Corrosion in Nuclear Reactors

While Zr alloys were chosen because of their low corrosion in high temperature water, things change in reactors!

Internal Corrosion:

- **Hydriding**
- **Stress Corrosion Cracking (SCC)**

External Corrosion (see figure)

	Out of Pile Corrosion Rate	
T °C	$\frac{mg}{dm^2\text{-}d}$	$\frac{micron}{year}$
310	0.006	1.2
360	0.3	6
400	1	20
510	20	400

-- Zr alloys typically absorb about 40% of the hydrogen liberated by oxidation.

-- Zircalloy-4 was developed to reduce the absorbed hydrogen.

-- The absorption of hydrogen was reduced by a factor of 3.

- ***See figure 6 for Zr-4 @ 400 °C***

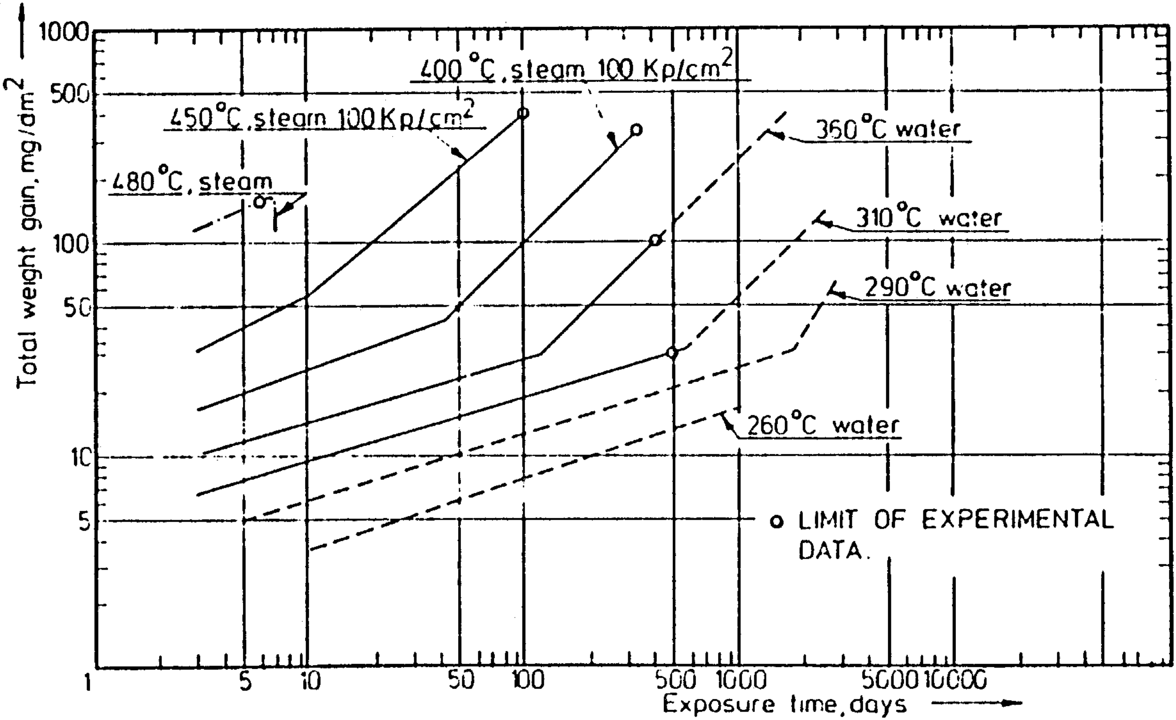
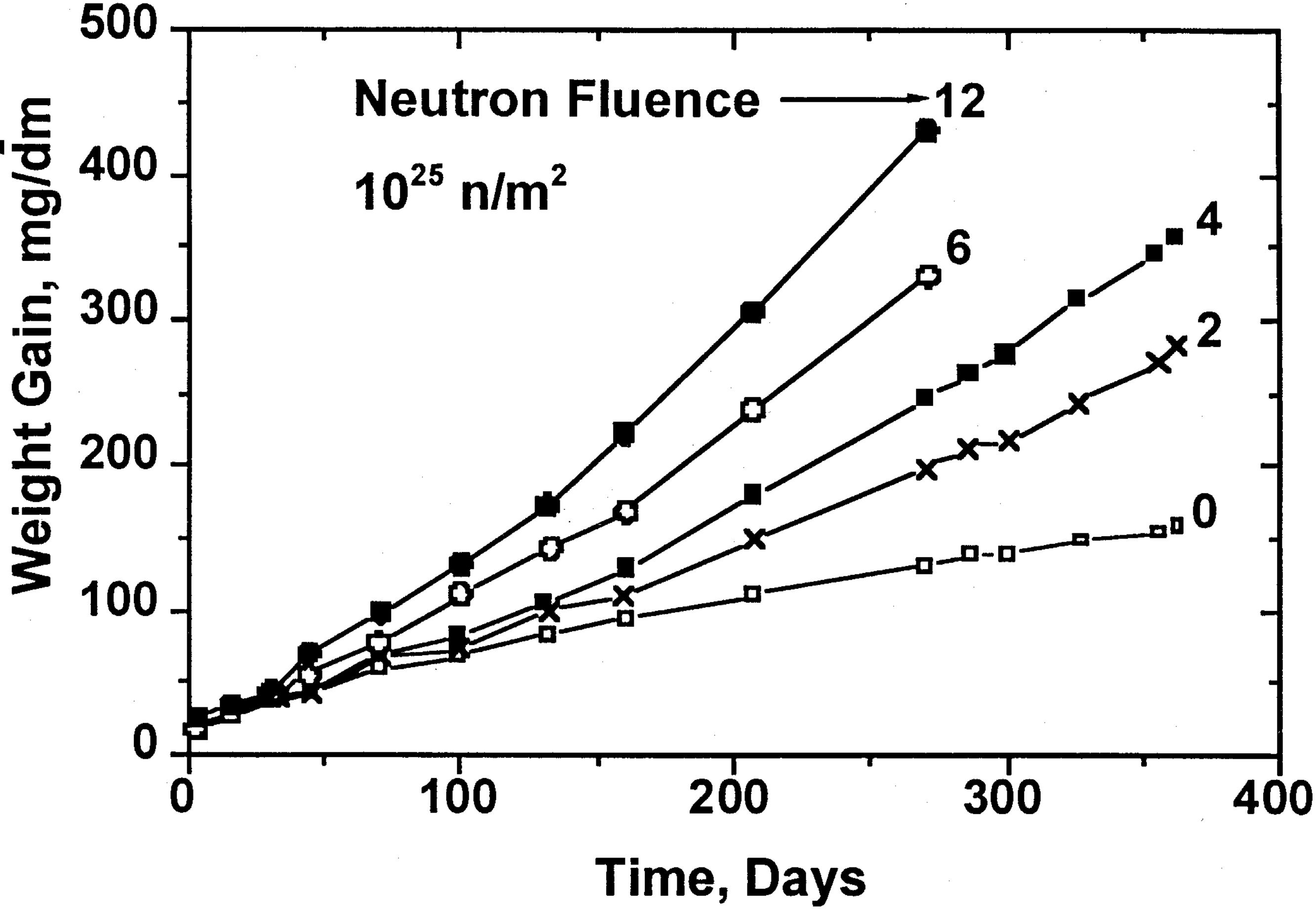


Fig. 1. Out of pile corrosion of zircaloy 2 and 4 [2].

1 mg / dm² = .05 μm of metal

1 mg / dm² / day = 20 μm / year



?ost-irradiation corrosion of Zircaloy-4 in 673K steam after different fluences [83

R. Adamson

Irradiation Effects

- **During irradiation, H_2O (D_2O) is decomposed to $H_2 + O_2$ ($D_2 + O_2$)**

- **In a BWR, liquid phase contains 0.05 to 0.2 ppm O_2, and vapor phase contains 5 to 20 ppm O_2.**

- **In PWR's, a hydrogen over pressure is used to suppress the evolution of O_2.**

- **In BWR's, irradiation increases corrosion rates by a factor of ≈ 100 @ 240°C, ≈ 10 @ 300°C, and ≈ 1 @ 400 °C.**

- **Irradiation also decreases the difference of absorption rates in Zr-2 and Zr-4.**

- **Even the highest BWR corrosion rates @ 325 °C lead to only 35 microns thickness lost per 5 years.**

- ***Nodular Corrosion (Mainly in BWR's)-2 figures***

  - **General corrosion of Zr alloys leads to thin black protective layers (ZrO_2).**

  - **These alloys also form localized, lens-shaped, white oxides.**

  - **Nodules generally grow much faster than the "uniform" films found in PWR's.**

  - **The extent of coverage depends on material, water chemistry, temperature, etc.**

  - **Adamson (GE) showed that irradiation dissolution of $Zr(Fe,Cr)_2$ precipitates cause Fe and Cr to go into solution, thus reducing nodular corrosion. (figure 3)**

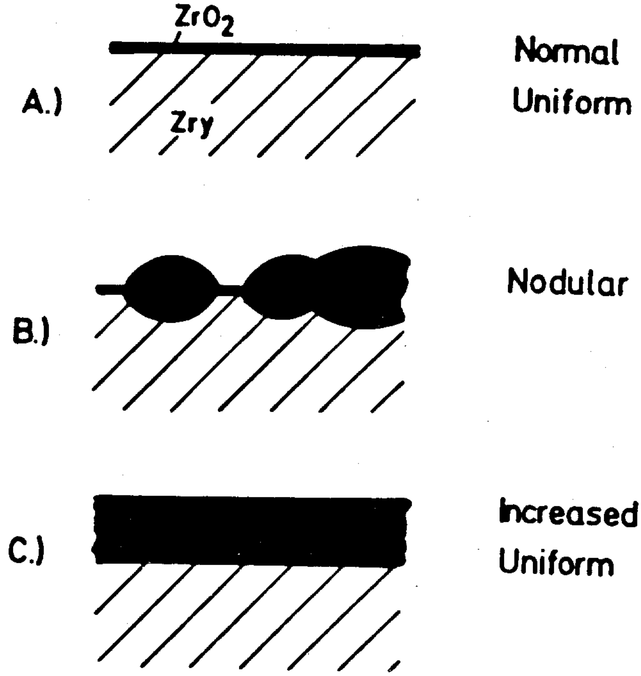
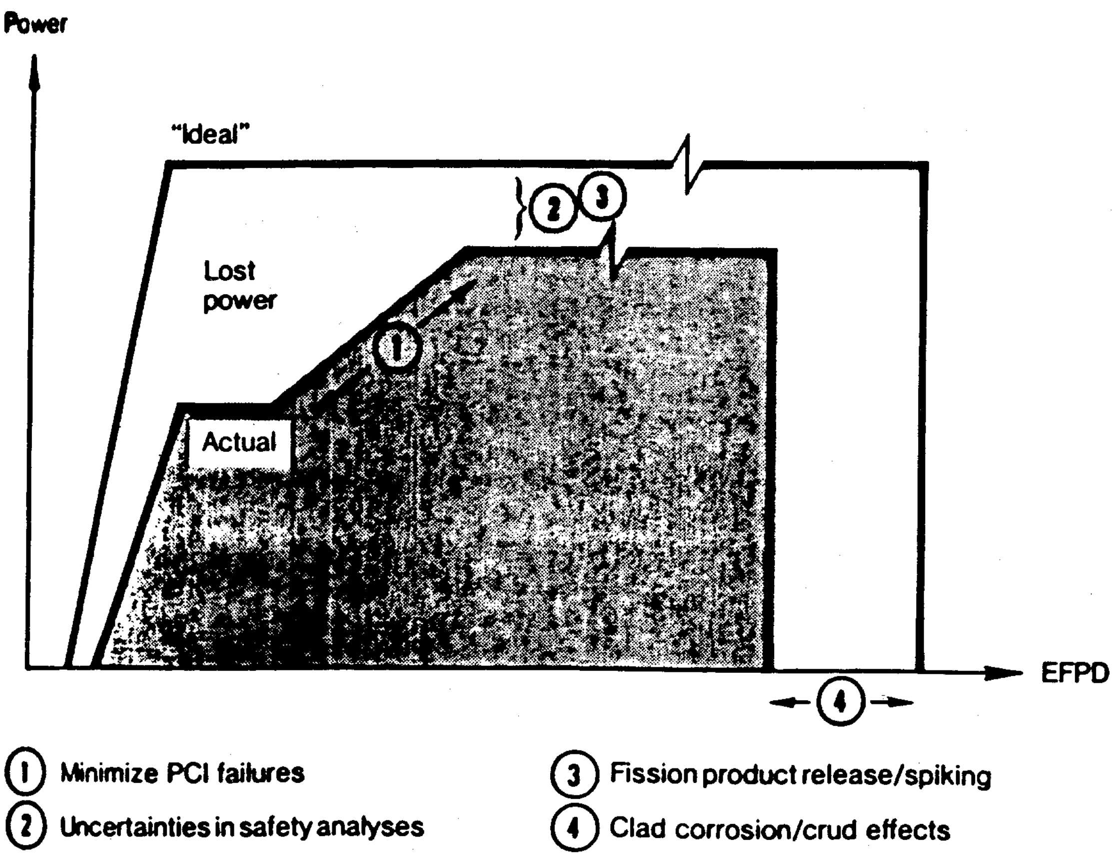
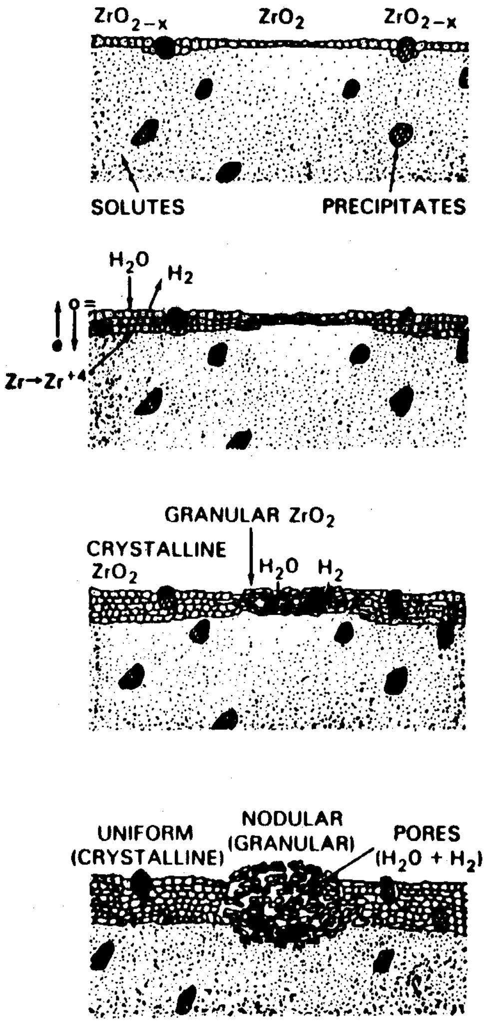


FIG. 2—*Type of oxide layers formed on Zircaloy in BWRs.*





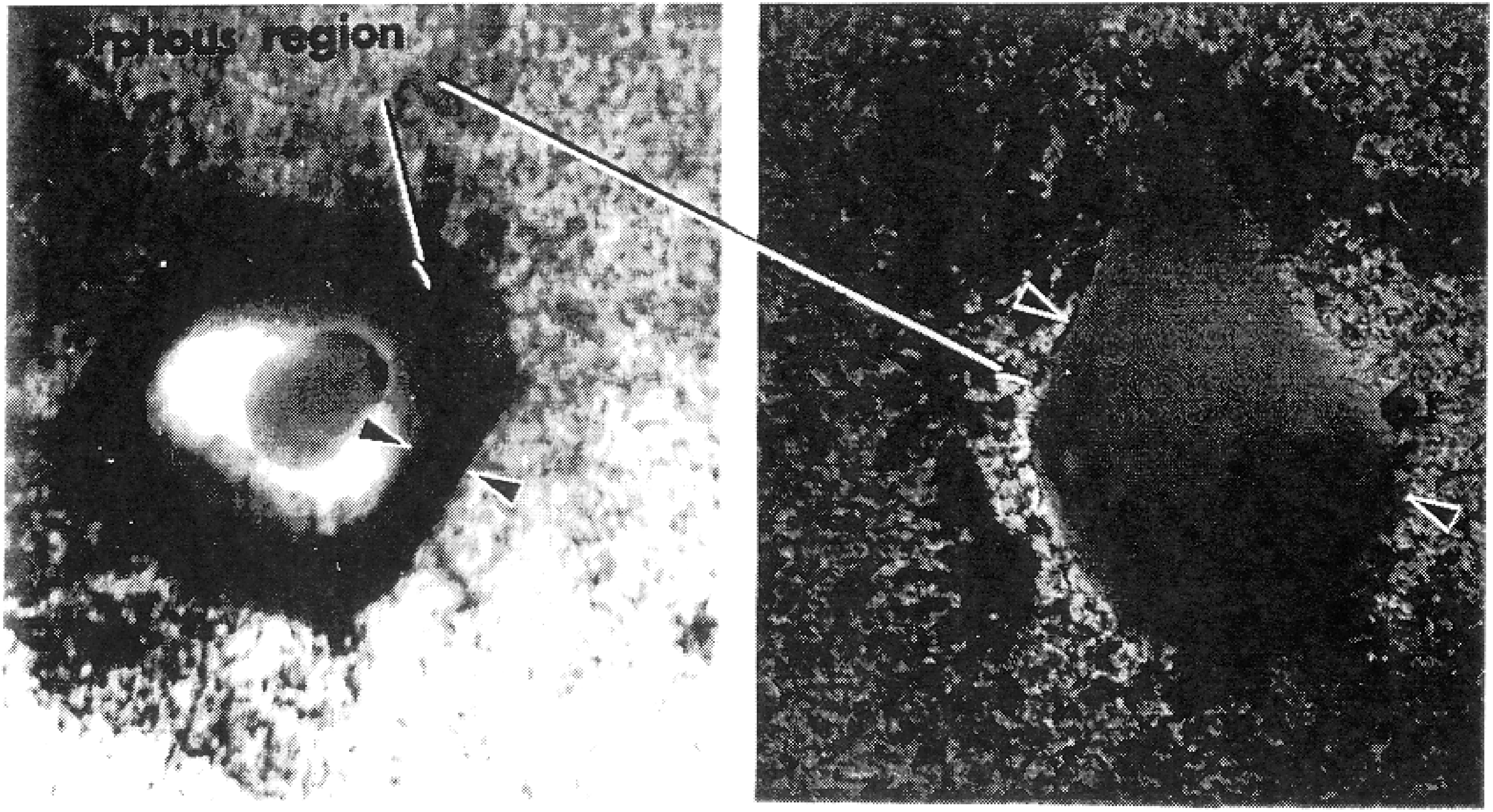
Step (a) Formation of initial uniform oxide, ZrO_2 or ZrO_{2-x}

Step (b) Thickening of initial uniform oxide

Step (c) Rupture of near stoichiometric ZrO_2 leading to direct access of H_2O to the interface.

Step (d) Repetitive formation and rupture of ZrO_2 leading to highly porous, granular ZrO_2, which retains corrosion hydrogen and prevents repassivation of the metal surface.

Figure 18. A schematic showing the steps leading to the nucleation of nodular oxide on Zircaloy.



Amorphization of originally $Zr(Fe,Cr)_2$ precipitates in Zircaloy-4 [31,33]. The precipitate on the right is totally amorphous.

Figure 3 - Adamson

Crud-Induced Localized Corrosion (CILC)

- **CILC is found in 12-15% of operating BWR's containing GE fuel.**

  - **It tends to occur in BWR's with brass condensers**

  - **CILC is also more common in $(U,Gd)\,O_2$ fuels.**
    => $(U,Gd)\,O_2$ rods are referred to as burnable poisons. Gd has a high absorption cross-section.

$$\sum_a^{thermal}(Gd) = 1400\ /\ cm$$

  - **Two types of crud formed in BWR's**

    1.) Low density, loosely adherent crud (Fe_2O_3) with excellent thermal conductivity.

    2.) High density, tightly adherent crud (CuO) scale with poor thermal conductivity.

  - **CILC involves scale-type crud containing >50% Cu cations.**

  - **Local pits (3 mm to 6 mm diameter) are found in failure regions.**

Contributing Factors

Environment:

- CILC requires Cu content to be sufficient. (Figure)

- Cu does 3 things:

    1.) Promotes scale formation.
    2.) Deposits between nodules.
    3.) Deposits in layers with oxides, forming steam pockets, which cause the temperature to rise, which causes enhanced corrosion + pitting

Duty Cycle

- CILC is more likely in $(U,Gd)O_2$ because low initial power allows nodules to form, higher power later leads to CILC. See Figure.

Materials

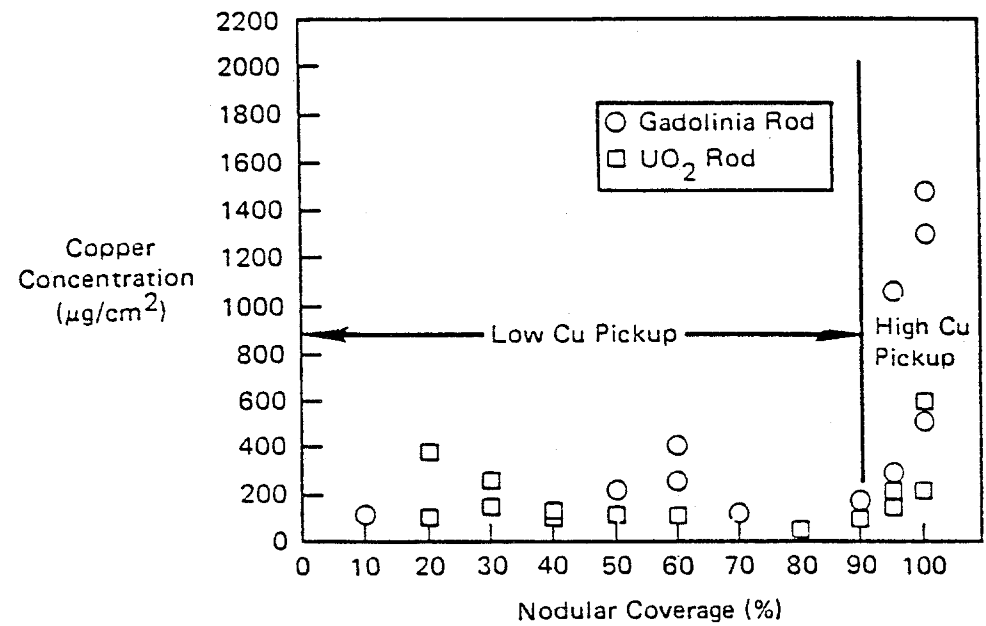
- Zircaloy's are particularly susceptible to CILC.

- Heat treatment of the cladding can increase the resistance to nodule formation by changing the precipitate size and density.

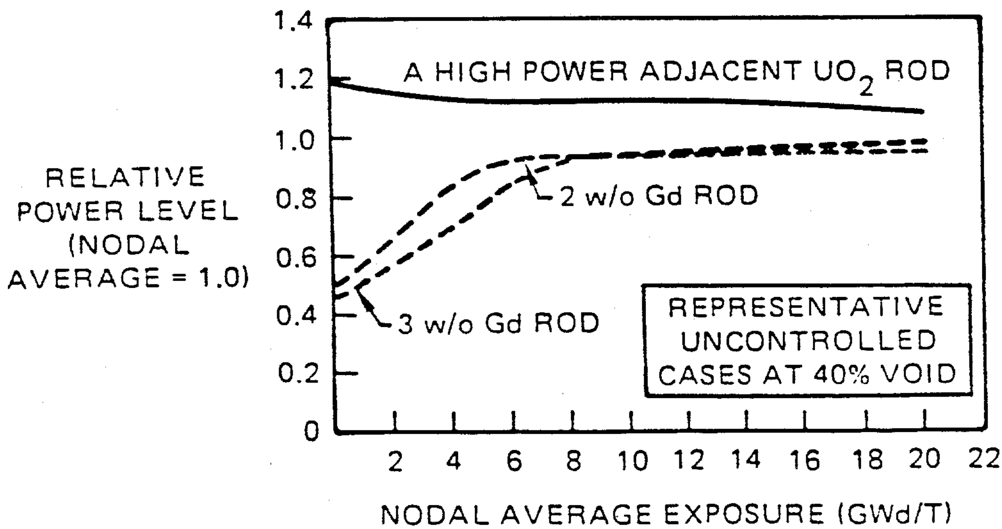
- BWR's require small precipitates that dissolve quickly

- PWR's require large precipitates that dissolve slowly

Figure 7. Effect of Extent of Nodule Coverage on Copper Bearing Crud Deposition



Relative Power History of (U,Gd) O_2 and Nearby High Power UO_2 Fuel Rods



<u>Radiation Damage - Zr</u>

(See D. O. Northwood, Atomic Energy Review, Vol. 15, No. 4, p. 547, 1977)

(See R. B. Adamson, "Effects of Neutron Irradiation on Microstructure and properties of Zircaloy, 12^{th} Intn. Symp. On Zirconium in the Nuclear Industry, ASTM STP-1354, pp. ?? (1999)

• ***Note that the operating temperature for Zircaloy in LWR's is 100 - 350°C but mainly 300 to 350 °C***

• ***Most typical damage structure is a high density of dislocation loops (20 - 100 Å in diameter).*** **See Figure**

<u>Neutron Fluence Effects on Zircaloy - II</u>

1.) no damage observed below 2×10^{19} n cm^{-2} (E> 1 MeV)

2.) Density of loops decreases with increasing n fluence

3.) Loop size increases with increasing fluence

4.) Saturation in visible defects at ≈ 1×10^{21} n cm^{-2} (Figure 7-23)

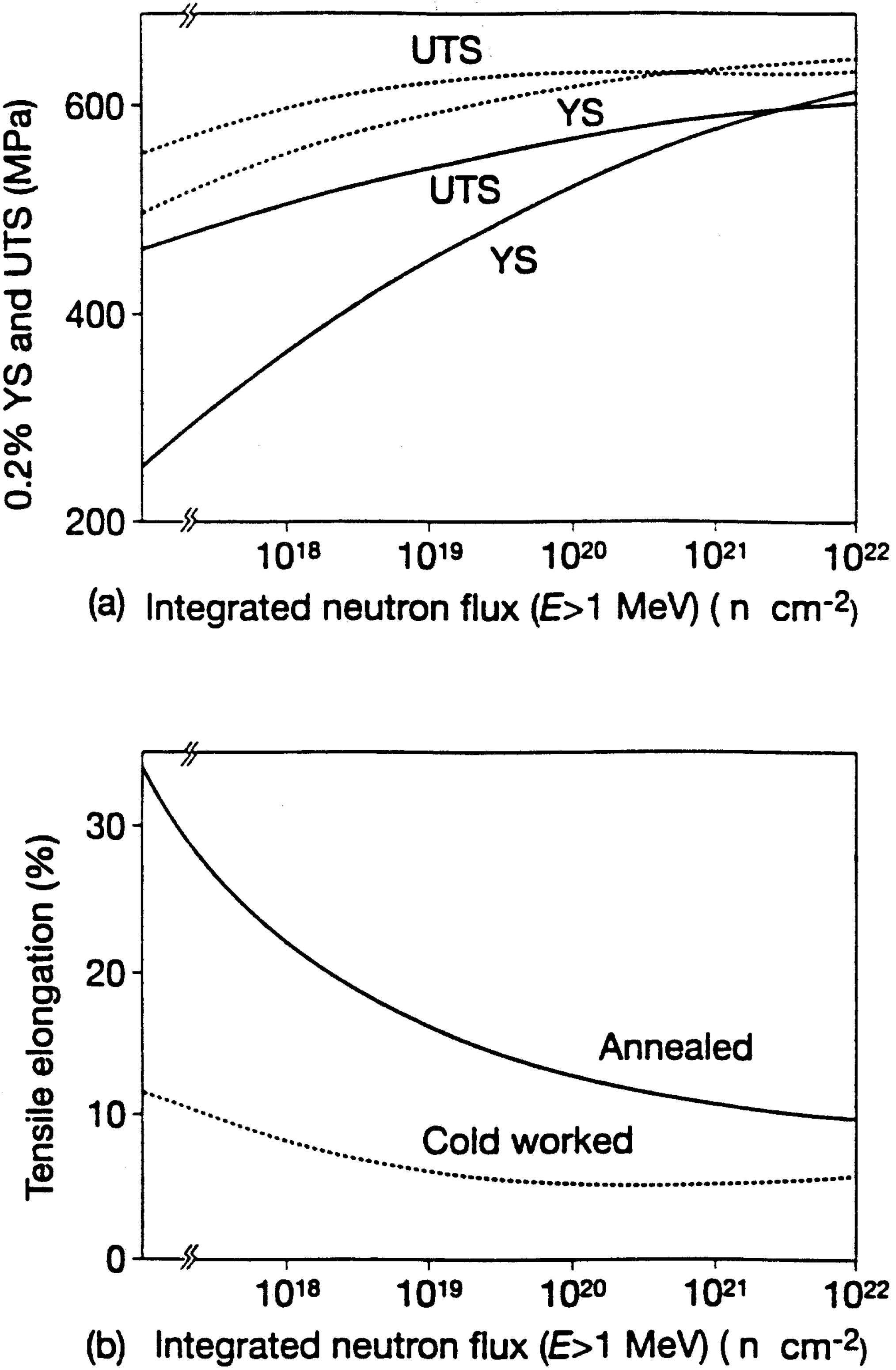


Figure 7-23. Effect of irradiation on the mechanical properties: (a) Due to defect build-up, the yield strength (YS) and fracture strength increase with dose, but the effect saturates at about $10^{24}\ \mathrm{n \cdot m^{-2}}$ (dashed lines: 10% cold worked, solid lines: annealed yield strength). (b) The same effect occurs on ductility. In the case of cold worked material, the initial high dislocation density masks the effect of irradiation.

<u>Temperature</u> <u>Effects</u>

- **Above ≈ 500 °C, no visible damage found**
- **At T > 400 °C, mainly vacancy loops**
- **At T< 400 °C, mainly interstitial loops**
- **Voids only found in ion bombarded samples when gas atoms are preinjected**

<u>Alloying</u>

Increasing alloying elements in solid solution, decreases loop size and increases loop density

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For the effects of microstructure and stress, see Northwood

Recent Information From Dr. Ron B. Adamson
Manager
Zircalloy Division
General Electric Corp.

• <u>Performance to date of BWR and PWR fuel</u>

@ 40,000 MWd/MT ($8x10^{21}$ n/cm^2, E>1 MeV)

only 1 failure in 100,000 rods

• The use of Zr sleeves has solved the PCI prob. (10 years ago the major mode of fuel failure was Pellet Clad Interaction (PCI)) See Figure.

• Crud Induced Localized Corrosion (CILC) definitely linked to Cu in BWR water. Many utilities have replaced copper based condenser tubes with stainless steel or Ti tubes.

• <u>Near term goal for BWR's and PWR's</u>

- 45,000 MWd/MT for BWR's
- 60,000 MWd/MT for PWR's

- only 1 failure in 1,000,000 rods

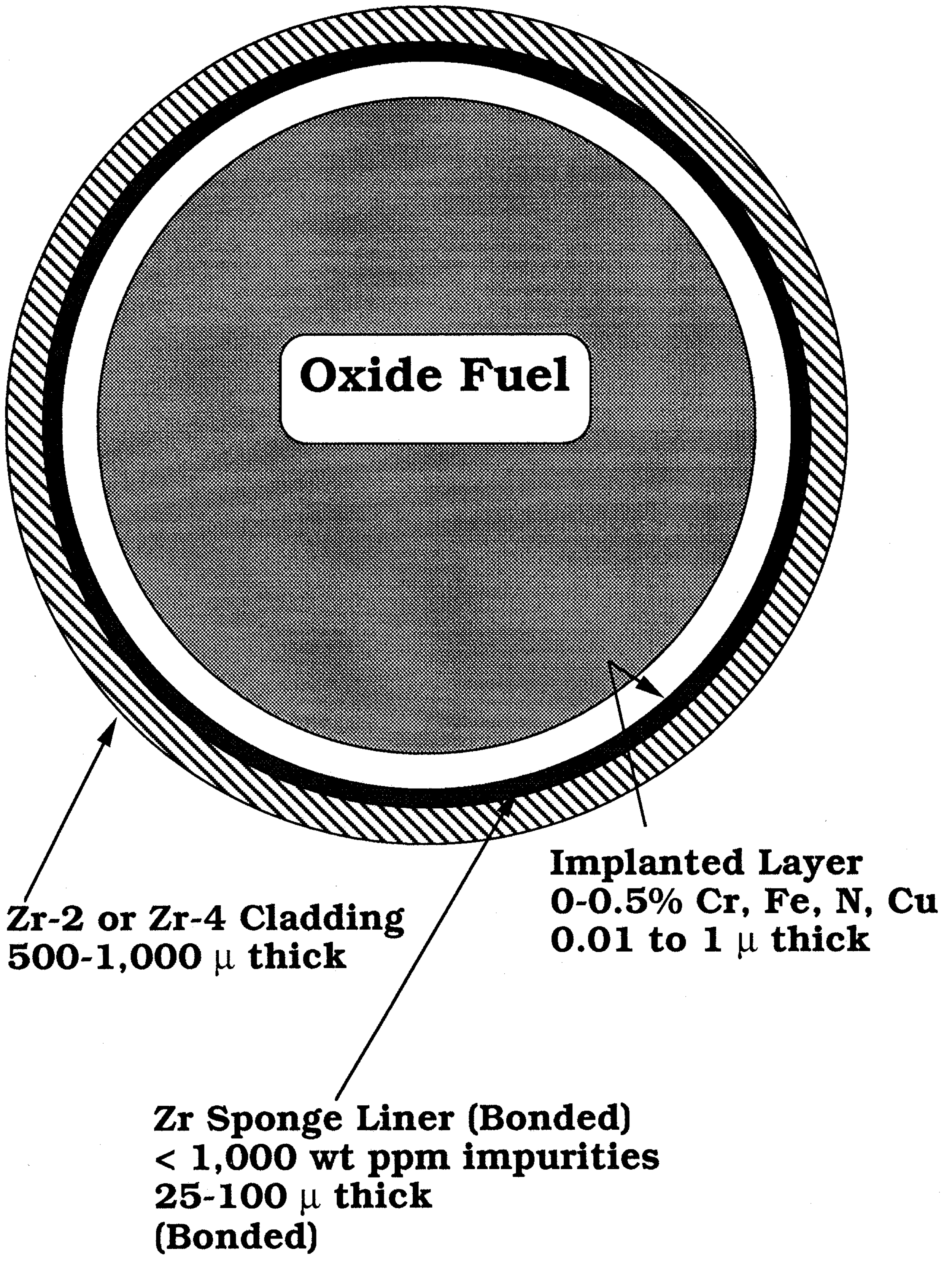
• Irradiation makes $Zr(Cr,Fe)_2$ precipitates amorphous by 1×10^{21} n/cm^2

• Radiation Effects

- Fatigue (Fig)
- Growth (Fig)
- Creep (Fig)
- Fracture (Fig)

GE Method to Reduce FCI in LWR's - After Adamson

Patent # 4,894,203



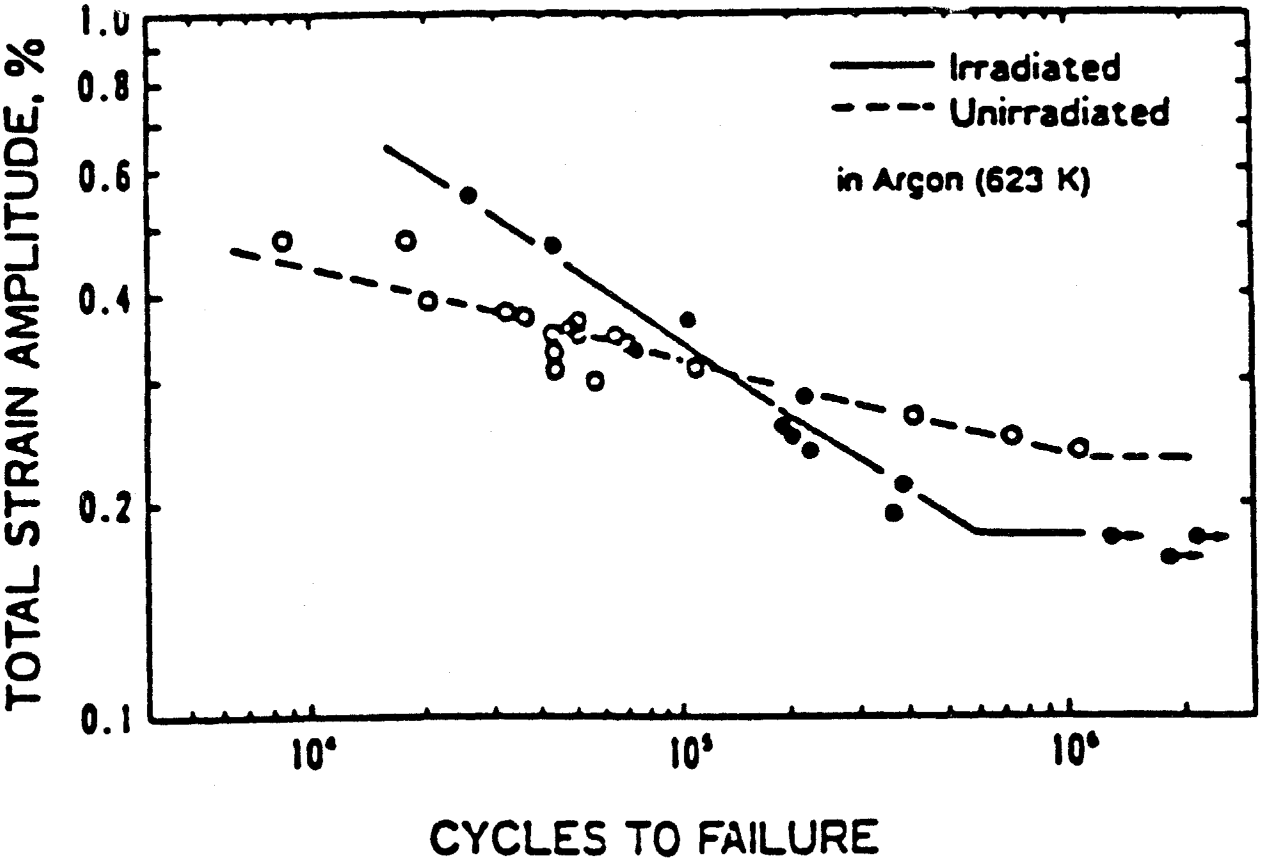


Fig. 12. Change in Failure Cycles due to Neutron Irradiation (Ref. 51)

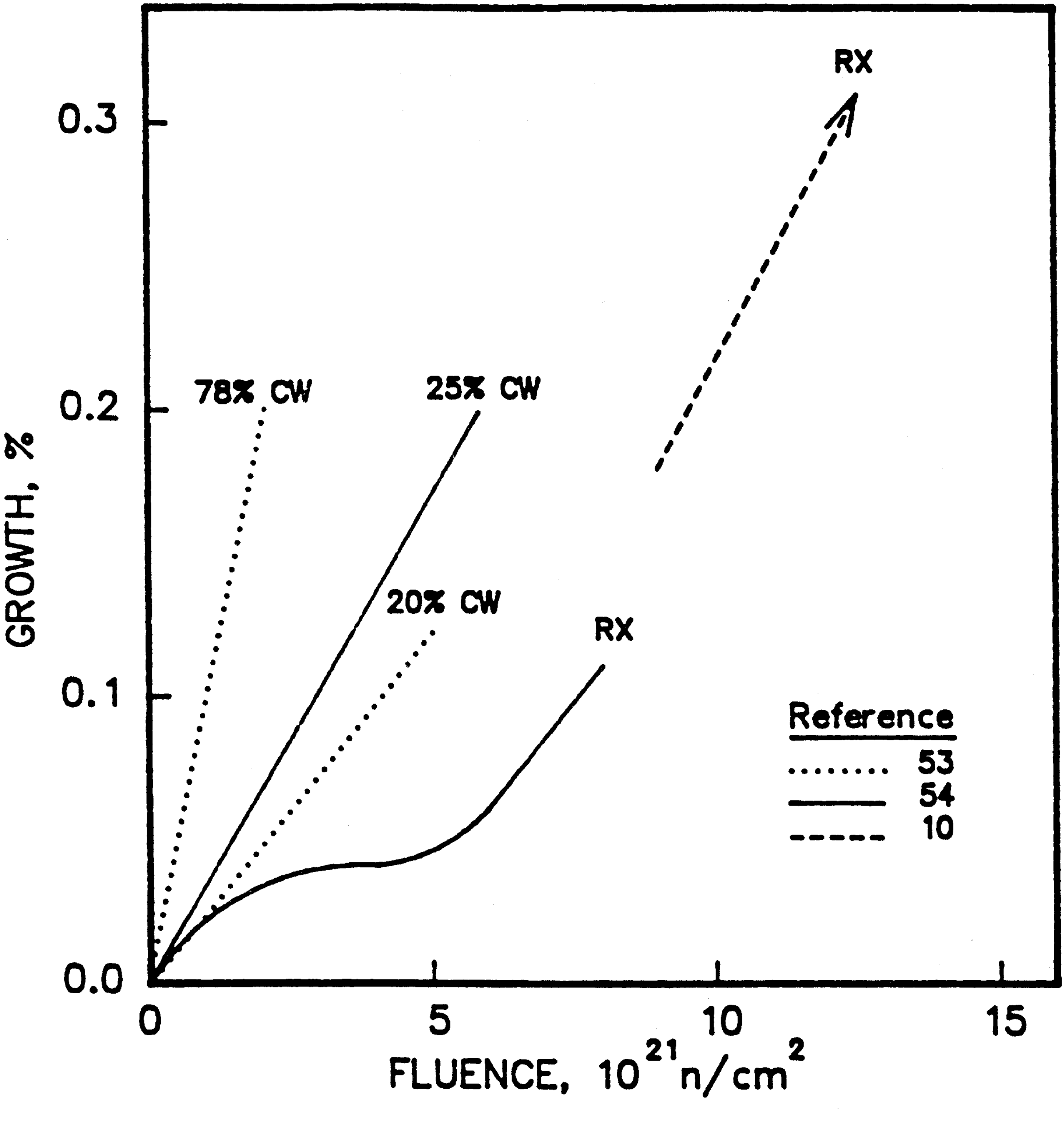


Fig. 13. Irradiation Growth of Zircaloy Near 300°C

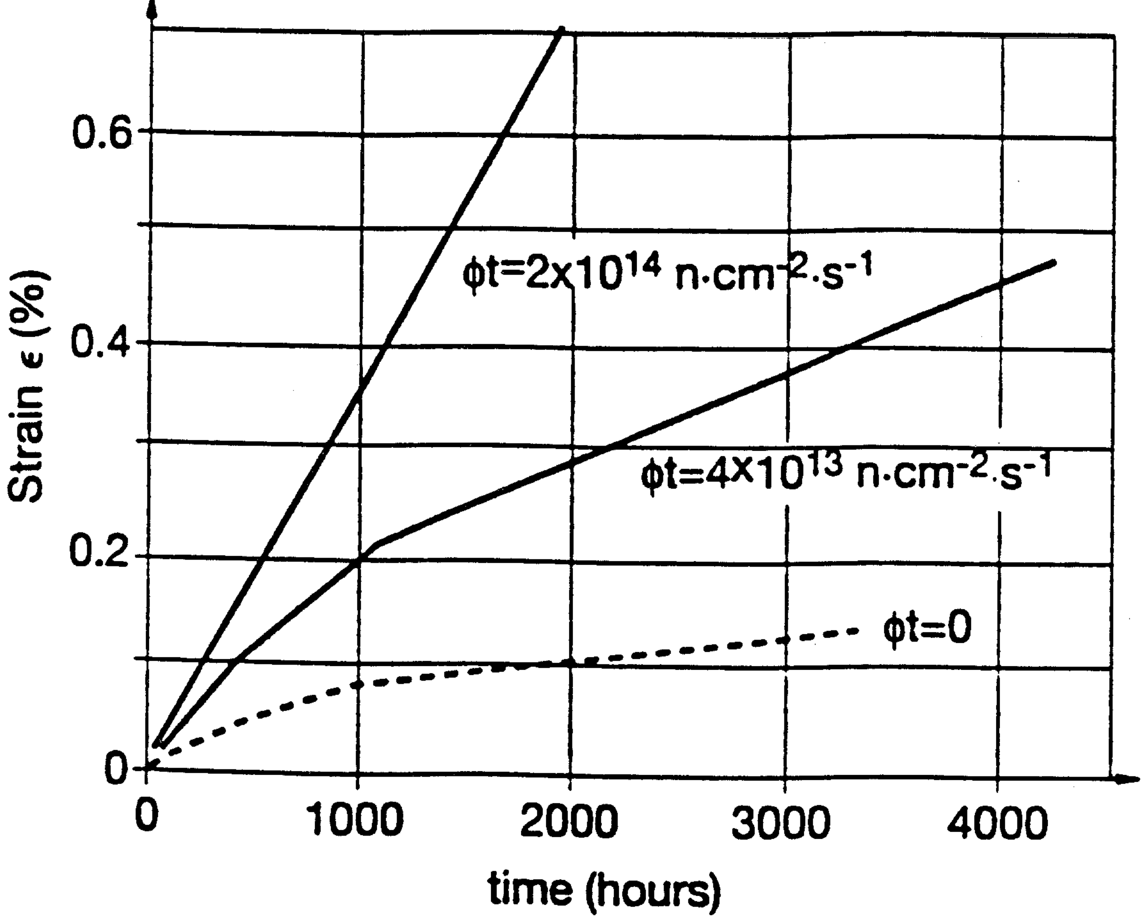


Figure 7-22. Diametral creep of RX Zircaloy under internal pressure (330 °C, $\sigma_H = 150$ MPa). The irradiation affects both the primary and the secondary creep, and the creep rate is increased in proportion to the dose rate.

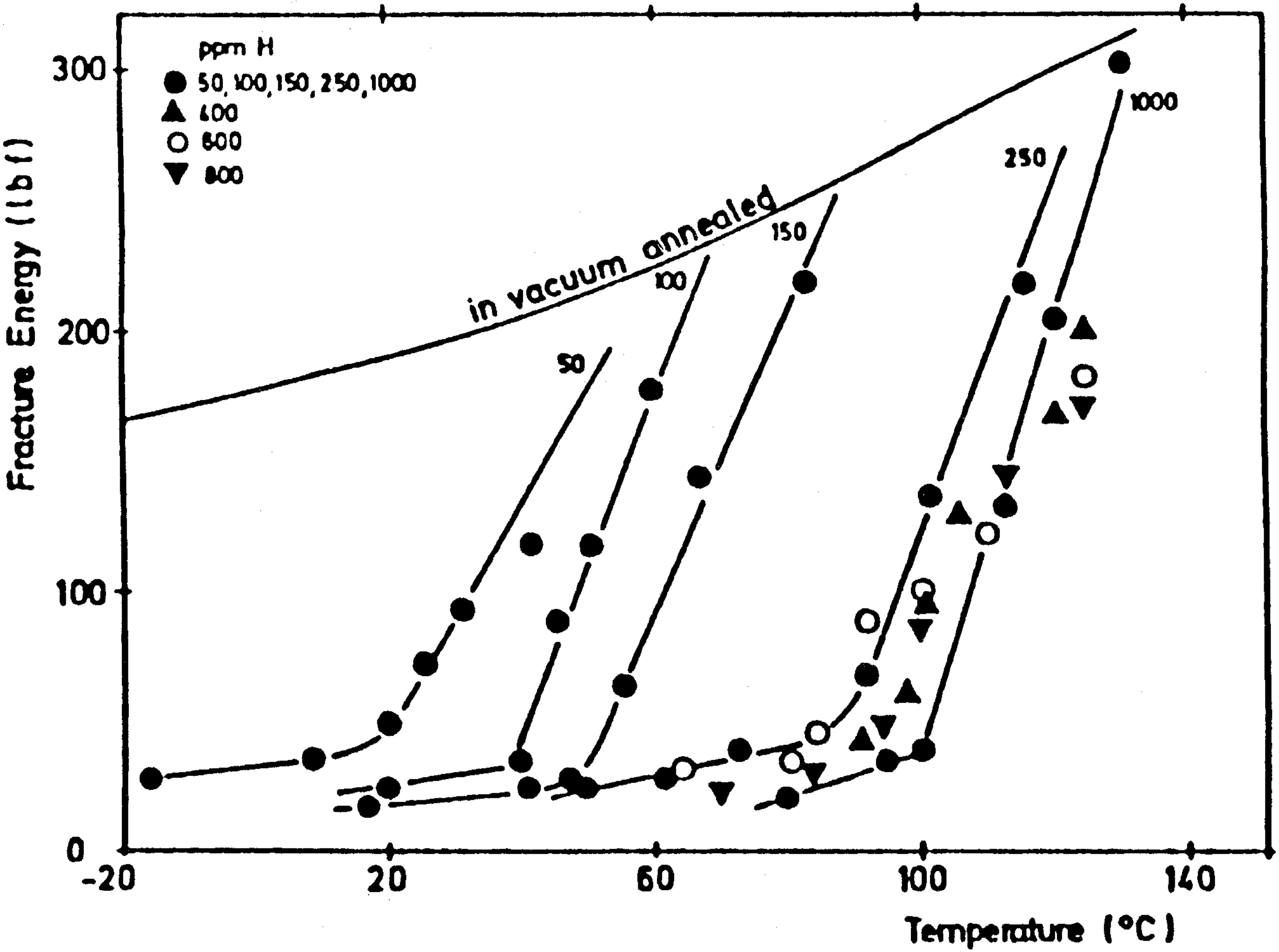


FIG.27. Influence of hydrogen on the fracture energy transition temperature [50].