# Zirconium Cladding

**Why ?**

- **Physical Properties**
- **Corrosion Resistance**
- **Radiation Effects**

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***In the early 1950's the Navy was looking for a material with***

- ***low $\sigma_a$***
- ***high corrosion resistance***
- ***high strength***

***Disadvantages of Zr in early 1950's;***

- ***poor ductility***
- ***poor corrosion resistance***
- ***high cost***
- ***difficult fabrication***

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**1943 - Zr produced by iodide process**
**≈ 1400 $/kg**
**≈ 0.05 kg in entire country**
**$\sigma_a$ = 105 barns**

**1948 - cost 280 to 500 $/kg**
**production rate ≈ 40 kg/y**
**$\sigma_a$ = 0.4 barns (removed Hf impurity, 1.5 to 2.5% in most Zr ores)**

**1953 - cost 30 to 70 $/kg**
**125,000 kg/y**
**$\sigma_a$ = 0.18 barns**
**( first Mark I STR core - Zr)**
**( second Mark II STR core - Zr alloy)**

**1958 - cost 10 to 18 $/kg**
**1,000,000 kg/y production**
**(Shippingport Reactor)**

| Table 1<br>Neutron Economy of Various Metals Compared to Zr | | | |
|---|---|---|---|
| **Base Metal** | **Ultimate Strength @ 300 °C (MPa)** | **Macroscopic Thermal Neutron Xsection, $cm^{-1}$** | **Relative Neutron Absorption for Given Design Stress** |
| **Zr** | 900 | 0.010 | 1 |
| **Be** | 350 | 0.001 | 0.5 |
| **Mg** | 90 | 0.005 | 5 |
| **Al** | 90 | 0.014 | 14 |
| **Fe** | 1100 | 0.170 | 14 |
| **Ni** | 1100 | 0.310 | 25 |
| **Ti** | 1000 | 0.260 | 28 |

## Physical Properties

**Phase transformations;** *Phase Diagram*

**$\alpha$ - up to 865 °C - hcp**

**$\beta$ - 865 to 1845 °C - bcc**

## Mechanical properties;

- **Can increase the strength by cold working but the recrystallization temperature is ≈ 400 to 500 °C**

- **Oxygen-Strengthens and embrittles Zr**
- **Hydrogen-(hydrides) reduces ductility**

| Property | Al | Zr | Zircaloy-2 | 347 SS |
|---|---|---|---|---|
| Density, g/cc | 2.71 | 6.5 | 6.55 | 7.98 |
| | | | | |
| Melting T, °C | 660 | 1845 | ≈1830 | ≈1399 |
| | | | | |
| Trans. T, °C | - | 862 | ≈1000 | - |
| Recryst. T, °C | 150-290 | 450-550 | 550-600 | - |
| | | | | |
| α, x $10^{-4}$/°C | | | | |
| 25-100°C | 23.5 | 6.38 | | 16.5 |
| 25-200 | 24.6 | | | |
| 25-300 | 25.6 | 7.61 | | |
| 25-500 | | | | |
| 25-600 | | 9.46 | | 18.0 |
| 25-700 | | | 6.5 | |
| | | | | |
| k-cal/cm-s-°C | | | | |
| 25°C | 0.53 | 0.050 | 0.035 | |
| 50 | | 0.050 | | |
| 100 | | 0.049 | 0.034 | 0.038 |
| 200 | | | 0.033 | |
| 300 | | 0.042 | 0.033 | |
| 538 | | | | 0.051 |
| Thermal n Xsection-b | 0.22 | 0.18 | >0.18 | >2.5 |
| Ultimate Strength-psi | | | | |
| 25°C | 13,000 | 34,800 | 68,600 | 90,000 |
| 100 | 9,700 | | | |
| 200 | 6,000 | | | |
| 300 | 2,500 | 18,000 | | |
| 400 | 1,300 | 12,000 | | |
| 500 | | 8,000 | 22,000 | 65,000 |
| Yield Strength-psi | | | | |
| 25°C | 5,000 | 9,900 | 44,800 | 35,000 |
| 100 | 4,100 | | | |
| 200 | 3,000 | | | |
| 300 | 1,500 | 6,000 | | |
| 400 | 800 | 4,800 | | |
| 500 | | 5,000 | 10,500 | 31,000 |
| | | | | |
| Elongation-% | | | | |
| 25°C | 45 | 47 | 22 | 40 |
| 100 | 57 | | | |
| 200 | 65 | | | |
| 300 | 90 | 52 | | |
| 400 | 93 | 50 | | |
| 500 | | 48 | 36 | 35 |

## Corrosion

**Pure Zr exhibits fairly good resistance to corrosion by water at elevated temperatures, but the material can develop some weight gain**

**Figure on Mechanism**
**Figure on Flaking**

- ***At 316°C ,VHP Zr <u>does</u> <u>not</u> reach breakaway in 200 days***

- ***At 360 °C , VHP Zr does reach breakaway in less than 7 days***

***Figure 15-8***

## Effect of Impurities

**Table IV**

**Small amounts of Sn, Ta , and Nb can counter impurities.**

| | | |
|---|---|---|
| **Zircaloy (USA)** | **Bad Neutronics** | **Higher Strength (USSR) (Canada)** |

**Figures 15 - 6 and 15 -7**

• ***Even the rates @ 316 and 399°C ( 5 to 15 x 10 $^{-4}$ cm / y) are small compared to a 1 mm cladding thickness***
***(Figure 15-8)***

**Composition of Commercial Zr Alloys**
**w/o**

| **Alloy** | **Zr** | **Sn** | **Fe** | **Cr** | **Ni** | **Nb** | **O** |
|---|---|---|---|---|---|---|---|
| **Zir -II** | **98.2** | **1.5** | **0.12** | **0.10** | **0.05** | **--** | **0.13** |
| **Zir -IV** | **98.2** | **1.3** | **0.22** | **0.10** | **--** | **--** | **0.13** |
| **Zr -1Nb** | **99** | **--** | **--** | **--** | **--** | **1.0** | **---** |
| **Zr -2.5Nb** | **---** | **97.5** | **--** | **--** | **--** | **--** | **2.5** |
| **Zr - 3 Nb -1Sn** | **96** | **1.0** | **--** | **--** | **--** | **2.8** | **---** |

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**Pressurized Water Reactors (PWR's)**

**The coolant contains a highly reducing environment ;**

- **Hydroxide - LiOH**
- **Hydrogen to keep oxygen level to < 0.05 ppm (Figure)**
- **Boric acid ( 0 to 2500 ppm) for control shim**

**Irradiation can accelerate corrosion by a factor of 8 to 10 (Figure)**

**( 11 μ in 41,000 EFPH's, 8 x 10$^{21}$ n cm$^{-2}$)**

## Boiling Water Reactors (BWR's)

- **Can not control oxygen by adding hydrogen because it will just boil away;**

*Oxygen levels*
*0.3 ppm in water*
*20 ppm in steam*

- **Irradiation reduces the temperature sensitivity to oxygen level**

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**Note: the reason we use Zr-4 (in PWR's) instead of Zr-2, is because Zir - IV has about one half the $H_2$ pickup compared to Zr-2 (Ni picks up $H_2$)**

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## Zr - Nb Alloys

**Zr -1Nb ( Figure 5)**

- **No apparent advantage at short times and at low temperatures**

- **USSR icebreaker - LENIN**

**Zr - 2.5 Nb (Figure 6)**

**Great Deal of Work reported !**

**1.) Zircaloy is not affected by oxygen alone but oxygen and neutron flux is more of a problem in Zr - Nb alloys.**

**2.) Zr - Nb is affected by increased oxygen levels, but the n flux lowers the temperature effect.**

**3.) In a deoxygenated environment, Zr - 2.5Nb has far superior properties compared to Zircaloy in the long run (Figure 7)**

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## Conclusions

**1.) Corrosion and hydride resistance of Zr -IV is more than adequate**

**2.) Zr -Nb offers no real benefit over Zircaloy for normal ( 1-2 years ) runs.**

**3.) For long exposures, Zr -Nb has a better corrosion resistance ( in high n fluence)**

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**See "Corrosion in Nuclear Systems"**
**by**
**Professor J. Blanchard**

**Video Tape (50 mins.)**

**Engineering Library**

**TV-0423-35**

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## Corrosion in Nuclear Reactors

***Internal Corrosion:***

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

***External Corrosion***

| | 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.**

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***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 leads to only 35 microns thickness lost per 5 years.**

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- ***Nodular Corrosion***

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

**• These alloys also form localized, lens-shaped, white oxides (especially in BWR's).**

**• Nodules generally grow much faster than "uniform" films.**

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

**<u>Crud-Induced Localized Corrosion (CILC)</u>**

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

  - **It tends to occur in BWR's with brass condensers and determines filter demineralizer condensate water cleanup systems.**

  - **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.**

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## Contributing Factors

***Environment:***

- **CILC requires Cu content to be sufficient.**

- **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**

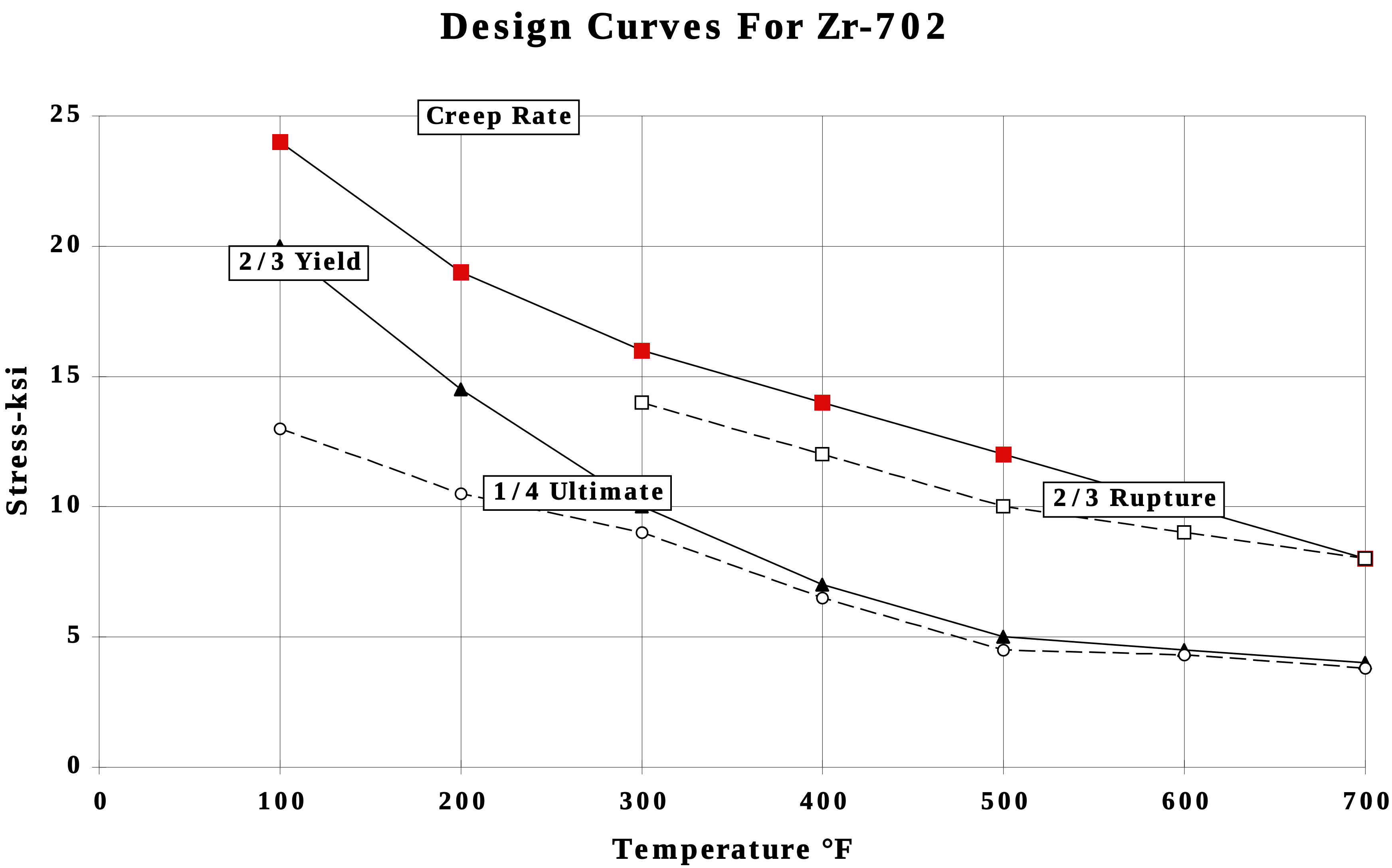
***Duty Cycle***

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

***Materials***

- **Zircaloy's are particularly susceptible to CILC.**

- **Heat treatment of the cladding can increase the resistance to nodule formation.**


Design Curves For Zr-702
Stress-ksi
Temperature °F
Creep Rate
2/3 Yield
1/4 Ultimate
2/3 Rupture
0
5
10
15
20
25
0
100
200
300
400
500
600
700