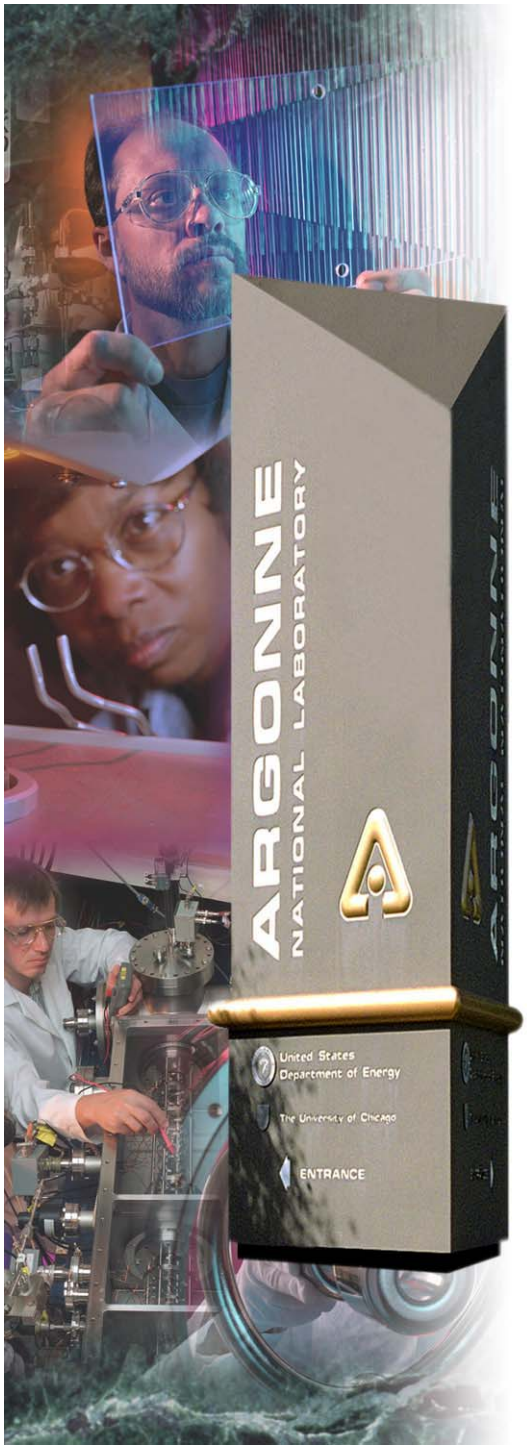

The Effects of Aliovalent Elements on Nodular Oxidation of Zr-Base Alloys

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Objective

- Develop a model that explains the contrasting susceptibility of E110 (Zr-1Nb) and M5 (Zr-1Nb) to nodular oxidation in steam under high-temperature LOCA-like conditions.

Nb-Containing Alloys for Fuel Cladding

- E-110 Zr-1Nb (in wt.%)
- M5 Zr-1Nb
- E-635 Zr-1Nb-1.2Sn-0.4Fe
- Zirlo Zr-1Nb-1Sn-0.1Fe
- MDA Zr-0.5Nb-0.8Sn-0.2Fe-0.1Cr

- **All alloys contain O of ≈0.05-0.12 wt.%.**

Characteristics of Nodular Oxidation in High Temperature Steam (900-1120°C)

- Not observed in Zircaloys, M5, and Zirlo.
- Observed in standard E110 and E635.

- Initial development of white nodules.
- Coalescence and interconnection of nodules.
- Flake-off of gray-white continuous oxide layer.

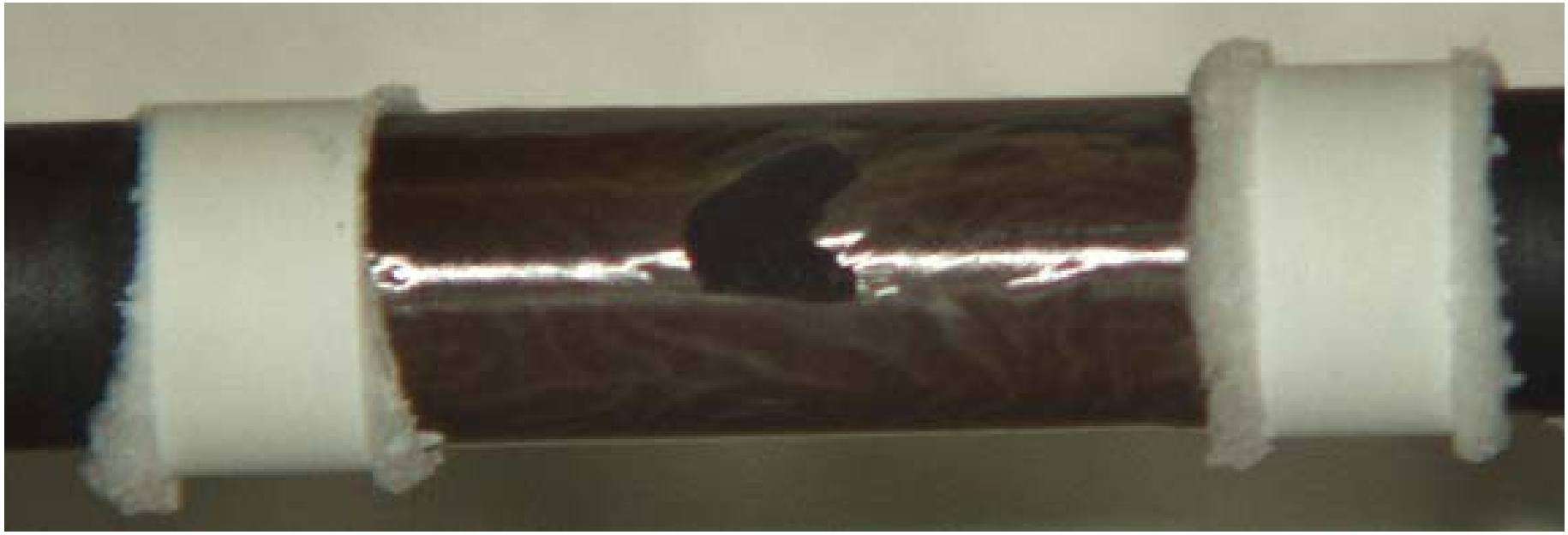
- **Breakdown of protective role of oxide, large H uptake.**

Zircaloys Not Susceptible to High-Temperature Nodular Oxidation (1100°C 14 min. in steam)

Protective black oxide on Zry-4, Y. Yan et al. 2003

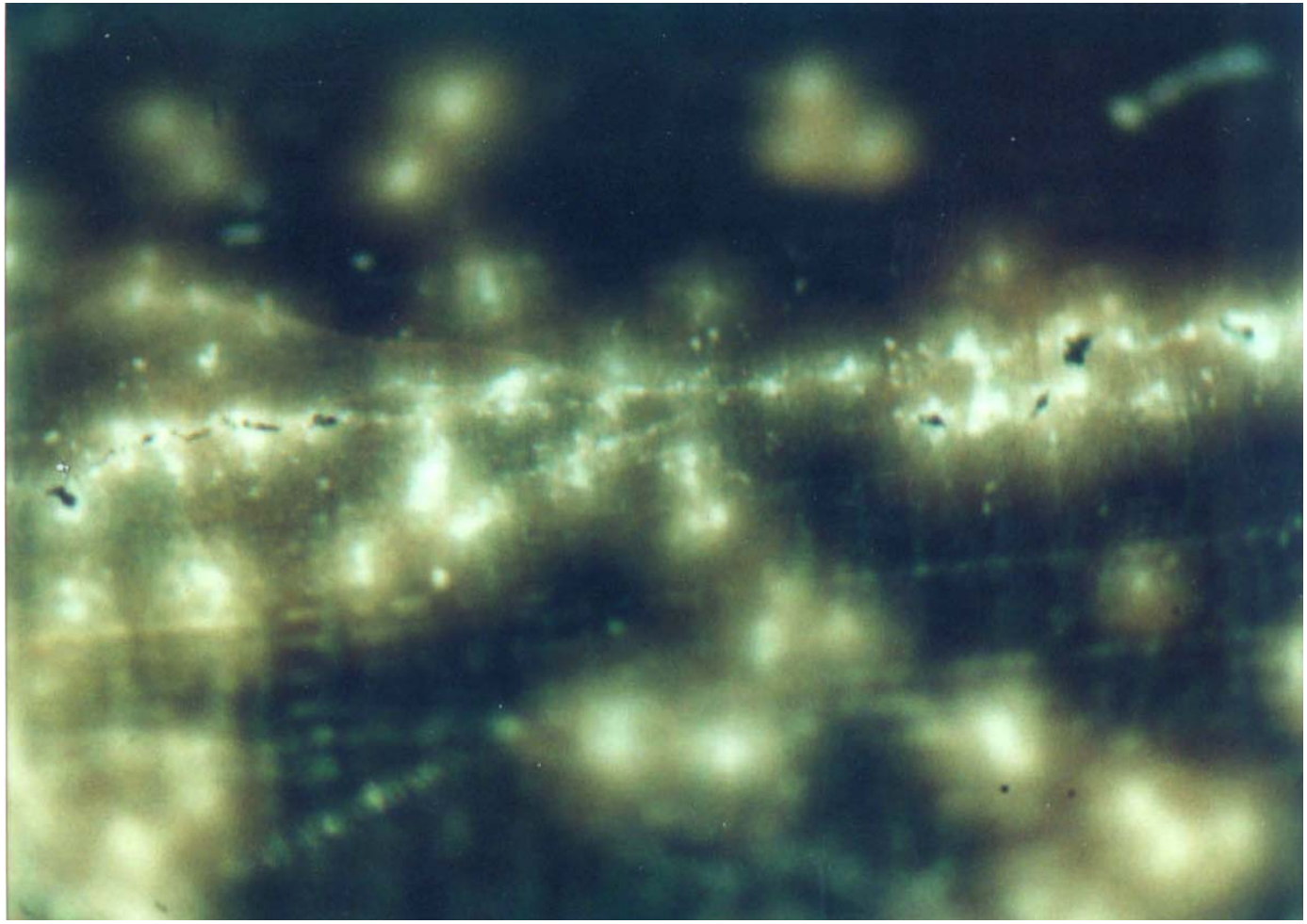
M5 Zr-1Nb Not Susceptible to High-Temperature Nodular Oxidation (1000°C 3 h in steam)

Protective black oxide, Y. Yan et al. 2003



E110 Zr-1Nb Susceptible to High-Temperature Nodular Oxidation (1100°C 40 min. in steam)

White surface spots, Y. Yan et al. 2003

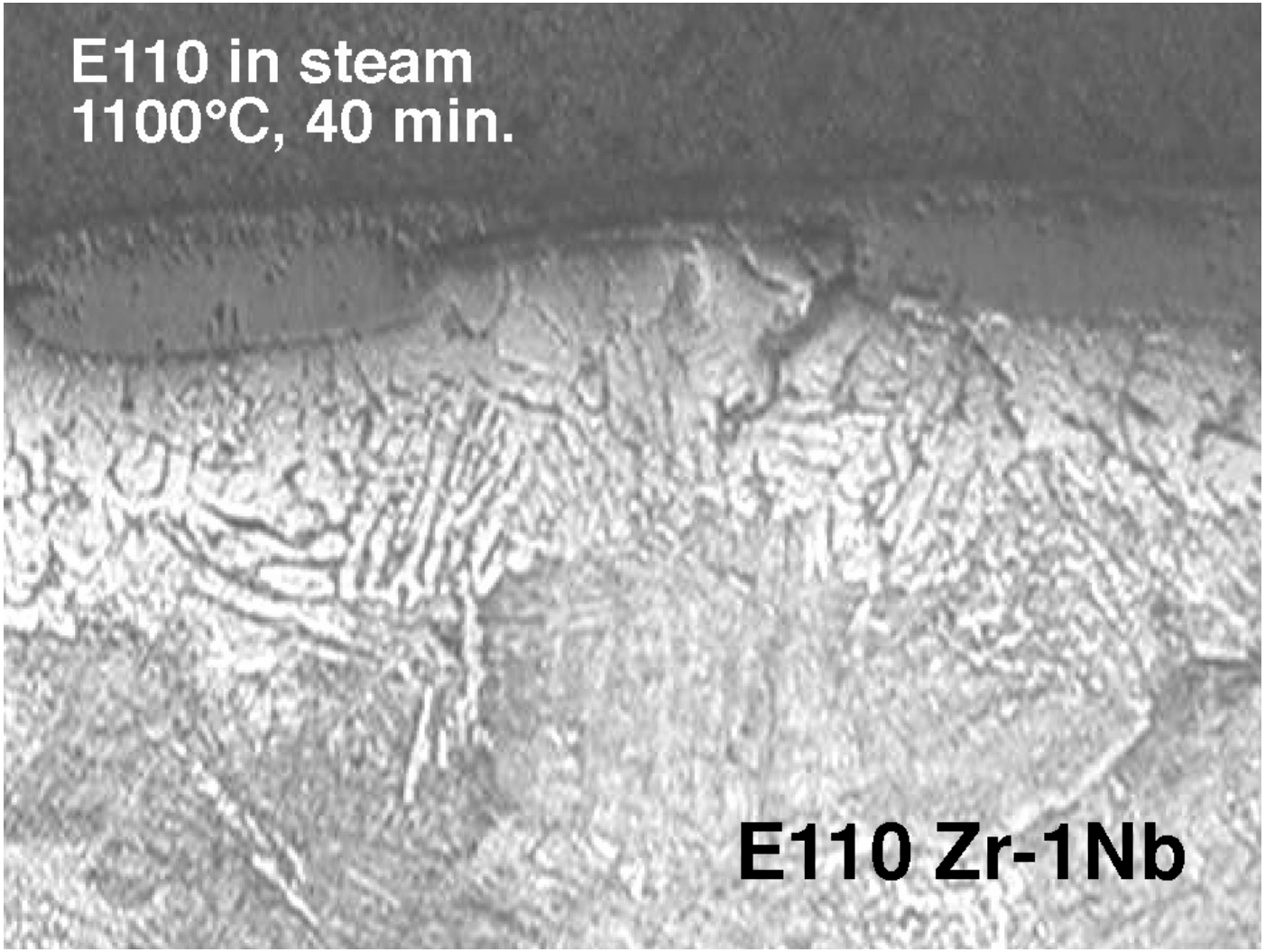


Oxide Flake-Off in E110 Following Nodule Coalescence (1000°C 23 min. in steam)

Y. Yan et al. 2003

Cross Section of Oxide Nodule in E110

(Etched Metallograph, Y. Yan et al. 2003)



Impact of Nodular Oxidation in High Temperature Steam

- Rapid uptake of H under LOCA situations.
- Locally enhanced oxidation.

- **Large H uptake leads to premature embrittlement of cladding after LOCA-like quenching, e.g., nil-ductility at ECR as low as ≈8% instead of >17%.**
- **Post-quench impact and bending properties are also degraded.**

Undervalent and Overvalent Elements

- Aliovalent element means an element of which valency differs from that of tetravalent Zr, i.e., $Zr^{++++}O^{--}_2$
- Two different types of breakaway oxidation not to be confused, nodular oxidation and uniform breakaway oxidation

- Undervalent Elements:
  double-valent: Ni^{++}, Ca^{++}, Mg^{++} in NiO, CaO, MgO
  triple-valent: Fe^{+++}, Cr^{+++}, Al^{+++} in Fe_2O_3, Cr_2O_3, Al_2O_3
- Overvalent Element:
  penta-valent: Nb^{+++++} in Nb_2O_5

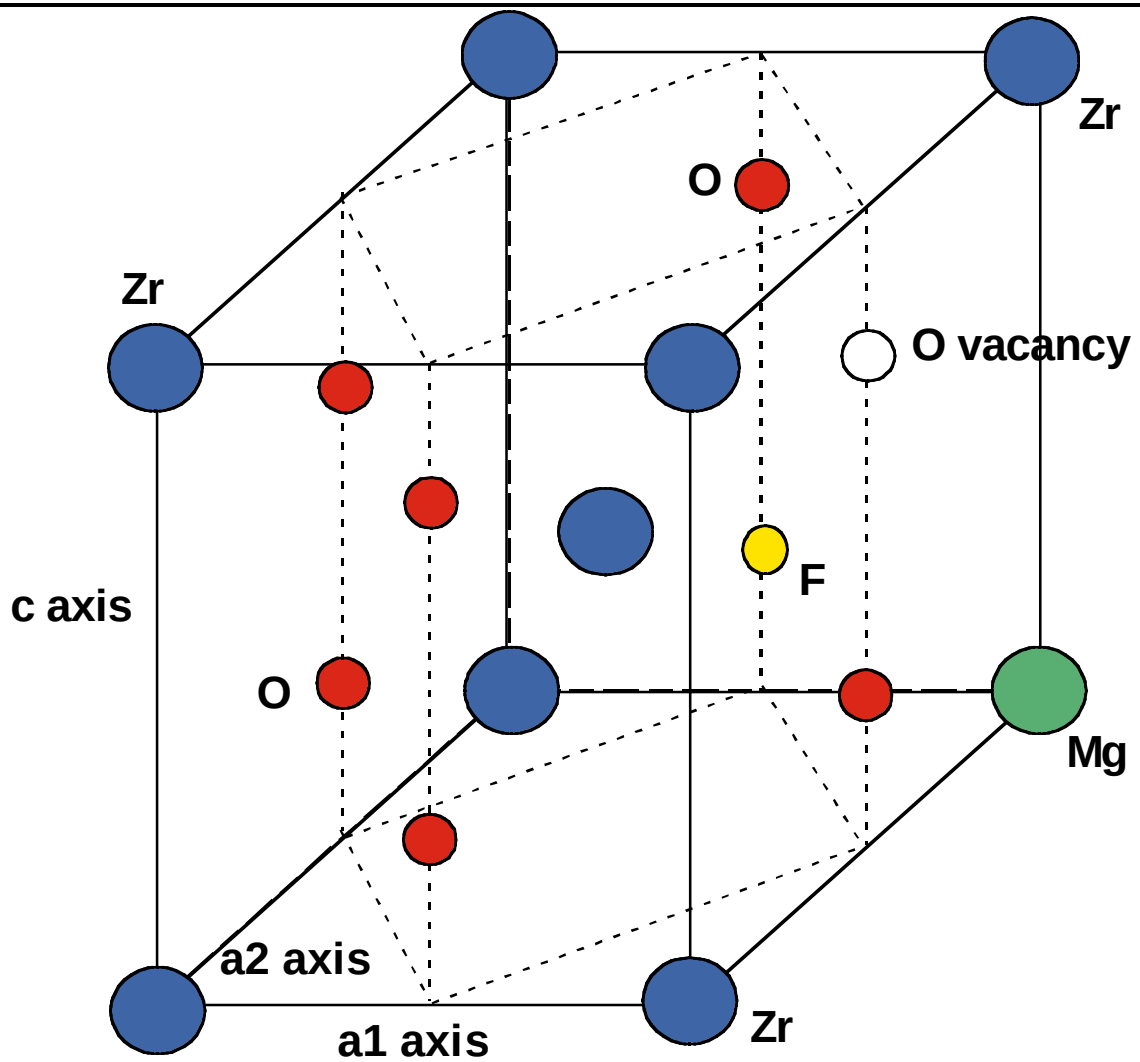
General Approach

Charge Balance, Valency, Defects, Stoichiometry

- During oxidation, overall electric charge of oxide unit cell is kept balanced (neutral).
- Effective cation valency determines the population of anion (O) vacancy in the oxide unit cell, hence, oxide stoichiometry.

- An overvalent element (Nb) in the unit cell leads to less O vacancy and makes the oxide more stoichiometric.
- An undervalent element (Ca, Mg, Al, Fe, Cr, Ni) leads to more O vacancy and keeps the oxide understoichiometric.

Zr Oxide Cell, Defects, and Impurities



Properties of Zr Dioxide

- Undervalent element incorporated
  More O vacancy, understoichiometric
  Tetragonal
  Higher fracture toughness
  Resistant to nodular oxidation

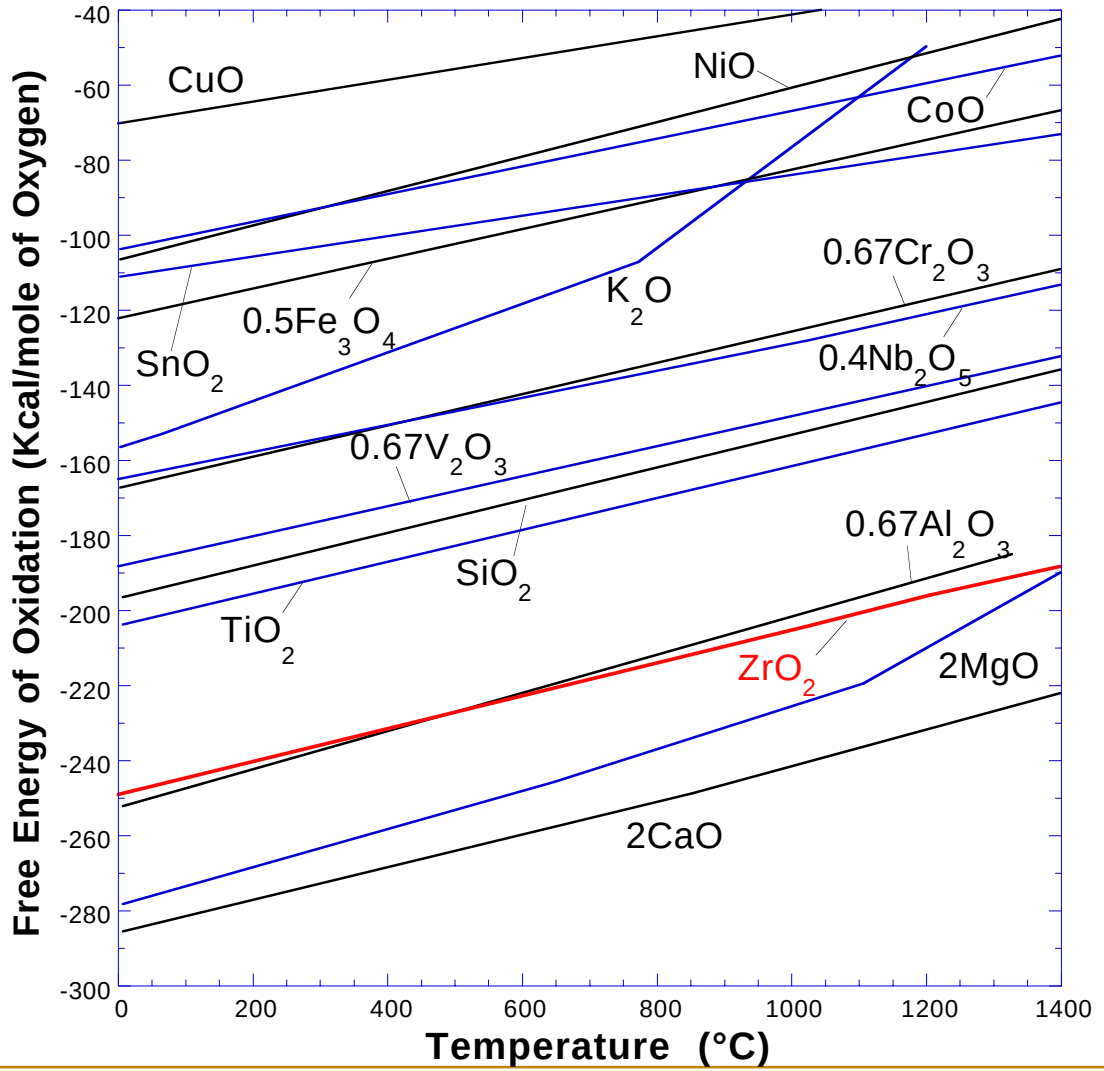
- Overvalent element (Nb) incorporated
  Less O vacancy, stoichiometric
  Monoclinic
  Lower fracture toughness
  Susceptible to nodular oxidation

Effective Undervalent Impurities

- Pure binary Zr-Nb alloys are inherently more susceptible to nodular oxidation at high temperatures than Zircaloys.
- However, all Zr-Nb alloys contain undervalent impurities which help to offset the deleterious effect of Nb.

- Effective Undervalent Impurities:
  - Double- or triple-valent.
  - Affinity to O is stronger than that of Zr.
  - Diffusion to O-rich alpha and oxide is fast.
- Ca, Mg, and Al (Ca or Mg role on stabilization of cubic or tetragonal oxide is well known).

Ca and Mg Oxidized More Readily Than Zr; Al Similar



Alloy Fabrication and Impurity Pick-Up

- Primary candidate for pick-up of beneficial or deleterious impurities is during fabrication.
- Fabrication processes for E110 and M5 are very different.

- **Details of both processes were critically examined.**

Production of Nuclear-Grade Zr

- Decompose zircon ore.
- Produce feedstock for Hf purification, ($ZrCl_4$ + $HfCl_4$) or (K_2ZrF_6 + K_2HfF_6), Hf ≈15,000 - 25,000 wppm.
- Separate the Zr and Hf compounds, produce low-Hf $ZrCl_4$ or low-Hf K_2ZrF_6.
- Reduce the low-Hf compounds to obtain low-Hf Zr metal, Hf <500 wppm.
- **Process changes and evolves.**

Decomposition of Zircon Ore (ZrO_2)(SiO_2)

- **Process E**
  - (ZrO_2)(SiO_2) + 2(KF)(SiF_4)= K_2ZrF_6 +2SiO_2
  - at 700-1000°C
  - **F contamination**

- **Process W**
  - Chlorinate mixture of (ZrO_2)(SiO_2) and graphite using $SiCl_4$, $TiCl_4$, or $AlCl_4$
  - Convert ore to $ZrCl_4$ and $SiCl_4$, at >1150°C

Common Methods of Hf Separation

- Methyl Isobutyl Ketone (MIBK) Process
- Extractive Distillation
- Fractional Crystallization of Zr and Hf Salts

- **Exact process for each producer changes with time.**

Hf Separation E, Fractional Crystallization

- K_2ZrF_6 from decomposed ore contains 1.5-2.5 wt.% K_2HfF_6.
- Solubility of K_2HfF_6 in distilled water is higher than that of K_2ZrF_6. Dissolve the mixture, cool off the solution; fractional crystallization occurs at different rates.
- After ≈15 steps, K_2ZrF_6 contains 400-500 wppm Hf.
- Crystallized K_2ZrF_6 is reduced to Zr metal by electrolysis.

- **Zr metal picks up F.**

Hf Separation E, Fractional Crystallization (Cont.)

- K_2ZrF_6 from decomposed ore contains 1.5-2.5 wt.% Hf.
- Solubility of K_2HfF_6 in distilled water is higher than that of K_2ZrF_6. Dissolve the mixture, cool off the solution; fractional crystallization occurs at different rates.
- After ≈15 steps, K_2ZrF_6 contains 400-500 wppm Hf.
- K_2ZrF_6 is converted to $Zr(OH)_4$.
- $Zr(OH)_4$ is calcinated to convert to Zr oxide: $Zr(OH)_4 + Ca = ZrO_2 + Ca(OH)_2$.
- ZrO_2 is converted to $ZrCl_4$ and then to Zr metal.

- **Zr metal picks up F and Ca.**

Zr Reduction E (E110), (Electrolytic Zr and Iodide Zr Mixed)

- Zr metal produced by electrolysis of Hf-purified K_2ZrF_6 in molten bath of KCl, NaCl, or mixed KCl-NaCl.
- Zr metal from decomposition of ZrI_4 on hot filament.
- Mix the electrolytic and iodide Zr, e.g., 60%-40%.

- **Zr metal contains F.**

Hf Separation W (MIBK Process)

- Start with $ZrCl_4$+$HfCl_4$ from ore decomposition.
- Convert to $ZrOCl_2$+$HfOCl_2$ in demineralized water.
- Convert to $ZrO(SCN)_2$+$HfO(SCN)_2$, use $(SCN)NH_4$.
- Remove $HfO(SCN)_2$ by liquid-liquid extraction, use methyl isobutyl ketone (MIBK).
- Treat remaining $ZrO(SCN)_2$ with HCl, form $ZrOCl_2$.
- Convert to $Zr(OH)_4$, use NH_4OH and H_2SO_4.
- Convert to ZrO_2: $Zr(OH)_4 + Ca = ZrO_2 + Ca(OH)_2$.
- Chlorinate ZrO_2 to $ZrCl_4$.
- **Low-Hf $ZrCl_4$ product picks up Ca.**

Hf Separation CZ (Extractive Distillation)

- $ZrCl_4$ + ≈2-2.5 wt.% $HfCl_4$ (from ore decomposition) is separated by extractive distillation using a solvent of molten KCl-$AlCl_3$.
- Low-Hf $ZrCl_4$ (Hf <100 wppm) product is fed to Kroll process to convert to Zr metal.
- **Hf-purified $ZrCl_4$ picks up Al.**

Zr Reduction W (Zry, Zirlo, M5) (Kroll Process)

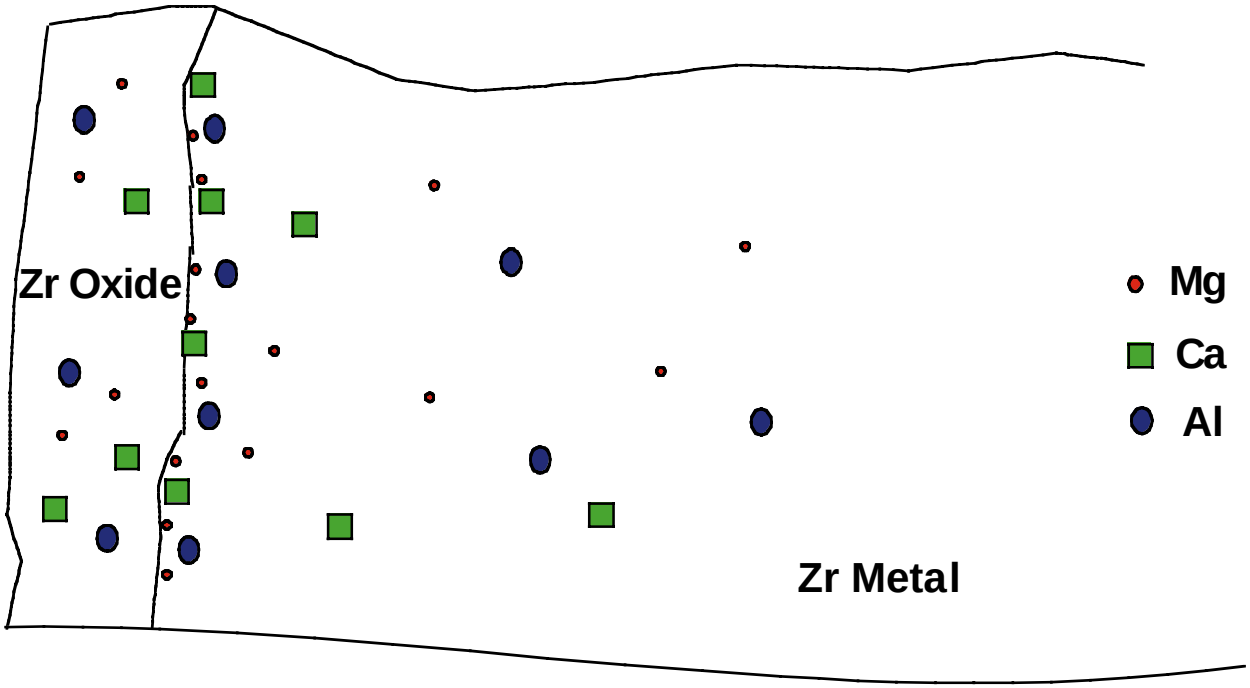
- Reduction of Hf-purified $ZrCl_4$ by Mg:
  $ZrCl_4$ (g) + 2Mg (l) = 2$MgCl_2$ + Zr (sponge)
- Hf-purified Zr sponge contains $MgCl_2$ residue and excess Mg.
- The concentrations of $MgCl_2$ and Mg are reduced by vacuum degassing or vacuum distillation.

- **Zr metal picks up Mg.**

Fabrication-Related Impurity Pick-Up Important to Nodular Oxidation

Process	Important Impurities Picked-Up	Deleterious or Beneficial
Hf separate, fractional crystallization	F	deleterious
Hf separate, MIBK	Ca	beneficial
Hf separate, extractive distillation	Al	beneficial
Conversion of $Zr(OH)_4$ to ZrO_2	Ca	beneficial
Zr reduction, electrolysis of K_2ZrF_6	F	deleterious
Zr reduction, Kroll process	Mg	beneficial
Multiple vacuum melting of alloy ingot	degass F or volatize ZrF_4	beneficial
Surface finish with Al_2O_3, Fe_2O_3, Y_2O_3	Al, Fe, Y	beneficial
Anneal test tube at high temp. in vacuum or inert atmosphere before exposure to steam	degass F or volatize ZrF_4	beneficial

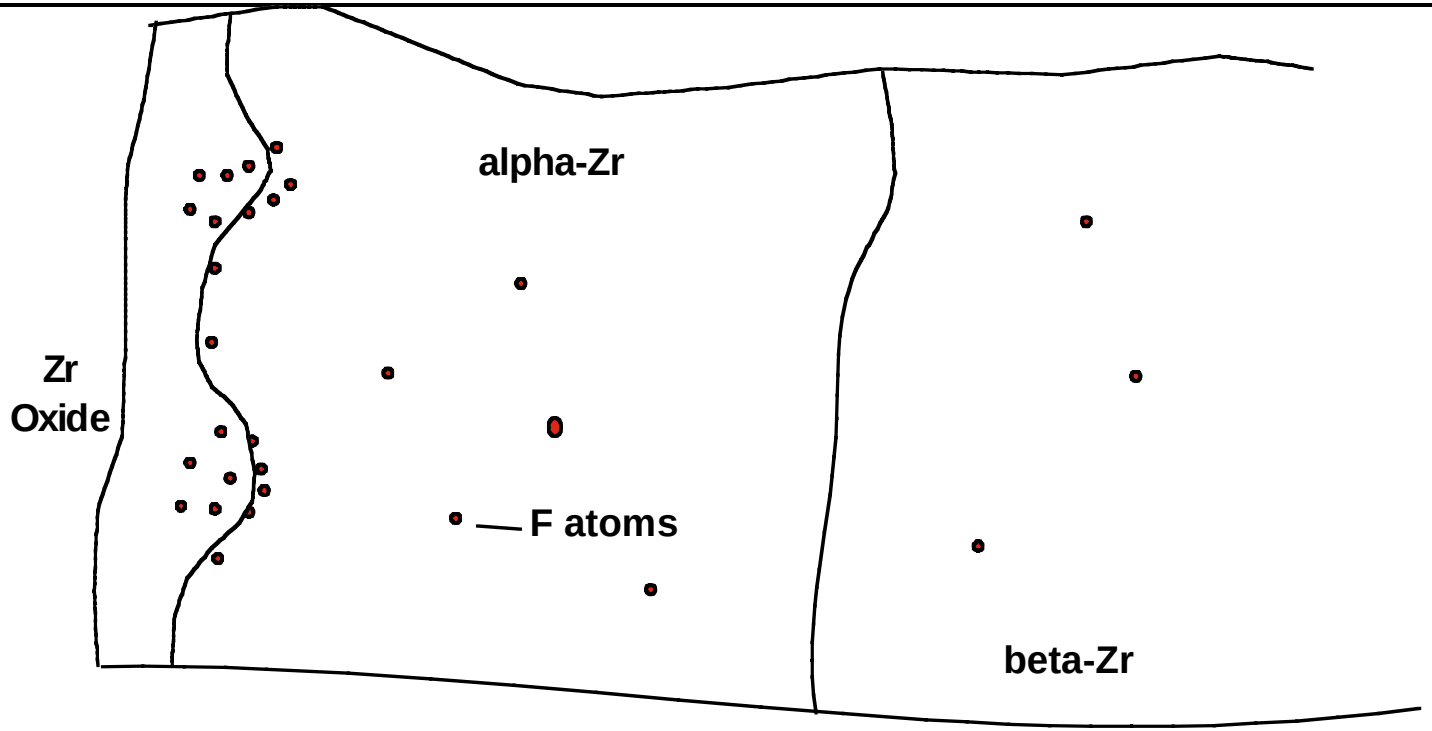
Mg, Ca, Al Incorporated in Oxide



Affinity to O of Mg, Ca, or Al is far greater than that of Zr. Mg, Ca, or Al diffuses to and accumulates a t oxide/metal boundary where O is cncentrated.

Mg, Ca, or Al is oxidized preferentially at the oxide/metal boundary. Although average concentration is low, Mg, Ca, or Al is preferentially incorporated in the oxide unit cell.

Role of F on Nodular Oxidation



F atoms accumulate at the oxide/metal boundary. (This has been reported for Ta and Fe oxides, but not for Zr oxide yet.) F and O behavior is similar. F atoms occupy O vacancy sites in the oxide converted from local region of metal higher in F content. This makes the oxide more stoichiometric, promoting formation of monoclinic oxide. Such a spot leads to nucleation of a nodule.

Role of F Contamination (Conti.)
(chemical analysis of F <100 wppm difficult and inaccurate)

- **F accumulation at oxide/metal boundary in Ta analyzed by SIMS and reported by:**

  K. Shimizu, K. Kobayashi, G. E. Thompson, P. Skeldon, and G. C. Wood, J. Electrochem. Soc. 144 (1997) 418.

- **Oxide flake-off ("slough-off") in steels contaminated by F was reported by:**

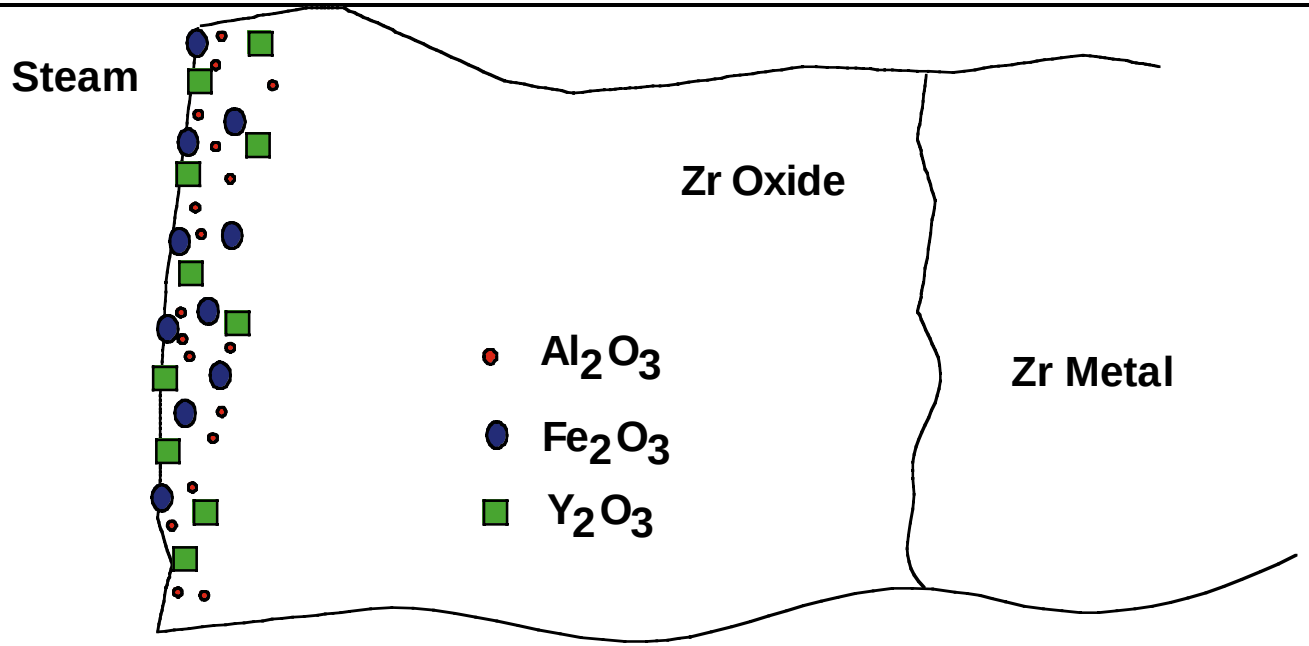
  C. T. Ward, D. L. Mathis, and R. W. Staehle, Corrosion, 25 (1969) 394.

  P. E. C. Bryant and P. R. Habicht, Combustion Engineering Internal Report TIS–5065, also in Proc. IAEA Workshop on Stress Corrosion Cracking, March 29-31, 1976.

  M. Takemoto, T. Shonohara, M. Shirai, and T. Shinogaya, Mater. Perform., 24 (1985) 26.

  H. M. Chung, W. E. Ruther, J.-H. Park, J. E. Sanecki, and N. J. Zaluzec, Paper #443, *Corrosion '99*, San Antonio, TX, April 25-30, 1999.

Effect of Surface Polishing



Surface polishing with fine powders of a hard oxide removes surface rough spots.

Oxide of undervalient element such as Al, Fe, or Y, incorporated in the surface layer, tends to make the Zr oxide understoi-chiometric and helps the oxide remain in tetragonal phase.

Overall effect is to delay the onset of nodular oxidation .

Summary and Conclusions

- A model was developed that can explain the contrasting behavior of high-temperature nodular oxidation of E110 and M5.
- Mg, Ca, or Al pick-up associated with Zr metal reduction or Hf purification is predicted to suppress the susceptibility to nodular oxidation. Absence of such pick-up is deleterious.
- F pick-up associated with some Hf-purification or electrolytic-Zr-reduction process is predicted to be deleterious.
- Multiple ingot melting or other treatments leading to degassing of F is predicted to be beneficial.