Zirconium Cladding

Why ?

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

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

- ***low σ_a***
- ***high corrosion resistance***
- ***high strength***

Disadvantages of Zr in early 1950's;

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

1943 - Zr produced by iodide process

≈ 1400 $/kg

≈ 0.05 kg in entire country

σ_a = 105 barns

1948 - cost 280 to 500 $/kg

production rate ≈ 40 kg/y

σ_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

σ_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
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*

α **- up to 865 °C - hcp**

β **- 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 does not 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)

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)

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

Video Tape (50 mins.)

Engineering Library

TV-0423-35

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.

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.**

- ***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.**

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

- **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.**

- **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