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

$\approx$ 1400 \$/kg

$\approx$ 0.05 kg in entire country

σ_a = 105 barns

1948 - cost 280 to 500 \$/kg

production rate $\approx$ 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

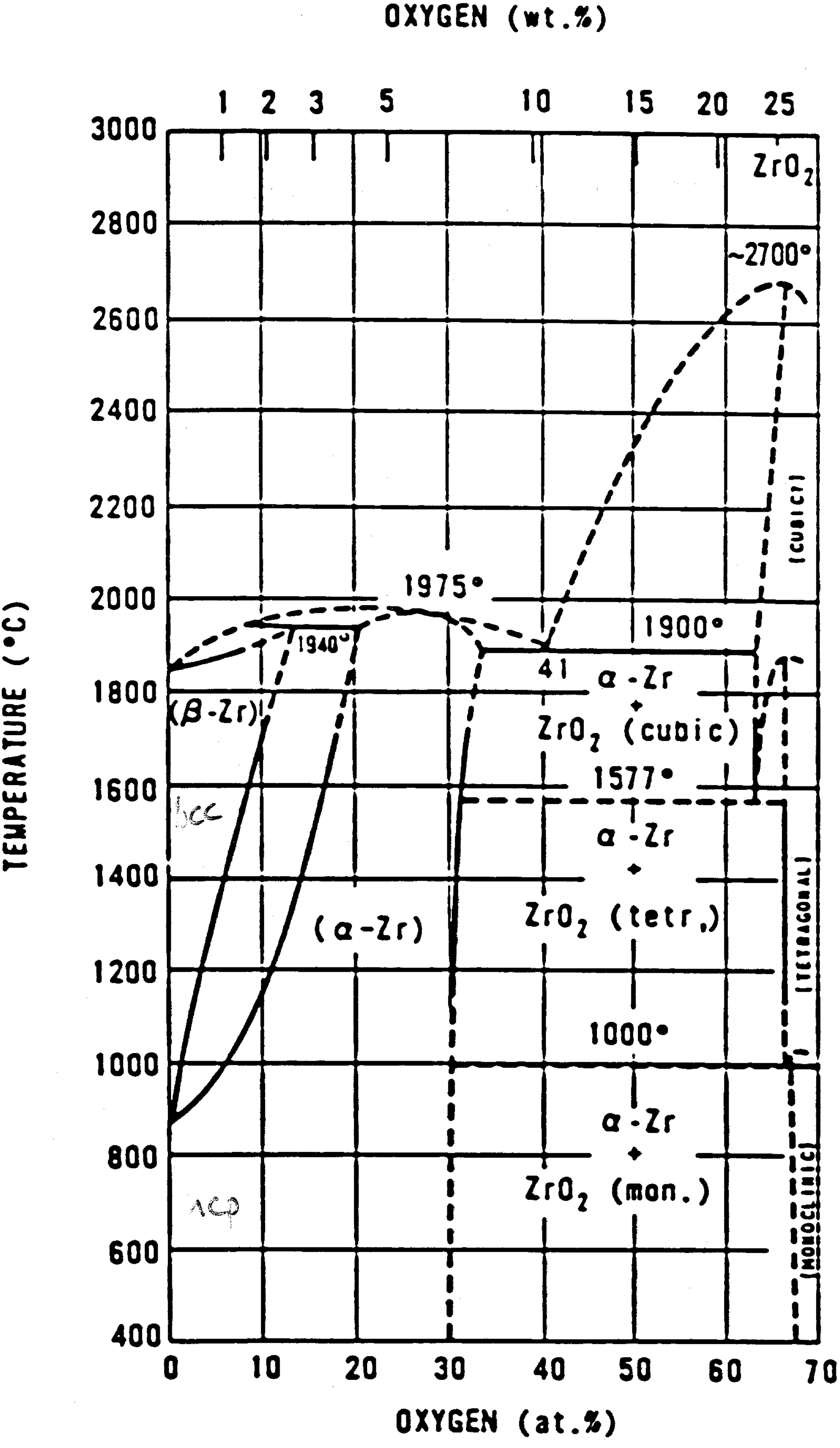
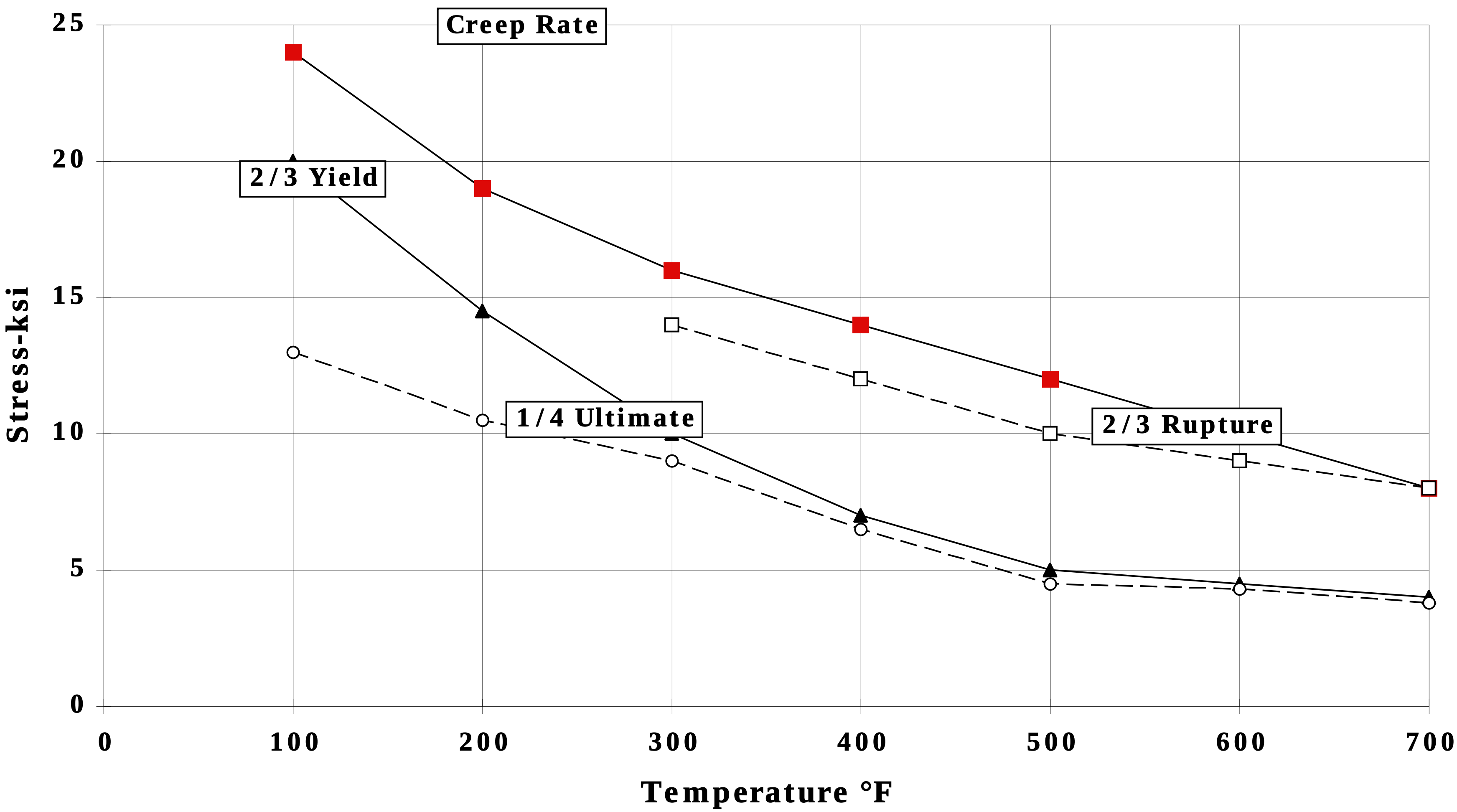


FIG. 8—*Zirconium-oxygen system.*

Design Curves For Zr-702



<u>Corrosion</u>

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

<u>Effect of Impurities</u>

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

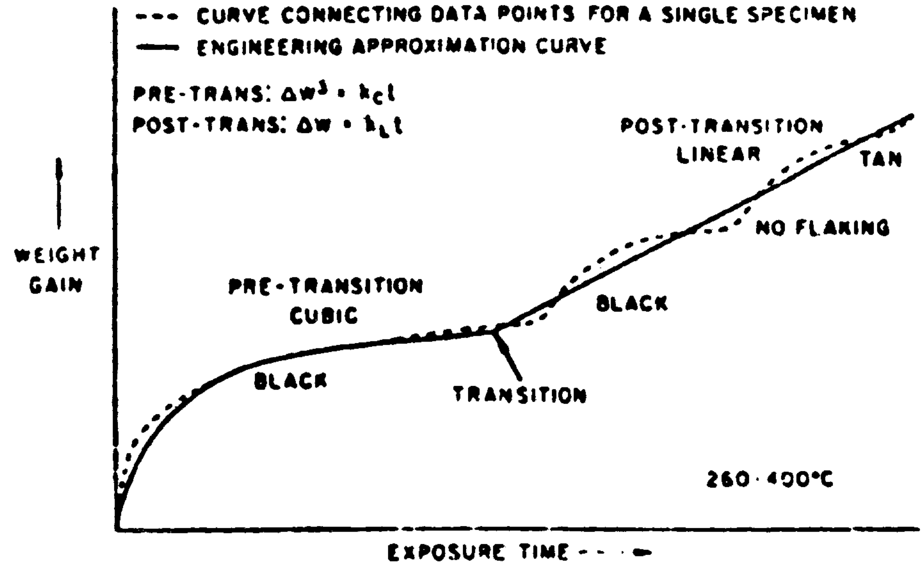
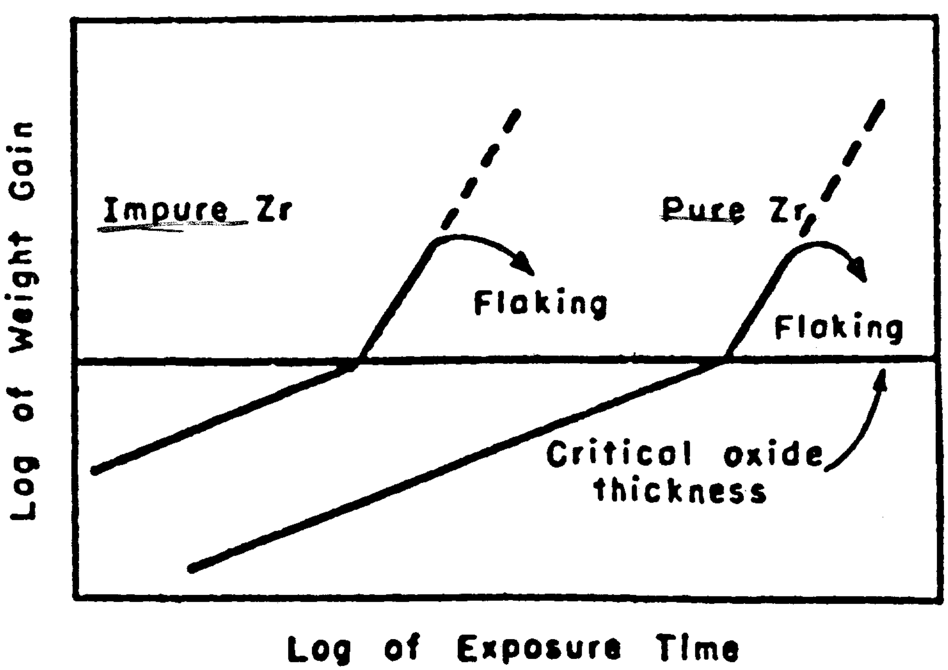


FIG. 2—*Schematic representation of the corrosion of Zircaloy-2 and Zircaloy-4 in the temperature range 260 to 400°C.*



15-5. Schematic representation of corrosion of unalloyed zirconium in high temperature water.

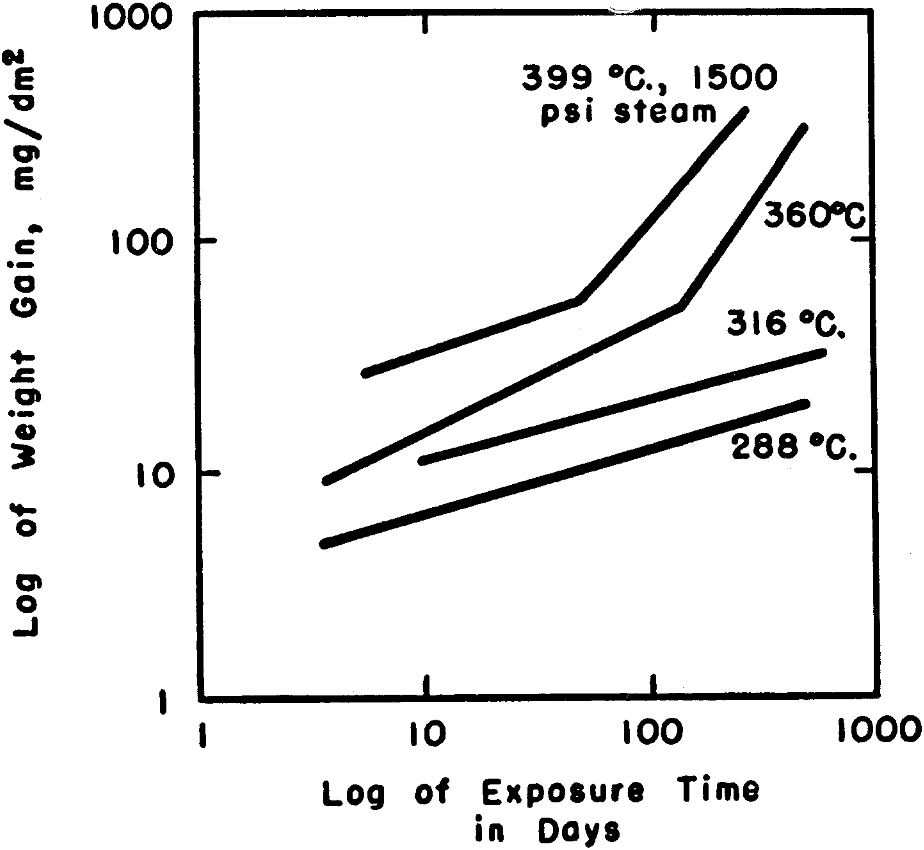


Fig. 15-8. Corrosion of Zircaloy-2.

TABLE IV EFFECT OF IMPURITIES ON THE CORROSION OF ZIRCONIUM IN HIGH TEMPERATURE WATER

Impurity	Effect	Conc. at Which Effect Is Noted, (w/o)	Nominal Composition of Arc Melted Crystal Bar (w/o)
N_2	Harmful	0.004	0.002-0.0025
C	Harmful	0.04	0.01
O_2	Very slight	0.05	0.04
H_2	None	<0.1	0.002
Ti	Harmful	0.1 to 20	0.002-0.003
Al	Harmful	0.1	0.0027-0.0037
Ca	Harmful	Uncertain	0.0025
Mg	Harmful	Uncertain	0.001
Cl	Harmful	Uncertain	0.0015
Si	Harmful	Uncertain	0.002-0.007
Pb	Harmful	~0.01	0.0025
Hf	None	0-100	0.01-0.015
Cu	None	~0.1	—
W	None	~0.1	<0.01
Fe[a]	None	<0.1	0.037-0.049
Cr[a]	None	<0.1	0.001-0.0018
Ni[a]	None	<0.1	0.0025-0.001

[a] Beneficial effects are found at about 0.1% of these elements.

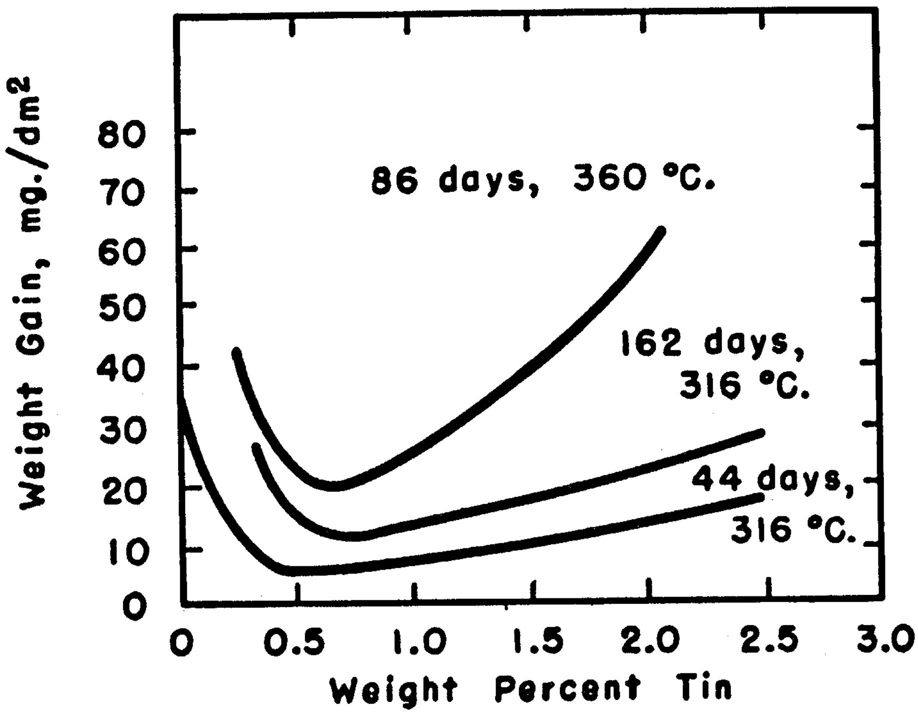
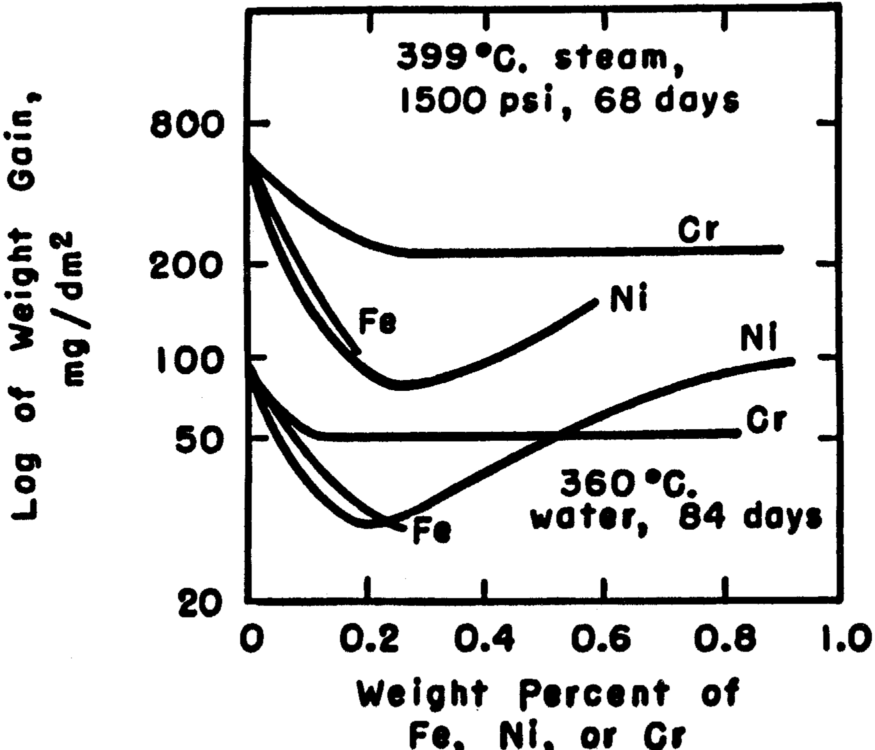


Fig. 15-6. Effect of tin content on the corrosion resistance of arc melted spong zirconium alloys. Poor corrosion resistance of unalloyed material was due to 60 ppm



15-7. Corrosion of 1.8% tin-zirconium ternary alloys with iron, nickel and chromium.

• *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})

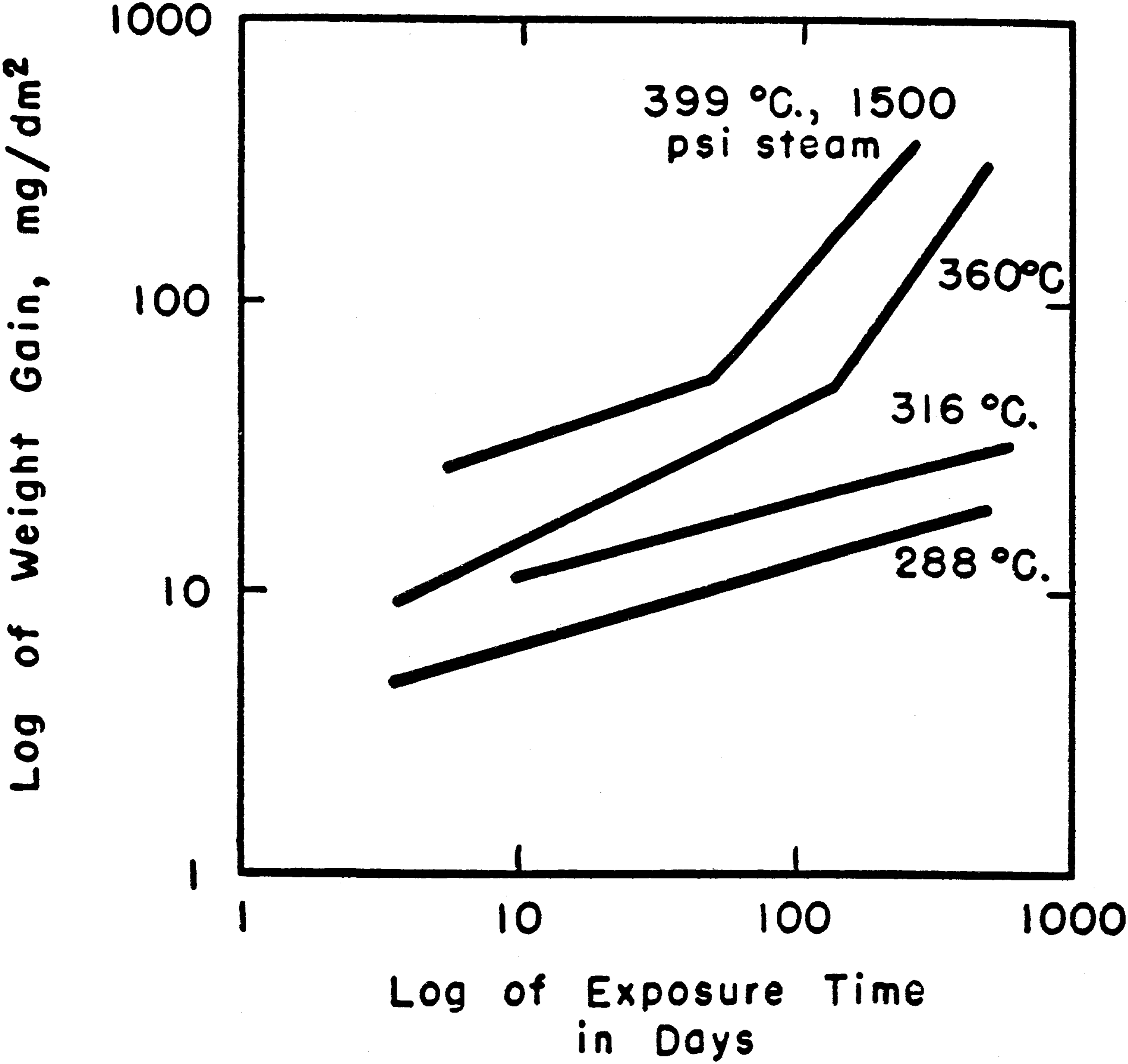

Fig. 15-8. Corrosion of Zircaloy-2.

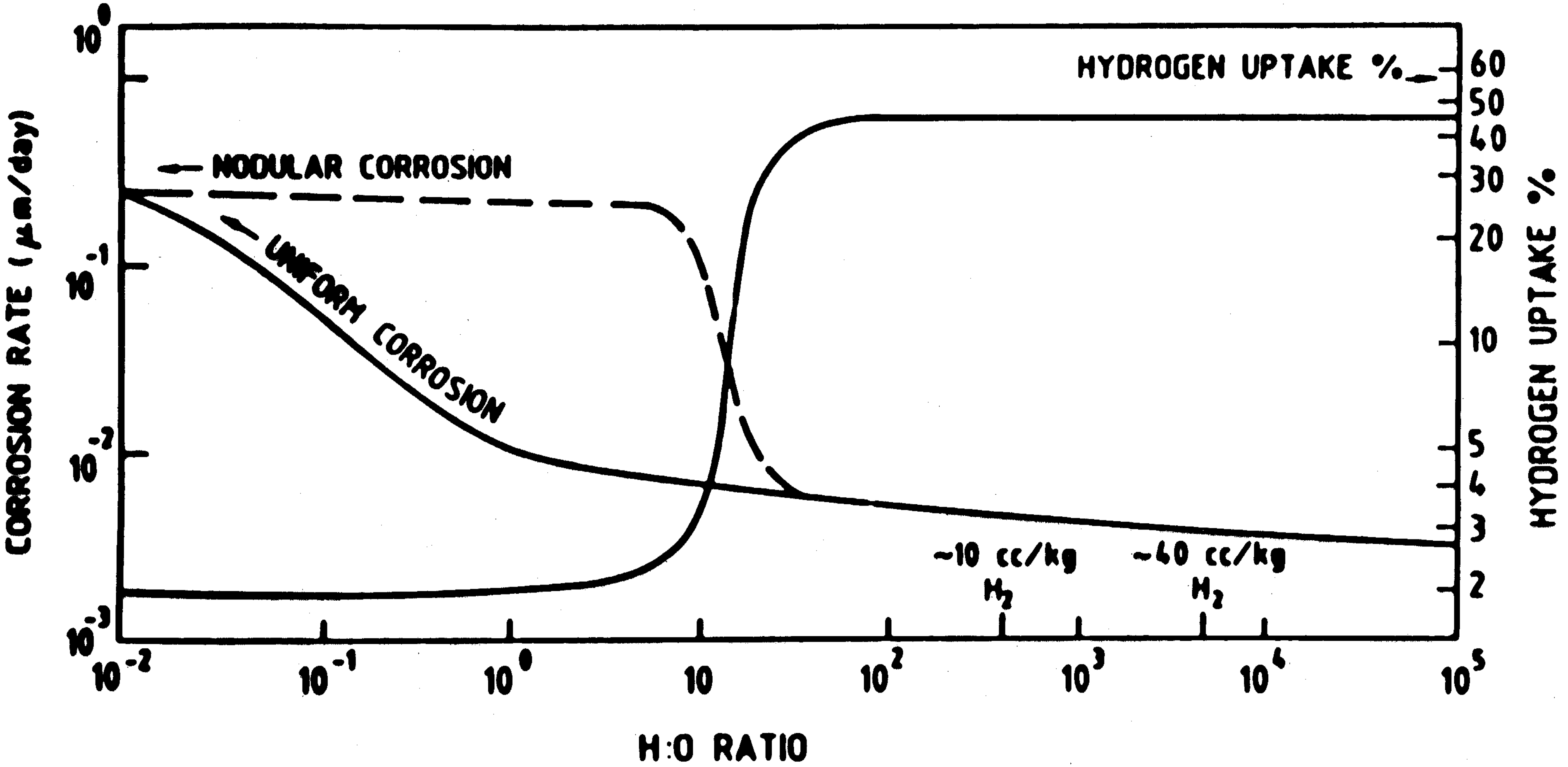

FIG. 1—*Effect of changing water chemistry on corrosion and hydriding of Zircaloy-2 in reactor (modified from Ref 8).*

There i nounting evidence for a difference in e responses of thin and thick oxide fil.. to a
... chemistry. In the FTR loop tests [10] samples with oxides greater than 20 μm

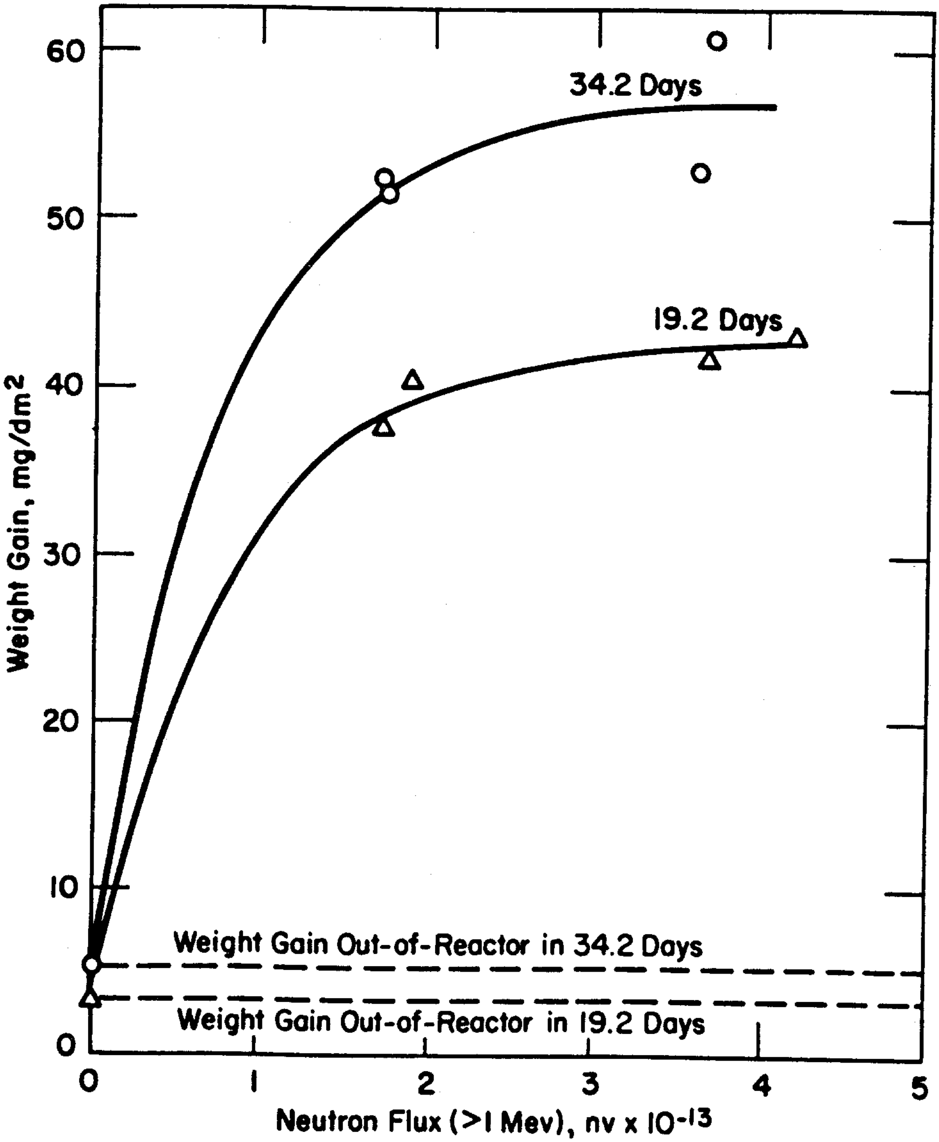

Fig. 32. Effect of fast neutron flux and time in flux at 280 C (540 F) on aqueous corrosion of Zircaloy-2. (Cited in Reference 5.)

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.

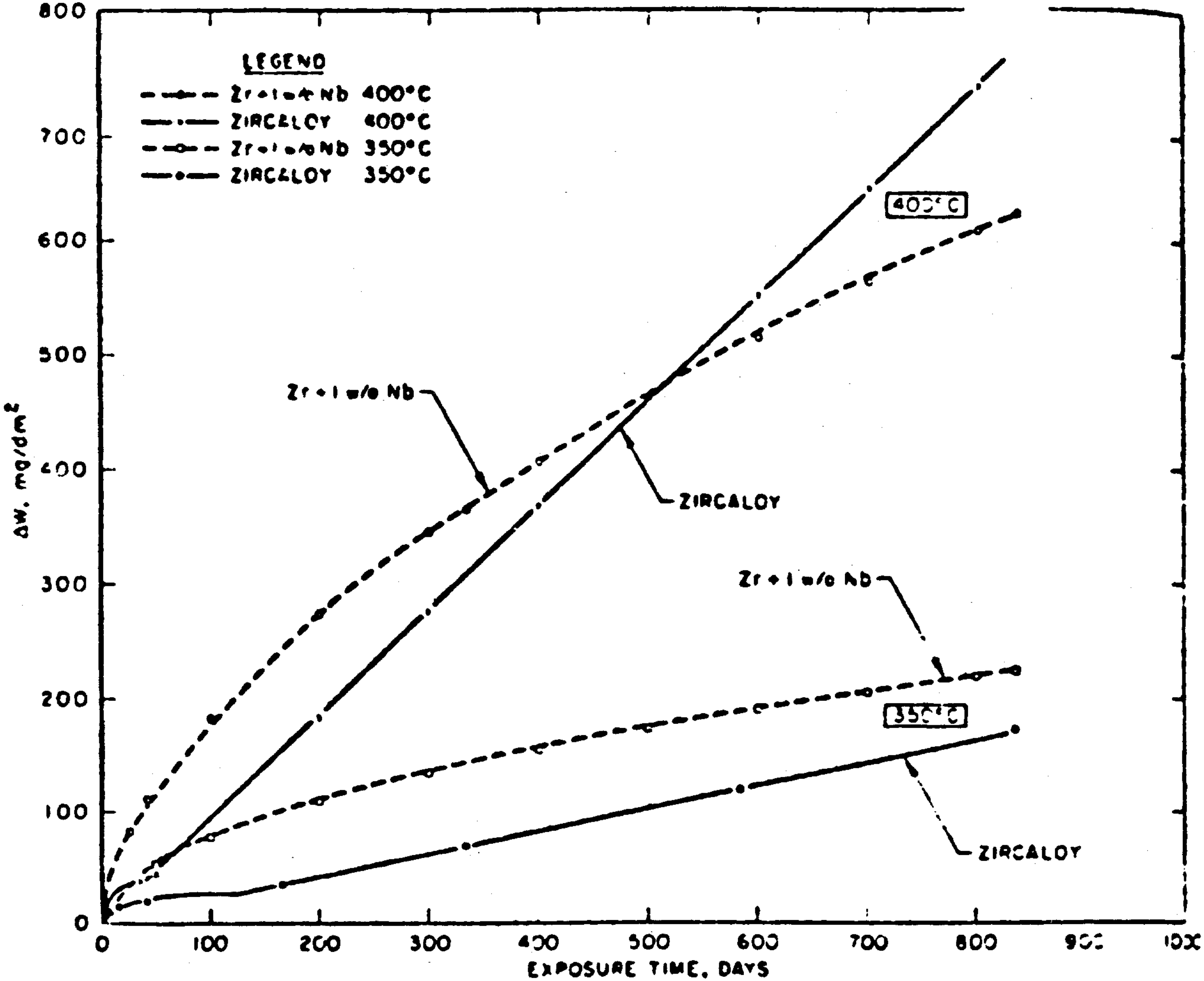

FIG. 5—*Ex-reactor corrosion of Zr-1Nb and Zircaloy in 350°C water and 400°C steam Zr-1Nb data from Ref 54.*

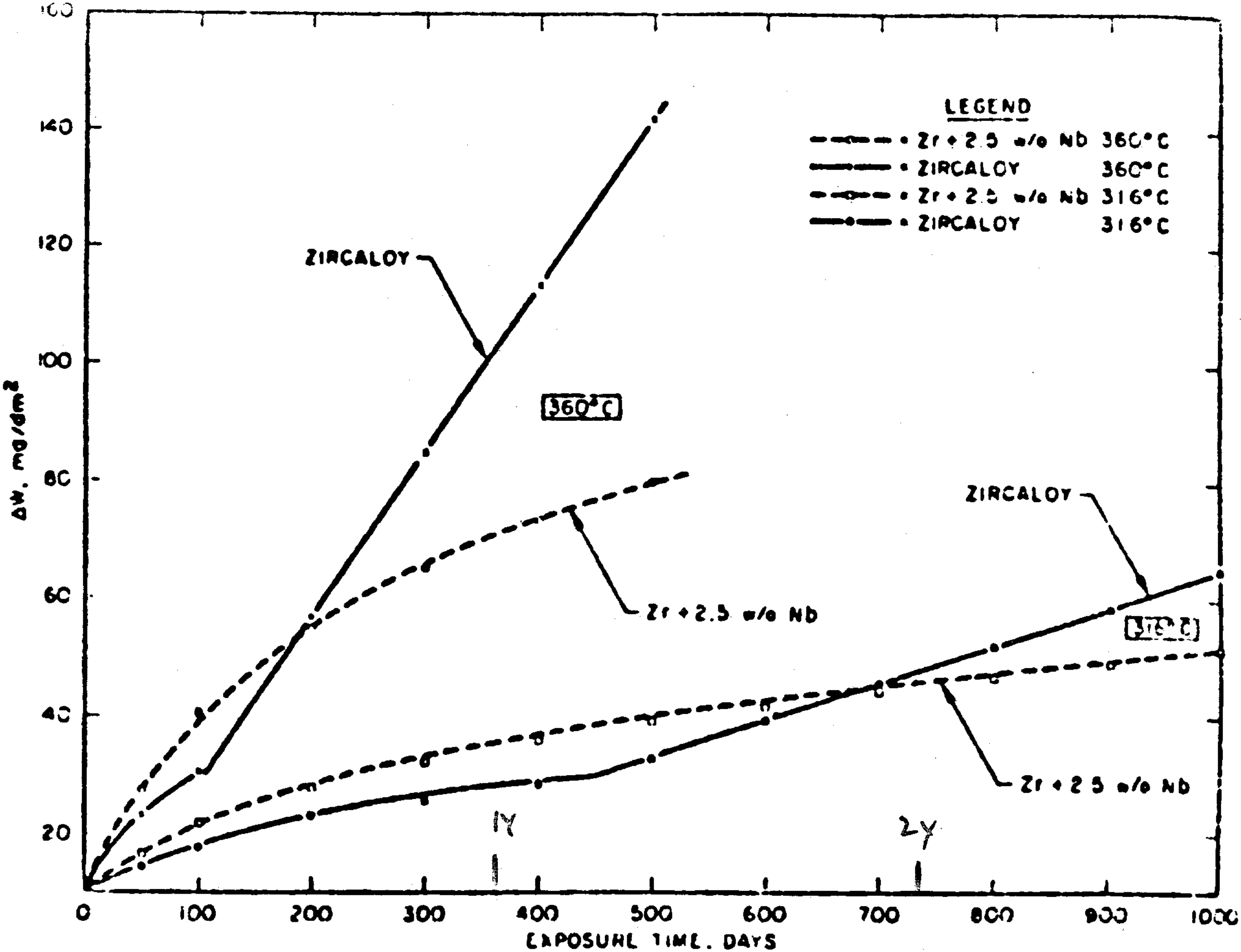

FIG. 6—*Ex-reactor corrosion of (Q.CW.A) Zr-2.5Nb and Zircaloy in 316 and 360°C water Zr-2.5Nb data from Ref 65.*

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

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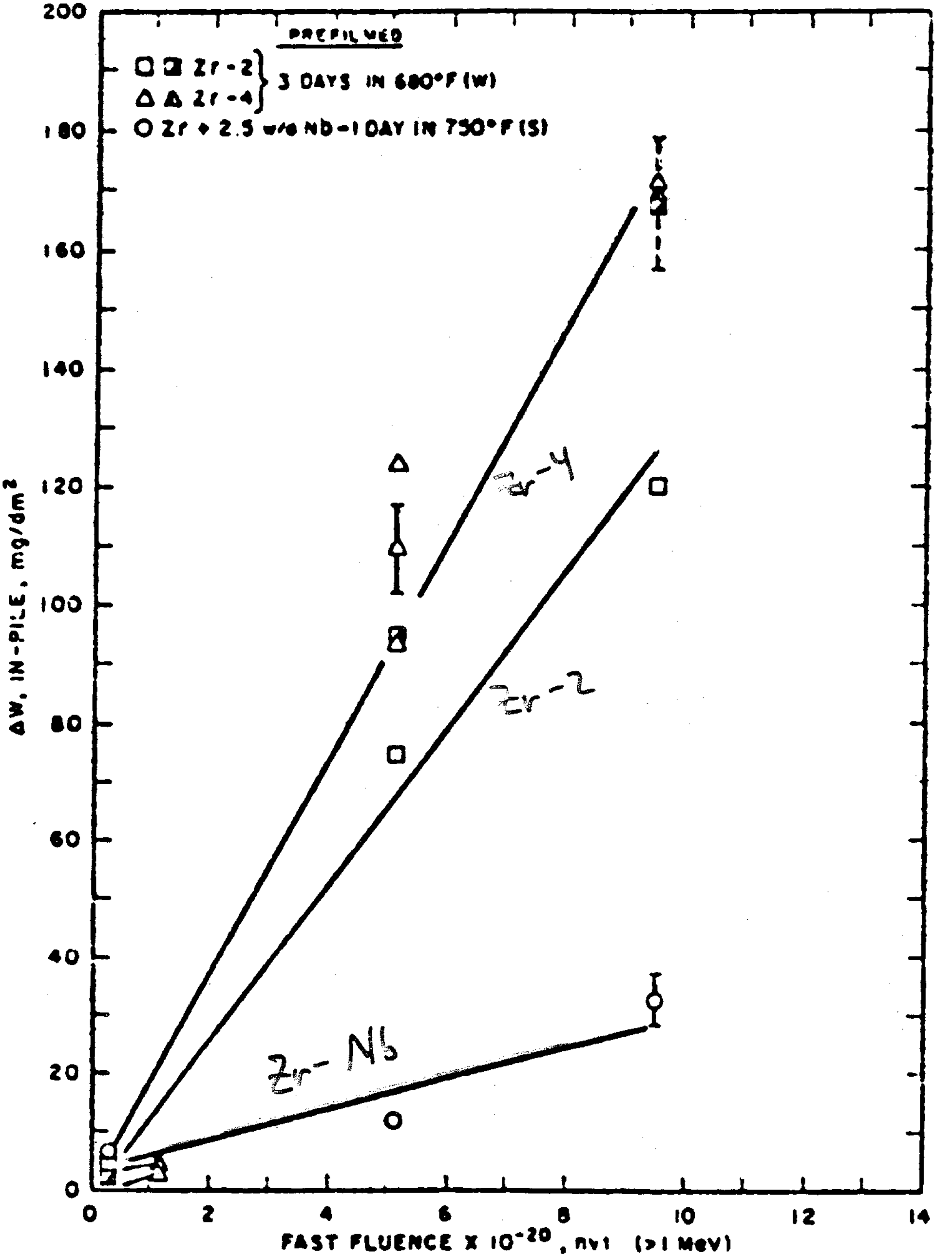

FIG. 7—*In-pile corrosion of three zirconium-based alloys as a function of fast fluer posure: 62 days in a PWR irradiation test loop with ~600 ppb oxygen. Calculated fro of Ref 26.*