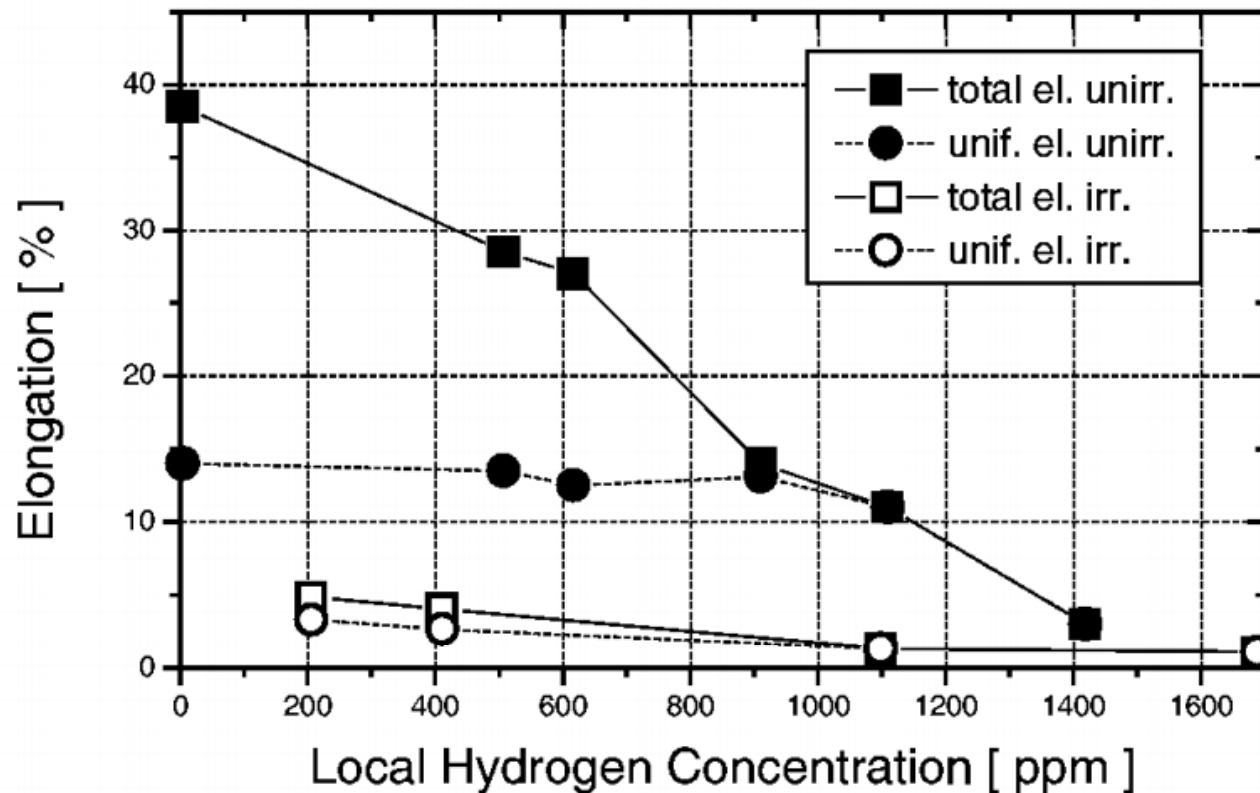
- Significant difference in oxygen concentration from different oxidation temperatures



- Oxygen concentration difference due to higher oxidation temperature is significant

Direct Impact of Hydrogen on Ductility

- Hydrogen by itself reduces ductility



- Is hydrogen and oxygen effects additive or interactive?

Hemann, A. et al, "Ductility Degradation of Irradiated Fuel Cladding", IAEA publication

Proposals

- For alloy chemistries bounded by testing experience (e.g., combined licensed alloy composition envelop of alloys tested)
 - Allow limits derived from non-irradiated hydrogen pre-charged testing

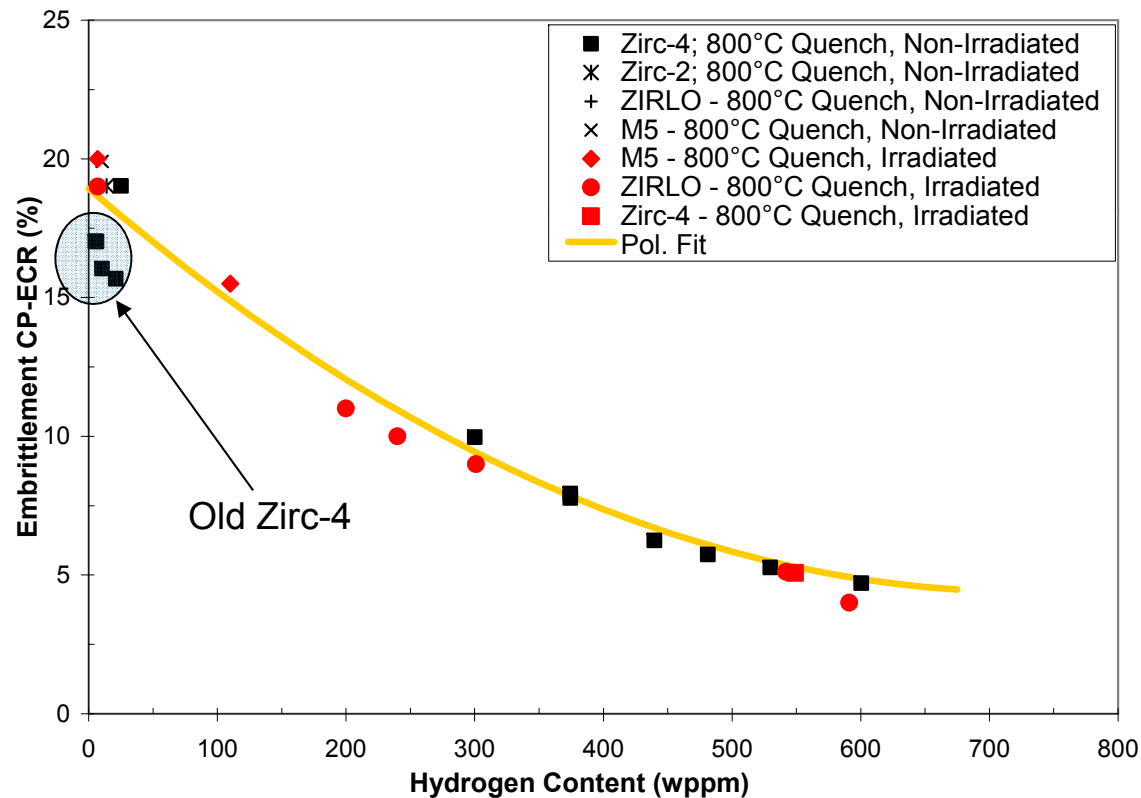
- New Alloy - chemistries outside of the experience database
 - Bulk of data to be generated using hydrogen pre-charge
 - Verification testing of irradiated cladding near the expected end of life hydrogen concentration or use as-fabricated materials with transmuted species
 - Allow operation within the hydrogen pre-charged test data range

Rationale for Proposal 1/3

- Ductility degradation at high temperatures is due to oxygen diffusion into the beta phase
 - Oxygen diffusion is controlled by the zirconium matrix bulk property
 - Oxygen diffusion could be modified if secondary phases form at LOCA temperature and have higher oxygen diffusion rates
 - Phase diagram of commonly used alloying element showed high solubility in the beta phase and therefore would not form secondary phases
- Testing of existing alloys manufactured by different processes showed no significant difference in ductility degradation
 - Verifying metallurgical data that the commonly used alloying elements do not form a “short-cut” for oxygen diffusion

Rationale for Proposal 2/3

- ANL Zircaloy-4, ZIRLO and M5 PQD ductile-to-brittle transition ECR



- Sample from multiple vendors fit on the same trend line
- Irradiated data also consistent with hydrogen pre-charged

Pre-hydriding is a good surrogate for irradiation

Rationale for Proposal 3/3

- ANL test data demonstrated transmuted species from currently used alloying elements do not lead oxygen diffusion short-cut

Therefore definition of new alloys from PQD testing perspective should be outside of the combined testing experience database



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