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THE PHYSICAL METALLURGY OF ZIRCONIUM ALLOYS

CRNL-1208

by

B.A. CHEADLE

Chalk River Nuclear Laboratories

Chalk River, Ontario

October 1974

Revised January 1975

ATOMIC ENERGY OF CANADA LIMITED

THE PHYSICAL METALLURGY OF ZIRCONIUM ALLOYS

A series of lectures prepared by B.A. Cheadle, C.E. Ells, E.F. Ibrahim,
R.A. Holt, C.E. Coleman, R.W. Gilbert, D.O. Northwood, W.J. Langford, R.R. Hosbons.

METALLURGICAL ENGINEERING BRANCH

Edited by W. Evans & J.A.L. Robertson

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*Double lectures.

ABBREVIATIONS USED IN THE REFERENCES

AECL	Atomic Energy of Canada Ltd.
AERE	Atomic Energy Research Establishment, Harwell (U.K.)
ASME	American Society of Mechanical Engineers
ASTM-STP	American Society for Testing Metals -- Special Technical Publication
USAEC	United States Atomic Energy Commission
BNES	British Nuclear Energy Society
Acta Met.	Acta Metallurgia
Can. Met. Quart.	Canadian Metallurgical Quarterly
J. Electrochem. Tech.	Journal of Electro-Chemical Technology
J.I.M.	Journal of the Institute of Metals (Britian)
J. Mat.	Journal of Materials
J. Met. Sci.	Journal of Metals Science
J. Nuc. Mat.	Journal of Nuclear Materials
J. Phys. E.	Journal of Physics E.
Mat. Sci. Eng.	Journal of Materials Science and Engineering
Nuc. Eng. and Design	Nuclear Engineering and Design
Phys. Stat. Sol.(a)	Physica Status Solidi Part (a)
Phil. Mag.	Philosophical Magazine
Reactor Tech.	Reactor Technology
Trans. AIME	Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers

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Trans. ANS

Transactions of the American Nuclear Society

Trans. ASM

Transactions of the American Society for Metals

Trans. JIM

Transactions of the Japan Institute of Metals

BNWL

Battelle Northwest Laboratories Report, U.S.A.

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LECTURE NO. 1

INTRODUCTION TO THE PHYSICAL METALLURGY OF ZIRCONIUM ALLOYS

by

B.A. Cheadle

1. HISTORY AND MANUFACTURE

Zirconium was discovered in 1824 by Berzelius. In 1925 Van Arkel and de Boer developed the iodide process for refining zirconium and produced high purity "crystal bar" zirconium. This was the first zirconium material that had good ductility and it was used in the electronics industry for residual gas gettering. Typical physical properties are given in Table 1. In 1947 the U.S. Bureau of Mines developed the zirconium sponge process and in 1949 its combination of mechanical properties and low neutron absorption cross section resulted in its being selected as the structural material for the nuclear reactors for submarines.

TABLE 1

TYPICAL PHYSICAL PROPERTIES OF ZIRCONIUM

Atomic number	40
Atomic weight	91.2
Density at 300K	6.5 $\frac{m}{mg/m^3}$
Melting temperature	2125K (1850°C)
Transition temperature $\alpha \rightarrow \beta$	1135K (862°C)
Coefficient of thermal expansion at 570K	[11 $\bar{2}$ 0] direction 6.3×10^{-6} /K [0001] direction 10.4×10^{-6} /K
Specific heat at 300K	276 J/Kg.K
Thermal conductivity at 300K	20 W/m.K
Thermal neutron capture cross-section	microscopic 0.18 barn macroscopic $0.008 \text{ cm}^2/\text{cm}^3$
Electric resistivity	$0.44 \mu\Omega.m$
Young's modulus at 300K	[11 $\bar{2}$ 0] direction 99GPa [0001] direction 125 GPa
Poisson's ratio at 300K	0.35
Lattice parameters	hexagonal α $a_0 = 0.323 \text{ nm}$ $c_0 = 0.515 \text{ nm}$
at 300K	body centered cubic β $a_0 = 0.359 \text{ nm}$

The current world production is about 4×10^6 kg per year and is used in the following general categories:

Commercial nuclear reactors	55%
U.S. naval nuclear reactors	30%
Non-nuclear uses (flash bulbs, chemical equipment, alloy additions, etc.)	15%

Teledyne Wah Chang produce 3×10^6 kg of zirconium sponge and zirconium alloys per year. Zirconium sand (zirconium silicate, ZrSiO_4) is melted with graphite to form zirconium carbon nitride. This compound is chlorinated and then reduced by magnesium to form magnesium chloride and zirconium which are separated by a distillation process. The zirconium product is zirconium sponge, Figure 1, which is broken up into small lumps. Any discoloured pieces are removed, Figure 2. The sponge is compacted together with alloying elements, Figure 3, and melted in an arc furnace to form an ingot, Figure 4. Ingots are usually double arc melted to homogenise the alloy and then forged in preparation for further processing into bar, sheet or extrusion billets.

2. ALLOYS AND MICROSTRUCTURES

The most common commercial alloys are Zircaloy-2, Zircaloy-4, Zr-1 wt% Nb and Zr-2.5 wt% Nb. Typical compositions are given in Table 2. Thus the most common alloying elements are tin, niobium and oxygen. Tin and oxygen stabilize the hexagonal alpha phase, and niobium stabilizes the cubic beta phase, Figure 5.

TABLE 2

TYPICAL COMPOSITIONS FOR THE COMMERCIAL ZIRCONIUM ALLOYS

Element	Zircaloy-2	Zircaloy-4	Zr-1 wt%	Zr-2.5 wt% Nb
Tin	1.20 – 1.70 wt%	1.20 – 1.70 wt%	—	—
Iron	0.07 – 0.20 wt%	0.18 – 0.24 wt%	—	—
Chromium	0.05 – 0.15 wt%	0.07 – 0.13 wt%	—	—
Nickel	0.03 – 0.08 wt%	—	—	—
Niobium	—	—	0.6 – 1.0 wt%	2.4 – 2.8 wt%
Oxygen	1400 ppm max.	1400 ppm max.	900 – 1300 ppm	900 – 1300 ppm
Balance	Zirconium plus impurities			

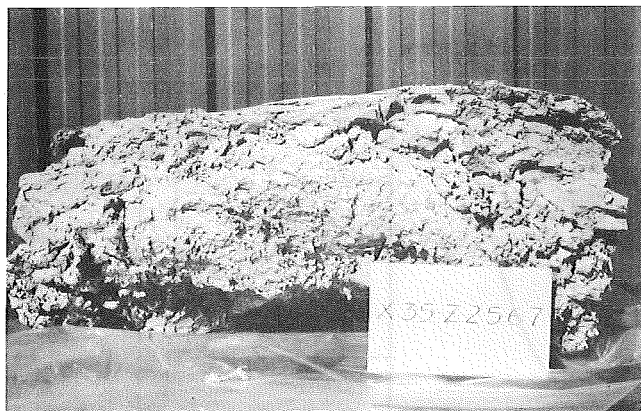


Figure 1 – Zirconium Sponge

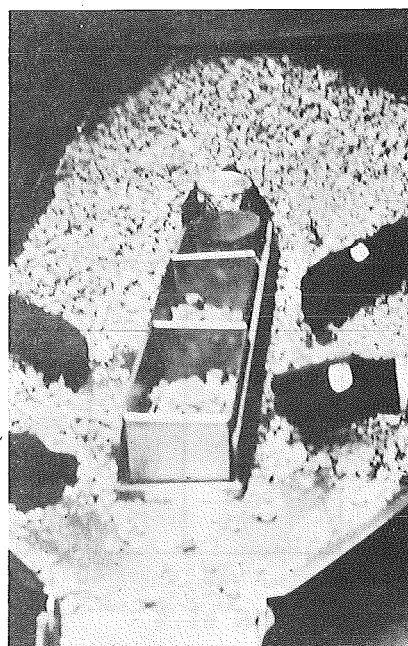


Figure 2 – Sponge Broken up into small lumps

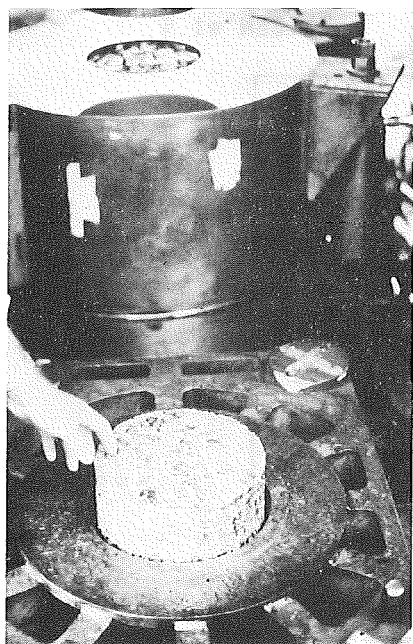


Figure 3 – Small lumps of sponge compacted with alloying elements

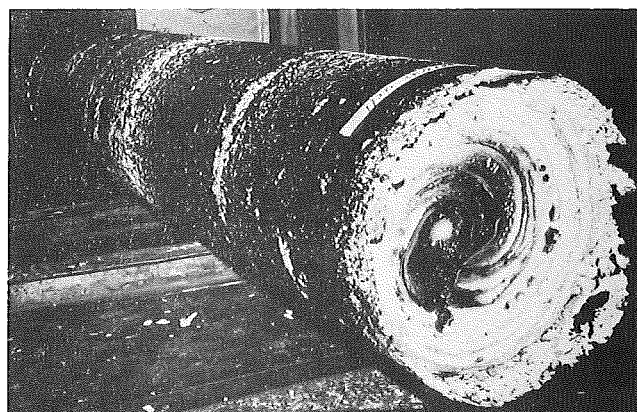


Figure 4 – Arc melted ingot of Zirconium Alloy

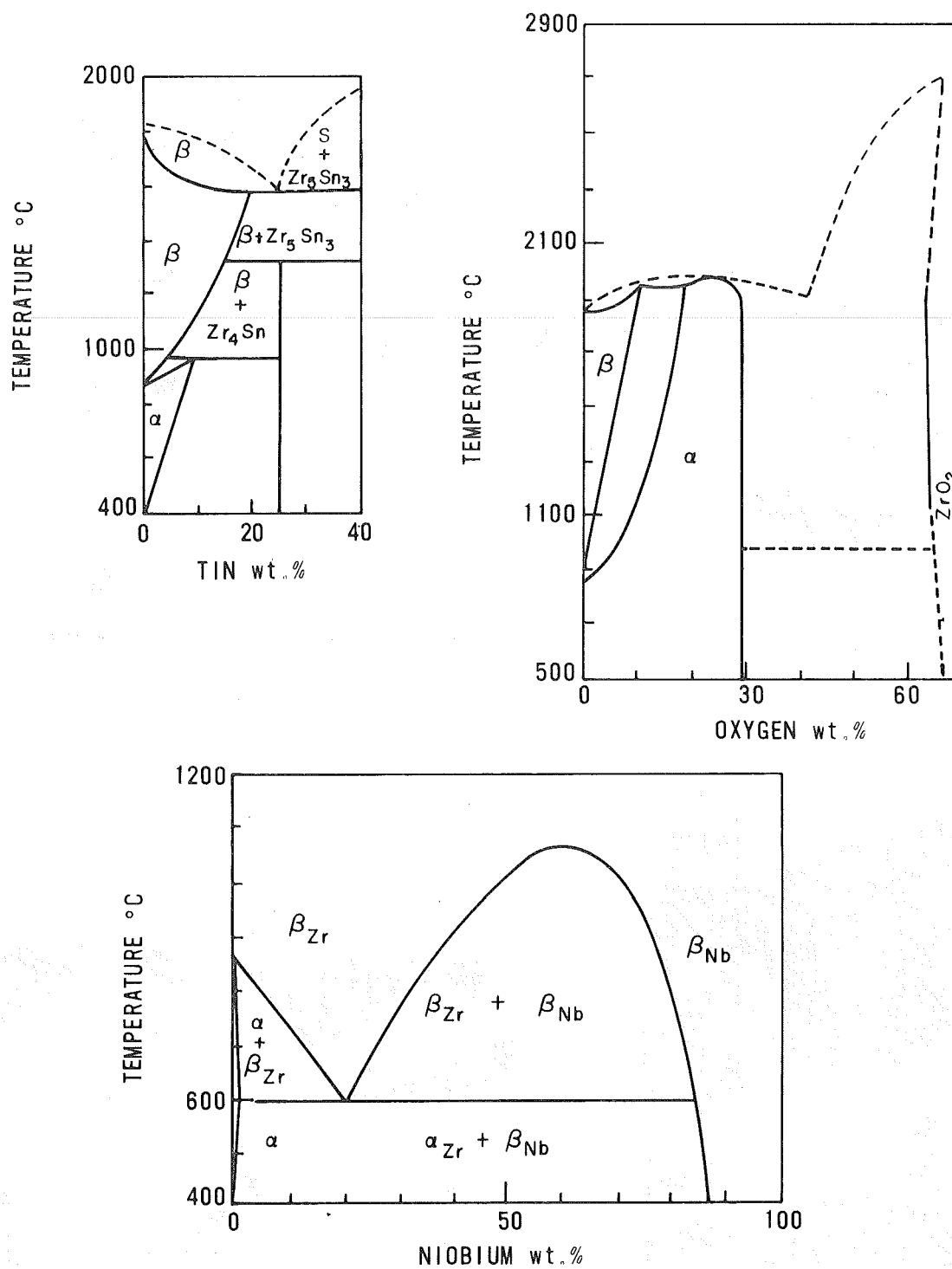
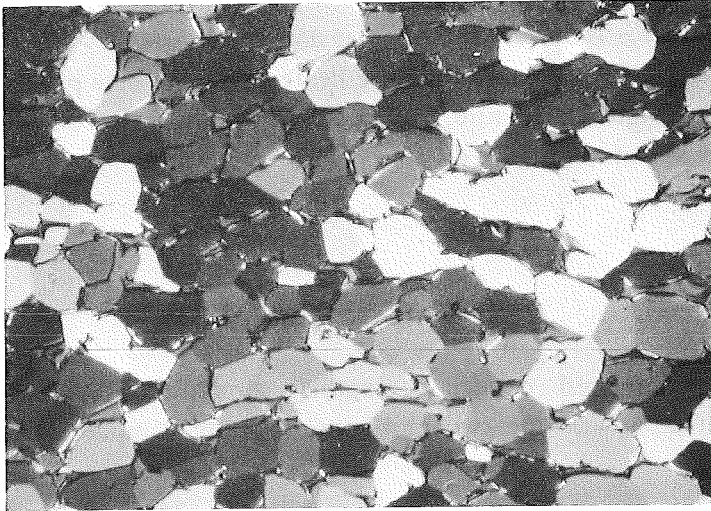
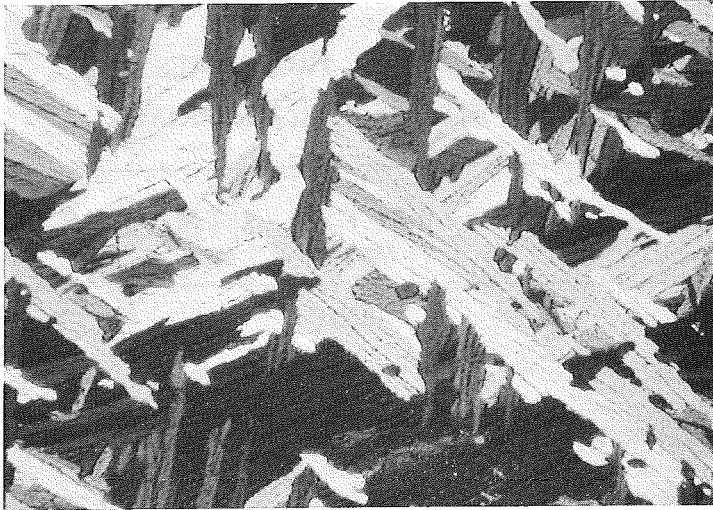


Figure 5 — Zirconium-Tin, Zirconium-Oxygen and Zirconium-Niobium partial phase diagrams



(a) annealed Zr-2.5 wt% Nb equiaxed α grains with β phase at grain boundaries

X500



(b) Widmanstätten structure in Zircaloy-2 slowly cooled from the β phase (1275K, 1000°C)

X500



(c) Martensitic α' structure in Zr-2.5 wt% Nb water quenched from the β phase (1275K, 1000°C)

X1000

Figure 6 – Typical microstructures of Zirconium alloys

Zirconium alloys have complex microstructures. In the annealed condition they have microstructures of equiaxed alpha grains, Figure 6a. If they are heated into the beta phase and cooled slowly they have a Widmanstätten structure, Figure 6b, but if they are cooled rapidly some alloys have a martensitic structure, Figure 6c.

3. MECHANICAL PROPERTIES

a) Effect of Alloying Addition

Alloying additions of tin, niobium and oxygen strengthen zirconium. Typical mechanical properties of the Zircalloys and the two niobium alloys are compared to other structural materials in Table 3.

TABLE 3
TYPICAL ROOM TEMPERATURE MECHANICAL PROPERTIES OF
ZIRCONIUM ALLOYS AND OTHER STRUCTURAL MATERIALS

Alloy	Condition	0.2% Y.S. MPa	U.T.S. MPa	% El.
Zirconium	Recrystallized	250	400	25-35
Zircaloy ⁺	Recrystallized	400	500	20-35
	Cold-worked 40%	550	600	10-20
Zr-1 wt% Nb ⁺	Recrystallized	430	480	30-40
	Cold-worked 60%	600	700	10-20
Zr-2.5 wt% Nb ⁺	Recrystallized	500	600	10-20
	Cold-worked 40%	650	750	10-20
Carbon/Manganese Steels	Hot rolled	280	550	20-30
Martensitic Stainless Steel (403)	Quenched and tempered	600	750	10-25
Austenitic Stainless Steel (304)	Annealed	200	550	40-50
	Cold-worked	1000	1200	5-10
Aluminum alloy (57S)	Annealed	100	200	20-30
	Half hard	200	250	5-15

⁺ plus about 1000 ppm oxygen

b) Effect of Texture

The hexagonal crystal structure of alpha zirconium results in anisotropic mechanical properties. When zirconium alloys are rolled into sheets, a texture is developed in the hexagonal alpha grains, Figure 7. The tensile properties of Zr-2.5 wt% Nb sheet in the longitudinal, transverse and short transverse directions, Figure 8, are given in Table 4. The orientation of the hexagonal alpha grains relative to the axes of the tensile specimens is similar in the longitudinal and transverse specimens and hence their mechanical properties are also similar. In the short transverse specimens the grains are differently oriented relative to the tensile axis and the sheet is strongest in that direction.

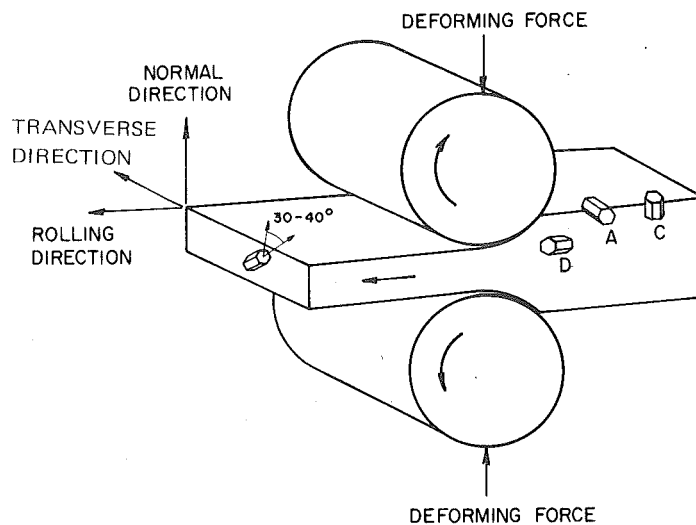


Figure 7 – Sheet Rolling

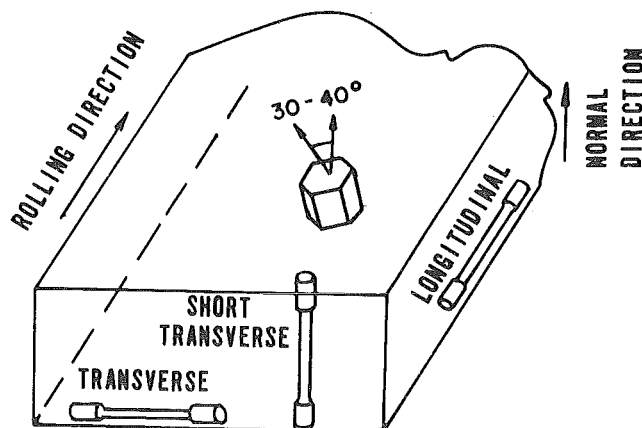


Figure 8 – The orientation of the tensile specimens in the Zr-2.5 wt% Nb sheet

TABLE 4
THE ROOM TEMPERATURE MECHANICAL PROPERTIES OF
ANNEALED Zr-2.5 Wt% Nb SHEET

Specimen Direction	0.2% Y.S. MPa	U.T.S. MPa	% El.
Longitudinal	380	500	27
Transverse	470	500	22
Short transverse	520	540	17

c) Effect of Microstructure

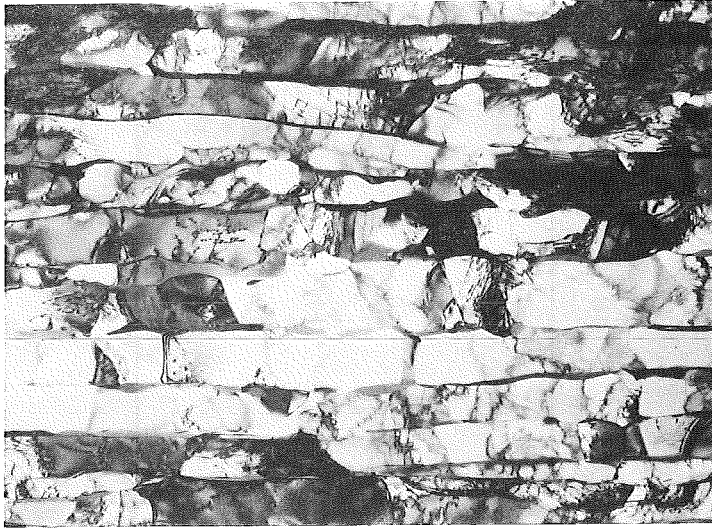
The strength of the Zircalloys is not affected very much by heat-treatment, Table 5. However the strength of Zr-2.5 wt% Nb can be increased considerably by water quenching from the beta phase (1275K), Table 5, due to the formation of the martensitic phase α' , (Figure 6c). Cold work produces a dislocation substructure, Figure 9, which increases the flow stress and increases the strength.

d) Effect of Irradiation

Irradiation increases the strength of zirconium alloys and reduces their ductility. The change in property is related to the neutron exposure or integrated flux, Figure 10. Irradiation temperature, metallurgical condition (heat-treatment, cold-work) and the alloy composition each affect the change in properties with irradiation.

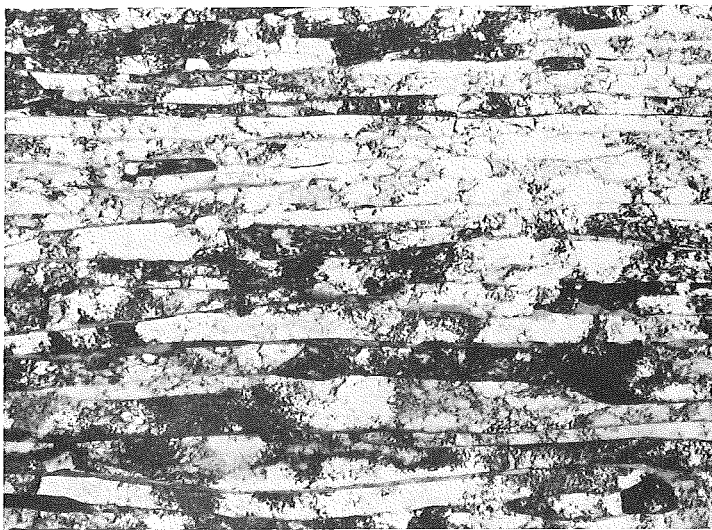
TABLE 5
TYPICAL ROOM TEMPERATURE TENSILE PROPERTIES OF ZIRCALOY-2 AND Zr-2.5 Wt% Nb

Alloy	Material Condition	0.2% Y.S.		U.T.S.		%EI	%RA
		kpsi	MPa	kpsi	MPa		
Zircaloy-2	slow cooled from 1025K (750°C)	48	330	72	500	22	40
	slow cooled from 1275K (1000°C)	48	330	68	470	22	35
	water-quenched from 1275K (1000°C)	68	470	84	580	16	50
	20% cold-worked	80	550	85	590	30	45
	40% cold-worked	85	590	90	620	10	35
Zr-2.5 Wt% Nb	slow cooled from 1125K (850°C)	50	350	74	510	28	48
	slow cooled from 1275K (1000°C)	76	520	89	610	13	46
	water-quenched from 1275K (1000°C)	106	730	115	790	9	38
	water-quenched from 1125K (850°C)	109	750	120	820	14	60
	20% cold-worked	85	590	90	620	15	46
	40% cold-worked	90	620	100	690	13	50



(a) as extruded the elongated α grains contain few dislocation networks

X7000



(b) extruded and cold worked 25%. The elongated α grains with a high dislocation density

X7000

Figure 9 – Typical microstructures of Zr-2.5 wt% Nb pressure tubes showing the α grains elongated in the axial direction

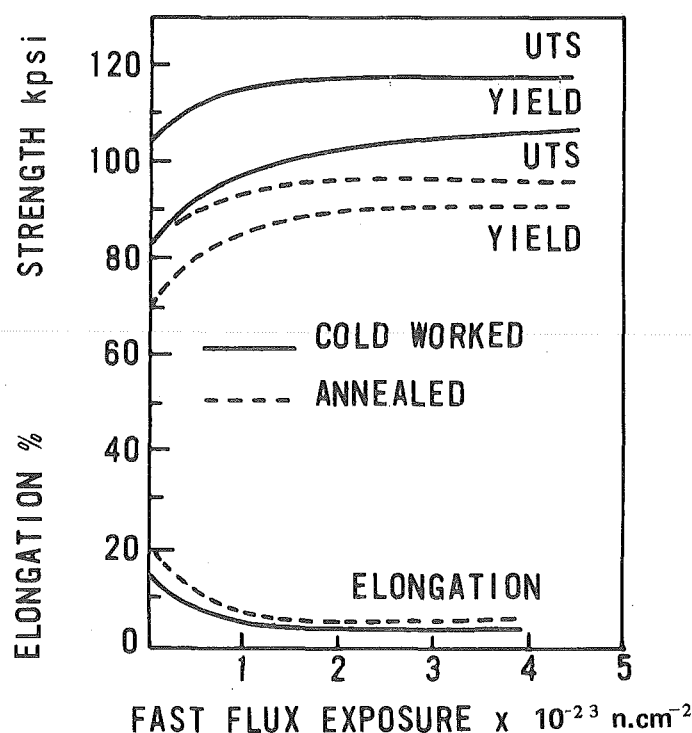


Figure 10 – The effect of irradiation at 330K on the room temperature tensile properties of Zircaloy-4.

E.N. Harbinson and C.J. Baroch
J. Mat. 3 1068 p.107

4. CANDU COMPONENTS MADE FROM ZIRCONIUM ALLOYS

CANDU reactors produce economic electrical power by utilizing natural uranium fuel and structural materials that have a low cross section for thermal neutrons. Zirconium alloys have a much lower neutron absorption per unit strength than other commercially available structural materials, Table 6, with the exception of beryllium which is unsuitable for nuclear applications due to poor ductility particularly after irradiation. Hence the following reactor components are made from zirconium alloys.

Fuel Bundles

The UO_2 fuel is clad in Zircaloy tubes sealed with welded end caps to form a fuel element. The cladding tubes have Zircaloy wear and spacer pads brazed on and several elements are held together by Zircaloy end plates to form the fuel bundle, Figure 11. Each bundle is about 50 cm long.

TABLE 6

NEUTRON ECONOMY OF VARIOUS METALS COMPARED WITH ZIRCONIUM

Base Metal	Ultimate Tensile Strength of Alloy ^{a)} at 575K		Macroscopic Cross Section for Thermal Neutrons ^{b)} $\Sigma c, \text{cm}^2/\text{cm}^3$	Relative Neutron Absorption for Given Design Stress
	MPa	kpsi		
Zirconium	900	130	.01	1
Iron	1100	160	.17	14
Nickel	1100	160	.31	25
Titanium	1000	145	.26	22
Aluminum	90	13	.014	14
Magnesium	90	13	.005	5
Beryllium	180 – 350 ^{c)}	25 – 50	.001 ^{c)}	.25 – .5

a) Based on presently available high strength alloys

b) Probable value for high strength alloy designed to minimize neutron absorption

c) For unalloyed beryllium

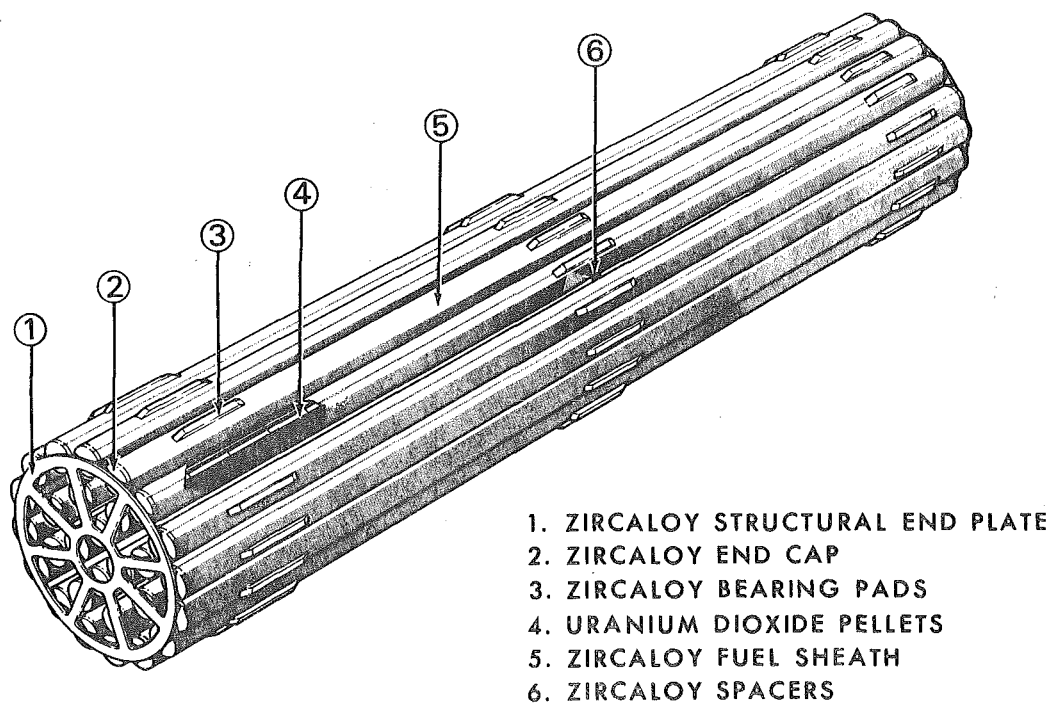


Figure 11 – Fuel bundle for a CANDU Reactor

Pressure Tubes

The fuel bundles are placed end to end in a pressure tube, Figure 12. The first pressure tubes were Zircaloy-2 but they are now made of Zr-2.5 wt% Nb. A comparison of mechanical properties is shown in Figure 13. The pressure tubes in the Pickering and Bruce reactors are 103 mm (4.07 in.) inside diameter with a 4 mm (0.160 in.) thick wall and are 6.1 m (20 ft.) long.

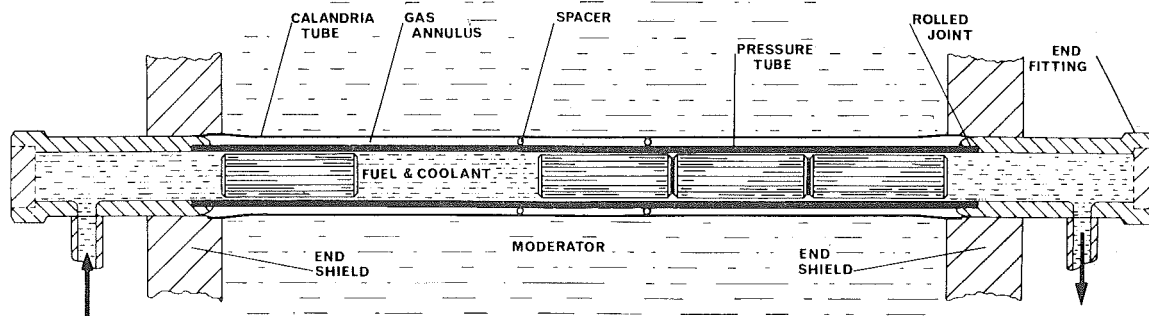


Figure 12 – Schematic of a fuel channel for a CANDU reactor with pressurized water coolant

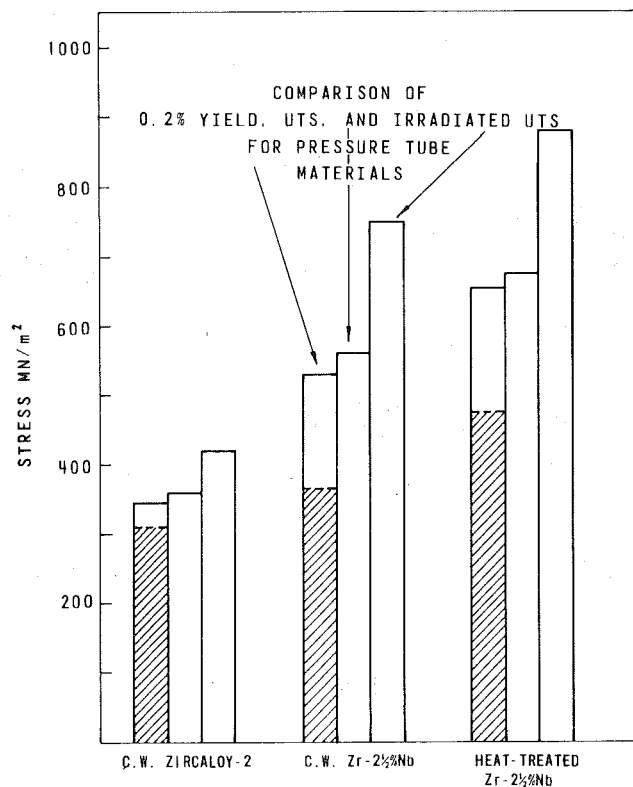


Figure 13 – Comparison of the mechanical properties of pressure tubes.

Garter Spring

A garter spring is wrapped around the pressure tube as a spacer between the pressure tube and the calandria tube. The garter spring is made from rectangular cross-section, 1.73 mm x 0.10 mm (0.068 in. x 0.041 in.) Zr-2.5 wt% Nb-0.5 wt% Cu wire wound into a coil, 6.6 mm (0.258 in.) diameter, Figure 14.

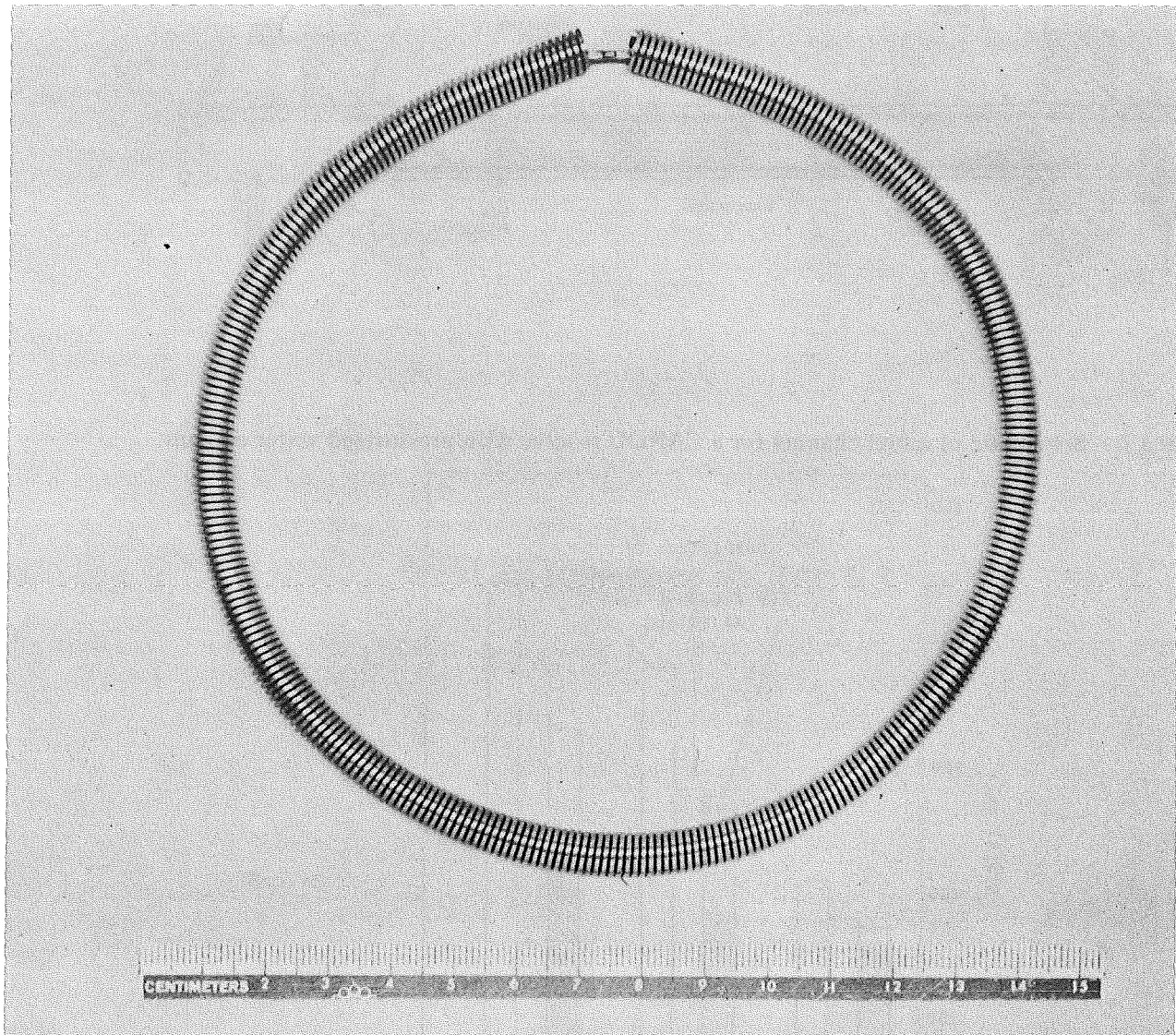


Figure 14 – Garter spring spacer assembly

Calandria Tube

The calandria tube goes around the outside of the pressure tube to make an insulating annulus of dry gas between the hot 575K pressure tube and the cooler heavy water moderator. The calandria tubes for Pickering and Bruce reactors are made from Zircaloy-2 and are 129 mm (5.08 in.) inside diameter, have a 1.4 mm (0.054 in.) thick wall and are 6.1 m (20 ft) long.

These components are shown assembled into a fuel channel, Figure 15, in a CANDU reactor in Figure 16.



Figure 15 – Model of an NPD channel assembly

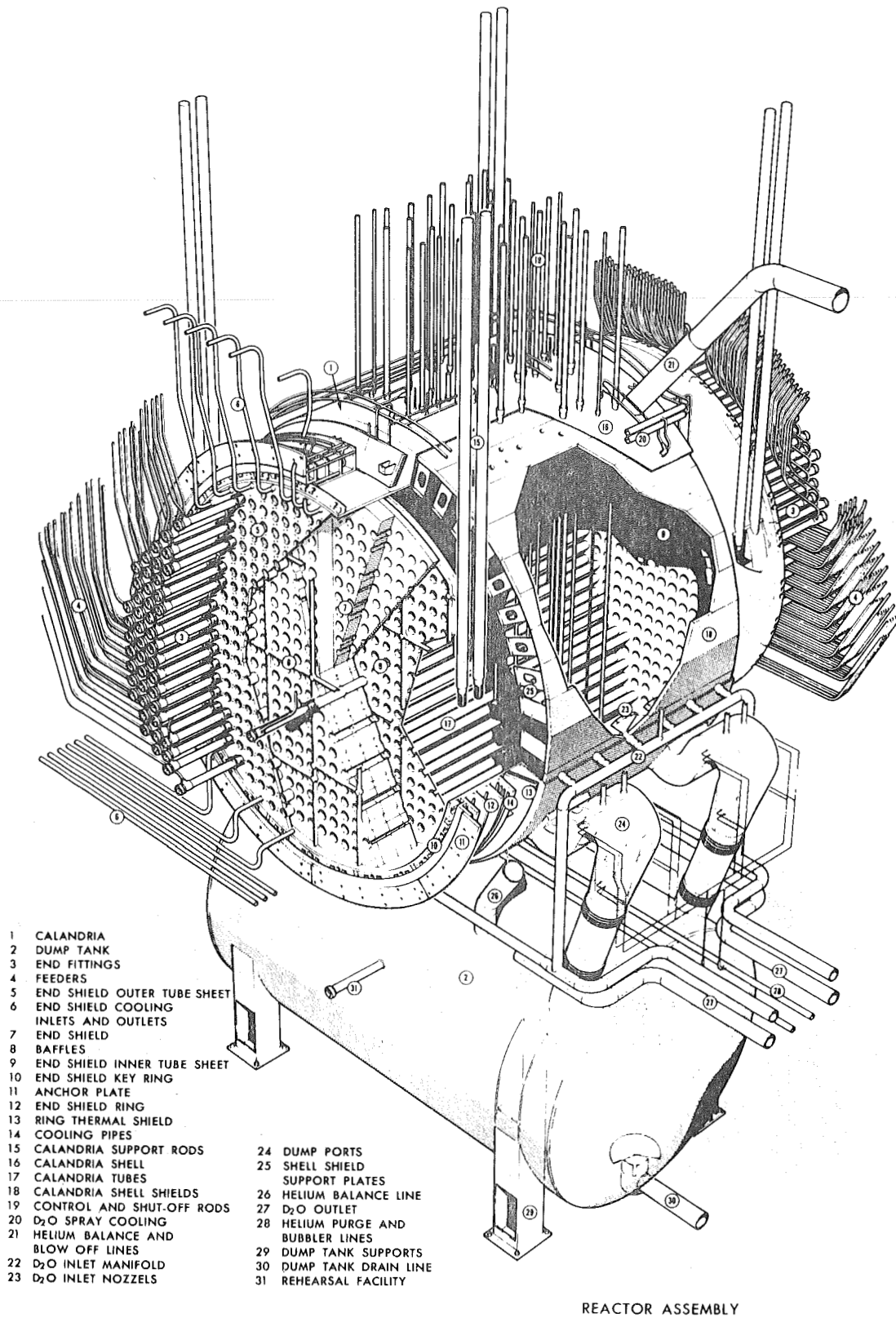


Figure 16 – A CANDU reactor assembly

Calandria Vessel

Although stainless steel is used for CANDU power reactor calandria vessels, Zircaloy-2 plate 6.5 mm thick was used to fabricate the calandria vessel of the Taiwan research reactor, Figure 17. This vessel is 2.7 meters diameter and 3.3 meters high.

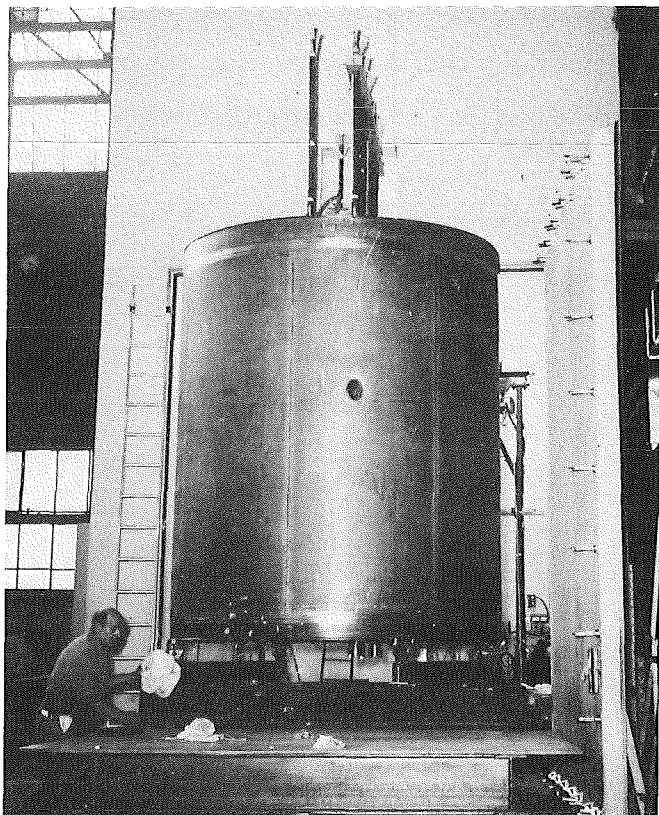


Figure 17 — Taiwan Calandria vessel made from Zircaloy-2 plate

5. SUMMARY

These reactor components demonstrate that zirconium alloys have an attractive combination of mechanical properties, corrosion resistance and neutron absorption cross section. Zirconium alloys can be fabricated into diverse shapes by conventional cold-working processes and can be joined by welding and brazing processes. Zirconium alloys have anisotropic mechanical properties and complex microstructures and fabrication processes must be carefully controlled to obtain the properties required.

REFERENCE BOOKS ON ZIRCONIUM

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- The Metallurgy of Zirconium, *D.L. Douglas, Atomic Energy Review, Vienna, 1972.*
- Zirconium and its Alloys, *Electrochemical Society, Inc., New York, 1966.*
- Applications — Related Phenomena in Zirconium and its Alloys, *ASTM STP, 458, 1968.*
- Zirconium *Canadian Metallurgical Quarterly, Vol. 11, No. 1, 1972*
- Zirconium in Nuclear Applications, *ASTM STP, 551, 1973.*

CRNL-1208

LECTURE NO. 2*

THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS

by

B.A. Cheadle

1. PHASES AND TRANSFORMATION

Although many alloy systems have been studied only two alloys, Zircaloy and Zr-2.5 wt% Nb are of importance in nuclear engineering, Table 1. Sn stabilizes the hexagonal α -phase, thus an alloy of Zr-9 wt% Sn is still α at 1200K (925°C), Figure 1. In contrast Nb stabilizes the cubic β -phase, thus an alloy of Zr-20 wt% Nb is β at 880K (610°C), Figure 2.

TABLE 1

TYPICAL COMPOSITIONS FOR THE ZIRCALOYS AND Zr-2.5 Wt% Nb

Element	Zircaloy-2	Zircaloy-4	Zr-2.5 Wt% Nb
Tin	1.20 – 1.70 wt%	1.20 – 1.70 wt%	—
Iron	0.07 – 0.20 wt%	0.18 – 0.24 wt%	—
Chromium	0.05 – 0.15 wt%	0.07 – 0.13 wt%	—
Nickel	0.03 – 0.08 wt%	—	—
Niobium	—	—	2.40 – 2.80 wt%
Oxygen	1400 ppm max.	1400 ppm max.	900-1300 ppm
Balance	Zirconium plus impurities		

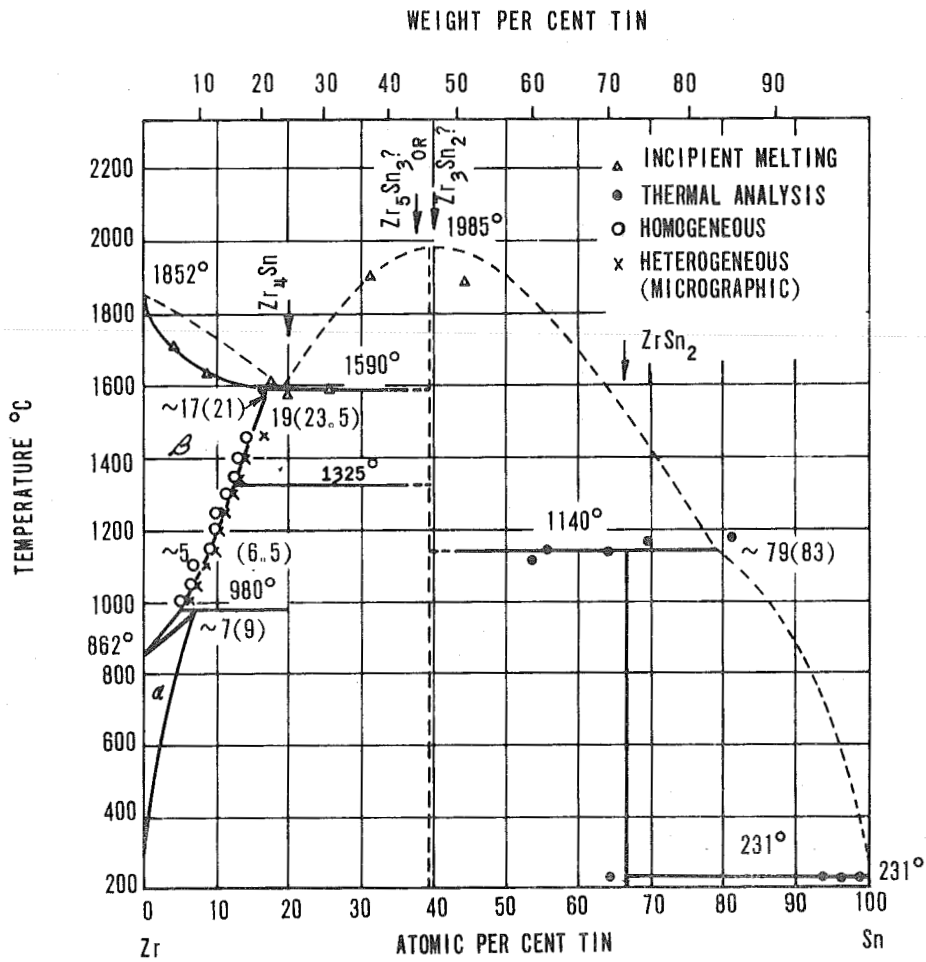


Figure 1 – The Zr-Sn equilibrium phase diagram

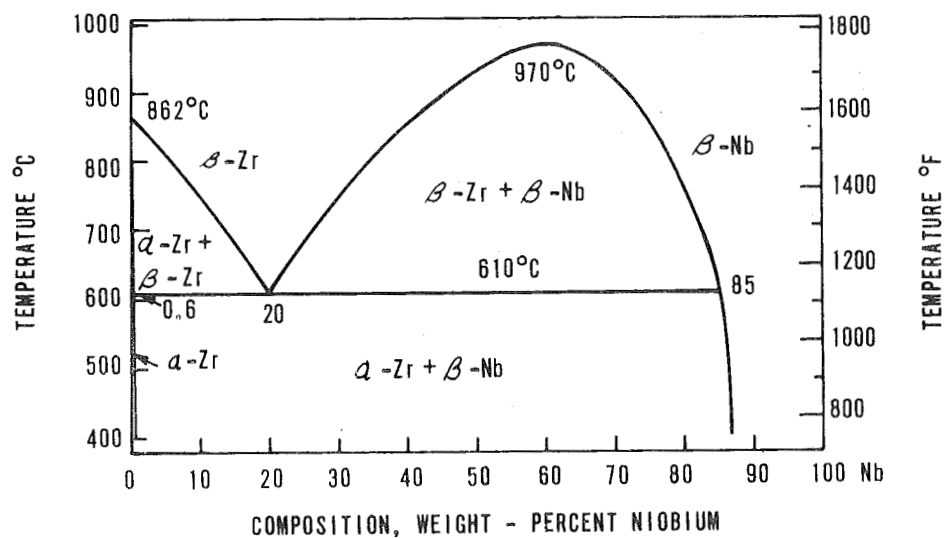
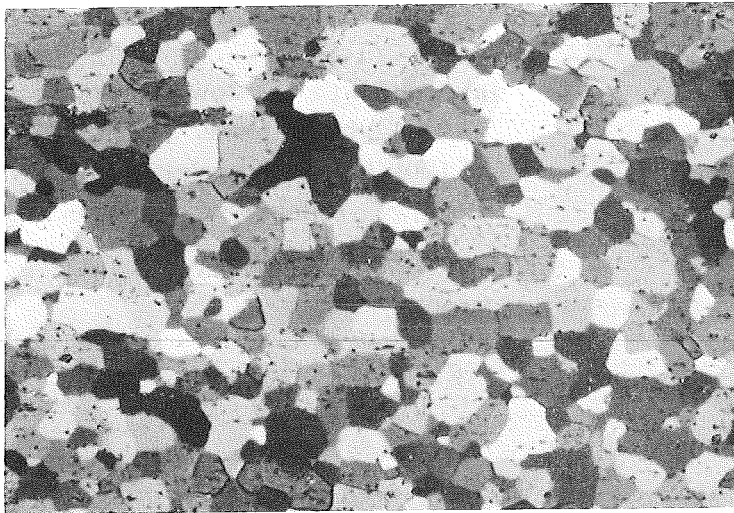
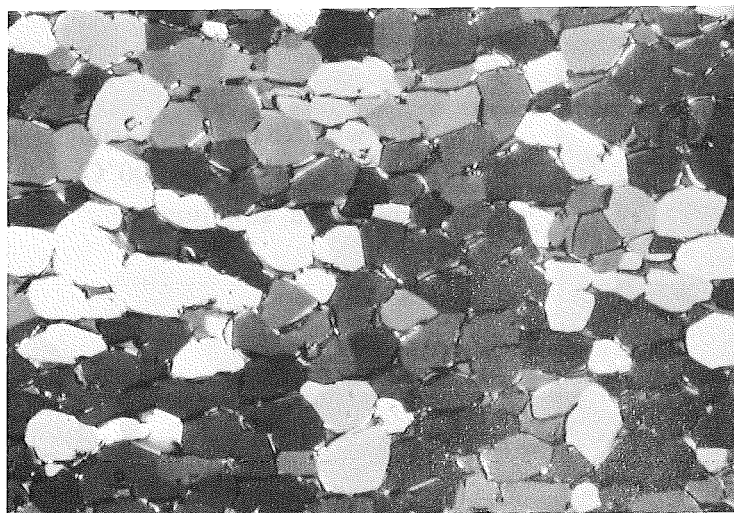


Figure 2 – The Zirconium-Niobium equilibrium phase diagram determined by Lundin and Cox



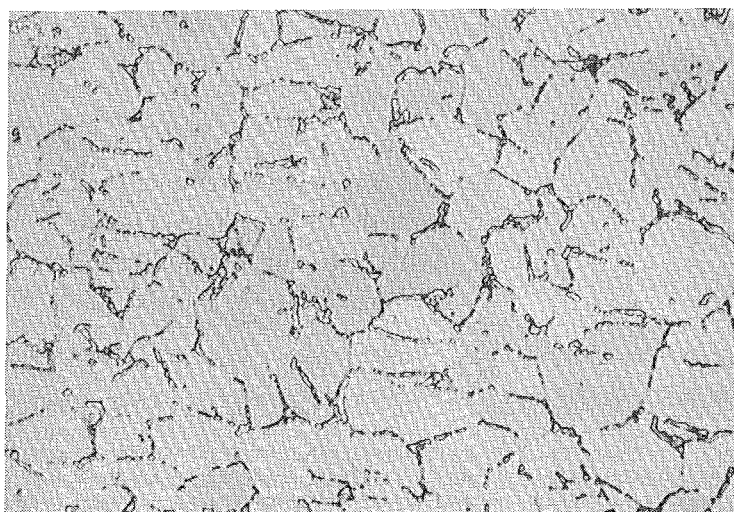
- (a) Annealed Zircaloy-2, equiaxed grains of α zirconium containing particles of a second phase (polarized light)

X500



- (b) Annealed Zr-2.5 wt% Nb, equiaxed grains of α with β at grain boundaries (polarized light)

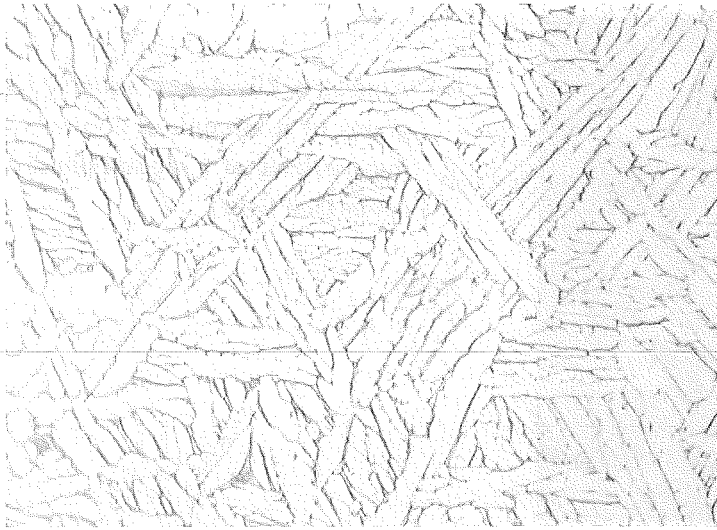
X500



- (c) Zircaloy-2 heated in the $\alpha + \beta$ phase region and air cooled which produces precipitates of a second phase at the grain boundaries. (bright field)

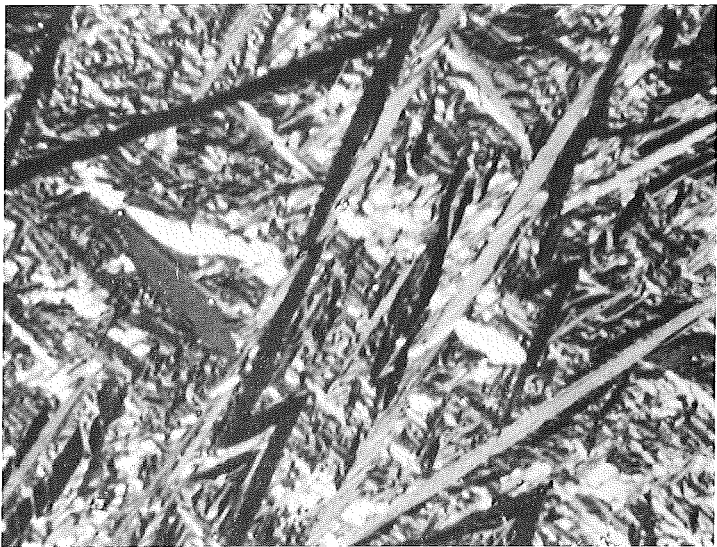
X1000

Figure 3 – Typical microstructures of Zirconium alloys



- (a) Zr-2.5 wt% Nb slowly cooled from the β phase. (1275K, 1000°C). α Zr nucleates and grows forming a Widmanstätten structure

X500



- (b) Zr-2.5 wt% Nb quenched from the β phase (1275K, 1000°C). Martensitic α' structure

X1000



- (c) Zr-2.5 wt% Nb water quenched from the ($\alpha + \beta$) phase (1145K, 870°C). Islands of equilibrium α in martensitic α' matrix

X500

Figure 4 – Typical microstructures of Zirconium alloys

Microstructure

Zirconium alloys have complex microstructures and great care must be exercised in their metallographic preparations to reveal phases, *W. Evans, Can. Met. Quart. LXIII, 1960, p.617*. In the annealed condition the Zircalloys and Zr-2.5 wt% Nb have microstructures of equiaxed α -grains, Figure 3(a) and (b). When they are heated into the $(\alpha + \beta)$ -phase region and slowly cooled to room temperature second phase particles precipitate at the grain boundaries of the Zircalloys, Figure 3(c) but the microstructure of annealed Zr-2.5 wt% Nb is not changed.

When the alloys are slow-cooled from the β -phase into the $(\alpha + \beta)$ -phase field, α nucleates at the β -grain boundaries and grows to form a Widmanstätten structure, Figure 4(a). In several zirconium alloy systems there is a martensitic transformation. The upper temperature at which martensite forms (M_s temperature) is a function of composition and generally decreases with increasing substitutional solute content of the β -phase. When Zr-2.5 wt% Nb is water-quenched from the β or high $(\alpha + \beta)$ -phase fields the β transforms to α' which has a martensitic structure, Figure 4(b)&(c). The limit of Nb solid solubility is about 0.6 wt% and hence the α' is supersaturated with Nb. Heating α' below the monotectoid temperature 880K (610°C) precipitates cubic β Nb within the α' needles and also at the twin boundaries, Figure 5, and the α' transforms to equilibrium α .

- *C.D. Williams and R.W. Gilbert, "Tempered Structures of a Zr-2.5 wt% Nb Alloy", J. Nucl. Mat. 18, 1966, p.161*

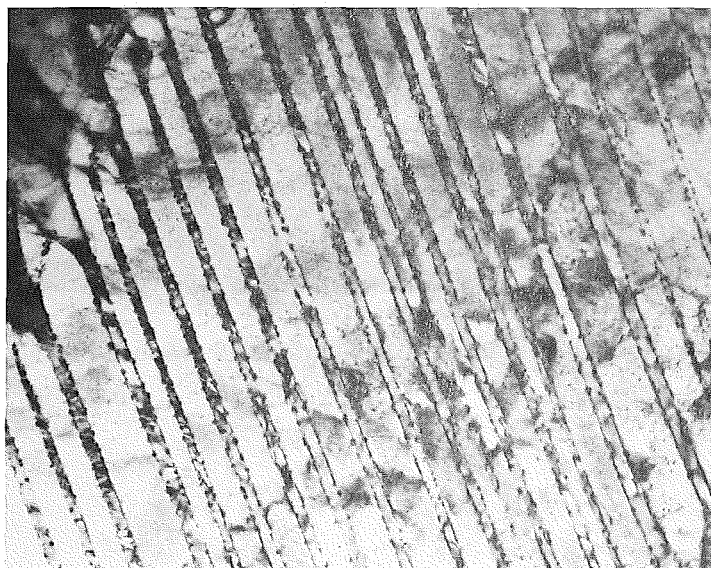


Figure 5 — Zr-2.5 wt% Nb water quenched from 1000°C and aged for 24h at 500°C showing twins in a needle of α' and β_{Nb} precipitates both at the twin boundaries and in the α' . 120,000 X

A metastable hexagonal ω -phase can form in zirconium-niobium alloys either by quenching the β -phase or by aging a niobium rich β -phase. The ω formed by aging is in the form of plates about 25 nm square. Figure 6. In Zr-Nb alloys the β must contain about 7 wt% Nb before quenched ω can be formed. This can be achieved in more dilute alloys by quenching from the $(\alpha + \beta)$ -phase field when the β fraction is enriched in niobium. In a 2.6 wt% Nb alloy this temperature is about 1030K (760°C); water quenching from this temperature produces ω and the maximum hardness, Figure 7. At lower temperatures the β -phase is more enriched in Nb but its volume is less. When the β contains more than 17 wt% Nb it is metastable at room temperature. The crystal structures and lattice parameters of the α , α' , β and ω -phase are given in Table 2.

- J. Winton and R.A. Murgatroyd, "The Effect of Variations in Composition and Heat Treatment on the Properties of Zr-Nb", *Electrochem. Tech.* 4, 1966, p.358

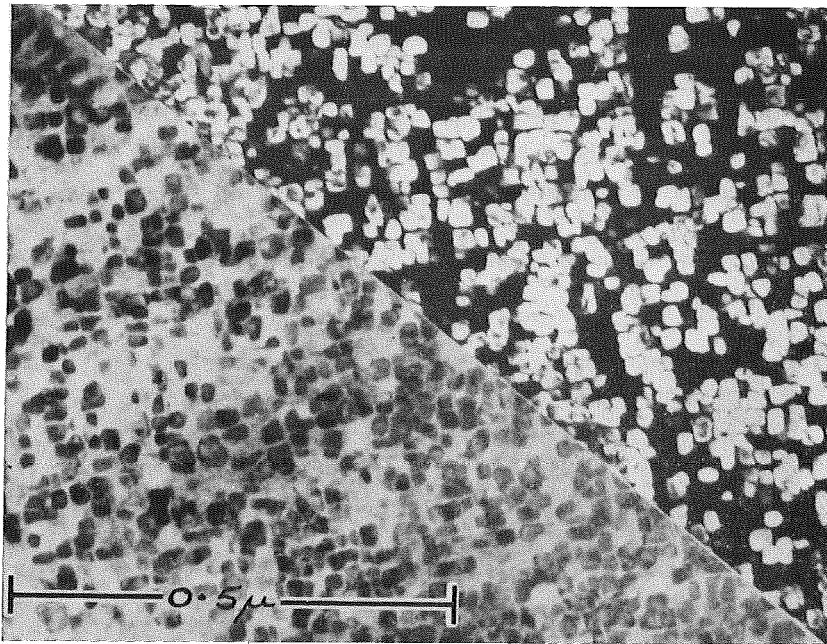


Figure 6 — Cuboidal ω morphology in a matrix of Nb-enriched β produced by aging Zr-20% Nb at 300°C.

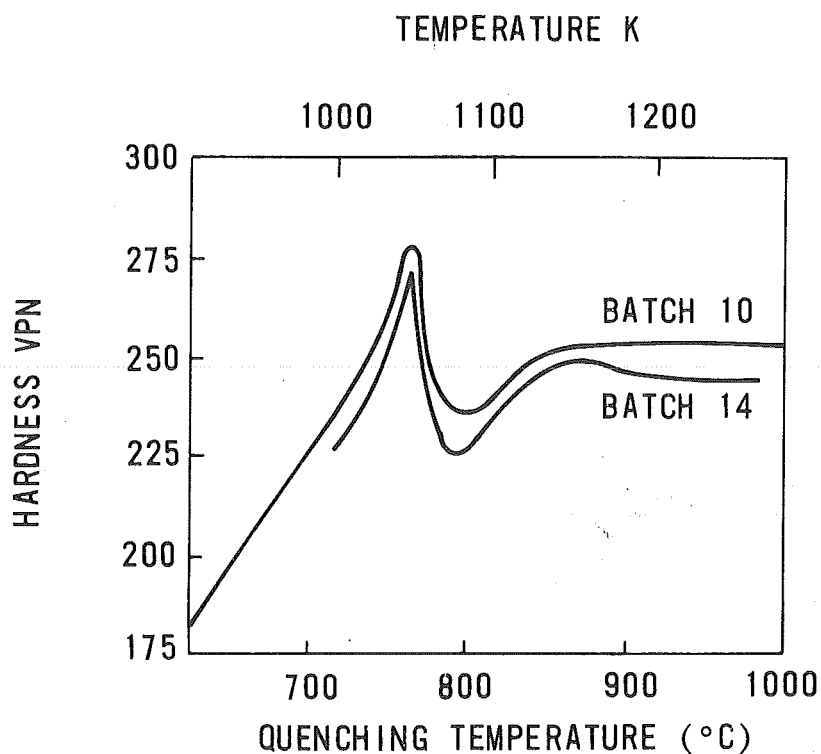


Figure 7 – Effect of quenching temperature on hardness of Zr-2.5% Nb

TABLE 2

THE CRYSTALLOGRAPHIC STRUCTURE AND LATTICE PARAMETER
OF PHASES IN ZIRCONIUM ALLOYS

Phase	Structure	Lattice Parameter Å		
α	close packed hexagonal	$a_0 = 3.23$	$c = 5.15$	$c/a = 1.59$
α'	close packed hexagonal	$a_0 = 3.25$	$c = 5.22$	$c/a = 1.61$
ω	close packed hexagonal	$a_0 = 5.04$	$c = 3.13$	$c/a = 0.621$
βZr	body centered cubic	$a_0 = 3.59$		
βNb	body centered cubic	$a_0 = 3.30$		

The isothermal transformation of Zr-Nb alloys has been extensively studied by R.F. Hehemann. Time-Temperature-Transformation diagrams for 12 wt% and 25 wt% Nb alloys are shown in Figures 8 and 9, R.F. Hehemann, *Transformations in Zirconium-Niobium Alloys*, *Can. Met. Quart.* 11, 1972, p.201.

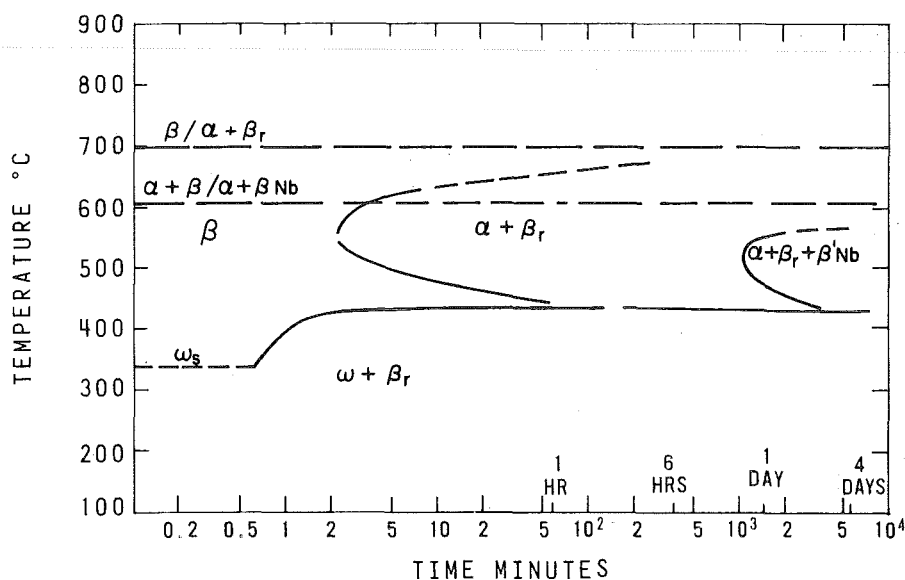


Figure 8 – TTT diagram for isothermal aging of the 12 wt% Nb alloy

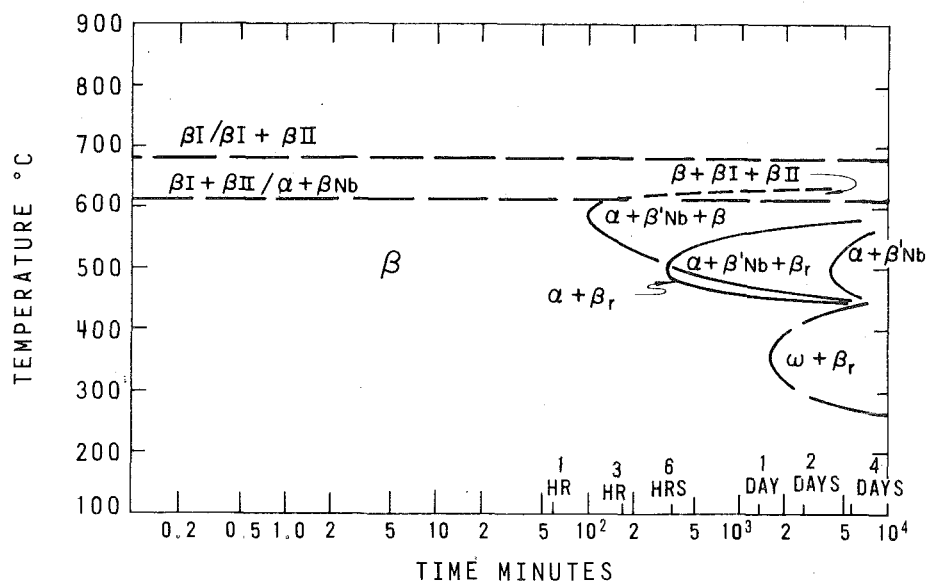


Figure 9 – TTT diagram for isothermal aging of the 25 wt% Nb alloy
(β_r is β enriched in Nb.)

When Zr-2.5 wt% Nb is slowly cooled from the ($\alpha + \beta$)-phase field the β transforms by growth on the existing α . The remaining β becomes enriched in Nb and when it contains about 17-20 wt% Nb it is metastable down to room temperature. Hence the microstructure consists of α grains and a grain boundary network of β which contains 17-20 wt% Nb, Figure 10. The isothermal transformation of a Zr-19 wt% Nb alloy has been studied in detail, Figure 11.

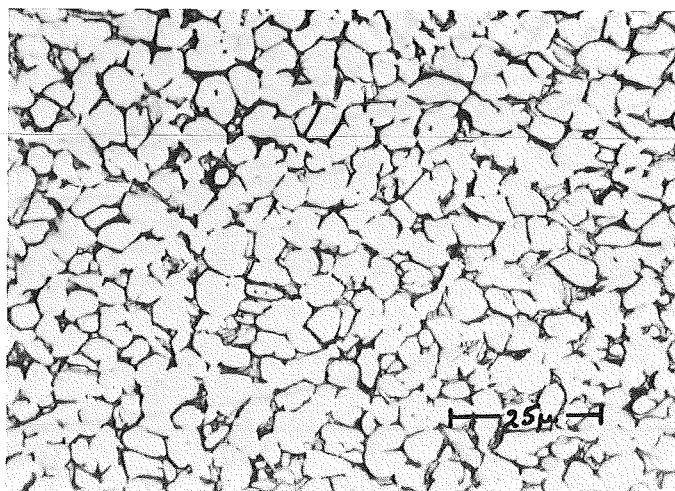
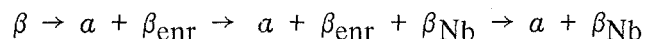
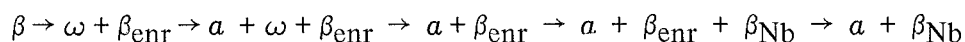


Figure 10 – Optical micrograph showing the dark etching β network in Zr-2.5 Nb furnace cooled from 1125K (850°C)

In the temperature range 800-875K (525-600°C) the β decomposes:



But below 800K (525°C)



The ω -phase precipitates as very small plates, Figure 6; the $\omega + \beta_{\text{enr}}$ structure can be twice as hard as the untransformed β , Figure 12.

— B.A. Cheadle and S.A. Aldridge, *J. Nucl. Mat.* **47**, 1973, p.255

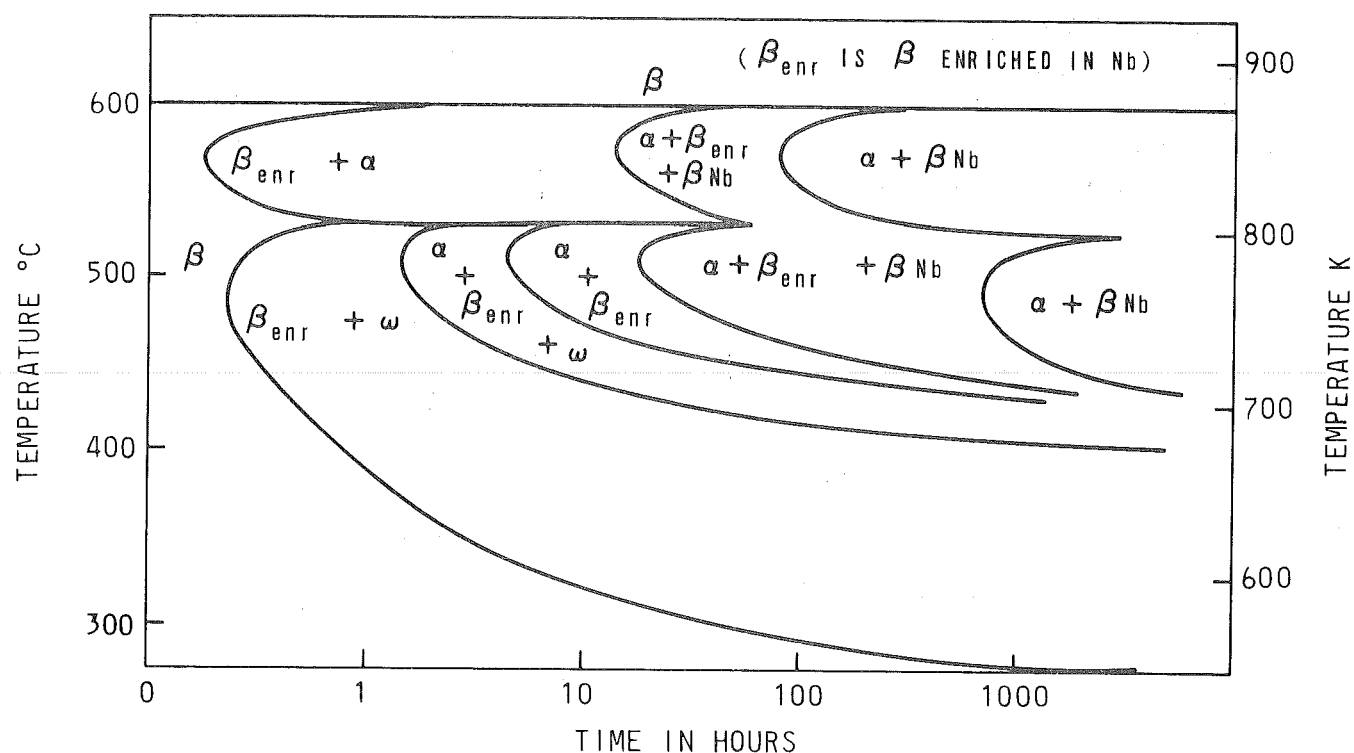


Figure 11 – The isothermal transformation behaviour of Zr-19 wt% Nb cooled from 1123K (850°C)

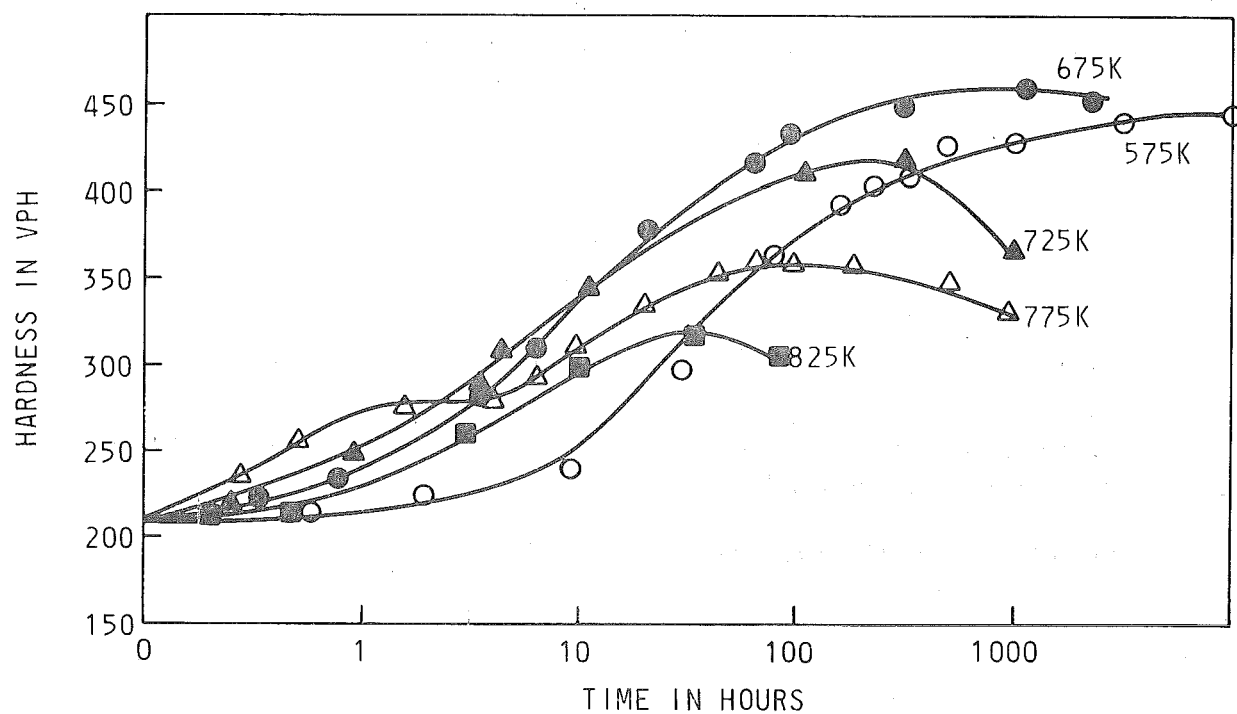


Figure 12 – The age hardening behaviour of the Zr-19 wt% Nb alloy cooled from 1123K (850°C)

2. MECHANICAL PROPERTIES

(a) Effect of Heat Treatment

Typical mechanical properties of Zircaloy-2 and Zr-2.5 wt% Nb in various heat treated conditions are given in Table 3. The strength of Zircaloy-2 cannot be increased very much by heat treatment. The higher strength of the β quenched Zircaloy-2 compared to the slow-cooled material is partially due to the finer grain size of the Widmanstätten structure. Zr-2.5 wt% Nb is much stronger in the β or ($\alpha + \beta$) quenched condition than in other conditions due to the martensitic α' -phase. Aging the martensitic α' at 775K (500°C) has only a small effect on the strength. The β_{Nb} precipitates increase the strength but at the same time the α' is recovering thus the net change in properties is small. The effect of time and temperature on the hardness is shown in Figure 13. When the α' -phase is heated to the ($\alpha + \beta$)-phase region ≈ 870 -1170K (600-900°C) it rapidly transforms to α with little Nb in solid solution and β enriched with Nb.

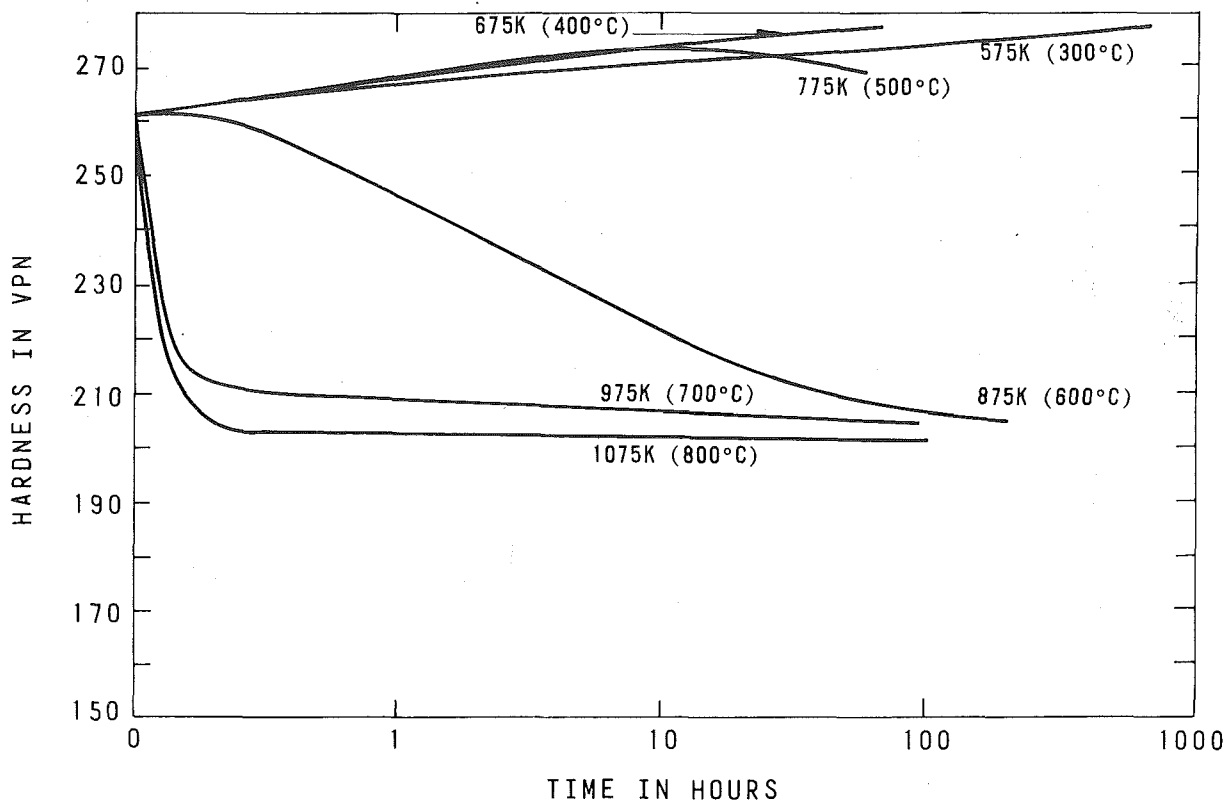


Figure 13 — The effect of heating at different temperatures on the hardness of Zr-2.5 wt% Nb water quenched from 1155K (880°C)

TABLE 3

TYPICAL ROOM TEMPERATURE TENSILE PROPERTIES OF ZIRCALOY-2 AND Zr-2.5 wt% Nb

Alloy	Material Condition	0.2% Y.S		UTS		%EI	%RA
		kpsi	MPa	kpsi	MPa		
Zircaloy-2	slow cooled from 1025K (750°C)	48	330	72	500	22	40
	slow cooled from 1275K (1000°C)	48	330	63	470	22	35
	water quenched from 1275K (1000°C)	68	470	84	580	16	50
	20% cold-worked	80	550	85	590	30	45
	40% cold-worked	85	590	90	620	10	35
Zr-2.5 wt% Nb	slow cooled from 1125K (850°C)	50	350	74	510	28	48
	slow cooled from 1275K (1000°C)	76	520	89	610	13	46
	water quenched from 1275K (1000°C)	106	730	115	790	9	38
	water quenched from 1125K (850°C)	109	750	120	820	14	60
	20% cold-worked	85	590	90	620	15	46
	40% cold-worked	90	620	100	690	13	50

(b) Effect of Cold Work

Cold work increases the strength of Zircaloy-2 and Zr-2.5 wt% Nb due to the dislocation structure increasing the flow stress, Table 3, Figures 14 and 15.

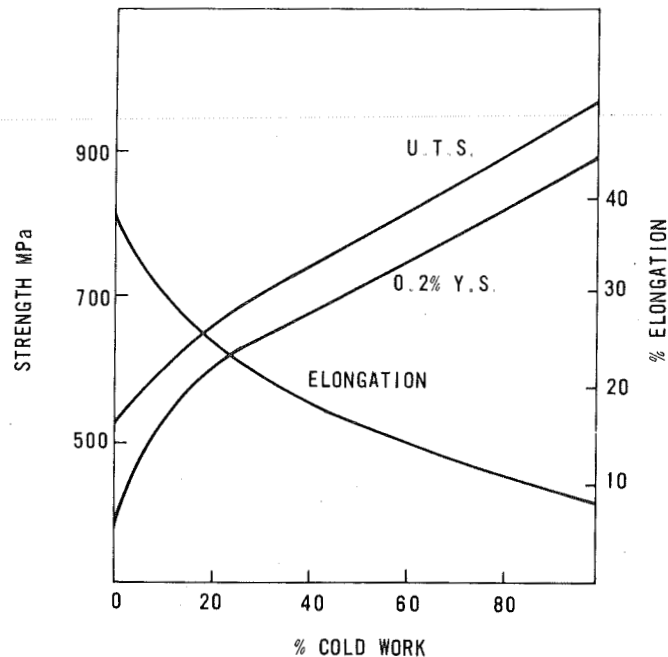


Figure 14 – The effect of cold work on the tensile strength of Zr-2.5 wt% Nb

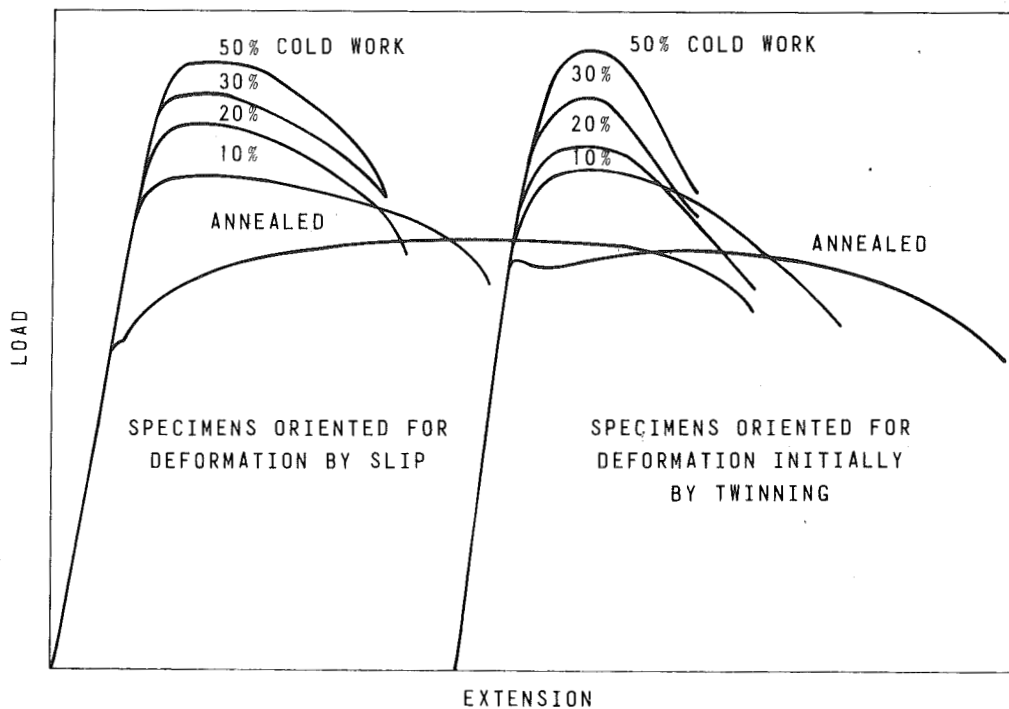


Figure 15 – The effect of cold work on the tensile properties of Zircaloy-2.

(c) Effect of Grain Size

Decreasing the grain size increases the strength of Zr alloys and the flow stress follows the Petch equation:

$$\sigma = \sigma_i + Kd^{-1/2}$$

where: σ is the flow stress

σ_i is the flow stress of a single crystal

K is a constant

d is the grain size

Results for annealed high purity zirconium by, *D. Weinstein, Electrochem. Tech. 4, 1966, p.307* are shown in Figure 16. The yield strength of hot worked Zr-2.5 wt% Nb can be increased to 75 kpsi (520 MPa) by decreasing the grain size, Figure 17.

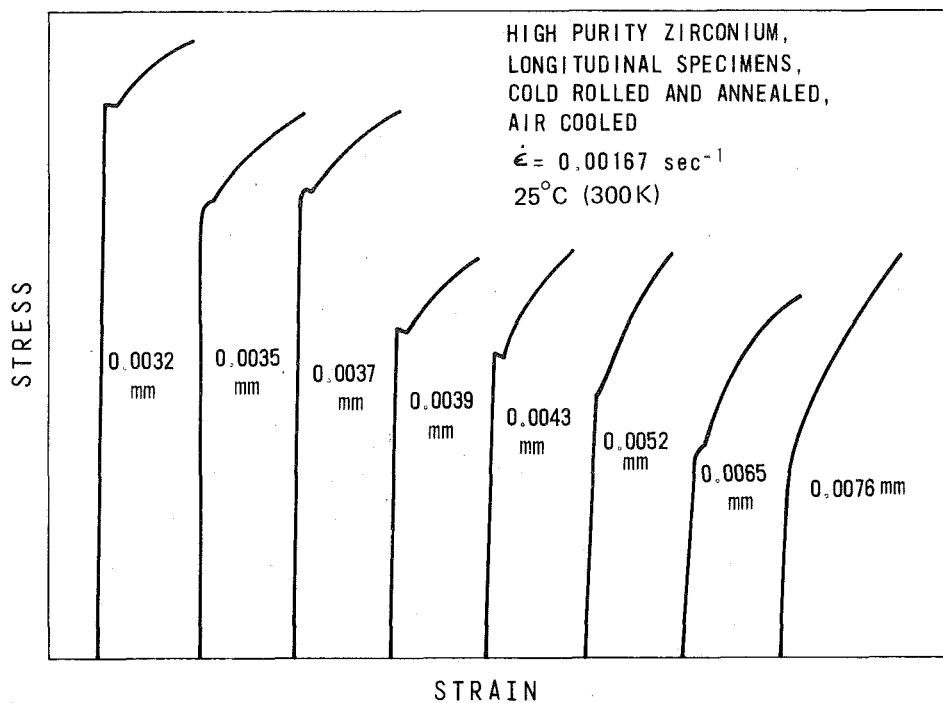


Figure 16 -- Yield point occurrence as a function of average grain diameter for air cooled specimens.

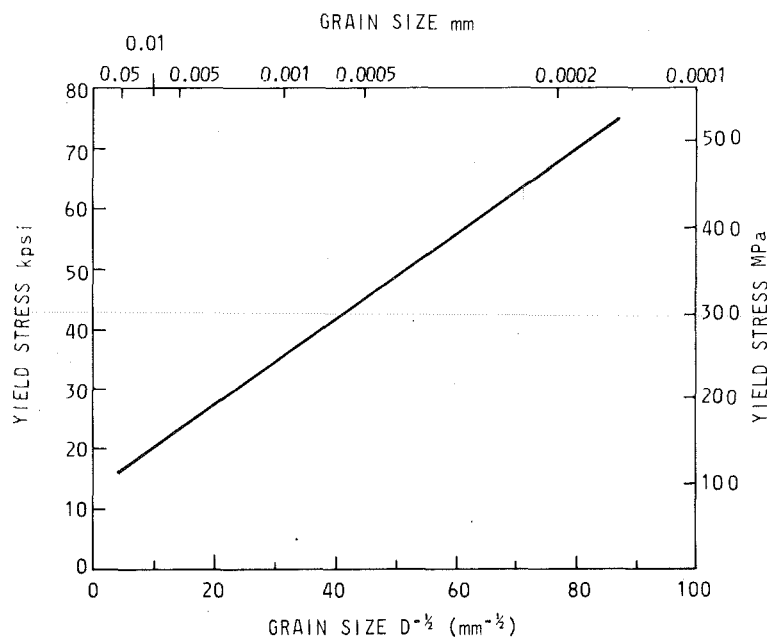


Figure 17 – Effect of grain size on the 0.2% yield stress of hot worked Zr-2.5 wt% Nb

(d) Age Hardening, Recovery and Recrystallization

Recovery is a thermally activated phenomenon and is affected by the prior amount of cold work, the direction of internal stresses, and crystallographic texture. Recovery is very slow below 575K (300°C) and very rapid above 875K (600°C). The rate of recovery in the 575-875K (300-600°C) range is faster the greater the amount of previous cold work. The strength of 70% cold-worked tubes decreases much more rapidly than 40% cold-worked tubes when they are heated in the temperature range 575-875K (300-600°C), Figure 18.

Recovery can be measured by the width of X-ray diffraction peaks. Measurements of the width of (0004) α -phase diffraction peaks of cold-worked Zr-2.5 wt% Nb, Figure 19 shows:

- 1) at 575K (300°C) recovery is slow;
- 2) at 775K (500°C) and 875K (600°C) there is rapid partial recovery followed by a much slower rate. The higher the temperature the greater the initial recovery;
- 3) temperatures higher than 875K (600°C) are required for full recovery in less than thousands of hours.

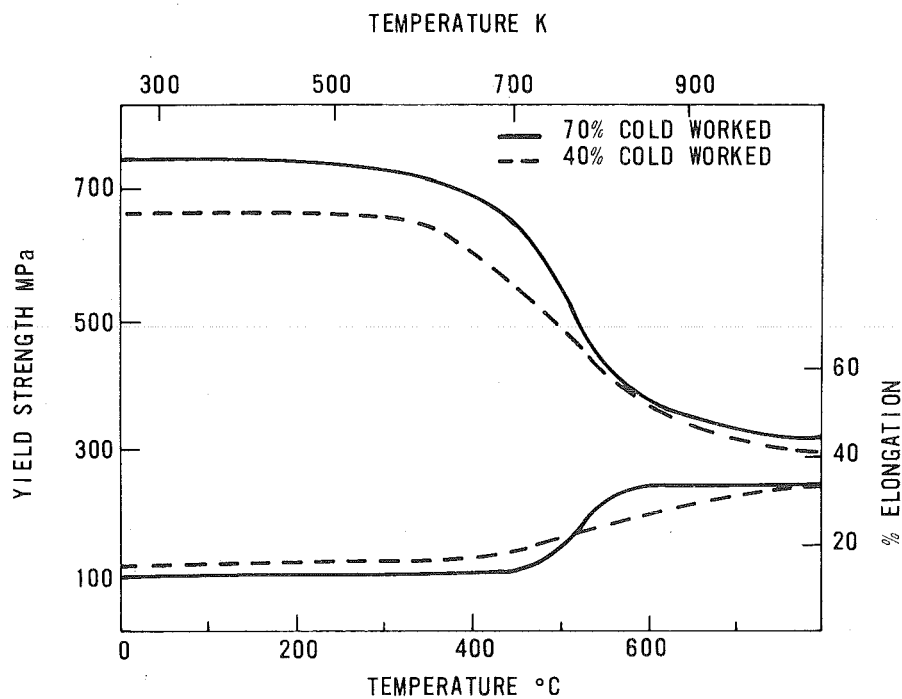


Figure 18 — The effect of heating for 1 hour on the tensile properties of 70% and 40% cold worked Zircaloy-2

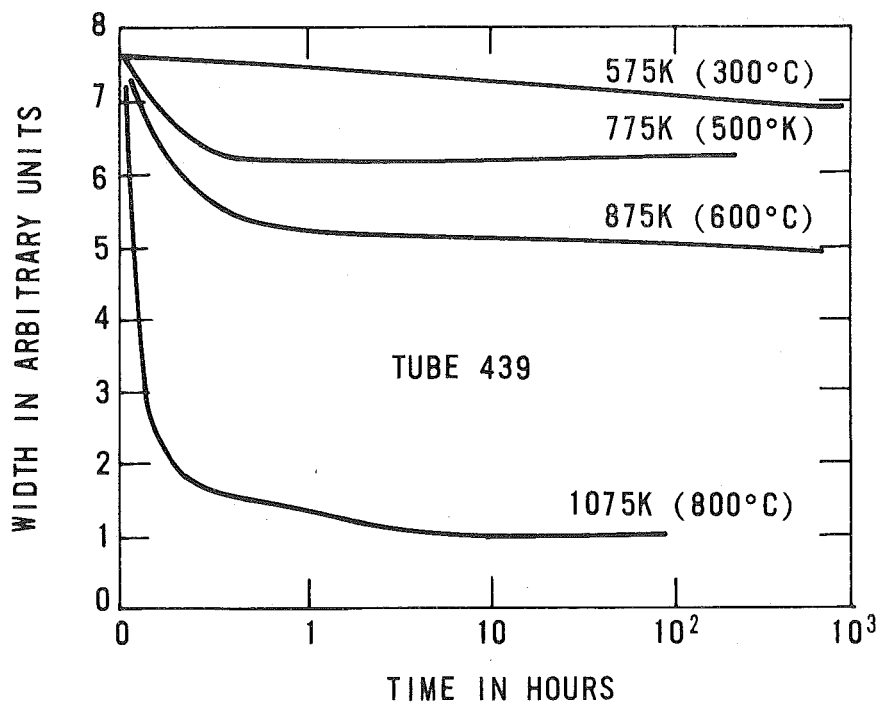


Figure 19 — The width of the (0004) X-ray diffraction peak of 20% cold worked Zr-2.5 wt% Nb after heating at different temperatures

Texture also affects recovery. 40% cold-rolled Zircaloy-2 sheet has a pronounced texture and specimens from the short transverse, transverse and longitudinal directions, Figure 20 show this effect. The short transverse specimens which initially deform by twinning hardened after heating in the range 575-775K (300-500°C), Figure 21. The increase in strength was partially due to a Bauschinger effect and partially due to a small amount of age hardening which had a greater effect when deformation was initially by twinning rather than by slip. *C.E. Ells and B.A. Cheadle, J. Nucl. Mat. 23, 1967, p.257.*

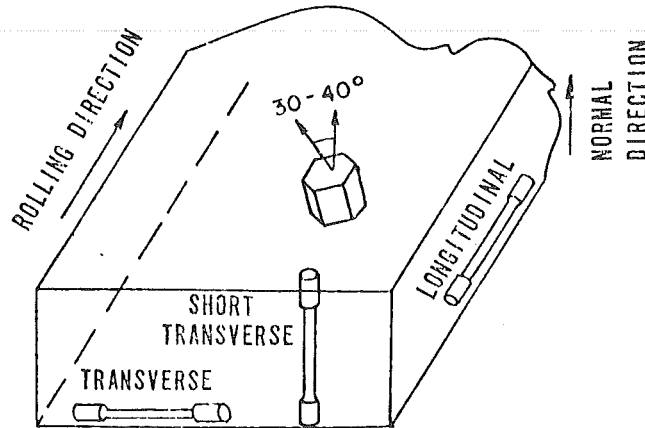


Figure 20 – Specimen orientation in the rolled sheet

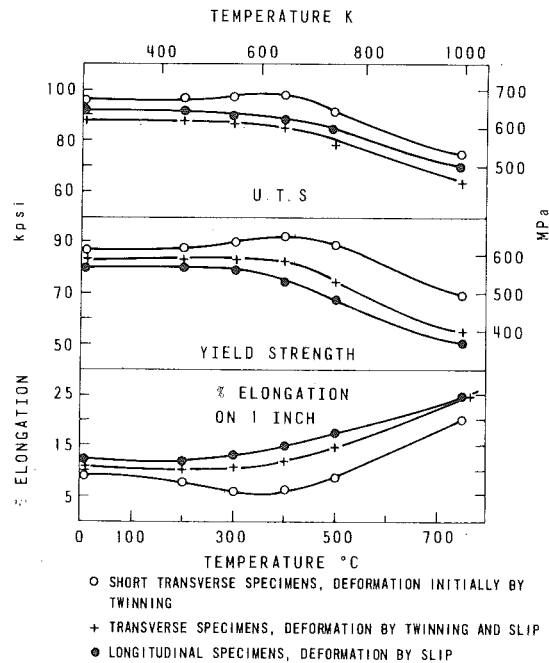


Figure 21 – The effect of heating for 1 hour on the tensile properties of 40% cold worked Zircaloy-2 sheet

The results for 40% cold-rolled Zr-2.5 wt% Nb were similar but more pronounced, Figure 22. The Bauschinger effect lowered the yield stress of the short transverse specimens below that of the longitudinal and transverse specimens. However after work hardening the UTS's were in the order expected from their textures with the transverse the strongest and the longitudinal the weakest. All the specimens aged hardened in the temperature range 575-775K (300-500°C) and again the effect was larger in specimens that initially deformed by twinning.

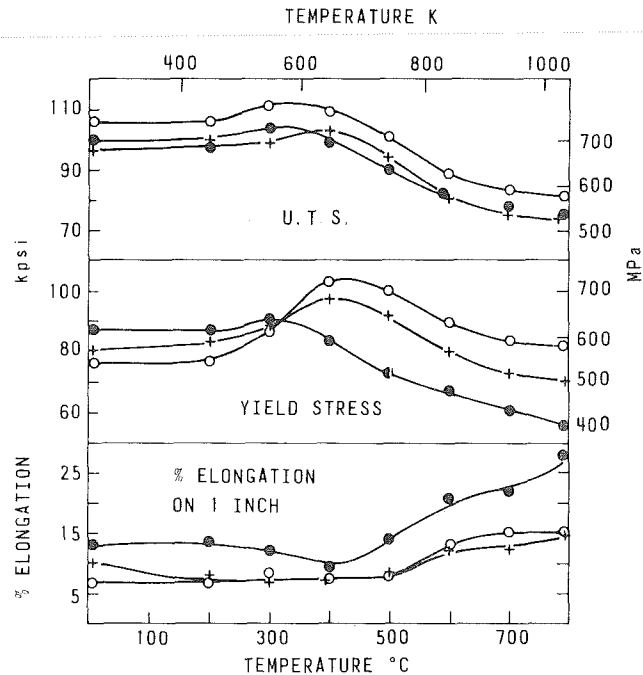


Figure 22 — The effect of heating for 1 hour on the tensile properties of 40% cold worked Zr-2.5 wt% Nb sheet (point identification as in Figure 21.)

The age hardening in this material has been attributed to the increase in strength of the niobium-enriched cubic β -phase when the ω plates form. The grain boundary $\omega + \beta_{\text{enr}}$ phase then behaves as a fibre strengthening phase, Figure 23. *S.A. Aldridge and B.A. Cheadle, J. Nucl. Mat. 42, 1972, p.32.*

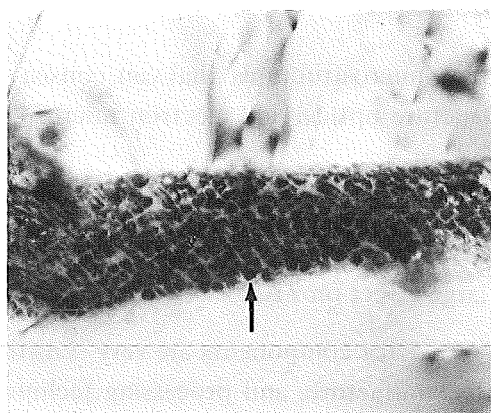


Figure 23 — Zr-2.5 wt% Nb pressure tube aged for 10 345 h at 575 K. The β network has a structure of ω plates in a matrix of niobium-enriched β phase (arrowed). (x70,000)

The isochronal recovery-age hardening of a 20% cold-worked tube is shown in Figure 24. At 575K (300°C) and 675K (400°C) the increase in the hardness of the grain boundary β -phase is greater than the recovery of the α -phase and there is overall small increase in hardness. Above 875K (600°C) the recovery of the α is the dominant factor and there is an overall softening. Recrystallization usually only starts when recovery is almost complete i.e. after many hours at 875K (600°C) or after a few minutes at 1075K (800°C).

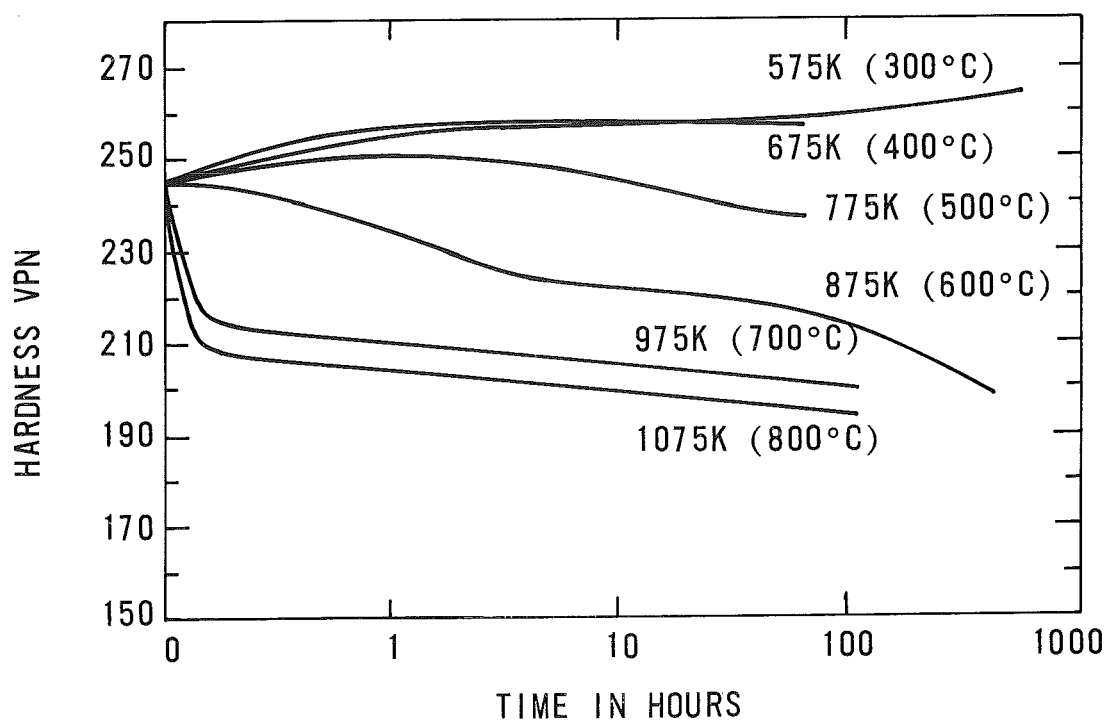


Figure 24 — Age hardening of a Zr-2.5 wt% Nb tube extruded at 1125K (850°C), air cooled and cold-worked 20%

3. SUMMARY AND CONCLUSIONS

Zirconium alloys have complex microstructures that can consist of α' , α , β_{Zr} , β_{Nb} and ω -phases. To study the microstructure optical and electron microscope and X-ray diffraction techniques are required.

Their mechanical properties are very anisotropic due to crystallographic texture developed by deformation. Heat treatment does not have a large effect on the tensile strength of Zircaloy-2 but has a large effect on Zr-2.5 wt% Nb.

The mechanical properties of reactor components are very sensitive to the deformation and heat treatment used in their manufacture, and processing techniques must be carefully selected and controlled.

CRNL-1208

LECTURE NO. 3*

TEXTURE IN ZIRCONIUM ALLOYS AND ITS EFFECT ON MECHANICAL PROPERTIES

by

B.A. Cheadle

INTRODUCTION

At room temperature, hexagonal α zirconium deforms by slip on the $(10\bar{1}0)$ planes in the $\langle 11\bar{2}0 \rangle$ directions, twinning under tension along the $\langle 0001 \rangle$ direction on the $(10\bar{1}2)$ and $(11\bar{2}1)$ planes and twinning under compression on the $(11\bar{2}2)$ planes, Figure 1. For intermediate directions deformation will be by slip or twinning depending on the orientation factor, Figure 2, and constraints from surrounding grains. The flow stress for slip is less than that for twinning and this results in higher strengths when tensile specimens have the majority of grains oriented with their "c" axes parallel to the stress axis rather than their "a" axes, Table 1. In addition the deformation is also anisotropic, Figures 3 and 4, and the different microstructures after deformation by slip and twinning are shown in Figure 5. Due to the limited number of deformation systems, when an ingot of a zirconium alloy is deformed the grains take up certain preferred orientations and a texture is developed.

-- *Structure of Metals by C.S. Barrett, McGraw-Hill Book Company Inc. 1952*

TABLE 1

TYPICAL COMPARATIVE ROOM TEMPERATURE STRENGTHS OF ZIRCALOY-2 AND Zr-2.5 Wt% Nb ALLOYS IN DIFFERENT CRYSTALLOGRAPHIC DIRECTIONS

Axis	YIELD STRESS kpsi		ULTIMATE STRENGTH kpsi	
	Zircaloy-2	Zr-2.5 Wt% Nb	Zircaloy-2	Zr-2.5 Wt% Nb
"a" Tension	48	55	63	74
"c" Tension	68	79	75	81
"a" Compression	67	—	—	—
"c" Compression	122	—	—	—

(The numerical values will vary with the oxygen concentration of the alloy and the amount of cold work.)

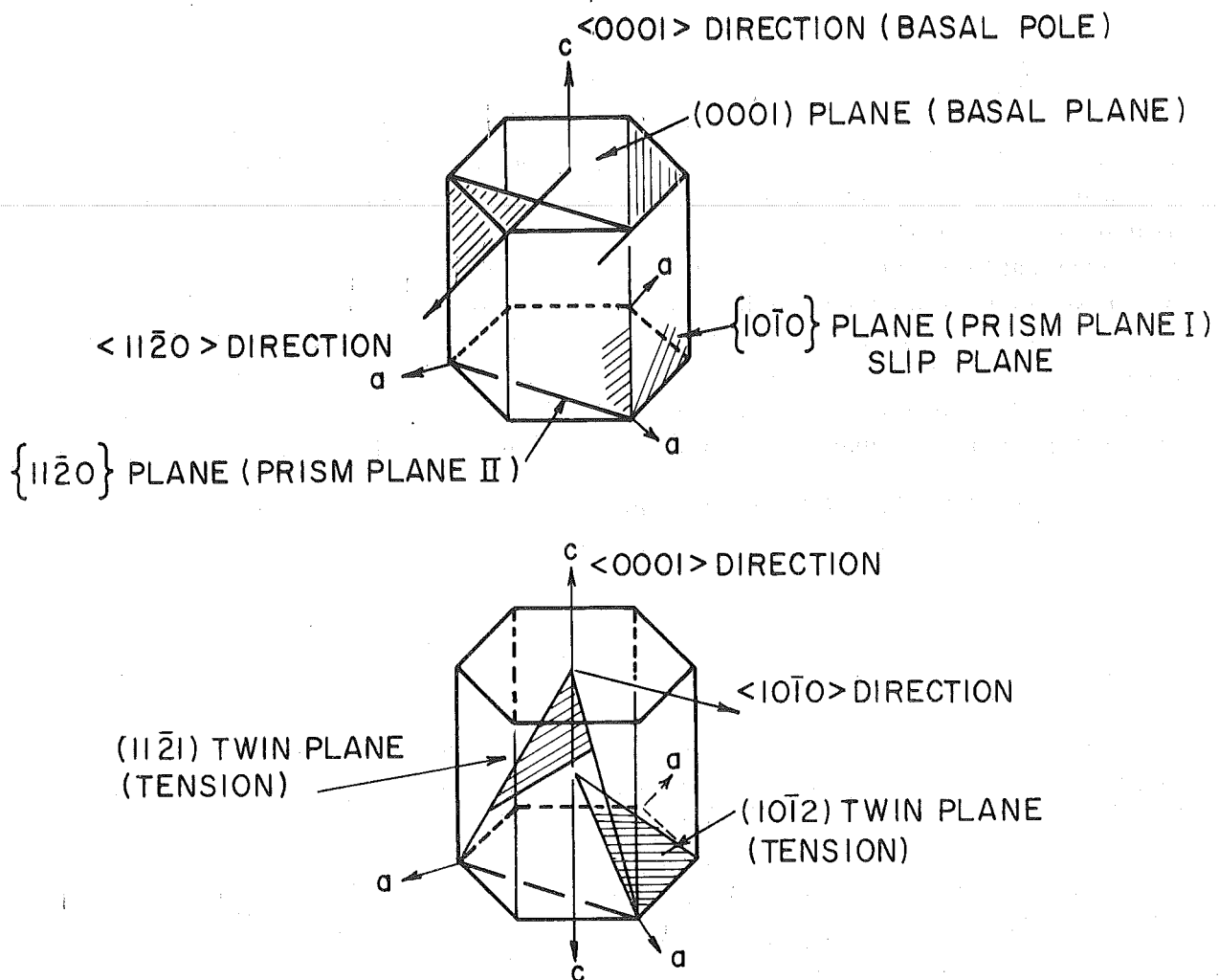


Figure 1 — Slip and twinning planes in α Zirconium

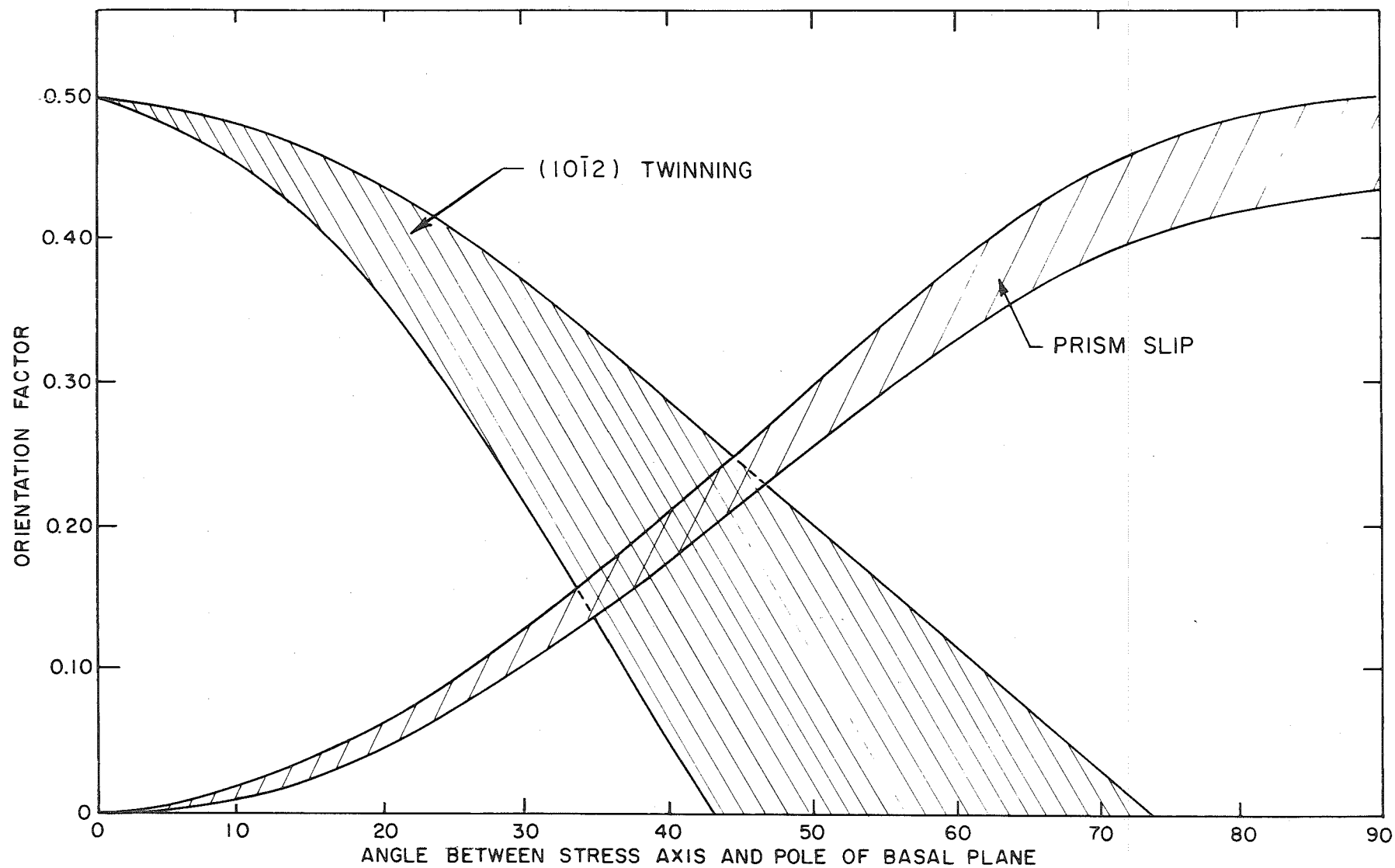


Figure 2 – The orientation factors for prism slip and $(10\bar{1}2)$ twinning as a function of the angle between the stress axis and the basal plane pole

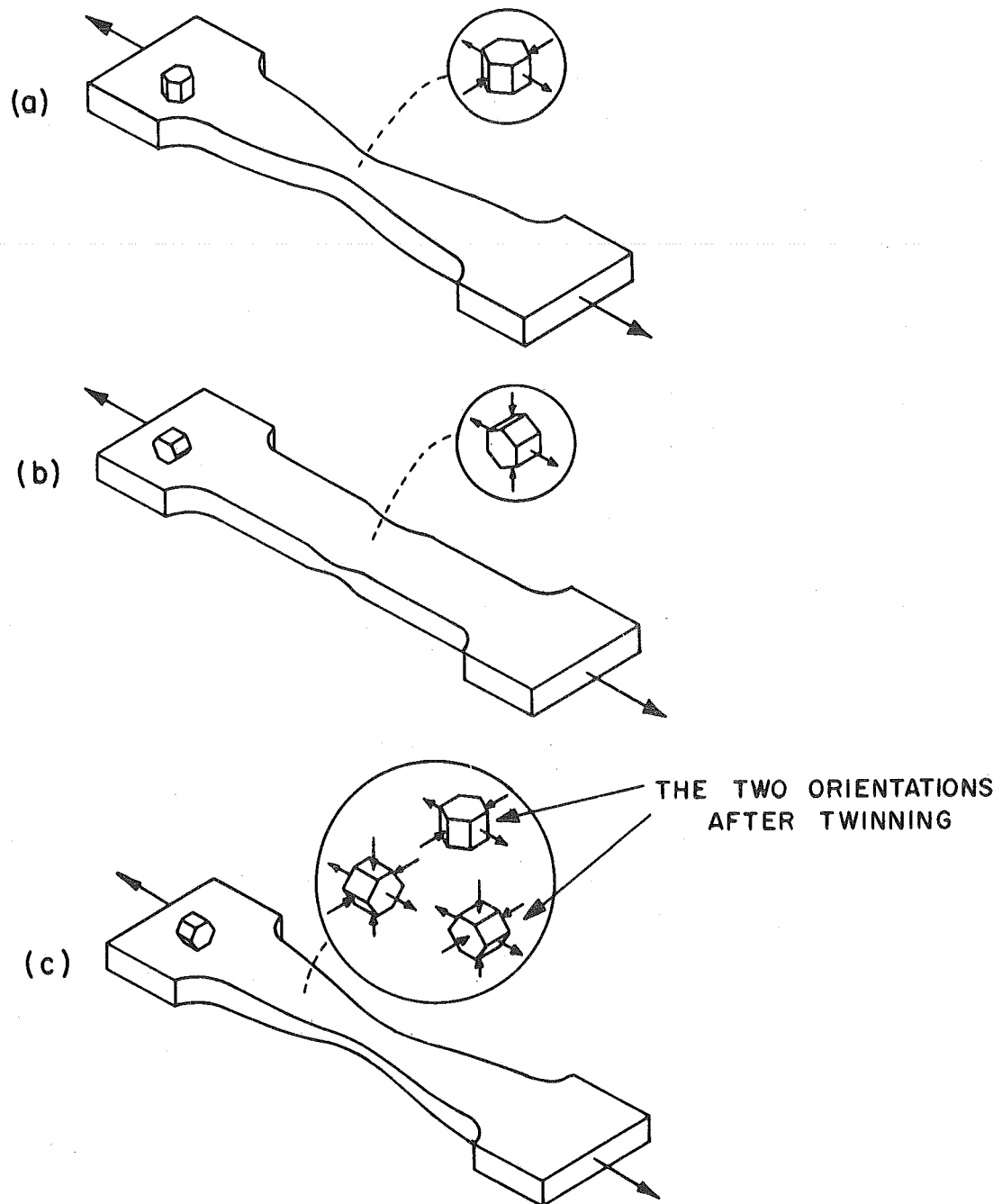


Figure 3 — Deformation behaviour of textured sheet tensile specimens of Zircaloy-2
(Picklesimer, Electrochem Techn, 4, No 7-8 1966)

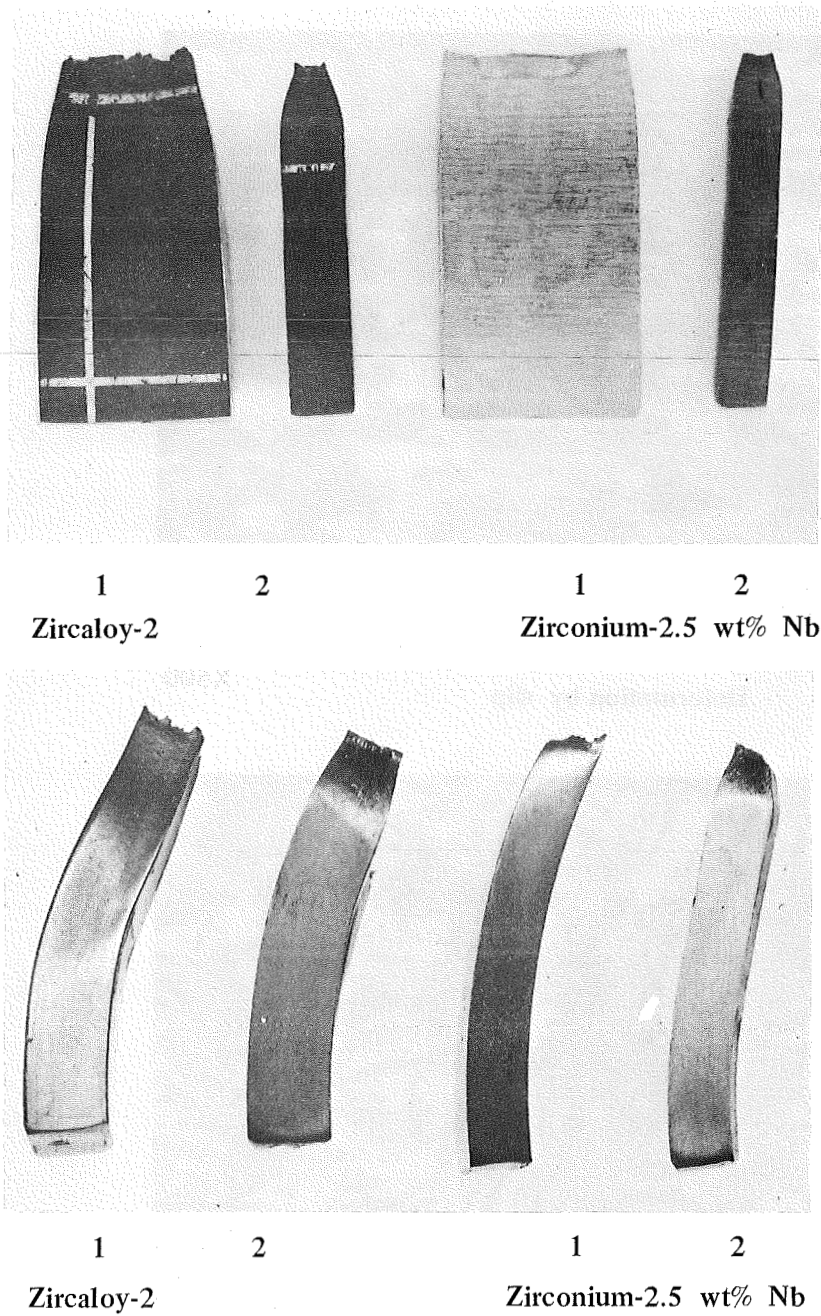
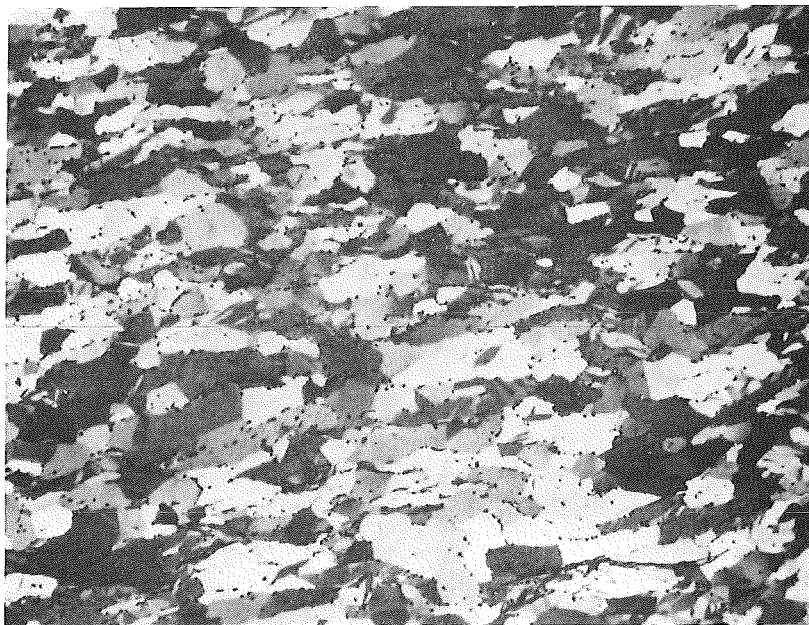


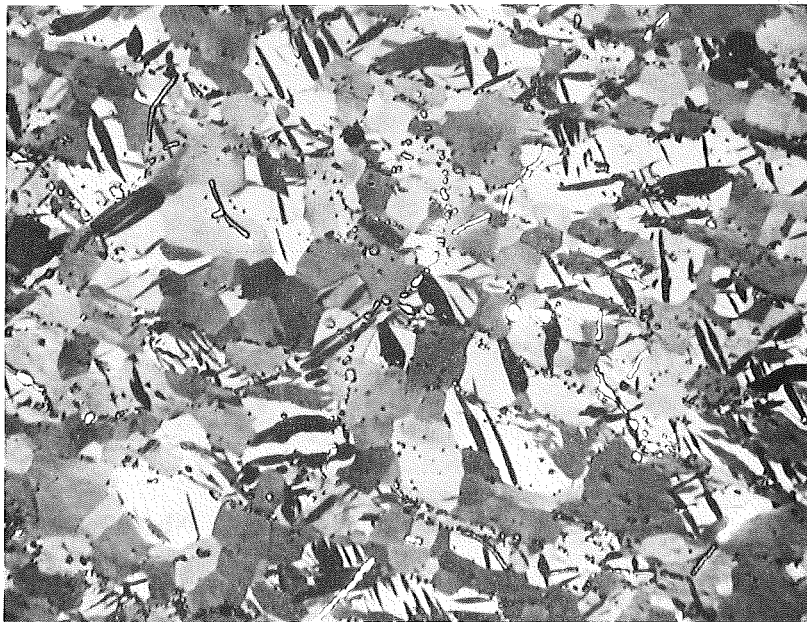
Figure 4 – Zircaloy-2 and Zr-2.5 wt% Nb fractured transverse ring specimens

- (1) with a cross section of 1/2 in. x the thickness of the tube
- (2) with a square cross section equal to the thickness of the tube



Deformation by slip

X500



Deformation by twinning

X500

Figure 5 — Metallographic Structure of the highly deformed regions of Zircaloy-2 tensile specimens.

MEASUREMENT OF TEXTURE

Crystallographic texture can be measured in several ways. The most common are the inverse and normal pole figure techniques. The inverse pole figure measures the intensities of all the crystallographic planes in a given direction. The normal pole figure measures the intensity of one plane in all directions. A comparison is shown in Figure 6.

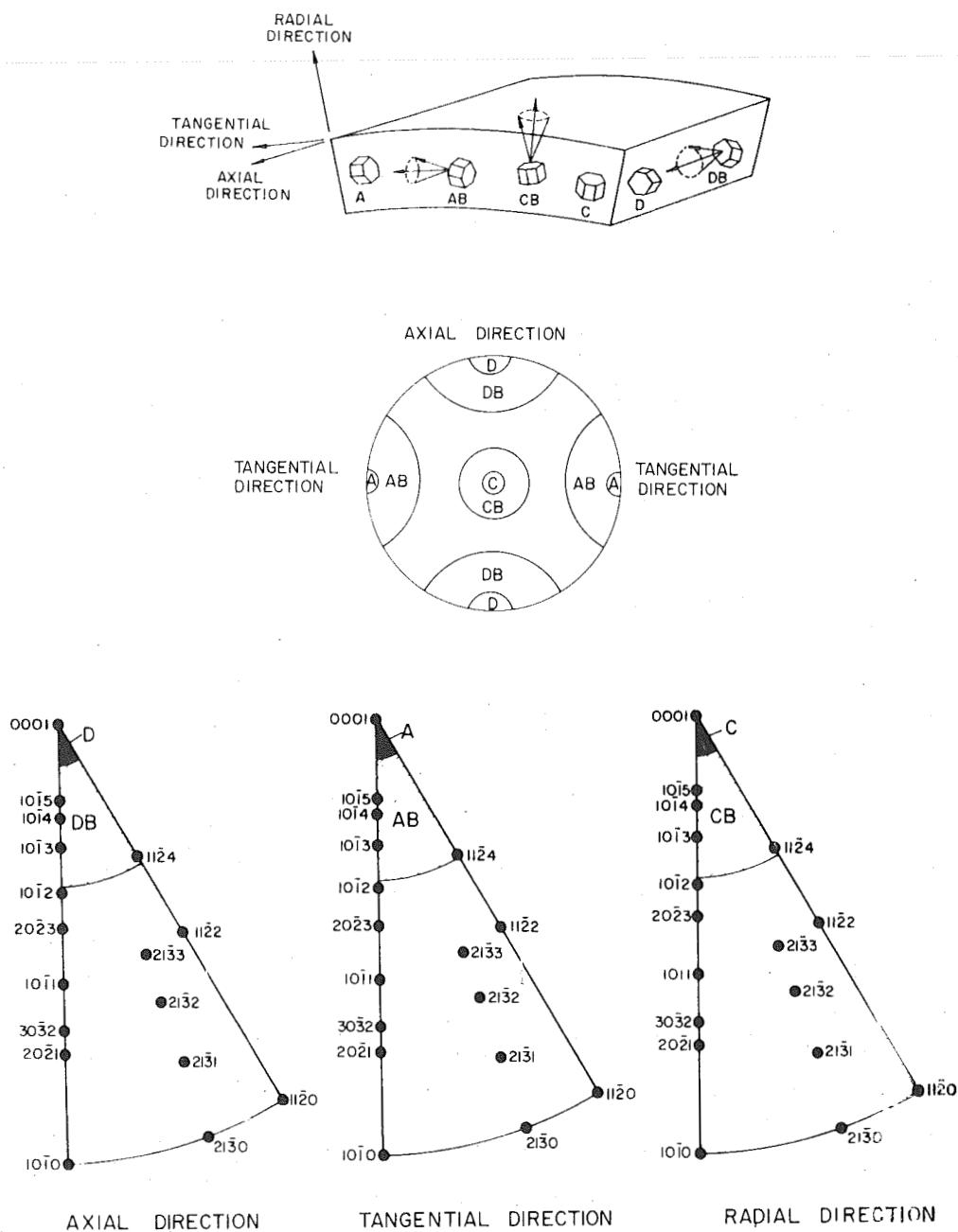


Figure 6 — The idealised orientations plotted on normal and inverse pole figures.

DEVELOPMENT OF TEXTURE

Texture is developed when material is deformed. When a grain deforms by slip there is no rotation of the basal pole, Figure 7. However when the basal pole is near the tensile axis and deformation is by twinning the material in the twin has a different orientation, Figure 8, and the proportion of grains with their basal poles close to the tensile axis is reduced, Table 2.

— B.A. Cheadle, C.E. Ells and W. Evans, "Development of Texture in Zirconium Alloy Tubes", *J. Nuc. Mat.* 23, 1967, p.199

TABLE 2

TEXTURE COEFFICIENTS OF DEFORMED ZIRCONIUM AND Zr-2.5 Wt% Nb BARS

	Zirconium		Zr-2.5 Wt% Nb	
	D	DB	D	DB
No deformation	3.0	3.0	1.0	2.5
Uniform deformation	—	0.4	1.0	2.5
Near the fracture	—	—	0.2	—

D = texture coefficient of the grains with basal plane normals parallel to the tensile axis;
DB = texture coefficient of the grains with basal plane normals within 40° of the tensile axis.

When zirconium alloys are rolled, a texture is developed with the basal plane normals perpendicular to the rolling direction and oriented up to 40° to the normal direction of the sheet, Figure 9. Additional rolling makes the texture more intense. In rolling, the major strain is compressive in the normal direction and is accommodated by a tensile strain in the rolling direction and a small tensile strain in the transverse direction.

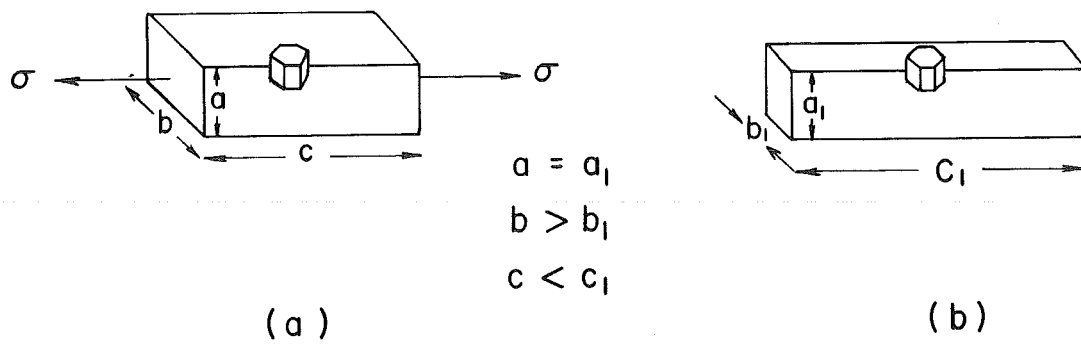
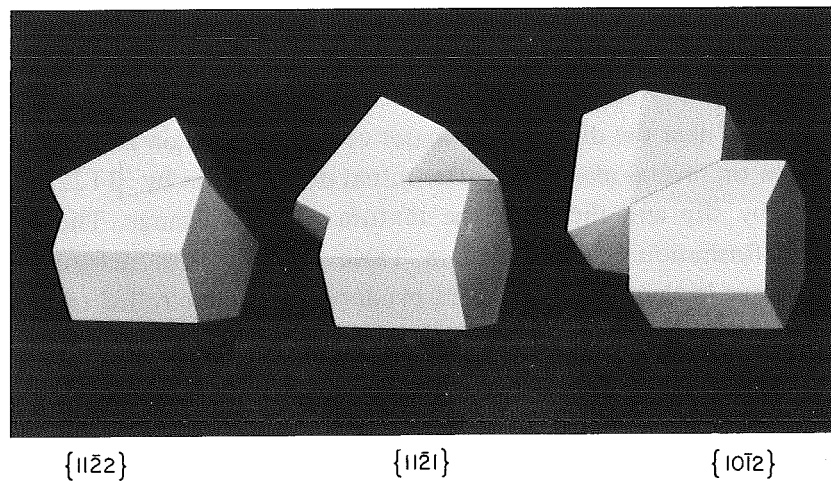
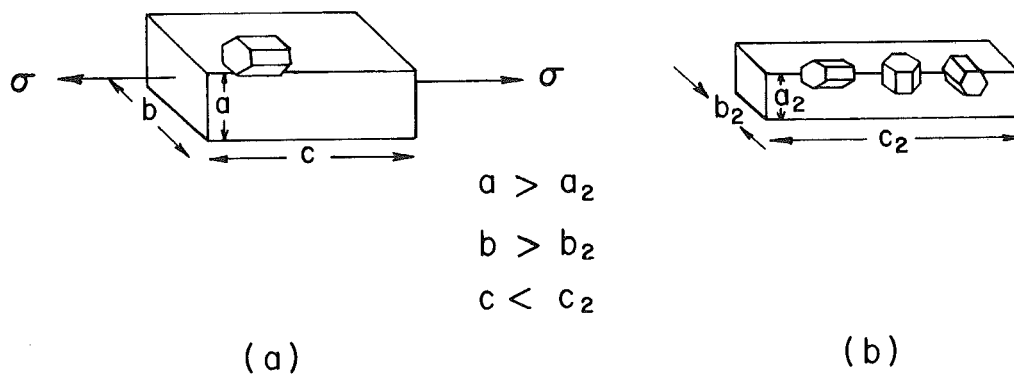


Figure 7 – Texture of a bar when deformation occurs by slip

THE THREE TWIN PLANES IN α -ZIRCONIUMFigure 8 – Texture of a bar when deformation occurs by $\{10\bar{1}2\}$ twinning

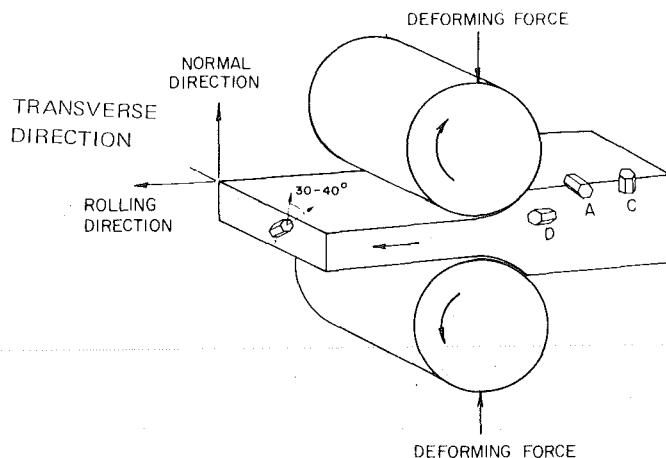


Figure 9 – The texture developed when sheet is rolled

No satisfactory explanation has been given for the stability of the observed rolling texture. Picklesimer, *Deformation, Creep and Fracture in Alpha-Zirconium Alloy, Electroch. Techn.* 4, 1966, p.289 suggests that the reason most of the material is oriented with the basal plane normal near the direction of major compressive strain is that slip occurs in the $[11\bar{2}3]$ directions on several planes and after initial deformation by $\{11\bar{2}2\}$ twinning further deformation is by slip and therefore the texture will not change. The degree of texture change with deformation is illustrated in Table 3. Only 10% deformation was required to initiate a change in the texture and 30% produced the stable rolled texture.

TABLE 3

EFFECT OF DEFORMATION BY ROLLING ON THE TEXTURE
OF Zr-2.5 Wt% Nb SHEET

Material Condition	Texture Coefficients					
	A	AB	C	CB	D	DB
As received	3.3	1.8	0.1	2.2	0.8	—
Plus slow-cooled from 1275K (1000°C)	0.8	1.3	0.1	2.1	1.3	1.8
Plus rolled 10%	0.8	0.8	1.7	2.1	1.7	0.7
Plus rolled further 20%	0.7	1.0	1.9	2.8	0.2	0.1

EFFECT OF TEMPERATURE DURING DEFORMATION

As long as the material remains in the α -phase, temperature during deformation does not have a large effect on the texture developed, Figure 10. In Zircaloy-2 and Zr-2.5 wt% Nb as the temperature is raised within their respective ($\alpha + \beta$) phase fields the proportion of α -phase is decreased, Figures 11 and 12. Deformation develops texture in the α -grains and on slow cooling the β transforms to α by growth on the existing α -grains which then have the same texture. If the alloys are deformed in the cubic β -phase then a texture is developed in the β . When the β is cooled and retransforms to α the α nucleates at grain boundaries and the orientation of the α is related to the β by the Burgers relationship:

$$[0001]_{\alpha} \parallel [110]_{\beta} \text{ and } \langle 11\bar{2}0 \rangle_{\alpha} \parallel \langle 111 \rangle_{\beta}$$

The texture of the sheet rolled at 1275K (1000°C) is the result of a $[100] \langle 110 \rangle$ cubic texture being developed in the β -phase and transformation to α after rolling produced the texture observed, Figure 10.

- B.A. Cheadle and C.E. Ells, "The Effect of Rolling Temperature on the Texture Developed in Rolled Zirconium Rich Alloys", *J. Nuc. Mat.* 24, 1967, p.240
- B.A. Cheadle, S.A. Aldridge and C.E. Ells, "The Effect of Temperature during Deformation on the Development of Texture in Zirconium Alloy Rolled Sheet", *J. Nuc. Mat.* 34, 1970, p.119

EFFECT OF HEAT TREATMENT

In the as-rolled condition the α grains have a $\langle 10\bar{1}0 \rangle$ fibre texture but when they recrystallise there is a 30° rotation about the "c" axis to a $\langle 11\bar{2}0 \rangle$ fibre texture. Cold-worked zirconium and Zircaloy-2 both recrystallise easily when heated in the temperature range 875-1075K (600-800°C). However in this temperature range Zr-2.5 wt% Nb is in the ($\alpha + \beta$) phase region. The matrix of β isolates the α -grains, preventing a change in their orientation, and on slow cooling the β transforms to α by growth on the existing α -grains so that there is no change in texture. If Zr-2.5 wt% Nb is heated at 850K (575°C) for many hours it will crystallize to the $\langle 11\bar{2}0 \rangle$ fibre texture.

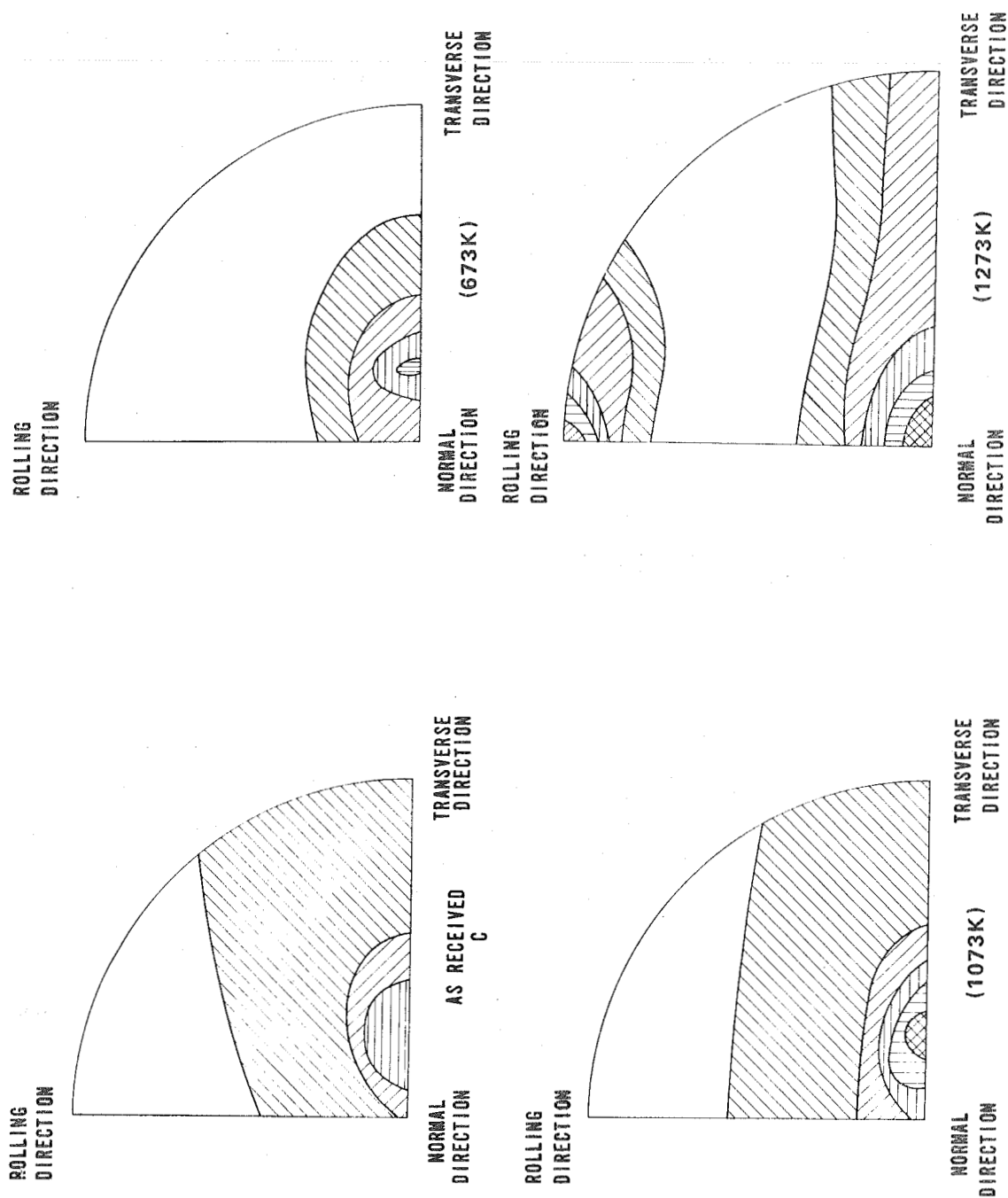


Figure 10 — Basal pole figures of Zr-2.5 wt% Nb rolled sheet showing the effect of temperature on the texture developed.

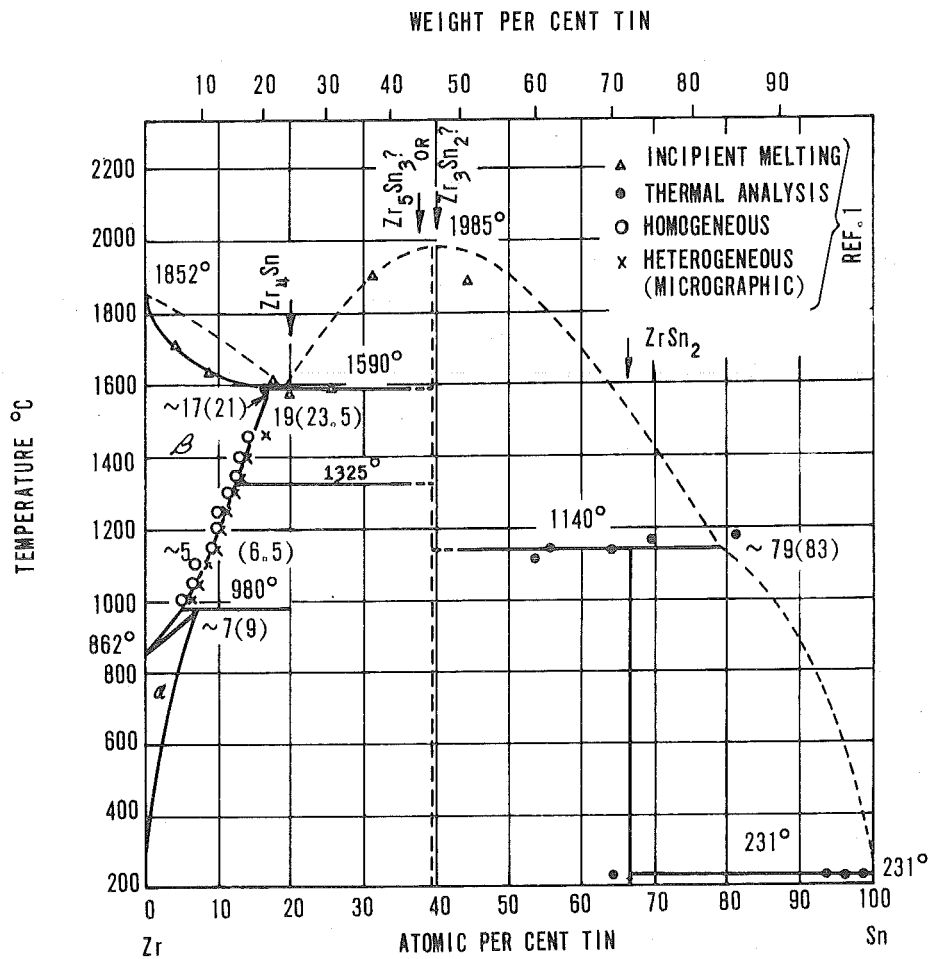


Figure 11 — The Zr-Sn equilibrium phase diagram

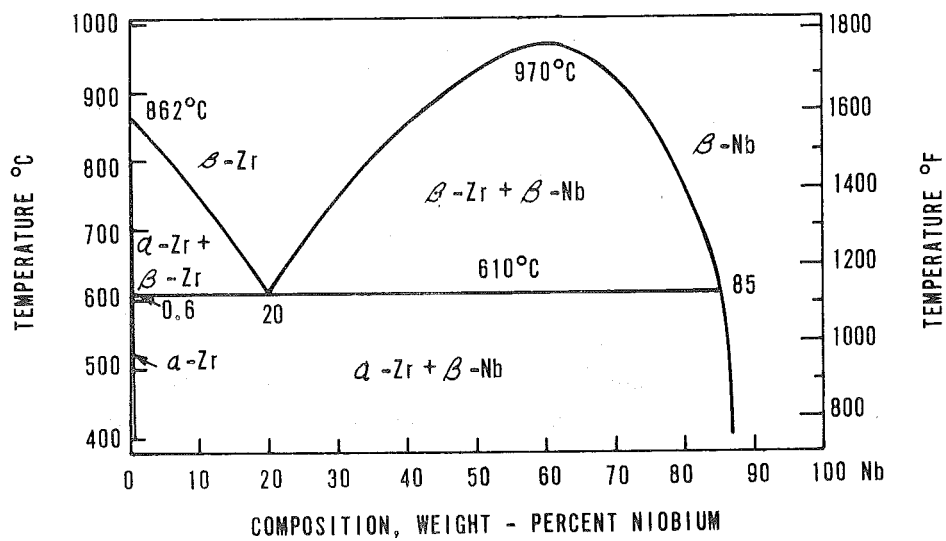


Figure 12 — The zirconium-niobium equilibrium phase diagram determined by Lundin and Cox

When zirconium alloys are heated into the β -phase then the orientation of the β -grains is related to that of the original α -grains by the Burgers relationship. When the alloys are cooled and the β transforms back to α the same relationship applies and an original α -grain may have its original orientation or 56 alternative orientations. In practice many of the 57 orientations are in groups and a completely random texture is not produced. If the alloy is heated into the β -phase and during heating in the α -phase region the α -grains recrystallize then the α -grains that transform to β are rotated 30° about the "c" axis and a different texture is produced in the β -phase. Hence the texture of the α -grains after an $\alpha \rightarrow \beta \rightarrow \alpha$ transformation sequence is different if recrystallization occurs, Figure 13.

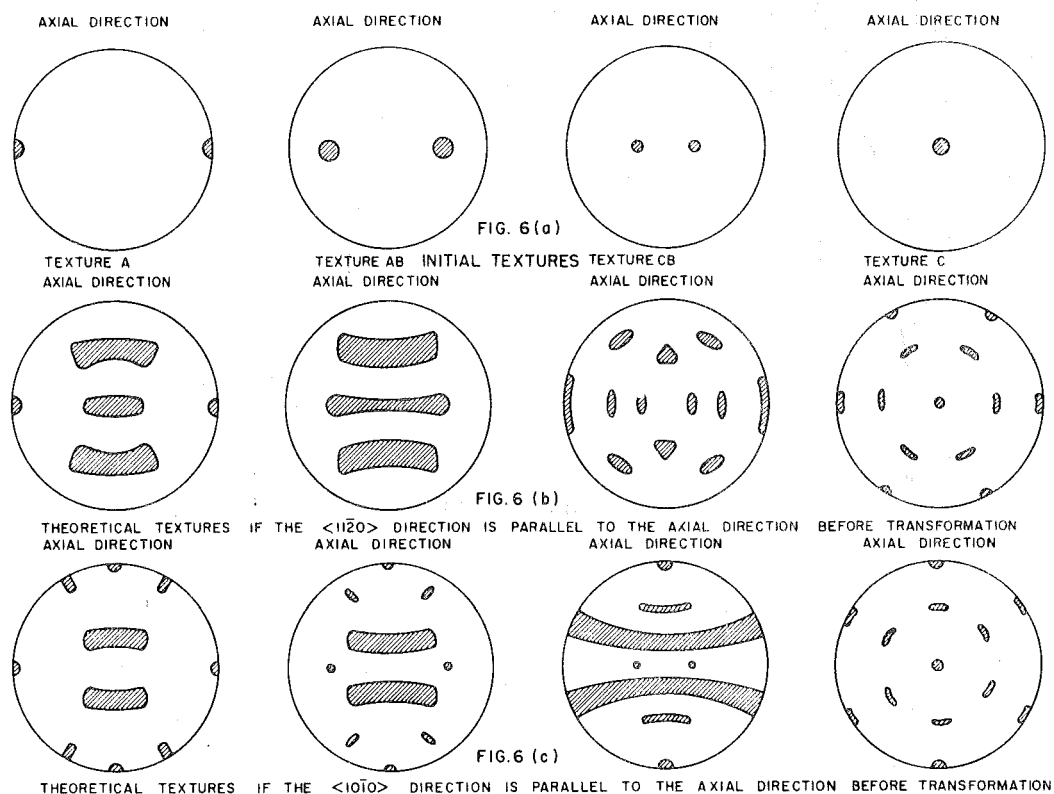


Figure 13 – Theoretical textures after an $\alpha \rightarrow \beta \rightarrow \alpha$ transformation plotted using the Glen-Pugh technique.

When Zircaloy-2 is heated into the β -phase region, while it is in the α -phase region it recrystallizes and when it is cooled and the β retransforms to α some grains are in the DB orientation, Figure 14. Zr-2.5 wt% Nb does not recrystallize during heating into the β -phase region and after retransformation to α some grains are in the D orientation rather than DB, Figure 14.

- B.A. Cheadle and C.E. Ells, "The Effect of Heat Treatment on the Texture of Fabricated Zr-Rich Alloys", *Electrochem. Tech.* 4, 1966, p.329

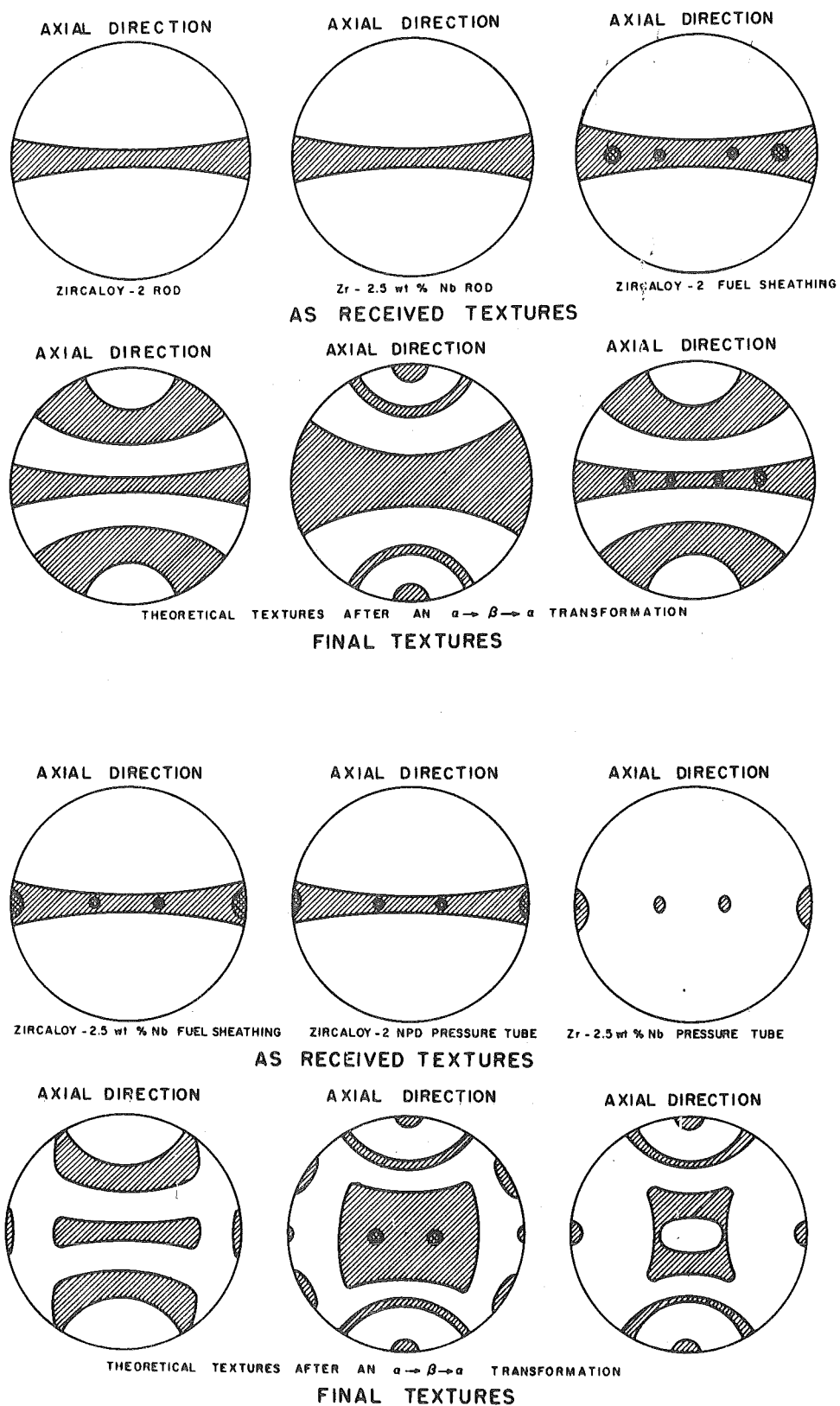


Figure 14 — Relevant (0001) pole figures for the tube and rod materials

THE TEXTURE DEVELOPED WHEN TUBES ARE COLD-WORKED

These general principles can now be applied to the development of texture in tubes. Most extruded tubes have the majority of grains in the A/AB orientations but this texture can be changed by cold work when making the finished tube. The two basic processes used for cold working extrusions to finished tubes are cold drawing and tube reduction.

The deforming force during drawing is axial tension, Figure 15, and the resultant strain is accommodated by compression in the circumferential and radial directions. Since extruded tubes usually have grains in the A/AB orientations, axial deformation will occur by slip, and reductions in circumference and wall thickness will also occur by slip. Thus, drawing does not generally have a large effect on the texture of most extruded tubes.

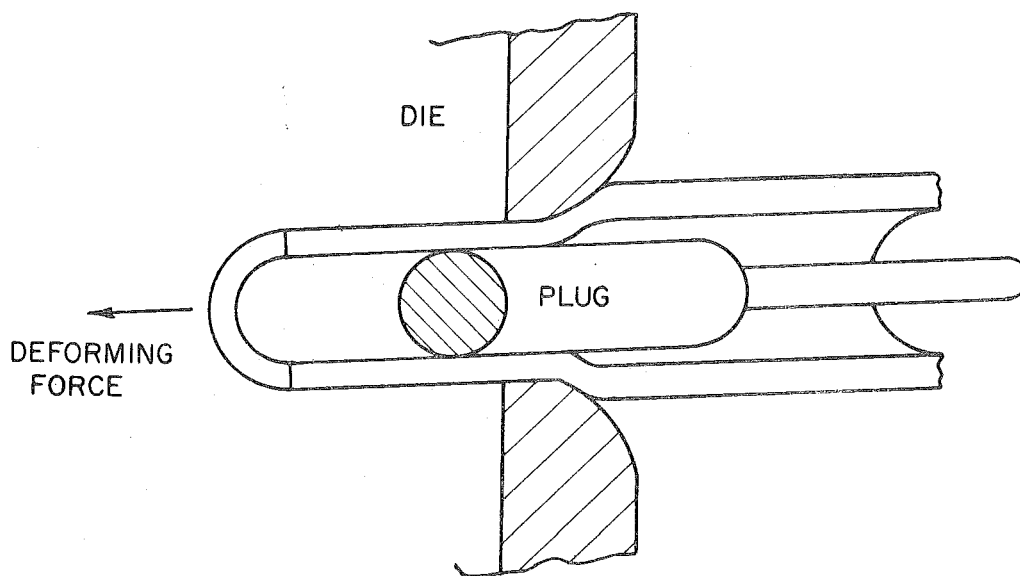


Figure 15 – Tube deformation by drawing

Tube-reduced tubes are deformed by two rolls which have tapered grooves and the inside of the tube is supported by a fixed tapered mandrel, Figure 16. The major strains are circumferential compression when the circumference is reduced, and radial compression when the wall thickness is reduced, with axial elongation in both cases. The direction of major compressive strain will depend on whether the circumference or the wall thickness of the tube has the greatest reduction. Hence tubes can be fabricated that have most of the grains in either the A/AB or C/CB orientations depending on the fabrication history, Figure 17.

- B.A. Cheadle, C.E. Ells and W. Evans, "The Development of Texture in Zirconium Alloy Tubes", *J. Nuc. Mat.* 23, 1967, p.199

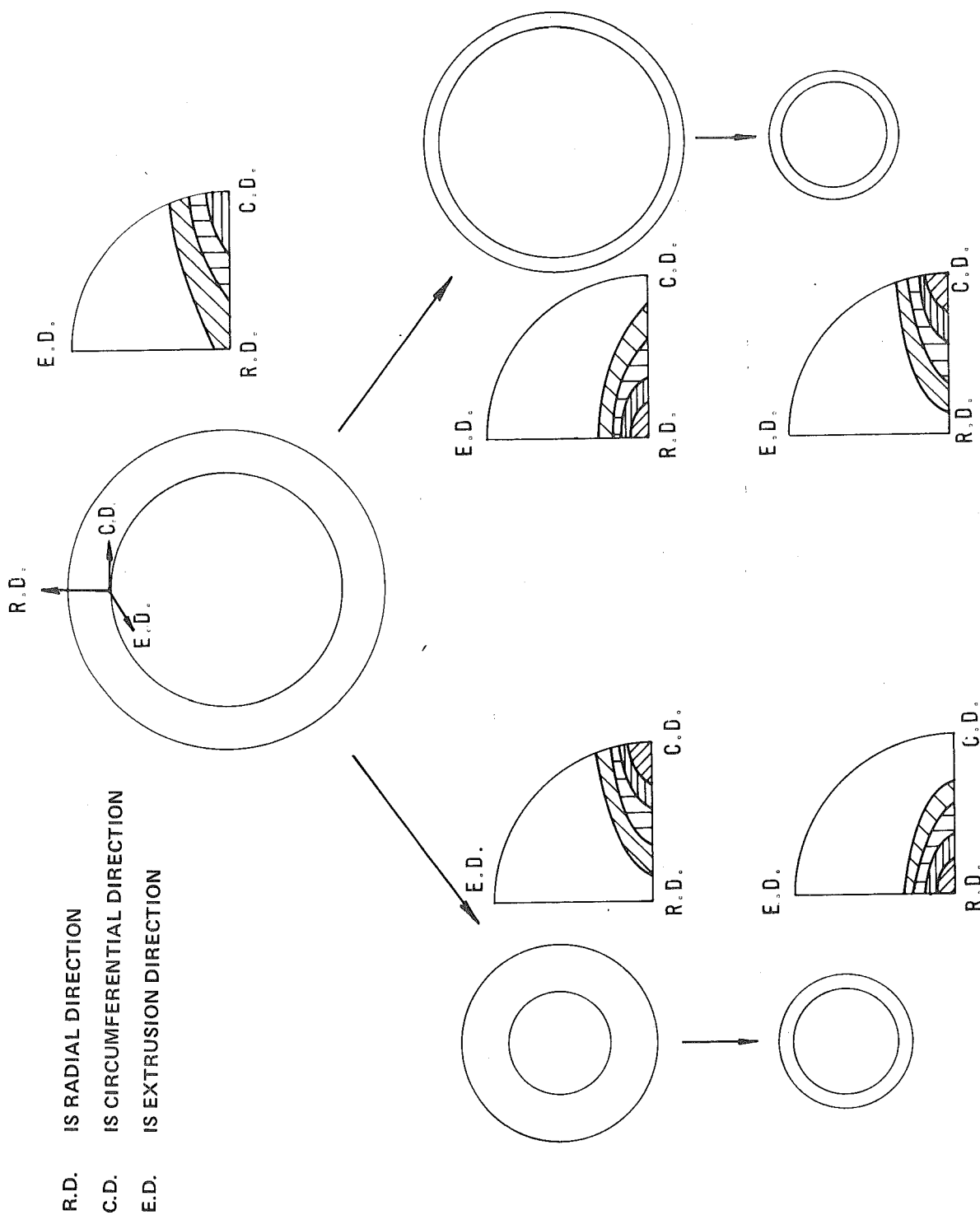


Figure 17 — Basal plane pole figures showing the effect of different fabrication routes on the texture developed by tube reduction

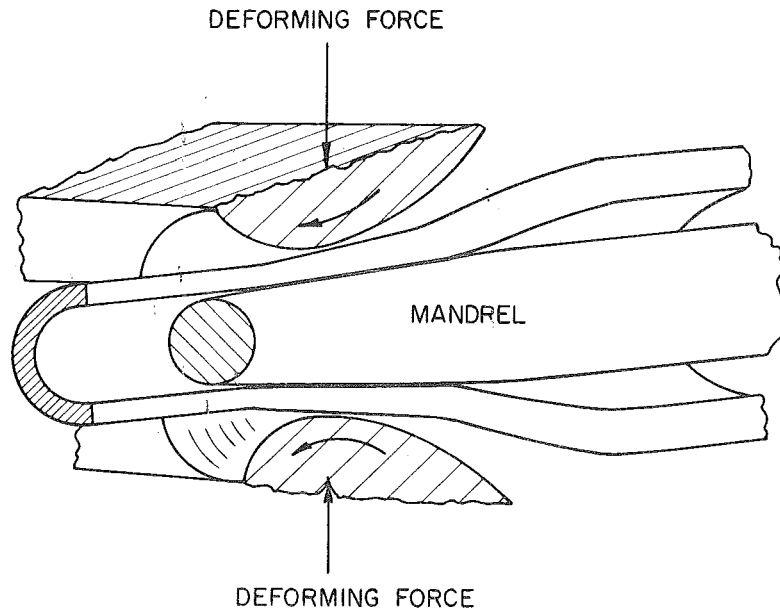


Figure 16 – Tube deformation by tube reduction

The development of texture in tubes by cold working can be summarized by Källstrom's texture rose, Figure 18, which relates strain in the three principle directions to the texture developed.

- K. Källstrom, "Texture and Anisotropy of Zirconium in Relation to Plastic Deformation", *Can. Met. Quart.*, 11, 1972, p.185

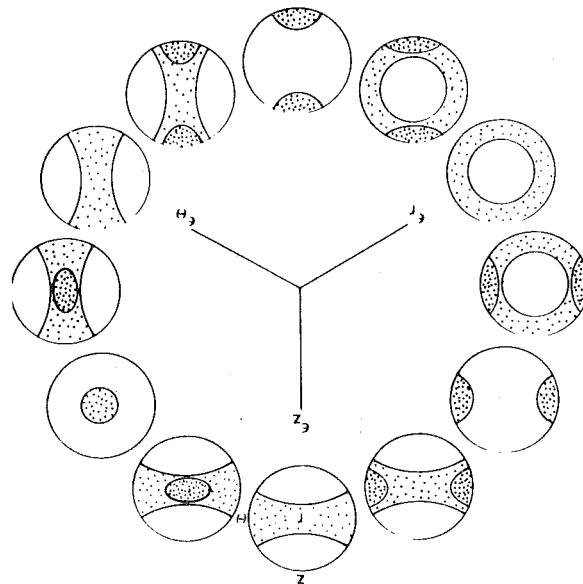


Figure 18 – Texture rose relating the strain ratio to the resulting stable basal plane pole figure.
When Z , θ and r are strains in the longitudinal, circumferential and radial directions.

TEXTURE DEVELOPED IN EXTRUDED TUBES

The texture developed when a tube is extruded is not well explained. The reduction in area of cross-section is usually very high and the direction of major compressive strain depends on the flow pattern. The examination of a partially extruded billet showed that most of the flow was down the conical die face, Figure 19. Hence the major strain was circumferential and most of the grains were in the A/AB orientations, Figure 20.

- B.A. Cheadle and S.A. Aldridge and C.E. Ells, "Development of Texture in Zr-2.5 wt% Nb extruded tubes", *Can. Met. Quart.*, 11, 1972, p.121

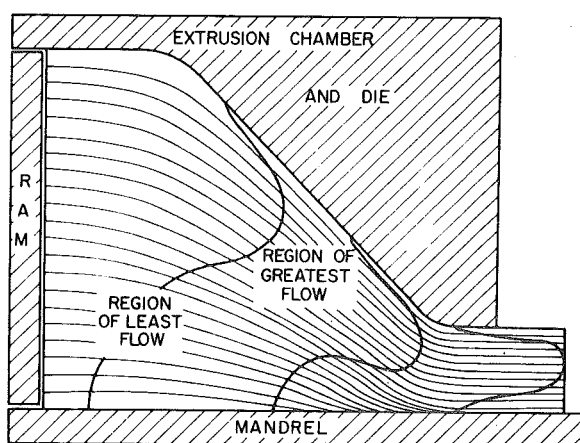
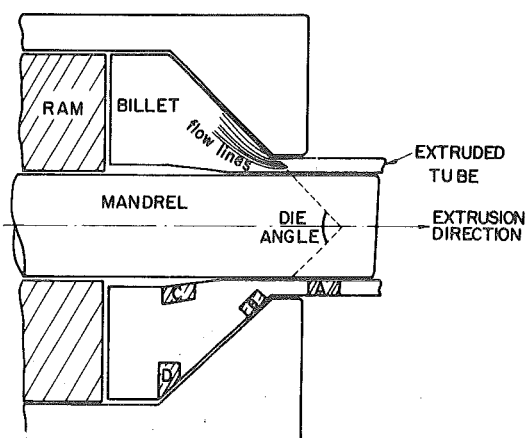


Figure 19 Diagrammatic representation of the flow lines



Position of the texture measurements on the partially extruded billet

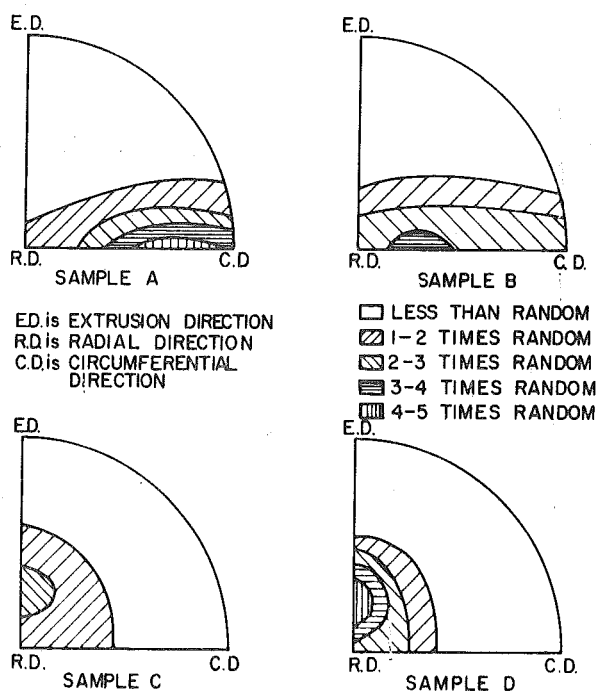


Figure 20 — The (0002) pole figures of samples A,B,C and D from the partially extruded billet

THE EFFECT OF TEXTURE ON THE MECHANICAL PROPERTIES OF TUBES

Texture has a large effect on the mechanical properties of internally pressurized tubes because the biaxial stress system imposes additional restraints on already anisotropic properties. This is shown in the properties of two batches of Zircaloy-2 tubes made by tube reduction but by different fabrication routes so that they had different textures, Table 4.

TABLE 4

THE IDENTITIES OF THE ZIRCALOY-2 SHEATHING BATCHES AND THEIR TEXTURE COEFFICIENTS*

		A	AB	CB	C
Batch 7	60% TR and SR	1.1	1.0	3.7	5.0
Batch 8	62% TR and SR	8.1	2.4	1.3	2.3

* A TC Value of 1.0 is Equivalent to Random Orientation.

TR and SR = Tube Reduced and Stress Relieved.

In the longitudinal tensile test all the grains are oriented for deformation by slip. Batch 8 was the strongest, Table 5, due to small differences in the amount of cold work, differences in composition and/or differences in the stress-relieving heat treatment. The properties in the transverse ring test depend on the relative number of grains that deform by twinning. Batch 8 had the majority of its grains in the A and AB orientations and hence was much stronger than Batch 7. Similarly in the free end burst test where a tube is internally pressurized with oil and the end seals are free to move Batch 8 was strongest.

In the closed end burst test, caps are welded to the ends of the tubes and the tube is under a biaxial stress ratio of 2:1 in the hoop to longitudinal direction. For the tube to form a bulge the wall thickness must decrease and for Batch 7 this can only occur in most grains by compression twinning which results in Batch 7 being significantly stronger than 8.

These two batches of tubes show the significant differences in the properties of cold-worked tubes with different textures. For a given amount of cold work a good combination of strength and ductility for an internally pressurized sealed end tube is obtained when the majority of grains are oriented with their basal plane normals in the radial direction. However, if a tube was required to have maximum hoop strength then the majority of grains should be oriented with their basal plane normals in the circumferential direction.

- K.P. Steward and B.A. Cheadle, "The Effect of Preferred Orientation on the Mechanical Properties and Deformation Behaviour of Zircaloy-2 Fuel Sheathing", AECL Report 2627

TABLE 5

THE ROOM TEMPERATURE MECHANICAL PROPERTIES OF ZIRCALOY-2 TUBES

Batch	Test	0.2% Y.S.		U.T.S. or Burst Strength	
		MPa	kpsi	MPa	kpsi
7	Longitudinal	560	79	700	100
8		590	84	730	104
7	Transverse ring	550	78	690	98
8		620	88	760	109
7	Free end burst	610	87	650	92
8		690	99	720	103
7	Closed end burst	780	111	860	122
8		740	106	780	111

SUMMARY

Zirconium alloys are anisotropic due to the hexagonal crystal structure of the α -phase and the limited number of deformation systems that operate. Pronounced crystallographic textures are produced when alloys are deformed which result in anisotropic mechanical properties. A basic understanding of the crystallographic processes involved allows reasonable predictions of the textures produced and their effect on mechanical properties.

FOR FURTHER INFORMATION

- T. Okada, H. Hirano, N. Kunimoto, "Texture and Microstructure of Thin Walled Zircaloy-2 Tubes", *Electrochem. Tech.*, **4**, 1966, p. 374
- D.O. Hobson, "Texture Changes Produced During Zircaloy-4 Tubing Fabrication: From Forged Billet to Finished Tubing". *Applications Related Phenomena in Zirconium and its Alloys*, Philadelphia, 1968, ASTM Special Technical Publication 458
- E. Tenckhoff and P.L. Rittenhouse, "Texture Development and Texture Gradients in Zircaloy Tubing". *Applications Related Phenomena in Zirconium and its Alloys*, Philadelphia, 1968, ASTM Special Technical Publication 458
- P.D. Kaufmann, "Texture Development and Phase Stability of 0.5 Cb-0.5 Mo Zirconium During Fabrication to Sheet Form". *Applications Related Phenomena in Zirconium and its Alloys*, Philadelphia, 1968, ASTM Special Technical Publication 458

CRNL-1208

LECTURE NO. 4

BEHAVIOUR OF HYDROGEN IN ZIRCONIUM ALLOYS

by

C.E. Ells

1. REASON FOR THE IMPORTANCE OF HYDRIDE

Zirconium and zirconium alloys absorb large quantities (up to about 50 at %) of hydrogen in solid solution at temperatures $\geq 775\text{K}$. This solubility decreases rapidly with decreasing temperature, and the excess hydrogen precipitates as a hydride phase, Figure 1.

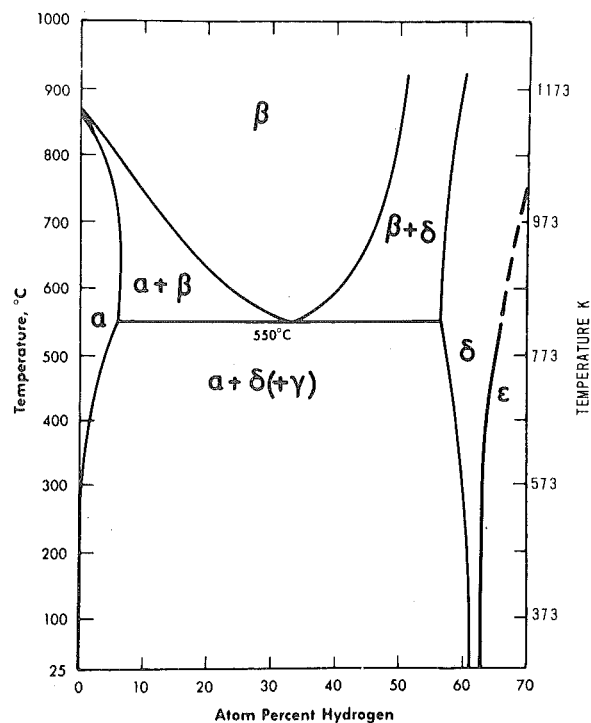


Figure 1 — The Zirconium — Hydrogen Phase Diagram.

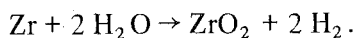
There are three stoichiometric hydride phases,

γ	—	face centered tetragonal — formed on fast cooling	} Zr-H_y where $y = 1.5 \text{ to } 1.67$
δ	—	face centered cubic — formed on slow cooling	
ϵ	—	face centered tetragonal — Zr-H_x where $x > 1.67$	

(Much of the literature on zirconium hydride uses ppm by weight as the unit of hydrogen concentration, 1 at % = 108 ppm).

The hydride phase generally exhibits very low ductility, and hence under some conditions has a deleterious effect on the mechanical behaviour of components made from zirconium alloy. These deleterious effects are particularly evident at temperatures $\leq 425\text{K}$ (150°C). The fabrication methods for zirconium alloy components are controlled so that

the hydrogen concentration in finished products has the acceptably low limit of 25 ppm. In power reactors, however, the zirconium alloys are used in contact with water. The corrosion reaction forming zirconium oxide, releases hydrogen by the reaction:



Some of this hydrogen enters the zirconium.

2. EFFECTS ON DUCTILITY

In some very special conditions hydride can increase the strength of the zirconium alloy. One condition is when very pure zirconium is quenched from a temperature at which all the hydrogen is in solution.

— *D.G. Westlake, Acta Met. 12, 1964, p.1373*

A second condition is when large quantities of hydride, several thousand ppm, are present.

— *H.H. Burton, Hanford Report HW-61077, 1959*

For alloys and conditions of practical interest, however, the hydrogen concentrations are so low (<200 ppm) that there is no appreciable affect on strength and we are concerned only with effects on ductility.

Stoichiometric hydride is so brittle that tensile tests on it have little real meaning, Figure 2.

— *K.G. Barraclough and C.J. Beevers, J. Met. Sci. 4, 1969, p.518*

It is not surprising, therefore, to find that small quantities of hydride can have an embrittling effect. Here it is very important to realize that the hydride phase is precipitated as platelets, Figure 3.

The platelets observed in optical microscopy, Figure 3(a), 3(b) have in turn a finer platelet substructure, Figure 3(c). The platelets may be at grain boundaries, or they may be intergranular. All the factors which determine the location of the hydride have not been established. However, Ambler has shown that certain grain boundaries are highly preferred sites for the hydride formation:

— *J.F.R. Ambler, J. Nucl. Mat. 28, 1968, p.237*

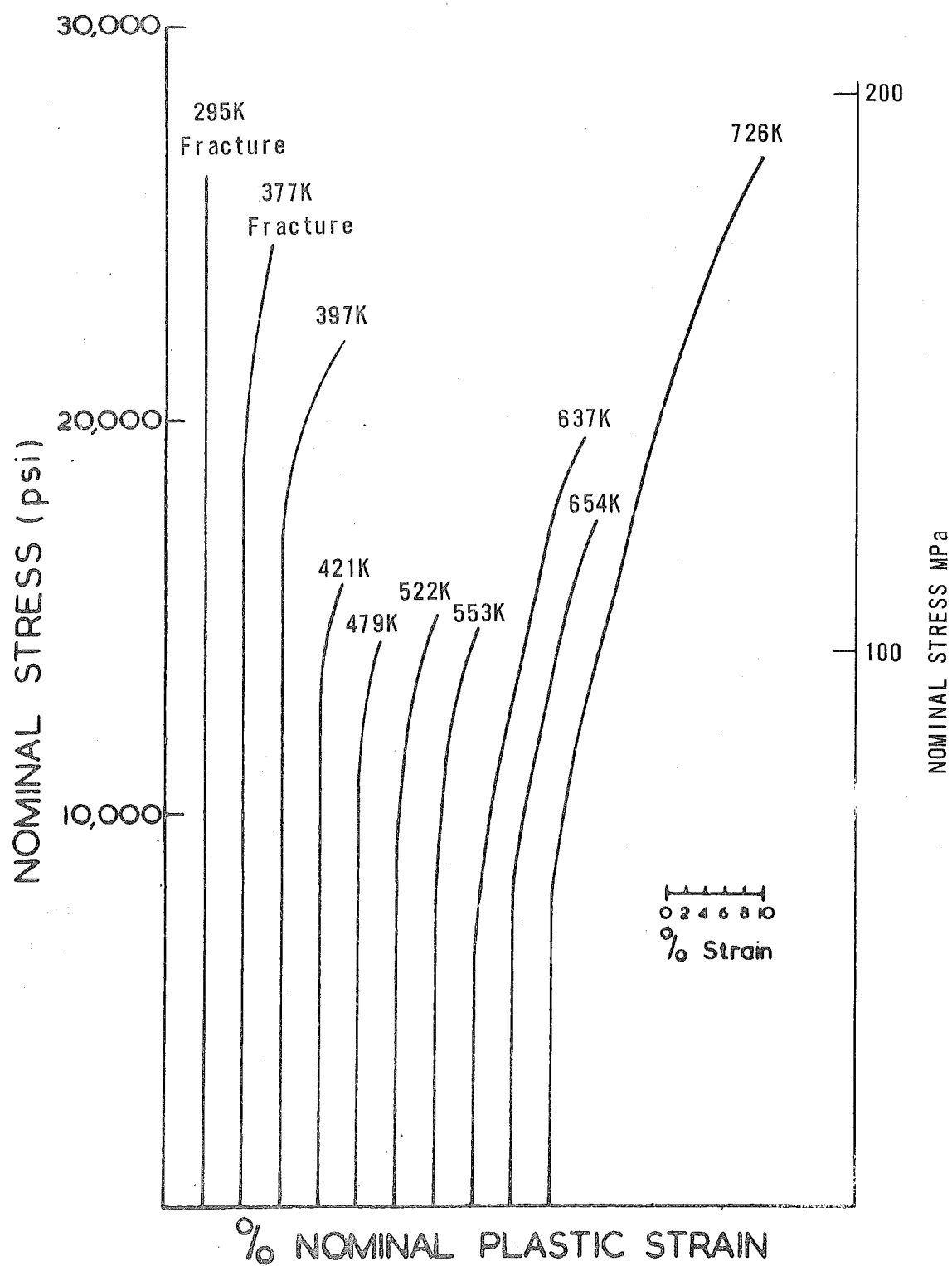
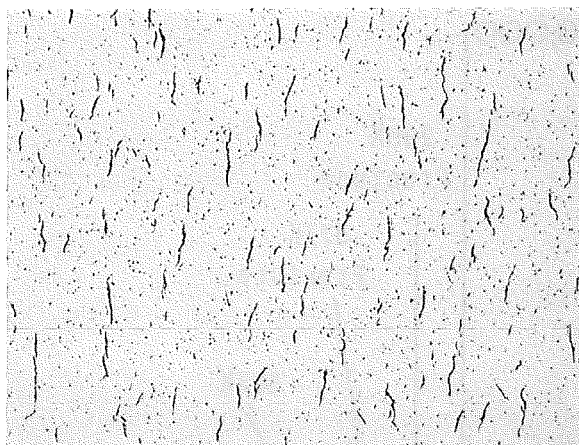


Figure 2 – Typical Nominal Stress-Strain curves of $\delta\text{ZrH}_{1.66}$.

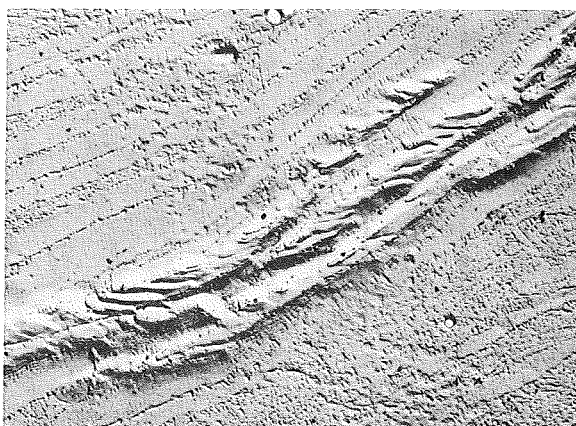


Figure 3 (a) – Hydride Orientation Observed on a Transverse Section Through the Wall of a Quenched and Aged Zr-2.5 Wt% Nb Pressure Tube, Viewed in Optical Microscopy.



200 X

Figure 3(b) – Hydrides Viewed in Optical Microscopy; Example of Highly Oriented Platelets.



10 000 X

Figure 3(c) – Showing Composite Structure of Hydrides in a Transverse Section. Replica Viewed by Transmission Electron Microscopy.

45 X

Figure 3 – The Form of the Hydride Platelets

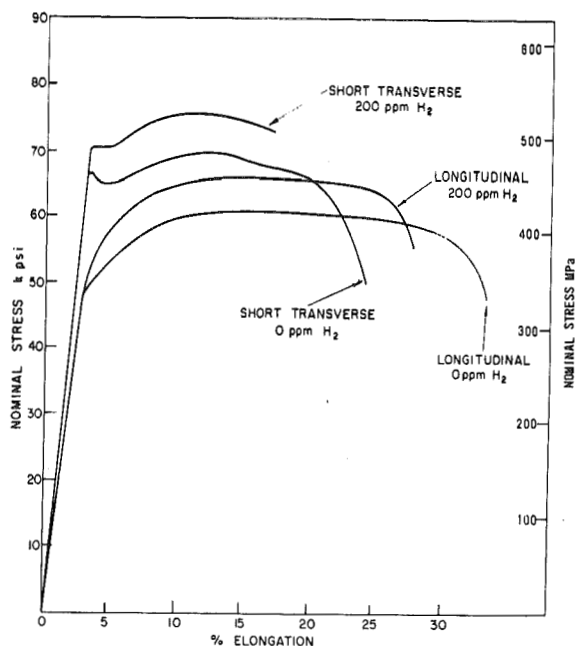


Figure 4 — Typical Load Elongation Curves for Annealed Zircaloy-2 Tested at Room Temperature. Normals to the hydride platelets were in the short transverse direction.

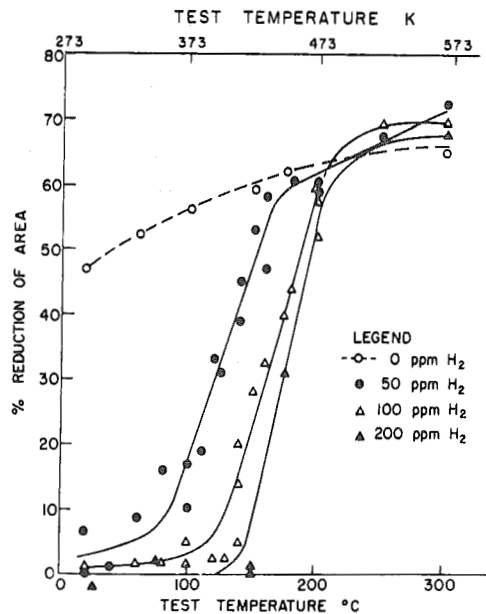


Figure 5 — Percent Reduction of Area as a Function of Test Temperature and Hydrogen Concentration for Cold-Worked Short Transverse Tensile Test Specimens.

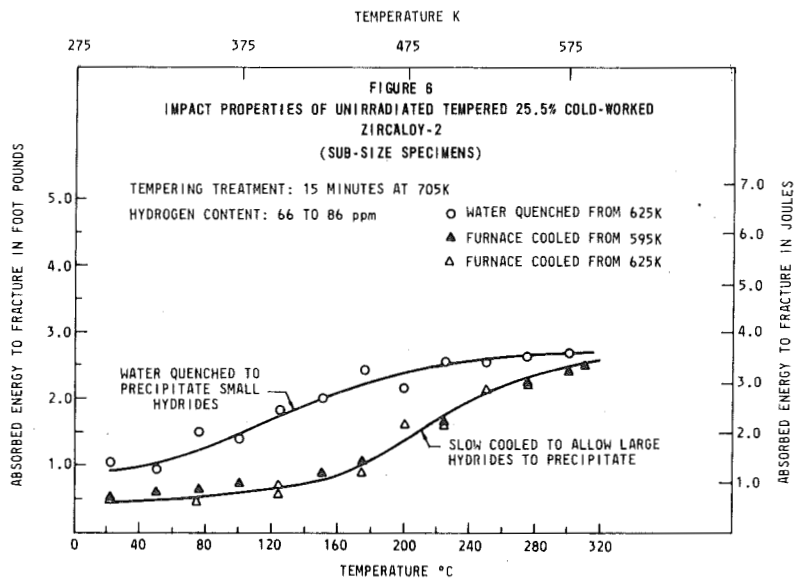


Figure 6 — Impact Properties of Unirradiated Tempered 25.5% Cold-Worked Zircaloy-2. Sub-Size Specimens.

The platelets can be randomly oriented, appear in bands, Figure 3(a), or they may have a high preferential orientation, Figure 3(b). If the latter, then the effect on ductility will be more deleterious when the plane of the platelets is perpendicular to the tensile stress axis (short transverse specimens). Conversely, platelets parallel to the tensile axis have little effect on ductility, (longitudinal specimens) Figure 4. In very adverse conditions, ductility can be markedly decreased by little as 50 ppm hydrogen.

— *R.P. Marshall and M.R. Louthan, Trans. ASM 56, 1963, p. 693*

Generally, however, at the hydrogen concentrations of interest, <200 ppm, there is no effect on tensile ductility at temperatures $>475\text{K}$ Figure 5.

— *W. Evans and G.W. Parry, Electrochem. Tech. 4, 1966, p. 225*

Other aspects of hydride effects on ductility have been studied extensively. It has been shown that large hydrides have a more deleterious effect on impact strength than do small hydrides (at the same hydrogen concentration), Figure 6.

— *L.M. Howe, AECL Report, AECL-1239, 1961*

Also the deleterious effect of the hydride is enhanced with increasing strain rate, as exhibited in bend tests, Figure 7.

— *C.E. Coleman and D. Hardie, J. Nucl. Mat. 19, 1966, p. 1*

For some of the stronger zirconium alloys a form of delayed failure occurs, Figure 8.

— *D. Weinstein and F.G. Holtz, Trans. ASM, 57, 1964, p. 284.*

Summarizing the effects on ductility we can say that the deleterious effect increases as:

- (a) temperature falls below $\approx 425\text{K}$,
- (b) hydrogen concentration increases,
- (c) hydrides become larger,
- (d) hydride platelets become oriented perpendicular to the tensile axis.

It is the task of the corrosion scientist to keep the hydrogen concentration low, and of the fabricator and physical metallurgist to maintain the desired platelet orientation.

3. THE DIFFUSION OF HYDROGEN IN ZIRCONIUM

In considering how to avoid having the hydride form in locations deleterious to ductility it has been necessary to study the diffusivity in detail. It has been found that gradients of each of concentration, temperature and stress are important. Hence it is sometimes

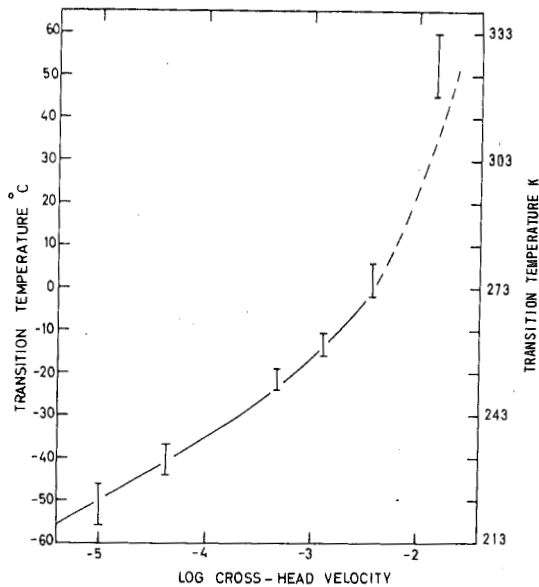


Figure 7 — The Effect of Strain Rate on the Fracture Transition Temperature in Bend Specimens. Hydrogen concentration in the specimens was 100 ppm and the units of cross-head velocity are inches.sec⁻¹.

necessary to use all three terms in the general diffusion equation:

$$J = -\frac{DC_x}{RT} \left[RT \frac{d \ln C_x}{dx} + \frac{Q^*}{T} \frac{dT}{dx} - \frac{V^*}{3} \frac{d\sigma}{dx} \right]$$

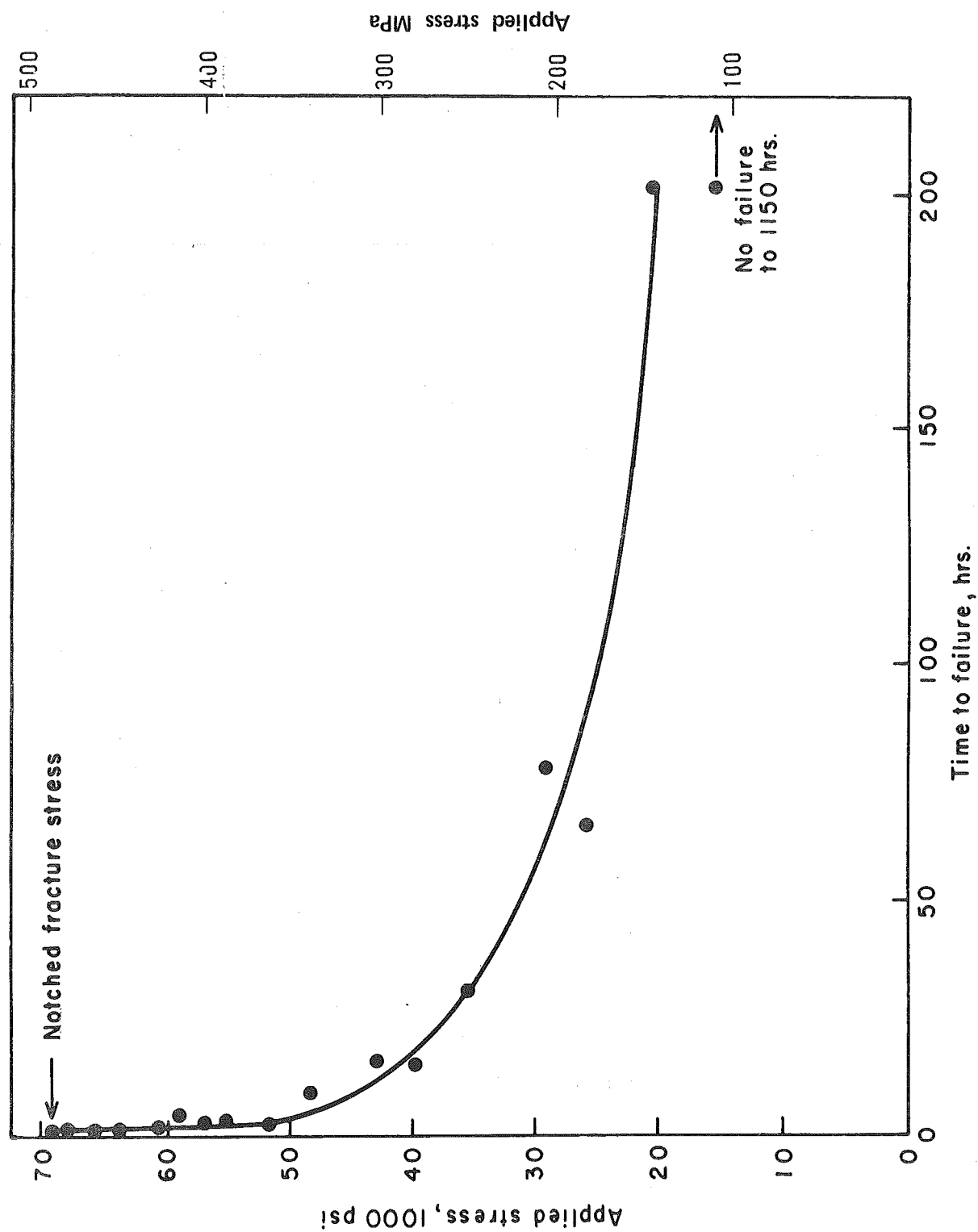
where:

- J is the hydrogen flux
- D is the diffusivity of hydrogen in the metal
- R is the gas constant
- T is the temperature
- C_x is the concentration of hydrogen at any point x
- Q* is the heat of transport of hydrogen in the metal
- V* is the volume of transport of hydrogen in the metal, and
- σ is the tensile stress (a compressive stress will have negative values)

The diffusivity is quite high

$$D = 0.217 \exp \left[\frac{-8380}{RT} \right] \text{mm}^2 \text{s}^{-1}.$$

J.J. Kearns, *J. Nucl. Mat.* 27, 1968, p.64



At 575K, for instance, $\sqrt{4Dt}$ is about 7 mm for 24 hours. Values of the heat of transport, about 6 k cal mole⁻¹.

— A. Sawatzky, *J. Nucl. Mat.* 2, 1960, p.321

and the volume of transport, about 200 mm³ mole⁻¹.

— C.E. Ells and C.J. Simpson paper in *Proceedings of Seven Springs Conf. on Hydrogen in Metals*, September 1973

results in slower, but still significant, movements of hydrogen.

There is yet another mechanism of hydrogen movement. When hydrogen is entering at the surface of a component, it should be possible to predict equilibrium hydrogen concentration throughout the component from the phase diagram in Figure 1. In practice the hydrogen concentration in the interior of the component is often higher than expected, a phenomenon known as 'supercharging'. For a recent article on supercharging see:

— G.P. Marino, *Mat. Sci. Eng.* 7, 1971, p.335

4. THE ORIENTATION OF THE HYDRIDE PLATELETS

In evaluating effects of the orientation of the hydride platelets it is convenient to have a quantitative description of the amounts of orientation. Normally the experimenters have quoted a parameter, f_x , defined as a percentage of hydrides, whose traces in the plane of observation make an angle with a reference direction in the range $x - 90^\circ$, Figure 9. Defined in this way, a high f_x value leads to a low tensile ductility when the stress axis is parallel to the reference direction.

Three factors, alone or in combination, affect the hydride orientation:

(a) Crystallographic — within given grains a few habit planes are preferred; notably (10 $\bar{1}$ 0) and (10 $\bar{1}$ 7).

(b) Prior strain — hydride platelets tend to form parallel to the rolling plane, Figure 10.

— G.W. Parry and W. Evans, *Chalk River Report*, AECL-1707, 1962

(c) Stress — hydride platelets become aligned perpendicular to the tensile stress axis, Figure 11.

— P.L. Rittenhouse and M.L. Picklesimer, *Oak Ridge Report*, ORNL-TM-844, 1964

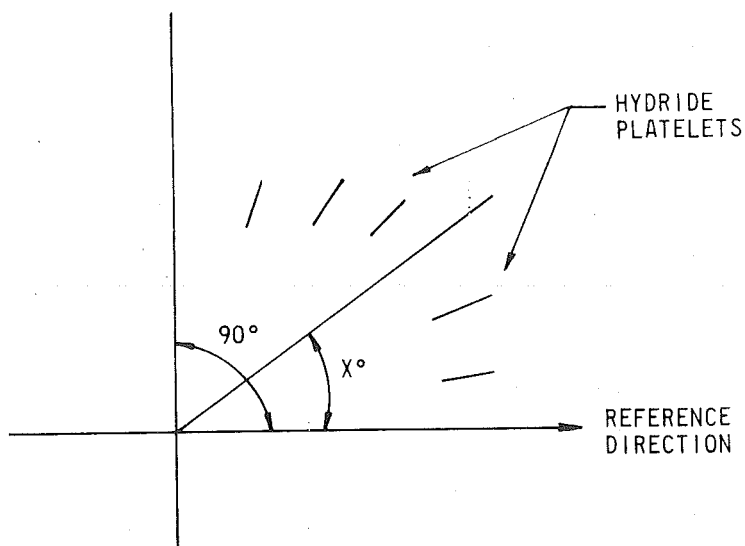


Figure 9 – A Quantitative Description of Hydride Orientation.

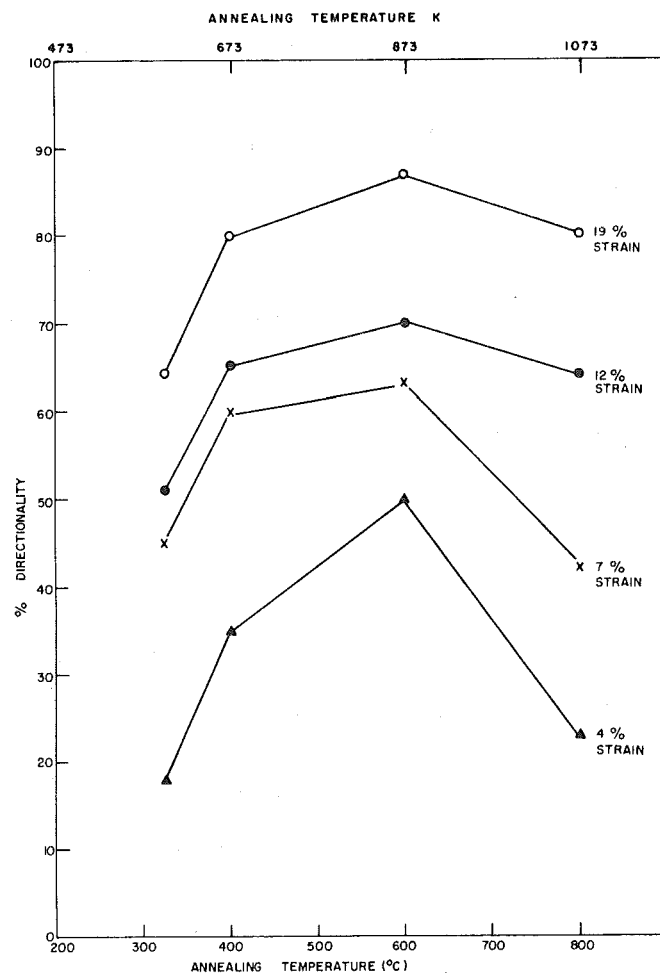


Figure 10 – Effect of Strain and Annealing Temperature on Hydride Orientation in Zircaloy-2 wire. Hydrogen Concentration 100 ppm. Specimens annealed 30 min at Temperature shown, after deformation. Here the % directionality is a measure of the proportion of platelets whose normals are parallel to the direction of thinning in the wire.

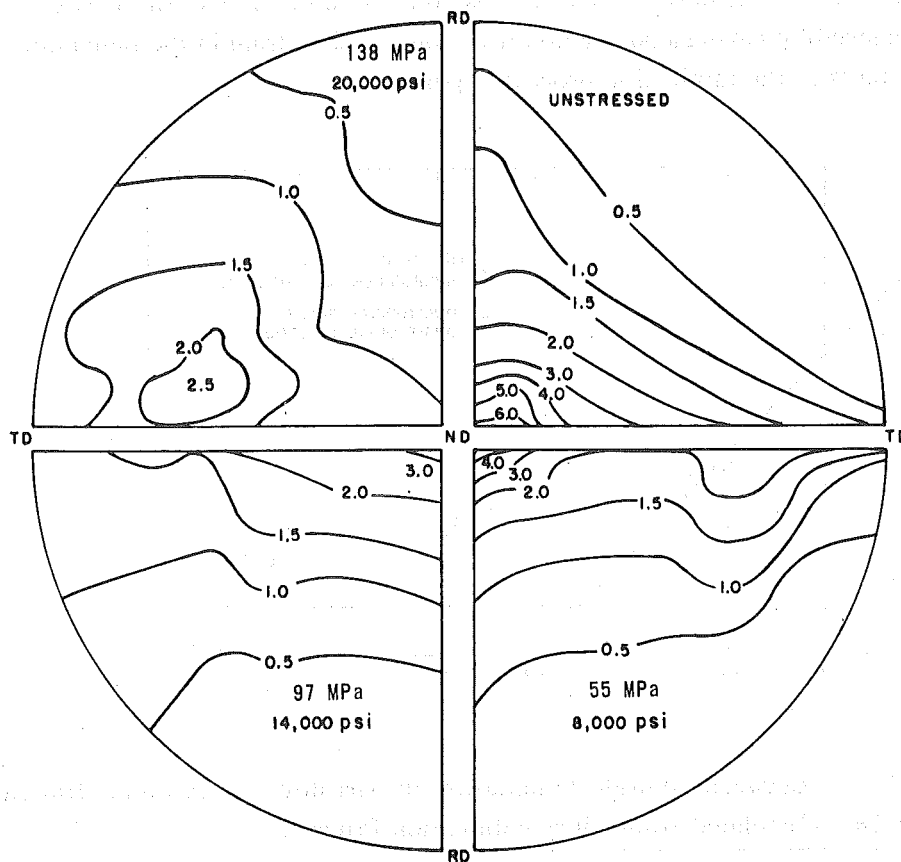


Figure 11 — Hydride Pole Distribution for Stress Oriented Zircaloy-2. Hydrogen Concentrations 170 ppm in Schedule J Material. Specimens Slowly Cooled from 400°C, Stressed in the Transverse Direction at the Stresses Shown.

5. THE HYDRIDE ORIENTATION IN TUBES

For most reactor applications, we are interested in the hydride orientation in the fuel sheath tubing and pressure tubes. Also, in these tubes the principal stress direction is circumferential. Hence, hydrides in the radial planes will be undesirable; rather any hydride present should be in circumferential planes. We must therefore:

- (a) ensure that the hydride platelets in the absence of applied stress are circumferentially oriented (strain orientation), and
- (b) minimize the reorientation under stress (stress orientation).

Of these, (a) is easier to achieve than (b). It is well established that the desired strain orientation is achieved by having a large amount of compressive strain in the radial direction during the final stages of the fabrication process, Figure 12.

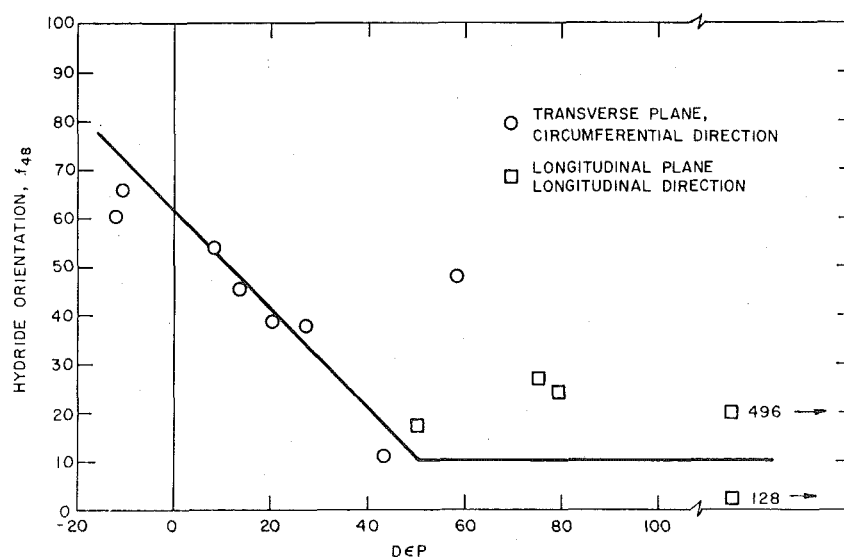


Figure 12 – Relation Between Hydride Orientation in Zircaloy-2 Tubes and Directional Strain Parameter DeP Calculated from Final Fabrication Process.

Tubing Plane	Reference Direction	Directional Strain Parameter (DeP)
Transverse	Circumferential	$[\Delta D - \Delta W]$,
Longitudinal	Longitudinal	$[\Delta L - \Delta W]$,

where ΔL , ΔW and ΔD are the percent change in length, wall thickness and mean diameter respectively.

— R.P. Marshall, *J. Nucl. Mat.* 24, 1967, p.49

All fuel sheathing and pressure tubes are fabricated to a schedule based on this rule.

The guide for avoidance of stress orientation is more complex. The stress orientation seems to occur by two mechanisms:

- (a) orientation of the hydride nuclei,

— C.E. Ells, *J. Nucl. Mat.* 35, 1970, p.306

(b) and growth of hydride platelets.

— C.E. Ells and C.J. Simpson, *Proc. Conf. on Hydrogen in Metals and Alloys, Seven Springs, Pa. September 1973*

Both mechanisms favour formation of hydride platelets perpendicular to the applied tensile stress. Experimentally, the degree of orientation is found to increase with stress, Figure 13.

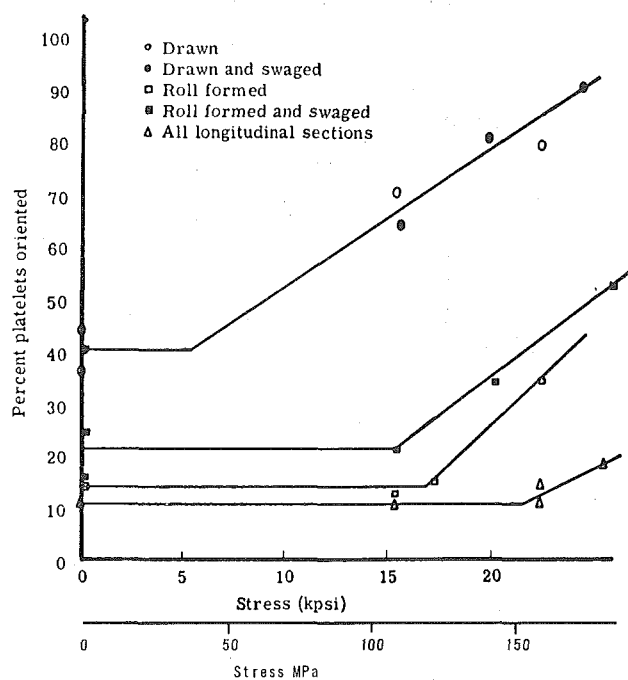


Figure 13 — Effect of Stress Level on Orientation of Hydride in Specimens Taken from Zircaloy-2 Tubes. Hydrogen Concentration ≤ 200 ppm. Constant Load Applied to Tensile Test Type Specimens Slowly Cooled from 675K at Stress Shown. The Ordinate is f_{50} .

— M.R. Louthan and R.P. Marshall, *J. Nucl. Mat.* 9, 1963, p.170

Also, the effect of stress on orientation becomes more pronounced as the component of basal plane normal parallel to the tensile axis is increased, Figure 14.

— P.L. Rittenhouse, *Trans. ANS* 10, 1969, p.464

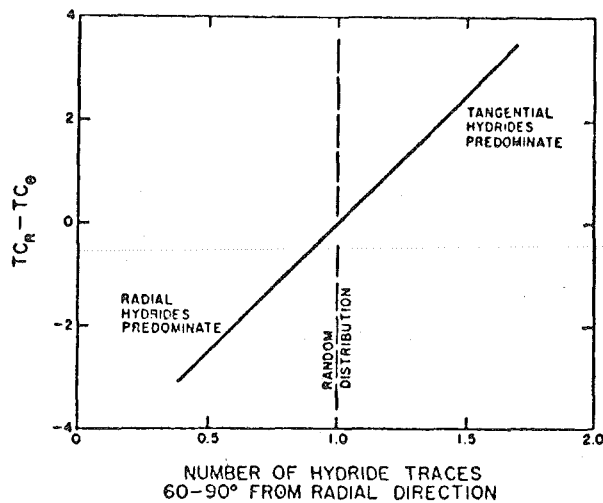


Figure 14 — Stress Orientation of Hydride in Internally Pressurized Zircaloy-2 and Zircaloy-4 Tubes Correlated with Crystallographic Texture. Hydrogen Concentration 150 ppm. Specimens Slowly Cooled While Stressed to 20 000 psi (hoop). Texture Variable Shown is Difference Between Texture Coefficient of Basal Plane Normal in Radial, TC_R , and in Tangential, TC_θ , direction.

6. FINAL SUMMARY

- (a) Hydrides can have a deleterious effect on the ductility of zirconium alloy.
- (b) Fabrication routes for tubes used in power reactors are chosen to minimize the formation of adversely oriented hydrides.
- (c) By maintaining a favourable strain hydride orientation, and by keeping the hydrogen concentration below about 200 ppm, hydride presents no serious problem to the operation of CANDU reactors.

FURTHER READING

- A paper "Delayed Hydrogen Embrittlement in Zr-2.5 wt% Nb", C.J. Simpson and C.E. Ells, *J. Nucl. Mat.* 1974 contains references which will lead back to much of the relevant literature on hydrogen in zirconium alloys.
- Note also that most of the literature on hydrogen in titanium is directly relevant to zirconium.
- The literature on oriented hydrides up to April 1968 is reviewed in C.E. Ells, *J. Nucl. Mat.* 28, 1968, p.120.

LECTURE NO. 5

IRRADIATION DAMAGE IN ZIRCONIUM AND ITS ALLOYS

by

D.O. Northwood and R.W. Gilbert

In 1946 Wigner, *Journal of Applied Physics* 17, p.857, first suggested that an energetic particle striking an atom in a crystalline matrix could impart sufficient kinetic energy to displace the atom from its normal position. Since that time many studies have been made of the properties and behaviour of radiation induced lattice or "point" defects and of their effects on the properties of materials.

Early studies were made on high purity crystals of the noble metals and revealed a very complex recovery spectrum starting at liquid He temperatures (4.2K). More recent studies arise from the need to understand and hopefully predict the changes in engineering properties of structural materials subjected to fast particle irradiation in nuclear reactors.

BASICS OF RADIATION DAMAGE

(1) Number of Atomic Displacements

A theoretical analysis of the number of atomic displacements produced when an incoming particle imparts a certain amount of energy to a lattice atom can be found in the paper by *Kinchin and Pease, Report of Progress in Physics*, 18, 1955, p.1-51. The first atom to receive the energy from the impinging particle is called the "primary knock-on atom" (PKA). If the PKA energy is:

(a) Greater than the *threshold displacement energy*, the atom is displaced from its lattice position, leaving a vacancy and forming an interstitial atom in the region where it comes to rest, Figure 1. This combination of a vacancy and an interstitial is called a "Frenkel pair".

(b) Less than the threshold displacement energy, the atom will recoil back to its own lattice site.

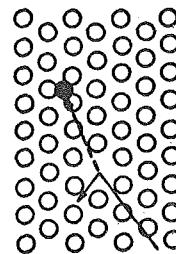


Figure 1 — Production of a Vacancy and Interstitial by a Primary Knock-On.

- NORMAL ATOM
- INTERSTITIAL ATOM
- PATH OF PRIMARY PARTICLE
- PATH OF KNOCK-ON ATOM

If the PKA has sufficient energy it may in turn dislodge other atoms and so on until the energy is expended to the point where no further displacements are produced. The entire process is known as a *collision cascade*. Calculations of the number of Frenkel pairs produced in such a cascade from 1 MeV neutron are typically 600-1000 assuming no defect rearrangement or annihilation.

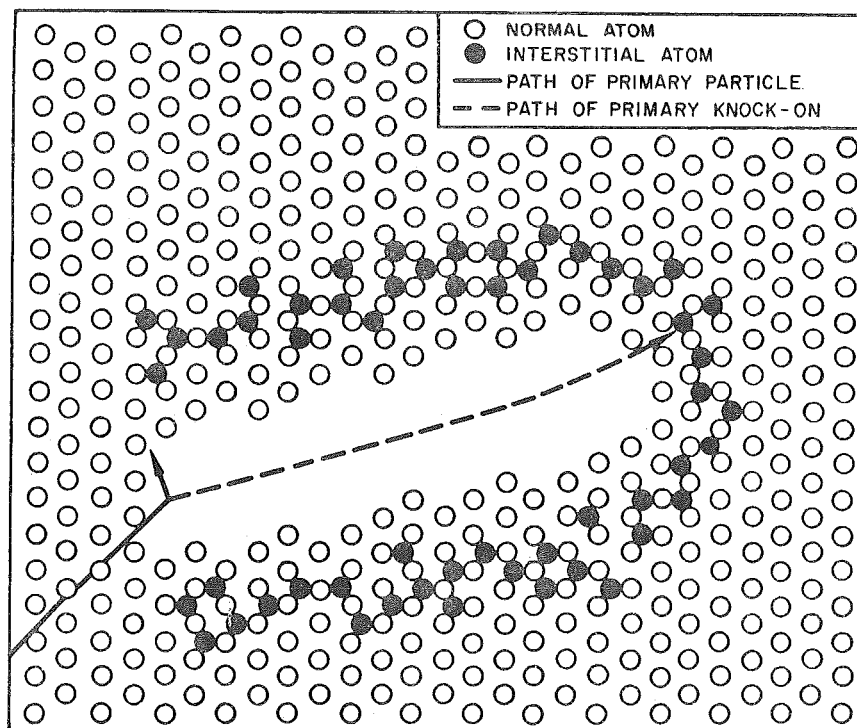
(2) Spatial Distribution of Defects

The basics of our understanding of the spatial distribution are to be found in the classic paper by Brinkman, *American Journal of Physics*, 24, 1956, p.246-267.

The essence of his reasoning is:

The PKA displaces essentially every atom in its path, some of which displace other atoms. The density of the damage increases as the energetic particle loses energy, producing at the end of each secondary knock-on track a region in which all atoms are dislodged. The ranges of the displaced atoms are short, only a few interatomic distances, resulting in a *displacement spike*, Figure 2. The interstitials form a shell around a large multiple vacancy (hole). The pressure from the interstitials and the violent motions of the individual atoms that have been displaced from their normal positions heat the region to a high temperature, well above the melting point, producing what is known as a *thermal spike*. The interstitials could then "fall back" into lattice positions thereby resulting in little permanent damage.

Figure 2 — Schematic Representation of a Displacement Spike (After Brinkman)



This model has since been refined, for example by *Seeger*, *Proceeding of the Symposium on Radiation Damage in Solids and Reactor Materials*, IAEA, Vienna, 1, 1962, p.101-127. His model is illustrated in Figure 3. He introduces the concept of:

- A *focuson*, focused momentum transfer along a crystallographic direction.
- A *dynamic crowdion*, a dynamic defect travelling along a close packed direction via a series of replacement collisions

Again there is a region with a large fraction of atoms missing which is surrounded by a "cloud" of interstitials. He however assumes that upon relaxation of the region, interstitials far enough away from the spike, do not feel its strain field and so do not return to it. The region of missing atoms at the centre of the cascade is termed a *depleted* or *Seeger zone* the size of which is estimated to be typically ≤ 1.0 nm.

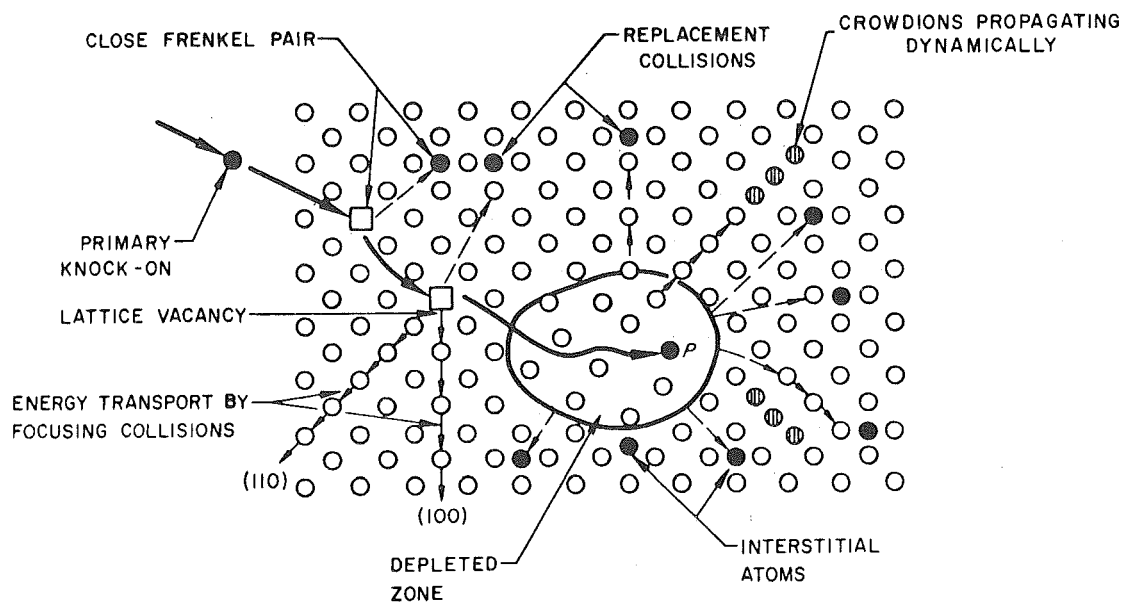
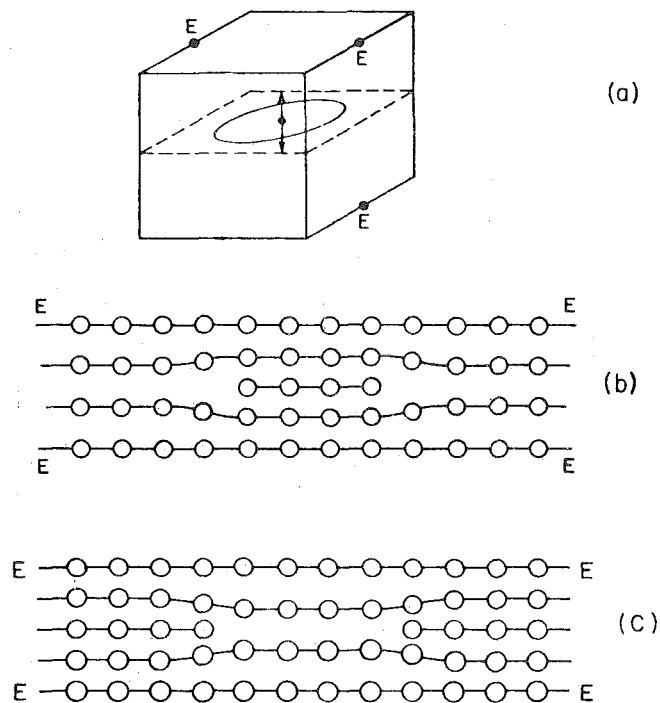


Figure 3 -- Schematic Representation of Radiation Damage (after Seeger).

At reactor operating temperatures the defects can be rearranged or annihilated. Collections of vacancies or interstitials can form dislocation loops which are schematically illustrated in Figure 4.

Figure 4 Schematic Representation of a Dislocation Loop (b) Interstitial (c) Vacancy.



The atomic lattice is distorted near a loop and it is this distortion, or strain field, that allows the loop to be seen in transmission electron microscopy (TEM). In the microscope, electrons passing through distorted areas are diffracted away from the transmitted beam and are prevented from reaching the image plane by an objective aperture. This *diffracted contrast* results in the imaging of loops as dark or electron deficient rings. Techniques exist for distinguishing between vacancy and interstitial loops but these do not work when the loops are too small. Loops or defect clusters smaller than ≈ 2 nm are difficult to resolve as loops and defects in this size range are often referred to as "black spot" damage.

Additional References

- F.A. Nichols, "Effects of High Neutron Exposures on the Properties of Materials", *Annual Review of Materials Science*, 2, 1972, p.463-500
- J.A. Brinkman and H. Wiedersich, "Mechanisms of Radiation Damage in Reactor Materials", *ASTM STP 380*, 1965, p.3-39
- J. Weertman and J.R. Weertman, "Elementary Dislocation Theory", *Macmillan Series in Materials Science*, 1964
- M.W. Thompson, "Defects and Radiation Damage in Metals", *Cambridge University Press*, 1969

TEM OBSERVATIONS OF IRRADIATION DAMAGE IN ZIRCONIUM ALLOYS

(1) Factors Affecting Size and Distribution of Damage

Exposure of zirconium alloys to fast neutron irradiation produces defects in the α -Zr phase of dimensions and distributions which are determined by:

fluence

temperature

alloy content.

(a) Neutron Fluence

The only data covering a wide range of neutron fluences were given by *Williams and Gilbert*, "Radiation Damage in Reactor Materials", IAEA, 1, 1969, p.235-247. Their results together with more recent CRNL data are given in Figure 5. The main points to be noted are that for zirconium alloys:

- No damage is seen by TEM at fluences less than $2-3 \times 10^{23} \text{ n.m}^{-2}$ although the yield strength is increased.
- At higher fluences 'black-spots' and dislocation loops are seen, the density increasing with fluence, Figure 6.

The defect size increases with increasing fluence.

N_d , the number of atom sites involved in the damage, saturates at a fluence of about $1 \times 10^{25} \text{ n.m}^{-2}$ which is about the fluence at which the yield strength levels off.

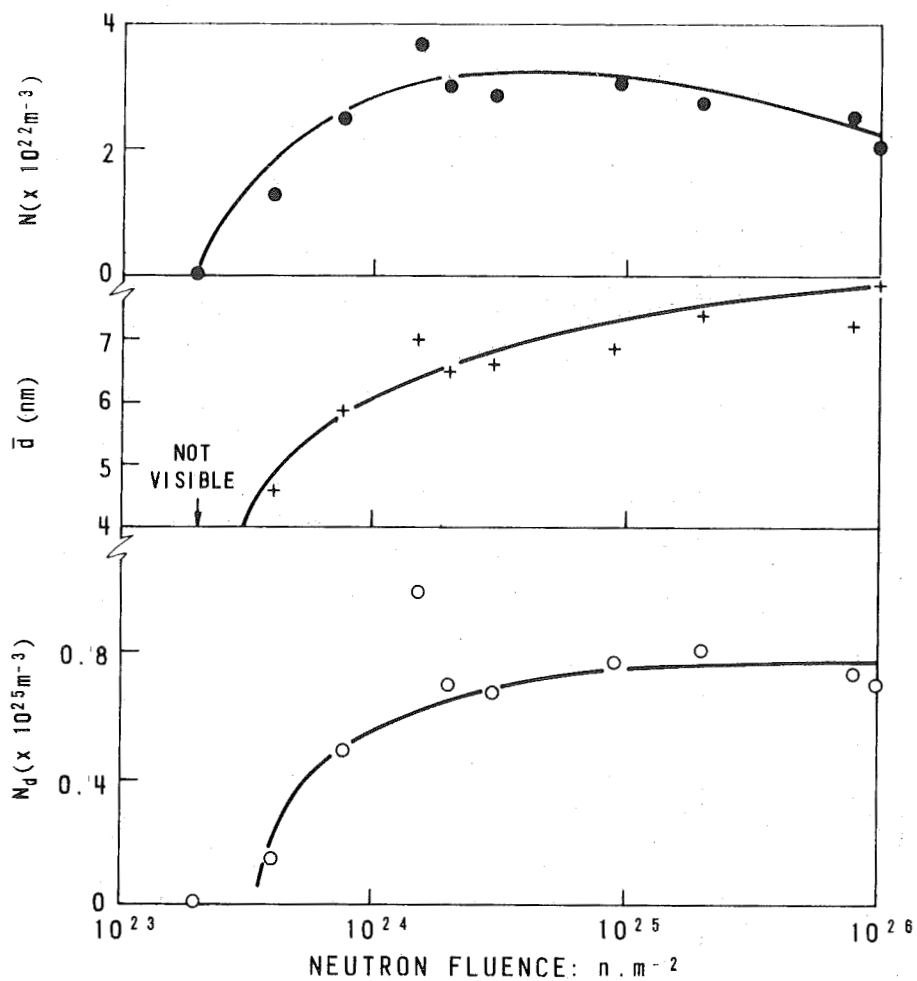
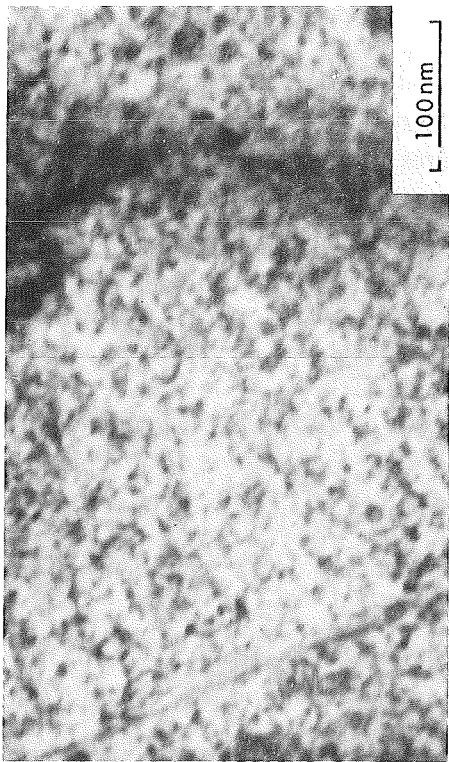


Figure 5 — Damage Accumulation in Annealed Zircaloy-2 Irradiated at $\approx 575K$

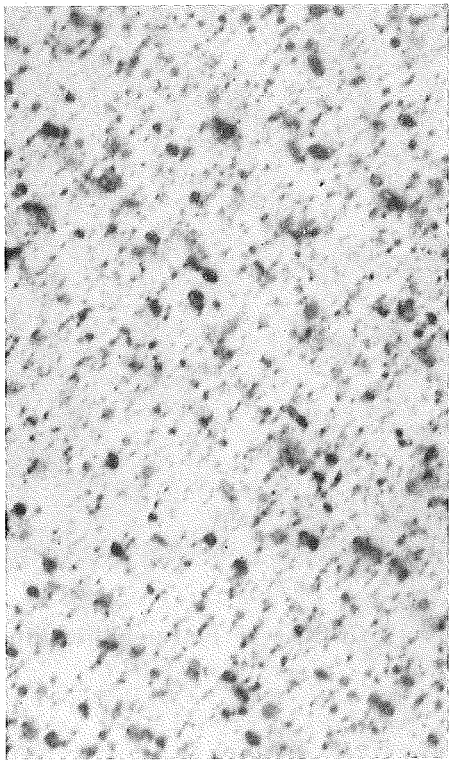
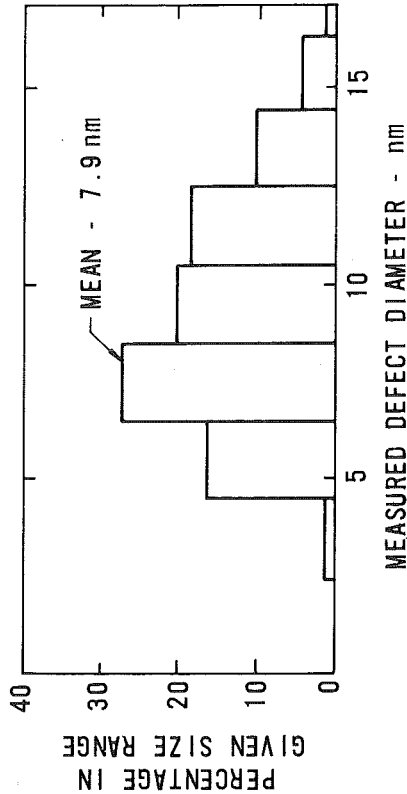
N = density of visible defects

$\bar{d}$ = mean size of defects

N_d = number of atom sites involved in damage assuming all perfect loops on prism planes



(b) $1.0 \times 10^{26} \text{ n.m}^{-2}$



(a) $7.7 \times 10^{23} \text{ n.m}^{-2}$

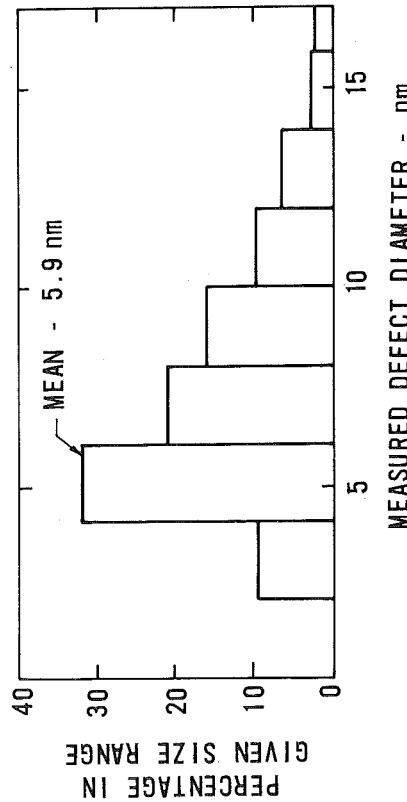


Figure 6 — Effect of Fluence on the Damage in Zircaloy-2 Irradiated at 575K.

(b) Temperature

As the irradiation temperature is increased above about 575K there is less irradiation hardening and the defects are larger and less numerous. More defects are resolvable as loops rather than 'black-spots'. Figure 7 compares the structures formed in Zr-1.15 wt% Cr-0.1 wt% Fe after irradiation at 575K or 775K. There is an irradiation temperature, which depends on alloy content and flux, above which no irradiation damage is seen, the defects being annealed out as fast as they form. With increasing flux there is less chance for recovery of the irradiation damage during irradiation at high temperatures. More detailed results can be found in the following references:

- C.E. Ells, C.E. Coleman and C.D. Williams, "The Temperature Dependence of Irradiation Damage in Zirconium Alloys", Presented at Symposium on Mechanical Behaviour of Materials, Kyoto, August 21-24, 1974
- A. Riley and P.J. Grundy, "A Study by Electron Microscopy of Neutron Damage in Zirconium and Zircaloy-2", *Phys. stat. sol. (a)* **14**, 1972, p.239-237
- D. Faulkner and R.C. Styles, "Neutron Radiation Damage in Zr-2.5 wt% Nb Alloys", *Proc. 31st Annual Electron Microscopy Society of America Meeting*, 1973. p.152-153

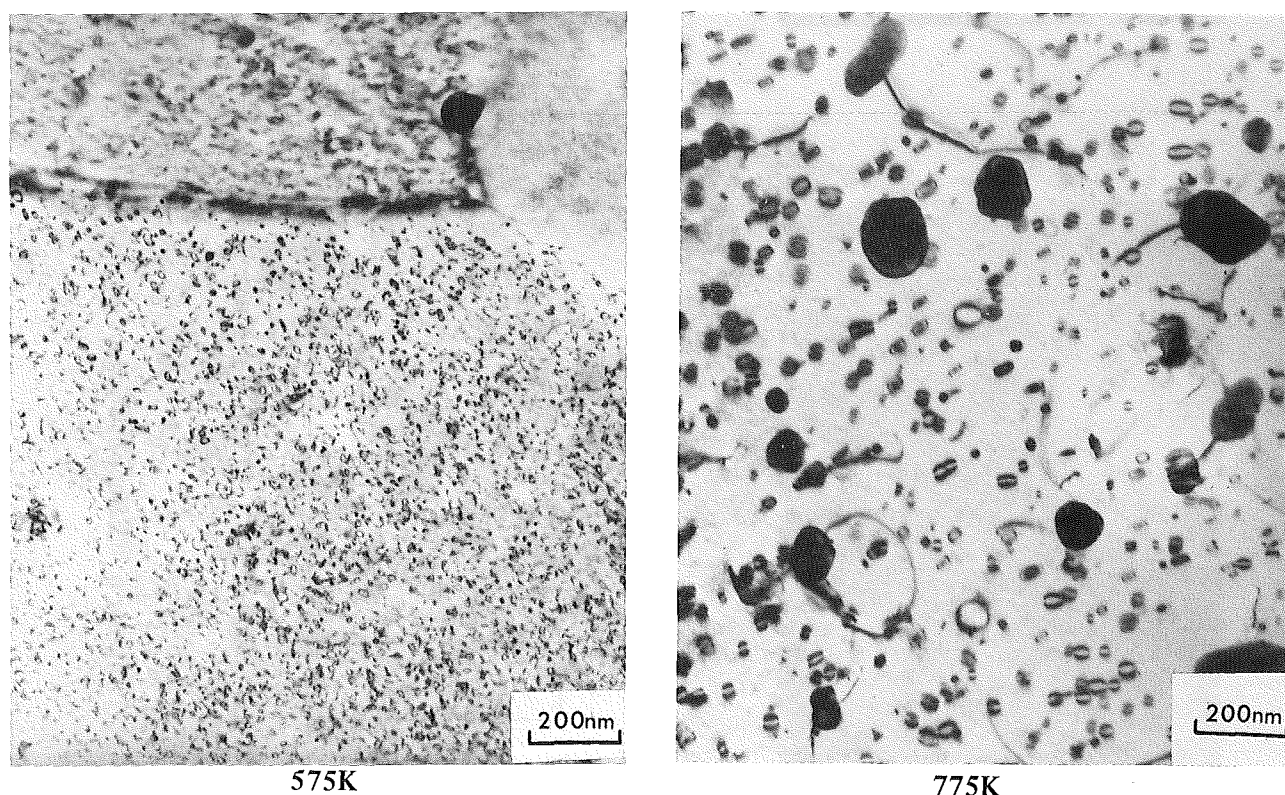
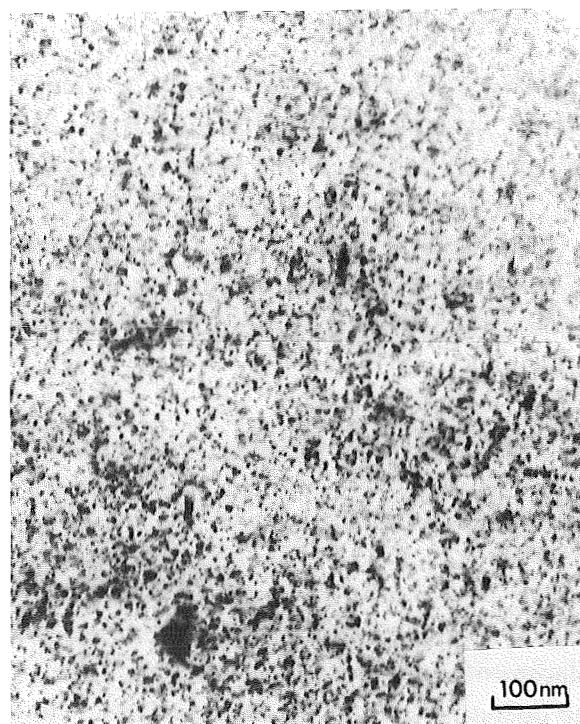


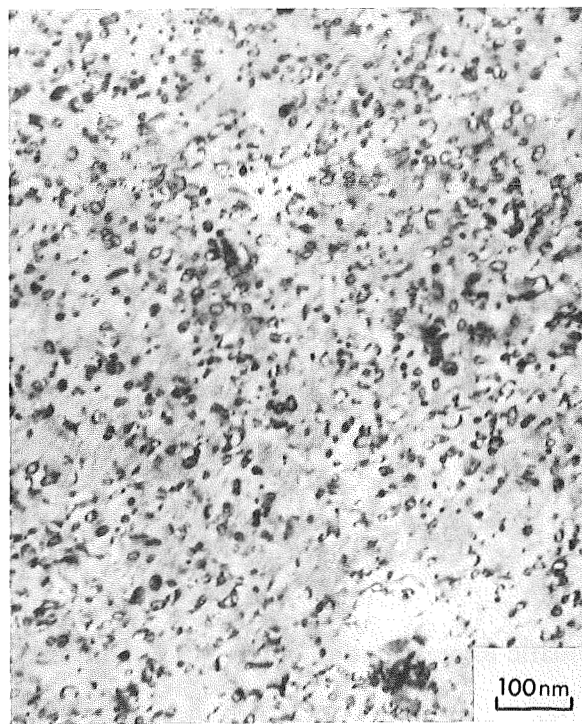
Figure 7 — Comparison of Irradiation Damage in Zr-1.15 wt% Cr-0.1 wt% Fe Fuel Sheathing Irradiated at 575K and 775K.



(a) Zircaloy-2 (1.0 - 1.5% Sn in solid solution)



(b) Zr-2.5% Nb (0.6 - 1.0% Nb in solid solution)



(c) Zr-1.15% Cr-0.1% Fe (<0.2% Cr in solid solution)

Figure 8 — Effect of Alloy Content (amount in solid-solution in h.c.p. α -phase) on Damage Produced at 575K and a Fluence of about $2 \times 10^{24} \text{ n.m}^{-2}$ ($E > 1 \text{ MeV}$).

(c) Alloy Content

Northwood, *Proc. 32nd Electron Microscopy Society of America Meeting, 1974, p.360-361*, has suggested that an important parameter affecting the size and distribution of the irradiation damage is the amount of alloy addition in solid solution in the h.c.p. α -Zr phase. For instance, Zircaloy-2 (1.0-1.5 wt% Sn in solid solution) and Zr-2.5 wt% Nb (0.6-1.0 wt% Nb in solid solution) irradiated to about $2 \times 10^{24} \text{ n.m}^{-2}$ at 575K contain the same density of similar size defects but Zr-1.15 wt% Cr-0.1 wt% Fe (<0.2 wt% Cr in solid solution) after a similar irradiation, contains considerably fewer defects of a much larger size, Figure 8.

(2) Characteristics of Damage

(a) Burgers Vector, Habit Plane, and Sign of Loops

The image contrast seen in the electron microscope arises from the strain field produced by atomic displacements near crystal imperfections. In the case of dislocations the displacement is the Burgers vector $\mathbf{b}$. A dislocation goes out of contrast when the reflecting plane operating contains its Burgers vector. This is often expressed as $\mathbf{g} \cdot \mathbf{b} = 0$, where $\mathbf{g}$ is the vector of the operating reflection. Since the scalar product $\mathbf{g} \cdot \mathbf{b}$ is equal to $g \cdot b \cos \theta$, where θ is the angle between $\mathbf{g}$ and $\mathbf{b}$, then $\mathbf{g} \cdot \mathbf{b} = 0$ when the displacement vector $\mathbf{b}$ is normal to $\mathbf{g}$, i.e. parallel to the reflecting plane producing the image, Figure 9.

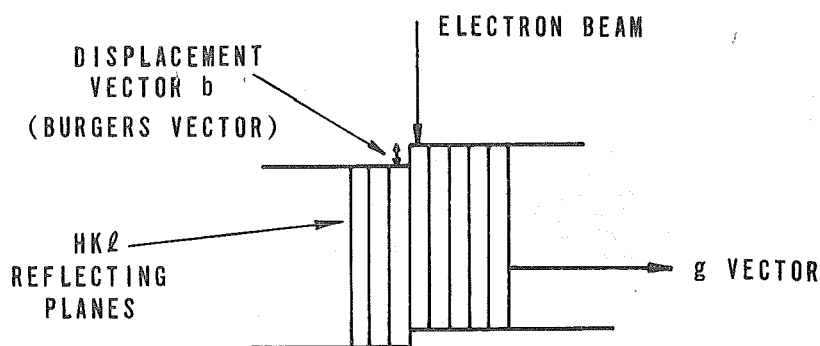


Figure 9 – Schematic Representation of $\mathbf{g} \cdot \mathbf{b} = 0$ Condition.

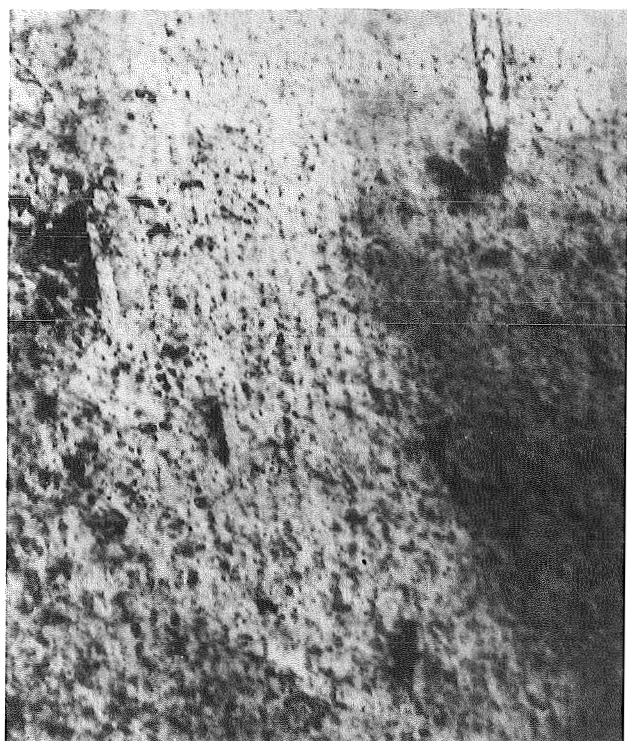
Results of such analyses by many investigators on a number of different zirconium alloys have shown that: $a/3 \langle 11\bar{2}0 \rangle$ is the most likely Burgers vector, Figure 10. *Riley and Grundy, Phys. stat. sol. (a)*, **14**, 1972, p.239-247, also suggest $a/3 \langle 11\bar{2}3 \rangle$ as a possibility, and *Adamson, Bell and Lee ASTM/AIME Symposium on Zirconium in Nuclear Applications, Portland, Oregon, August 22-24, 1973* state that some defects had Burgers vectors with a component parallel to the c-axis. All researchers seem agreed that the loops lie in or near the prism planes. *Kelly and Blake, Phil. Mag.* **28**, 1973, p.415-426, found the loops to be a mixture of interstitial and vacancy loops. Their data were, however, limited to post-irradiation annealed specimens.

Additional References

- *T.D. Gulden and I.M. Bernstein, "Dislocation Loops in Irradiated Zirconium", Phil. Mag.* **14**, 1966, p.1087-1091
- *C.D. Williams and C.E. Ells, "The Influence of Niobium in Irradiation Strengthening of Dilute Zr-Nb Alloys", Phil. Mag.* **18**, 1968, p.763-772
- *P.M. Kelly, "Irradiation Growth in Zirconium", Presented at International Conference on Physical Metallurgy of Reactor Fuel Elements, Berkeley, September 2-7, 1973*
- *P.B. Hirsch et al., "Electron Microscopy of Thin Crystals", Butterworths, 1965*

(b) Alignment

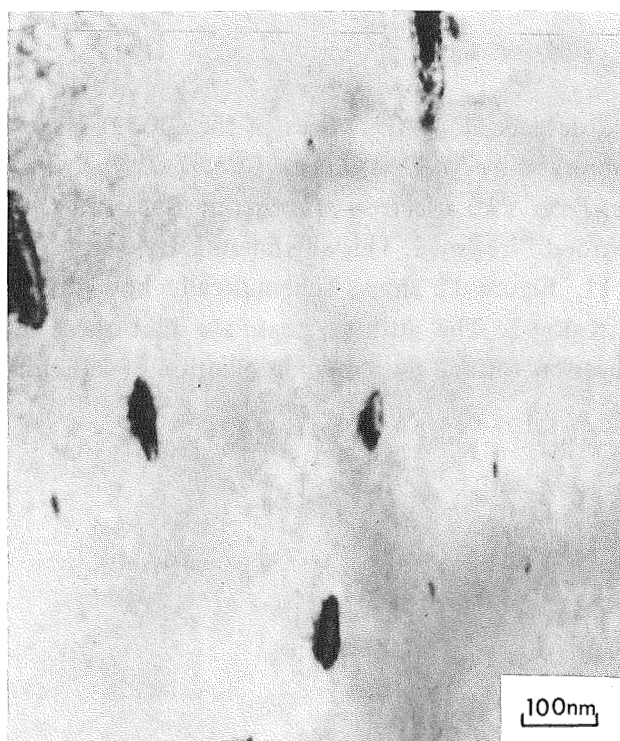
Alignment of the defects along the traces of the (0002) planes in neutron irradiated Zircaloy-2 has been observed by *Northwood and Gilbert, J. Nucl. Mater.* **51**, 1974, p.271-6, and by *Koch and Lee, Proc. 31st Electron Microscopy Society of America Meeting, 1973*, p.88-89, in ion bombarded Zircaloy-2. This alignment is only seen when the foil plane is the prism plane, Figure 11. Figure 12 shows schematically how the defects are arranged in neutron irradiated Zircaloy-2. The authors postulate that these arrays may represent a lowest energy configuration formed by some combination of self climb or prismatic glide of vacancy loops.



$g.b. \neq 0 \quad g = [10\bar{1}1]$



$g.b. \neq 0 \quad g = [10\bar{1}0]$



$g.b. = 0 \quad g = [0002]$

Figure 10 – Determination of Burgers Vector $a/3 \langle 11\bar{2}0 \rangle$ using g.b. Analysis in Zircaloy-2
Irradiated at 575K to $1.5 \times 10^{24} \text{ n.m.}^{-2}$.

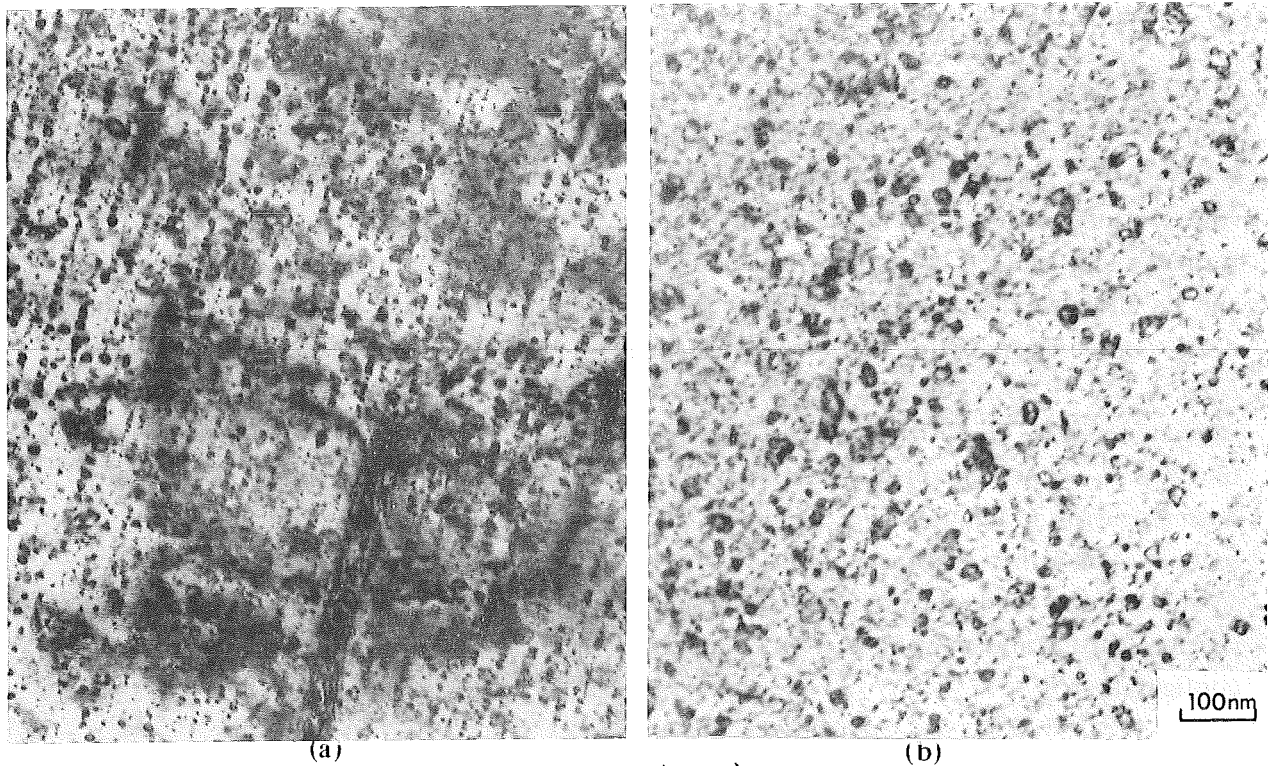


Figure 11 — Damage Alignment Along Traces of $\{0002\}$ Planes in Neutron Irradiated Zircaloy-2 Seen when Foil Plane is Prism Plane. (a) Foil Normal $[\bar{1}2\bar{1}0]$ (b) Tilted about 30° from (a)

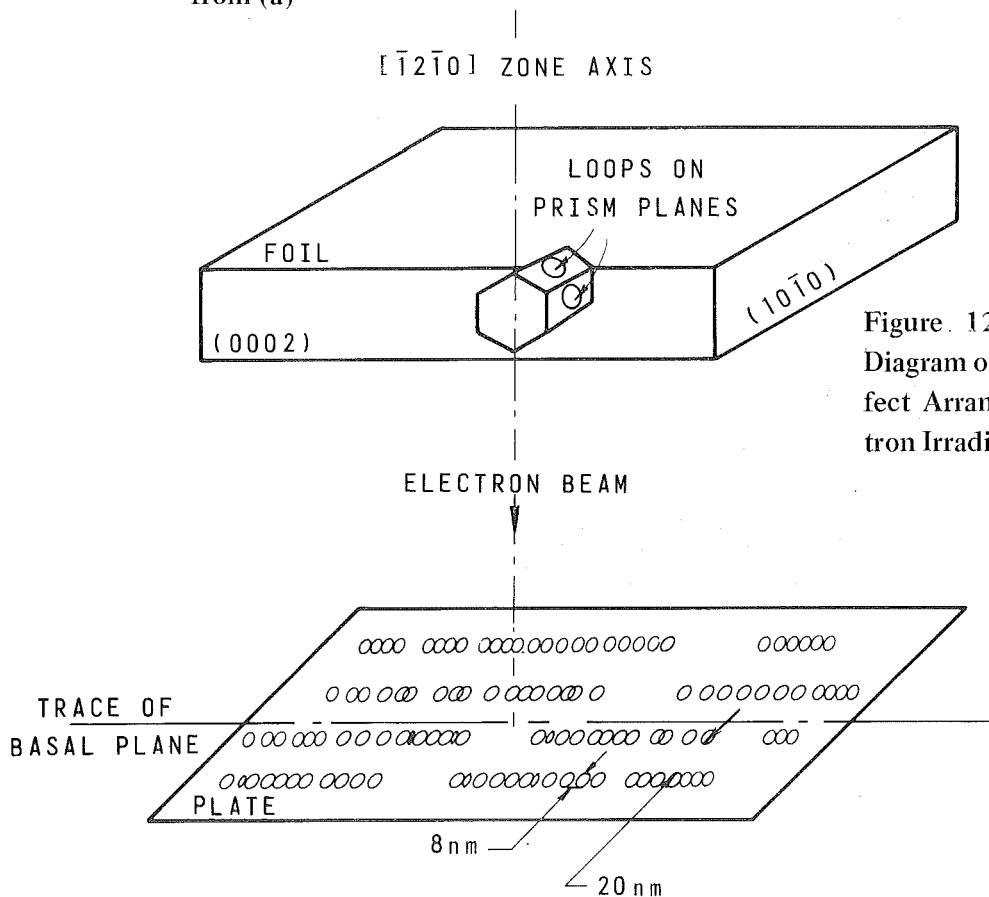


Figure 12 — Schematic Diagram of Postulated Defect Arrangement in Neutron Irradiated Zircaloy-2.

(c) Voids

Voids have been observed in a great number of neutron-irradiated metals at irradiation temperatures between 0.3 and 0.6 of their absolute melting temperatures, T_m . A fluence of $\approx 10^{26}$ n.m^{-2} is required to produce voids in practical alloys such as stainless steel while voids occur in many pure metals after a fluence of $\approx 10^{24}$ n.m^{-2} . Figure 13 shows void formations in neutron irradiated Nb. However, in any form of bombardment of zirconium and its alloys voids have formed only when there was prior seeding with an insoluble gas, *G.J.C. Carpenter, Radiation Effects, 19, 1973, p.189-190. Northwood and Gilbert, Radiation Effects, 22, 1974, p.139-140*, have not revealed the presence of voids in zirconium alloys irradiated at 475-775K (0.25-0.4 T_m) to fluences up to 10^{26} n.m^{-2} . They attribute the lack of voids to a low content of *insoluble* gas, for example helium. Little helium is produced during neutron irradiation since zirconium has a small fission spectrum averaged (n, α) cross section. Also other gaseous impurities such as hydrogen, oxygen or nitrogen are either soluble or form solid precipitates in zirconium. If present, the insoluble gas would stabilize a vacancy cluster and prevent it from collapsing to form a dislocation loop, a lower energy configuration.

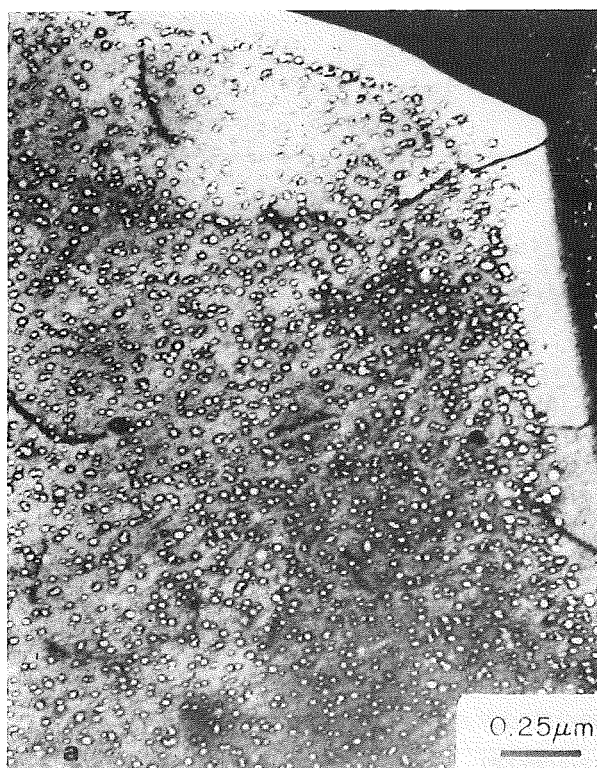


Figure 13 — Void Formation in Neutron Irradiated-Niobium

Additional References

- A. Wolfenden and K. Farrell, "On the Question of Void Formation in Neutron Irradiated Zirconium," *Scripta Met.* **6**, 1973, p. 127-130
- D.I.R. Norris, "Voids in Irradiated Metals", *Radiation Effects*, **14**, 1973, p.1-37

(d) General Comments

All the irradiation induced defects, whether 'black-spot' damage or dislocation loops, behave similarly in TEM contrast analysis showing a highly directional strain field. The 'black-spots' are probably small dislocation loops which can not be resolved as loops by TEM but are visible because of their strain fields. The defects produced at $\approx 575\text{K}$ at fluences less than $2\text{-}3 \times 10^{23} \text{ n.m}^{-2}$ are either very small loops with strain fields too weak to give sufficient contrast to be seen as 'black-spots'; or they are small clusters of vacancies such as Seeger zones.

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

The data generated to date on irradiation damage have enabled us to qualitatively relate the density of damage to the increment in yield strength. This is illustrated in Figure 14 for Zircaloy-2. Both the damage density and the increment in yield strength tend to saturate at fluences greater than about 10^{25} n.m^{-2} ($E > 1\text{MeV}$). The increment in yield strength at the low fluences ($< 2 \times 10^{23} \text{ n.m}^{-2}$), where no damage is seen using TEM, is probably due to small loops or Seeger zones. The relationship between fluence and mechanical properties is also to be found in Lecture 6. Our knowledge of Burgers vectors and habit planes of the dislocation loops has led Kelly, *International Conference on Physical Metallurgy of Reactor Fuel Elements, Berkley, September 2-7, 1973*, to re-examine a popular mechanistic theory for irradiation growth due to Buckley, *Properties of Reactor Materials and Effects of Radiation Damage*, Ed. D.J. Littler, p.413, Butterworths (1962) and *Journal of the Institute for Metals*, **97**, 1969, p.61, which is based on the aggregation of vacancy loops on basal planes and interstitial loops on prism planes. There is however, much more to be determined if we are to understand and predict the behaviour of in-reactor components.

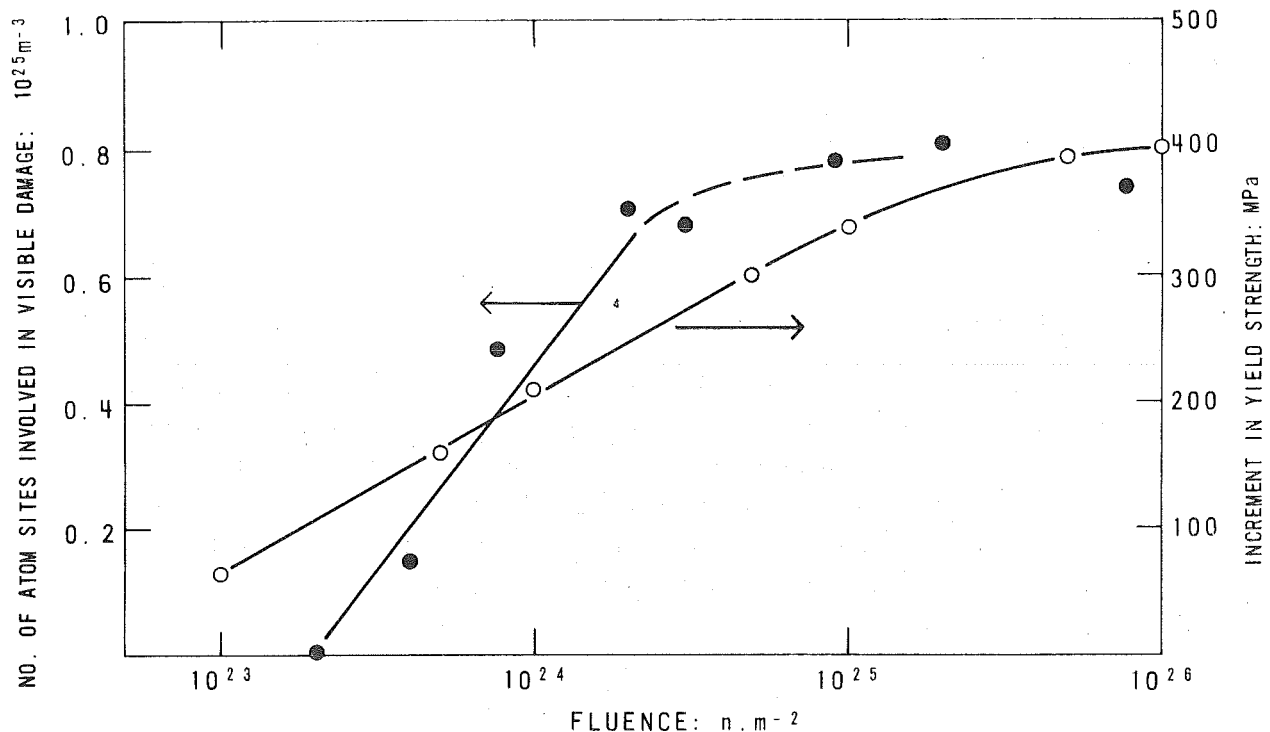


Figure 14 – Relationship between TEM Observations of Damage and Increment in Yield Strength (A.L. Bement et al, ASTM-STP 380, 364-384, 1964) for Zircaloy-2.

Further work is planned to determine:

- The character, i.e. vacancy or interstitial, and the habit planes of the dislocation loops in as-irradiated material. These data are required if we are to be able to relate the damage to the irradiation growth.
- The effect of irradiation temperature, alloy content, metallurgical condition (e.g. the amount of cold-work) and flux on the nature of the radiation damage. Although much information has already been generated much more is required to quantitatively relate the damage characteristics to the property changes.
- The effect of stress applied during the neutron irradiation (irradiation creep) on both the nature of the radiation damage and the dislocation production. There exists many theories for irradiation creep and a detailed TEM examination of creep specimens should help us in formulating a precise mechanism.

CRNL-1208

LECTURE NO. 6

FATIGUE AND FRACTURE OF ZIRCONIUM ALLOYS

by

R.R. Hosbons

INTRODUCTION

Current designs of CANDU reactors provide a base electrical load and we do not consider fatigue to be a factor in the service life of core components. However in future load following reactors some components may be subjected to a number of stress reversals. Some of these reversals may exceed the flow stress so that both high cycle and low cycle fatigue must be considered. The zirconium alloy tubes used in CANDU reactors have thin walls and the most important parameter in fatigue life is crack initiation.

1. Crack Initiation

The fatigue life of Zircalloys between 300 and 590 K and cyclic strains of 0.2 to 2% can be represented by O'Donnel and Langer's equation:-

$$S = \frac{E}{4 \sqrt{N}} \ln \frac{100}{100 - RA} + S_e$$

where E = Young's Modulus

RA = reduction of area from tensile tests (%)

S_e = endurance limit (170 MPa)

N = fatigue life

and S = hypothetical stress = $1/2 E \epsilon_T$

where ϵ_T = total cyclic strain.

Metallurgical condition has little effect on fatigue life. Irradiation reduces fatigue life at high strains but has little effect at low strains, Figure 1.

W.J. O'Donnel and B.F. Langer, Nuclear Science and Engineering, 20, 1964, p. 1.

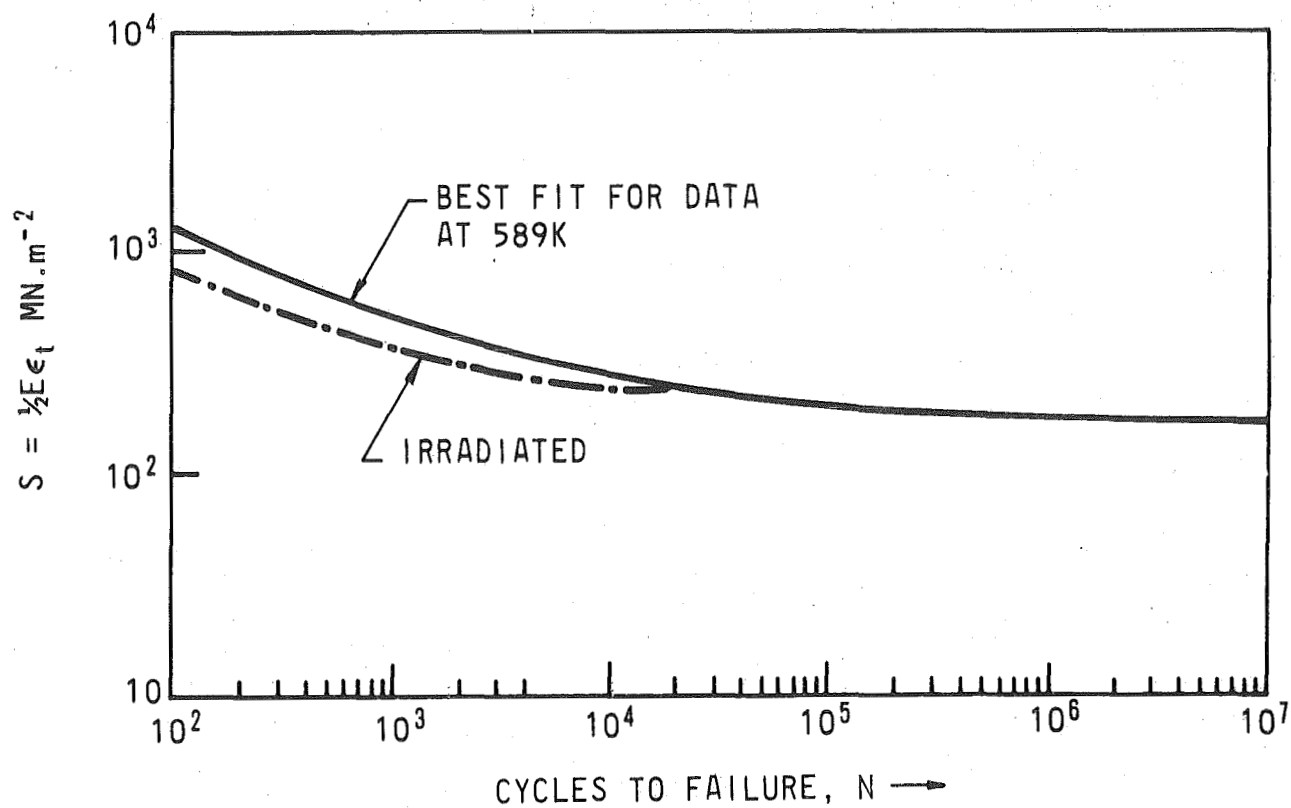


Figure 1 – Fatigue data on Zircaloy-2

The low cycle fatigue lives of candidate fuel sheathing alloys Zircaloy-2, Zr-2.5 wt% Nb and Zr-1.1 wt% Cr-0.1 wt% Fe at 575 K has been measured using both push-pull and reversed bend tests. The alloys were tested in the several metallurgical conditions which can be present in fabricated fuel bundles, Table 1.

TABLE 1
THE METALLURGICAL CONDITIONS OF THE ALLOYS

Material	Cold Work	Heat Treatment
Zircaloy-2	—	975 K _y for 2 hrs.
	6%	823 K for 4 hrs.
	12%	" " " " "
	20%	" " " " "
	41%	" " " " "
	—	1275 K Oil Quench
Zr-2.5 wt% Nb	—	850 K for 2 hrs
	—	1275 K Oil Quench
Zr-1.1 wt% Cr-0.1 wt% Fe	—	995 K for 2 hrs.
	15%	740 K for 4 hrs.
	—	1275 K Oil Quench

The fatigue lives of these alloys in the cold-worked and annealed, and in the cold-worked and stress relieved conditions are similar and can be represented by the same 95% confidence limits, Figures 2-4. β quenched Zr-2.5 wt% Nb and β quenched Zr-1.1 wt% Cr-0.1 wt% Fe have lower fatigue lives than the annealed materials. Long dwell times at maximum strain reduced the fatigue lives as shown for Zircaloy-2 in Table 2.

TABLE 2
THE EFFECT OF HOLD TIME ON LOW CYCLE FATIGUE
LIFE OF COLD WORKED ZIRCALOY-2

Dwell Time Seconds	Cycles to Failure
0	1320
900	1090
1,800	1425
3,600	1500
18,000	600-800

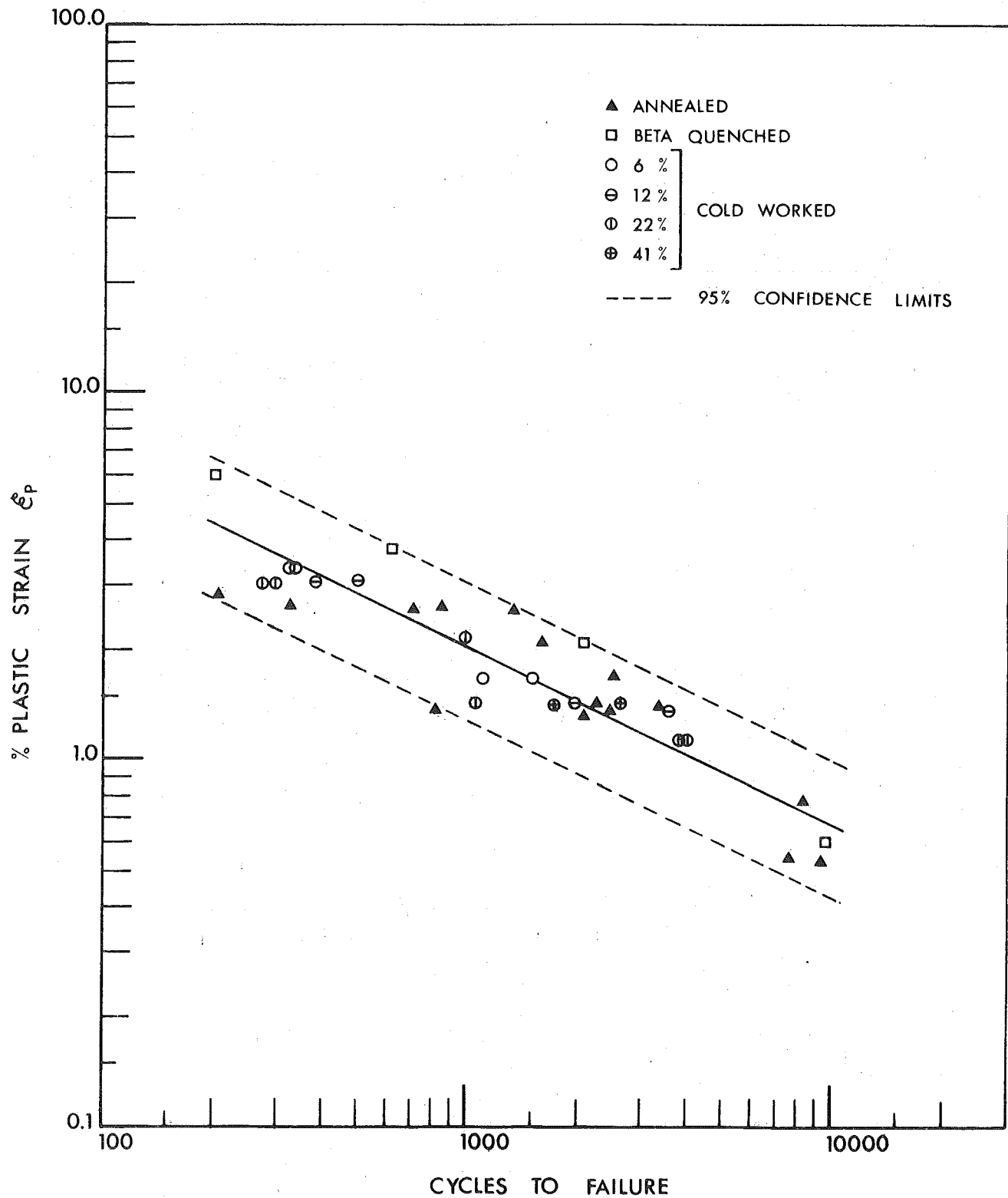


Figure 2 — Low Cycle Fatigue Data on Zircaloy-2 at 573 K.

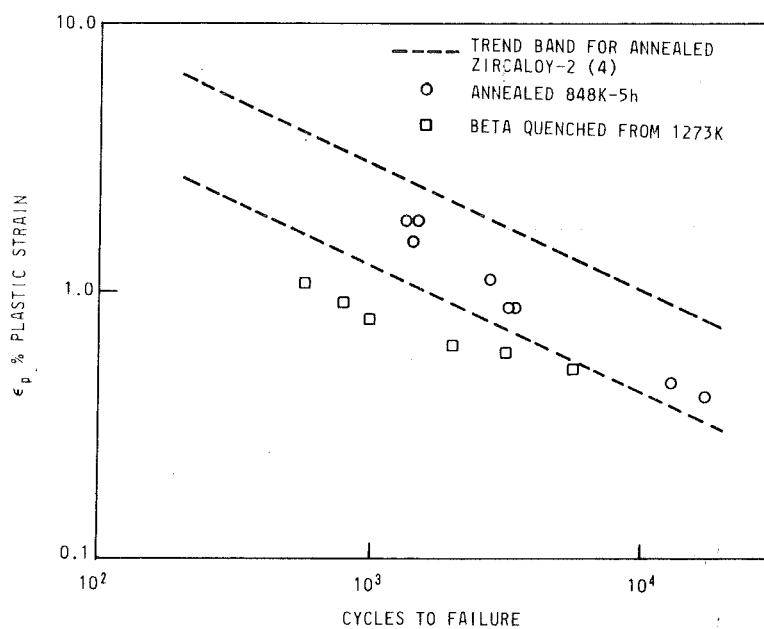


Figure 3 — Low cycle fatigue data for Zr-2.5%Nb alloy at 573K

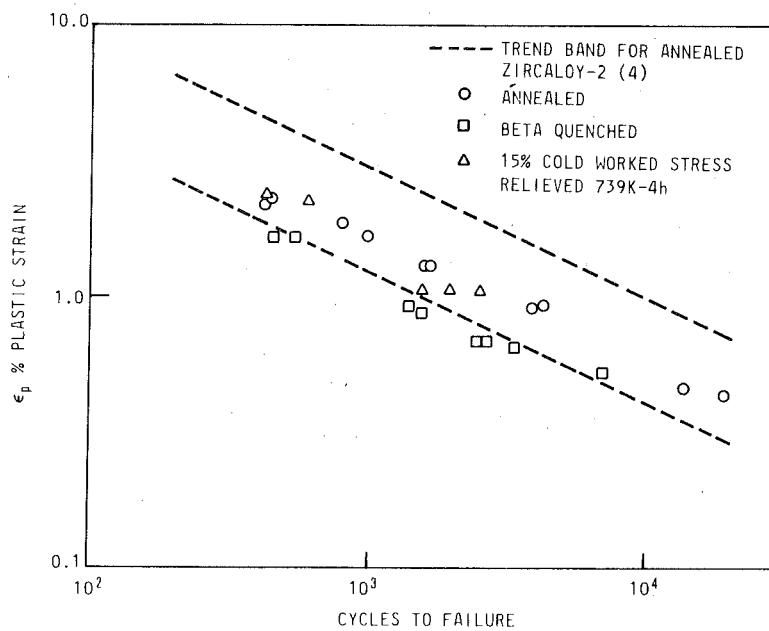


Figure 4 — Low cycle fatigue data for Zr-1.15%Cr - 0.10%Fe Alloy at 573K

TABLE 3

THE EFFECT OF AN ATMOSPHERE CONTAINING 0.03 Kg.m^{-2} IODINE ON
THE LOW CYCLE FATIGUE LIFE OF ZIRCONIUM ALLOYS

Material	Condition	Atmosphere	Hold Time s	Plastic Strain Range %	Cycles to Failure
Zr-2.5 wt% Nb	Annealed	Air	0	3	230
		Iodine	0	3	154
		Iodine	3600	3	50
Zr-Cr-Fe	Stress	Air	0	3	291
	Relieved	Iodine	0	3	164
		Iodine	3600	3	44
Zircaloy-2	Stress	Air	0	3	227
	Relieved	Iodine	0	3	136
		Iodine	3600	3	42

Zirconium alloys are susceptible to stress corrosion cracking in an atmosphere containing more than 0.03 Kg.m^{-3} of iodine. Reverse bend tests showed that an atmosphere containing 0.03 Kg.m^{-3} of iodine considerably reduced the number of cycles to failure, Table 3, particularly with a 3600 s (one hour) hold time at maximum strain. A much lower iodine concentration of 0.003 Kg.m^{-2} had very little effect on fatigue life, Figure 5.

R.R. Hosbons, Fatigue at Elevated Temperatures, ASTM STP 520, 1973.

R.R. Hosbons, Proceedings of the International Conference on Creep and Fracture in Elevated Temperature Applications, Philadelphia, Sept. 1973.

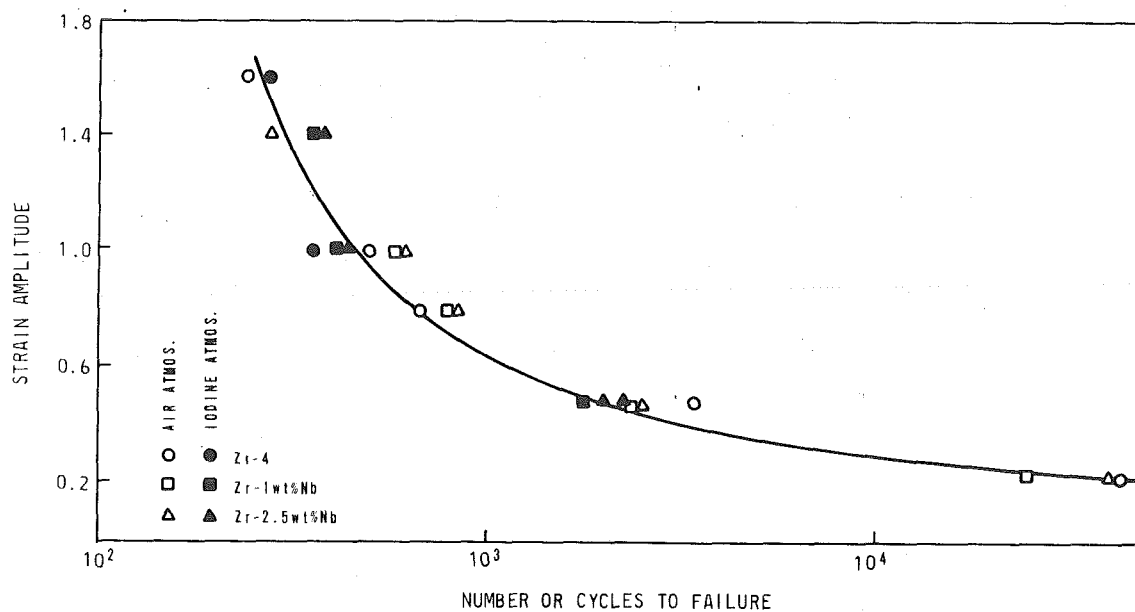


Figure 5 — Low cycle fatigue life at 575 K in air or 0.003 KG/MM² iodine atmosphere

Zircaloy-2 tested at 675 K in air had a lower fatigue life than found by O'Donnell and Langer and this was attributed to oxidation during the test, Horton — EURAEC report 1299, Oct. 1964. A comparison of fatigue data for zirconium alloys in Figure 6, shows the good agreement between the test results of O'Donnell and Langer and of Hosbons.

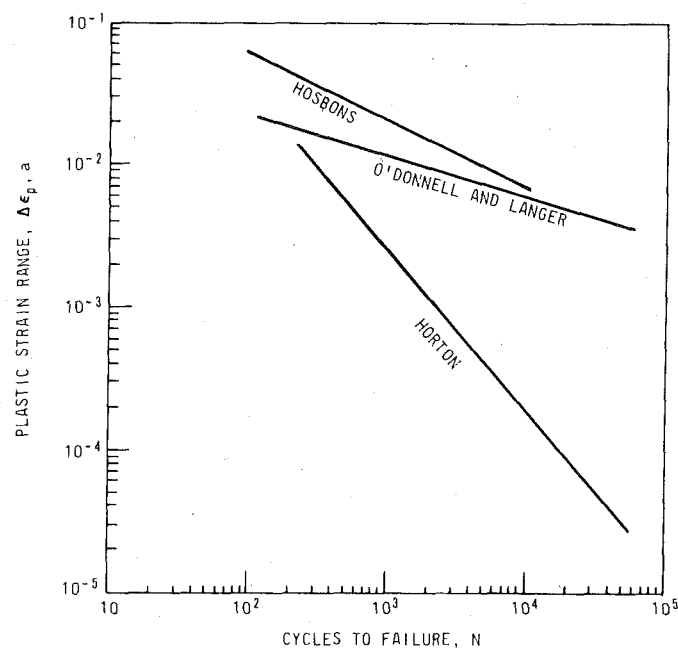


Figure 6 — Fatigue test results for Zircaloy-2

In most investigations specimens are machined from bar and strip and cyclicly stressed in the longitudinal direction in which deformation predominantly occurs by slip. However specimens machined from the short transverse direction of thick Zircaloy-2 slab, Figure 7, deform initially by twinning, and they had a much shorter fatigue life than specimens machined from the longitudinal direction, Figure 8. This agrees with metallographic observations that permanent fatigue damage in zirconium alloys occurs by twinning.

M.R. Warren and C.J. Beevers, Met. Trans. 1, 1970, p.1657.

D. Lee, Met. Trans. 3, 1972, p.315.

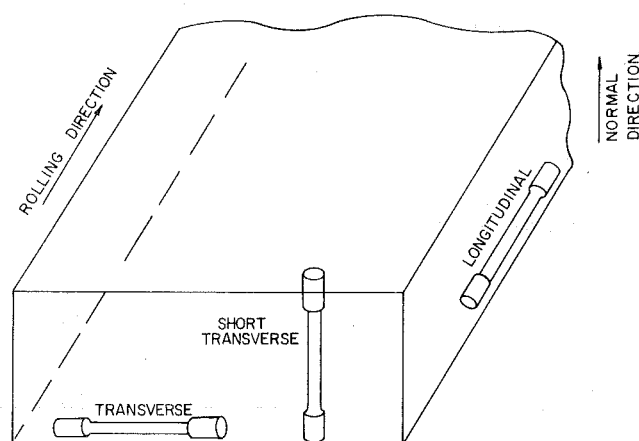


Figure 7 — Specimen orientation in the rolled sheet

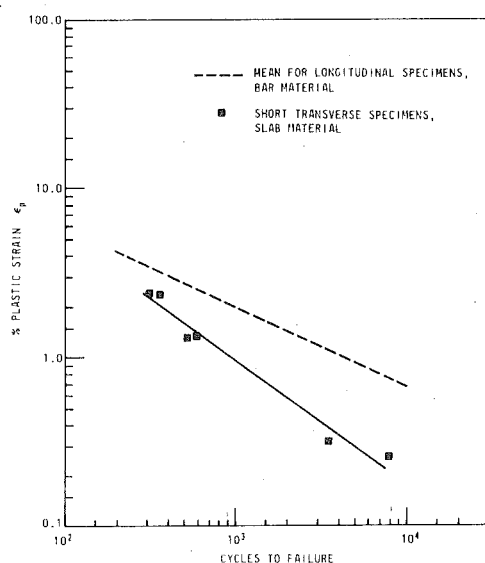


Figure 8 — The 575K low cycle fatigue properties of Zircaloy-2 specimens from both bar and slab material

2. Crack Propagation

Crack growth rates are affected by metallurgical condition, atmosphere, temperature and stress. In Zircaloy-2, a water environment, increasing temperature and increasing cold work all increase the crack growth rate, Figure 9. The results obey the fracture mechanics 'power law' relationship.

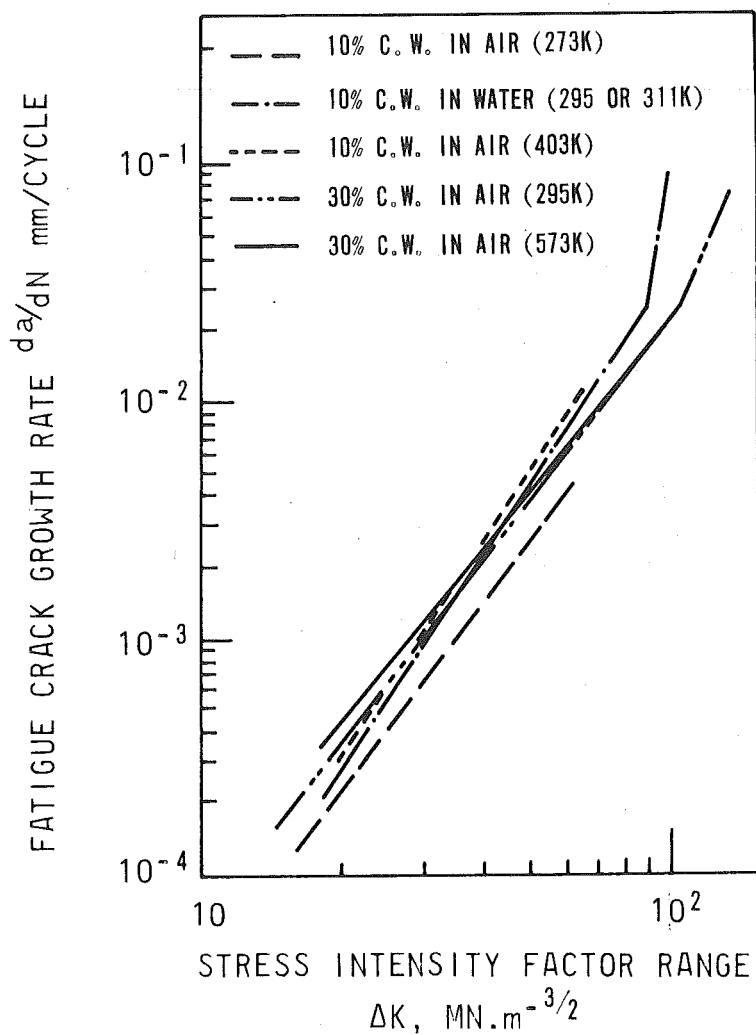


Figure 9 — Summary of fatigue crack propagation results

where $\frac{da}{dN} = C (\Delta K)^n$

where $\frac{da}{dN} = \text{crack growth/cycle}$

$\Delta K = \text{stress intensity factor range}$

and C, n are constants.

L.E. James, Nuclear Applications, 6, 1969, p.307.

L.E. James, Nuclear Applications and Technology, 9, 1970, p.260.

P.J. Pankaski, ASTM STP 458, 1969.

R.L. Knecht and P.J. Pankaski, BNWL-746, 1968.

3. Fatigue Life of Reactor Components

Irradiation damage increases the flow stress and reduces the ductility of zirconium alloys. Hence the fatigue life changes with fluence. Fatigue life can be estimated from short term tensile properties by Manson's Universal Slopes equation:- *S.S. Manson, International Journal of Fracture Mechanics 2, 1966, p.327.*

$$\epsilon_T = 3.5 \frac{\sigma_n}{E} N_f^{-0.12} + D^{0.6} N_f^{-0.6}$$

where ϵ_T is total strain

σ_n is U.T.S.

E is Young's modulus

D is tensile ductility = $\ell/n \left(\frac{100}{100-RA} \right)$

N_f = fatigue life.

If the conditions change during fatigue then the life can be determined by using Manson's Double Linear Damage Rule, *S.S. Manson, International Journal of Fracture Mechanics 2, 1966, p. 327*, which states that

$$\sum \left(\frac{n}{N_o} \right) = 1 \quad \text{for initiation}$$

$$\sum \left(\frac{n_1}{(\Delta N)_f} \right) = 1 \quad \text{for complete failure}$$

where n = number of cycles at a given stress
 n_1 = number of cycles after crack initiation
 N_o = number of cycles to cause crack initiation at that stress
 $(\Delta N)_f$ = number of cycles to propagate a crack to failure at that stress

Hence $N_f = N_o + (\Delta N)_f$

for $N_f \geq 730$, $\Delta N_f = 14 N_f^{0.6}$

and for $N_f < 730$, $N_o = 0$

Thus if the change in the short term tensile properties with neutron irradiation is known the in reactor fatigue life can be estimated.

The fatigue life of Zircaloy-4 fuel sheathing has been estimated and Figure 10 shows the relationship between the cycle frequency and strain to cause failure in 700 days, the length of time fuel bundles remain in CANDU reactors.

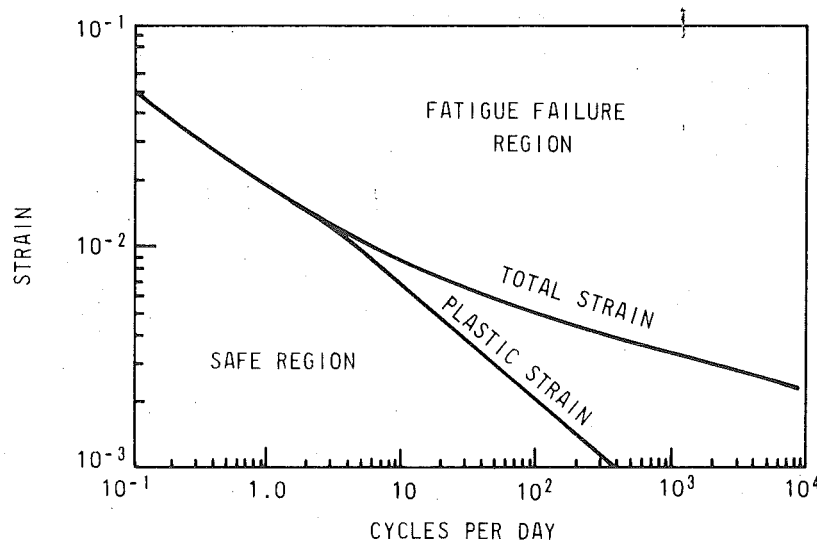


Figure 10 – Strain to produce failure in 700 days

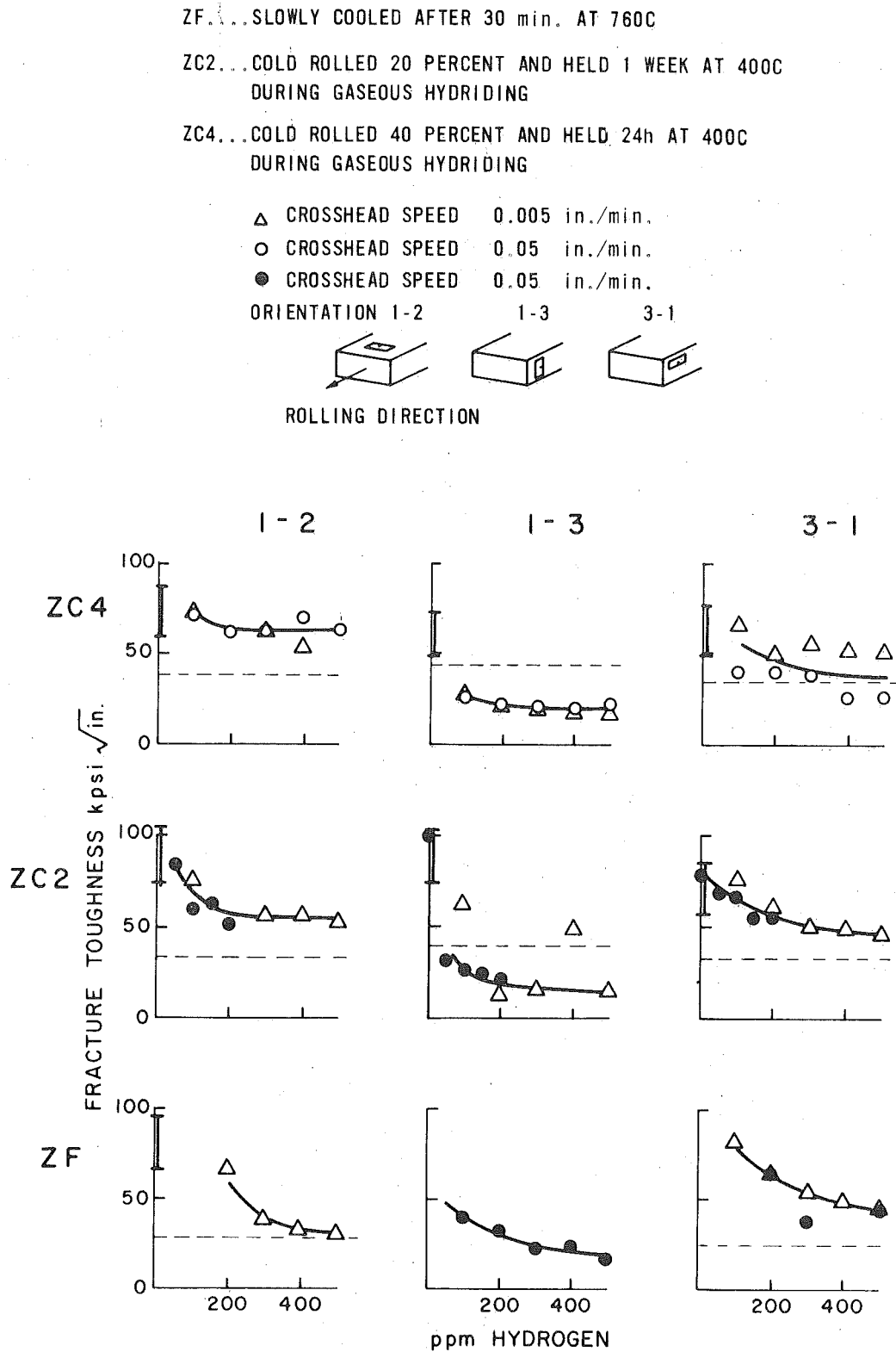


Figure 11 — Effect of orientation and hydrogen on the room temperature fracture toughness of Zircaloy-2

4. Fracture Toughness

Zirconium alloy tubes in CANDU reactors have thin walls and plane strain conditions are not met. At operating temperature (575 K) zirconium alloys have good fracture toughness. At temperatures below 423 K hydrogen can reduce the plane strain fracture toughness by up to 50% depending on the orientation of the hydride plates.

Crystallographic texture and grain shape have very little effect on fracture toughness. However in cold-worked materials hydrides generally precipitate parallel to the rolling plane and when the tensile axis is perpendicular to the hydrides the reduction in fracture toughness is very pronounced, Figure 11. *I. Aitchison, ASTM STP 458, 1969, p.160.* Fracture toughness increases with temperature especially above 300 K, Figure 12. *T.J. Walker and J.N. Kass, ASTM STP 551, 1974, p.328.* Walker also found that irradiation does not decrease fracture toughness and may in fact increase it, Figure 13.

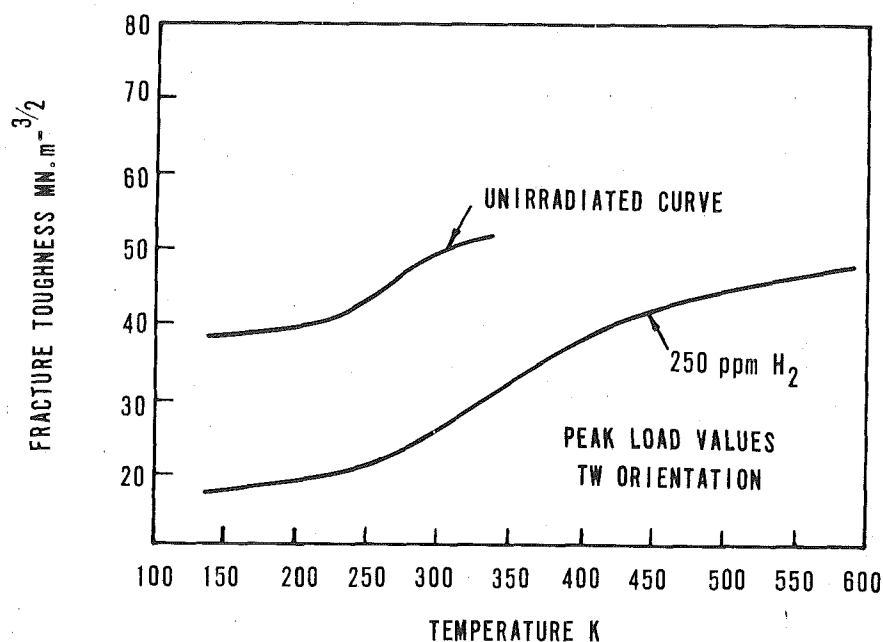


Figure 12 — K_{IC} values corresponding to peak load values for the TW orientation.

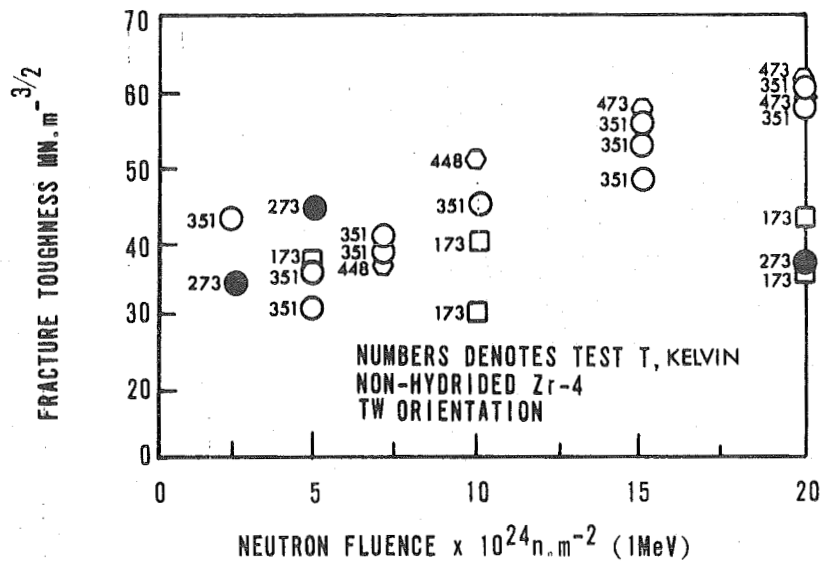


Figure 13 – Dependence of fracture toughness on irradiation.

5. Fracture Surface Appearance

When fracture occurs the fracture surface can be examined by optical microscopy, electron microscopy using plastic replicas and on the scanning electron microscope. The fracture faces can have a distinctive appearance which depends on the mode of failure.

(a) Fatigue

At the point of initiation the crack has a feathery cleavage type of surface, Figure 14. At low stress intensities the surface rapidly becomes characterized by straight striations and sharp changes in elevation between plateaus typical of brittle fatigue, Figure 15. At higher stress intensities the fracture appearance changes to ductile fatigue, Figure 16, which is characterized by wavy striations.



Figure 14 – Feather cleavage at start of fatigue crack
(3000 X)



Figure 15 – Brittle fatigue (3000 X)



Figure 16 – Ductile fatigue (3000 X)

(b) Fast Fracture

Zirconium alloys can exhibit fracture surfaces which contain cleavage, quasi-cleavage and dimple failure. Cleavage occurs by the direct separation of low index crystallographic planes and is characterized by flat areas on the fracture surface, Figure 17. Cleavage generally occurs in material fractured below 375 K when hydrides are present.

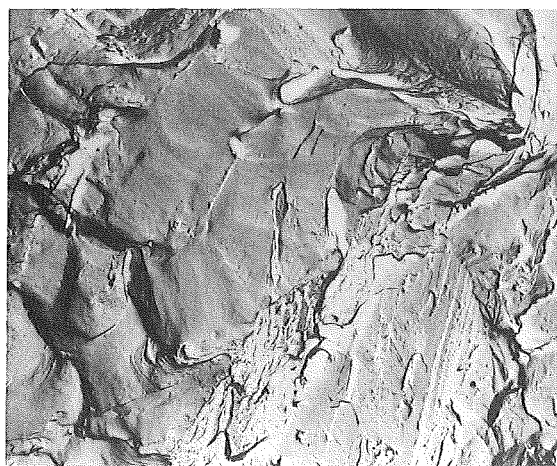


Figure 17 – Cleavage in Zircaloy-2

Quasi-cleavage, Figure 18, also occurs in Zircaloy-2 at 375 K and is similar in appearance to cleavage but is accompanied by some deformation.



Figure 18 – Quasi-cleavage in Zircaloy-2

In Zircaloy-2 fractured above 575 K and in zirconium 2.5 wt% niobium above 300 K the fracture surface is dimpled, Figure 19. The dimples occur by micro void coalescence ahead of the propagating crack and if elongated indicate shear deformation, Figure 20.

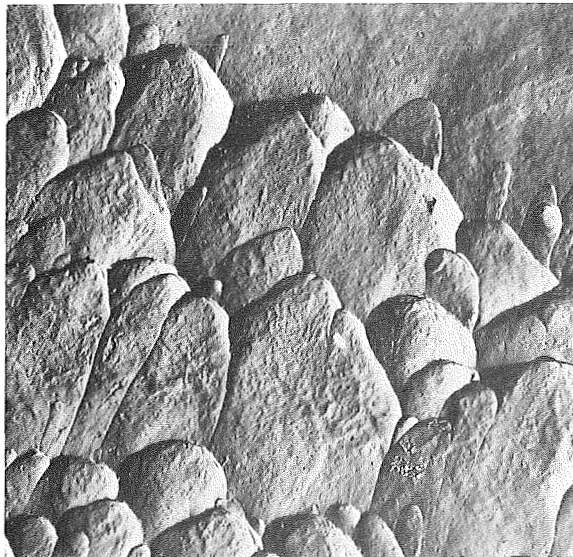


Figure 19 – Dimpled rupture in Zirconium-2.5 wt% Niobium

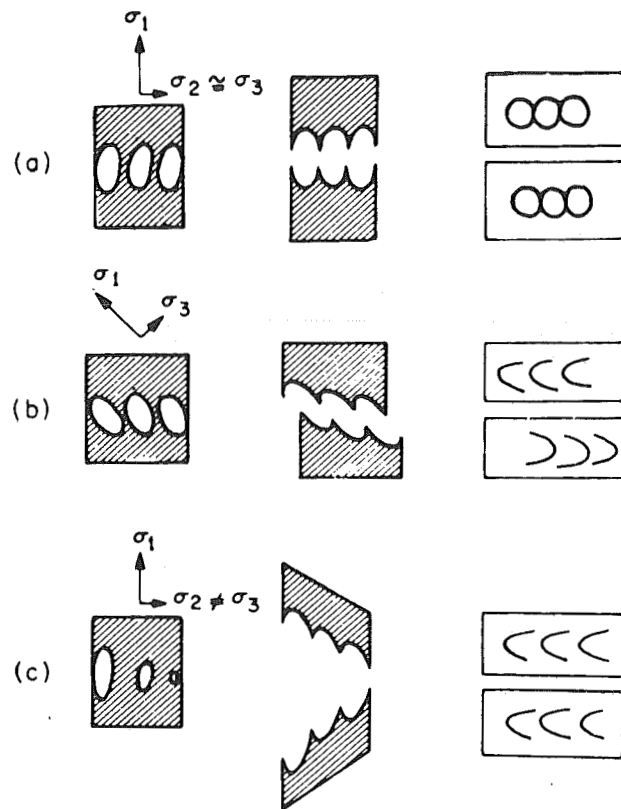


Figure 20 — Formation of dimples by coalescence of micro voids
(a) normal dimpled (b) shear rupture (c) tearing.

The pressure of hydrogen in the alloys usually makes the dimples smaller and introduces some cleavage into the fracture surface, Figure 21.

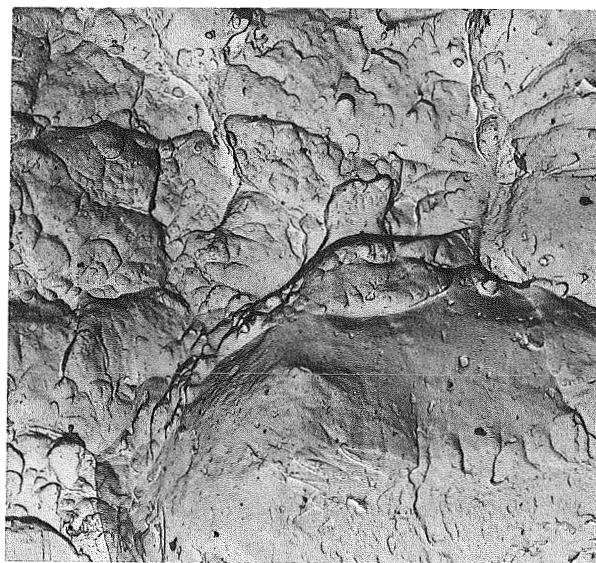


Figure 21 — Dimpled rupture with cleavage in hydrided Zirconium 2.5 wt% Niobium

SUMMARY

The fatigue properties of zirconium alloys show that it is not a probable failure mechanism in reactor components. The fracture behaviour of zirconium alloys depends upon specimen orientation, hydrogen concentration and temperature and there is some evidence that radiation has little effect. The fracture surfaces have distinctive features which can be used to analyse the mode of failure.

CRNL-1208

LECTURE NO. 7

ZIRCONIUM ALLOY CREEP AND GROWTH

by

E.F. Ibrahim

PRESSURE TUBES

In CANDU reactors, fuel is contained in zirconium alloy pressure tubes 8 or 10 cm inside diameter and up to 6 m long. They operate at about 573K (300°C) with an internal pressure of about 10 MPa (1 kg/mm²).

DESIGN CRITERIA

Design criteria for pressure tubes are based on Section III of the ASME Pressure Vessel Code (although the code does not deal with zirconium alloys). The restrictions on maximum design stress are:

- < 1/3 of Ultimate Tensile Strength (UTS)
- < 2/3 of 0.2% Yield Stress
- < 60% of the stress estimated to give a rupture life of 100 000 h
- < Stress to give a creep rate of 10⁻⁷ /h

The desire for neutron economy provides considerable incentive to avoid unnecessary reduction in the stress in the tube by increasing the wall thickness.

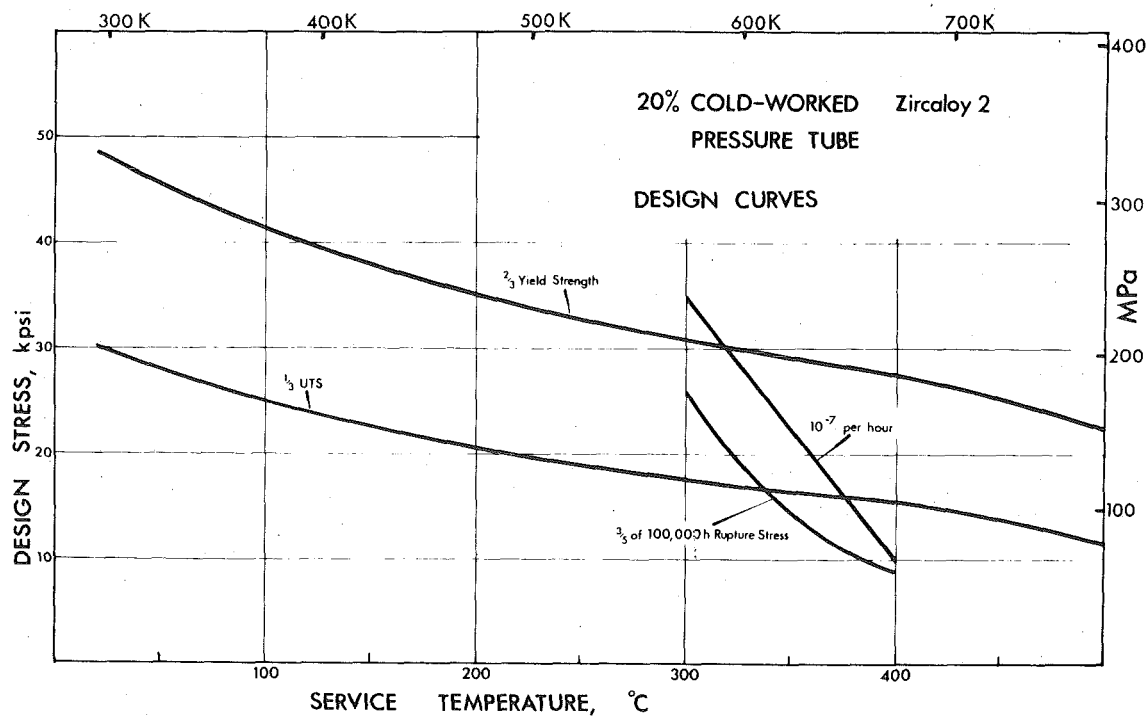


Figure 1 — Design curves for 20% cold-drawn Zircaloy-2 pressure tube material.

Figure 1 shows design curves for cold-drawn Zircaloy-2 based on out-of-reactor tests. At 573K the lowest stress on the design curves is for 1/3 UTS and this is therefore the limiting property for design. Design curves for Zr-2.5 wt% Nb are similar (but with higher values) with 1/3 UTS the design limitation.

CREEP DESIGN CRITERIA

Initially, creep did not appear to be important particularly as out-of-reactor tests show creep rate to diminish rapidly with increasing test time.

— *E.F. Ibrahim, AECL-2528, 1965*

Creep rate at 573K $\propto t^{-0.8}$. However in the early 1960s, uniaxial creep specimens from pressure tubes were tested with sufficient accuracy in-reactor to show that creep rates are considerably higher in a fast neutron flux than in the laboratory and that the rates do not decrease very rapidly with time.

— *V. Fidleris, ASME publication 62-WA-325*

Figure 2 — Out- and in-reactor creep test on 20% cold-worked Zircaloy-2 at 573 K and 210 MPa.

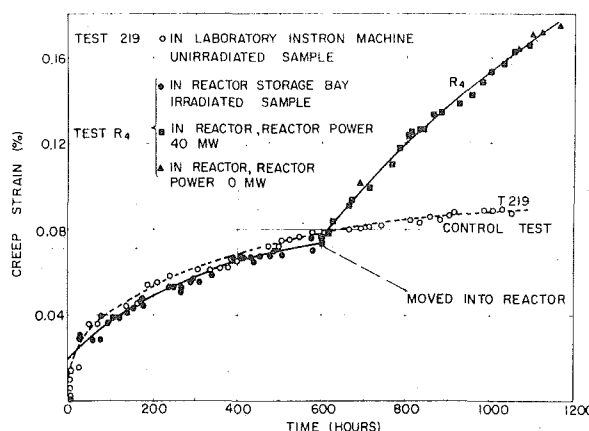


Figure 2 shows the first creep curves which clearly demonstrated how fast neutron flux increases creep rates.

Later measurements on full-size pressure tubes installed in NRU (an experimental reactor) confirmed that the conclusions from the uniaxial specimens were applicable to internally pressurized tubes in-reactor.

— *P.A. Ross-Ross and C.E.L. Hunt, J. Nucl. Mat. 26, 1968, p.2*

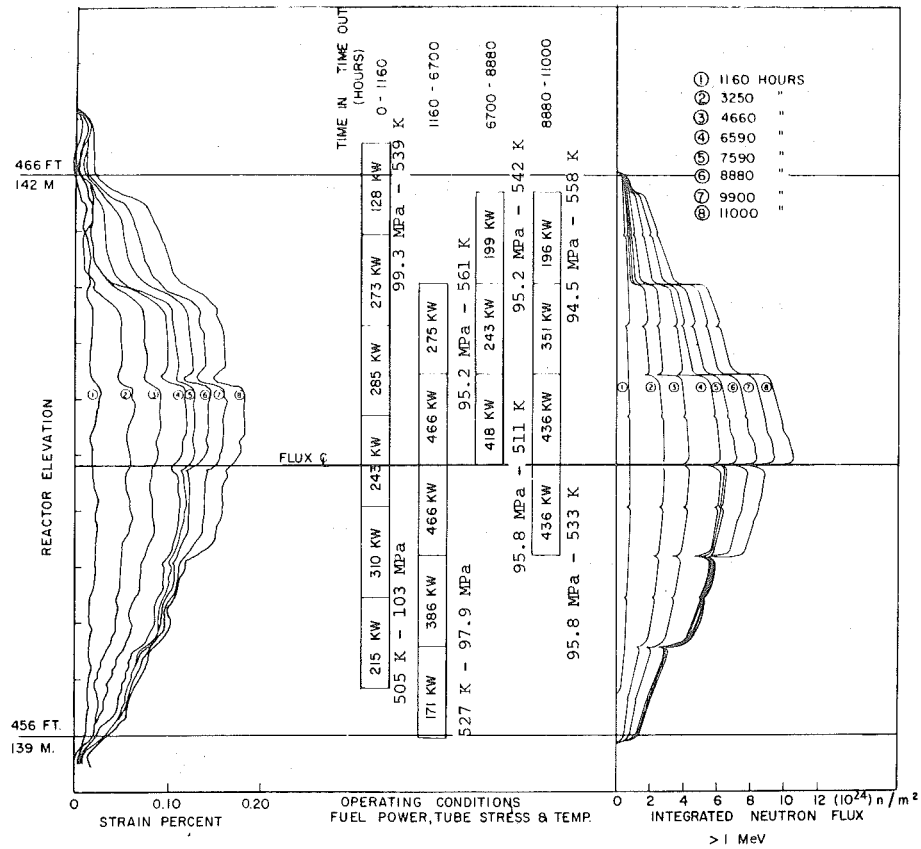


Figure 3 — 18% cold-drawn Zircaloy-2 pressure tube in NRU — stress, strain, temperature and integrated neutron flux vs. elevation.

Figure 4 — 18% cold-drawn Zircaloy-2 pressure tube — strain vs. integrated neutron flux at different elevations.

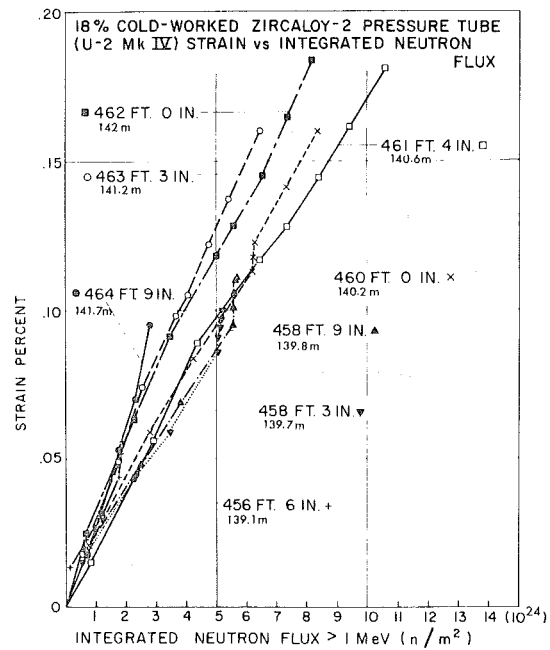


Figure 3 presents strain measurements and the corresponding integrated fast neutron flux, showing how closely related strain is to neutron flux. Figure 4 plots strain against integrated flux for various positions in the tube.

Although $1/3$ UTS is the design criterion for pressure tubes, creep rates estimated from tests in-reactor are necessary to ensure that total strains are within acceptable limits for the life of a reactor.

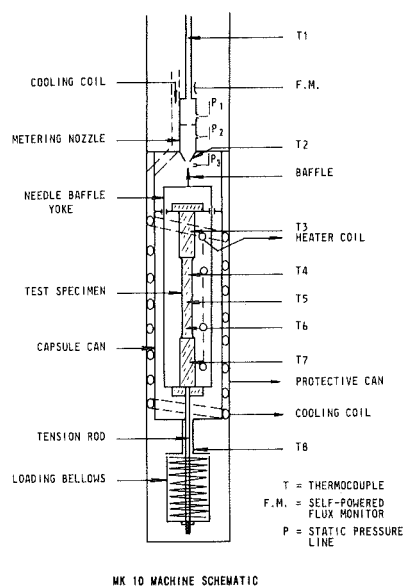
TYPES OF IN-REACTOR CREEP TESTS

Test types can be roughly classified as follows:

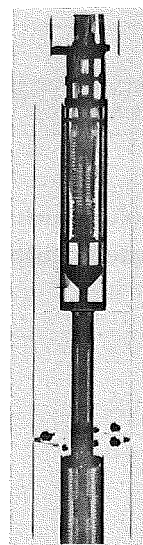
Uniaxial Creep Tests

Tests (usually in tension) on specimens with gauge lengths about 5 cm. Figure 5 shows a schematic of an in-reactor creep machine.

— V. Fidleris et al., *J. Phys. E*, 5, 1972, p.442



(a) schematic diagram



(b) radiograph

Figure 5 — Mk 10 uniaxial in-reactor creep machine

The advantages of uniaxial tests are:

Temperature and stress can be easily changed.

Specimens can be machined from small samples of the material.

Strain measurement is continuous.

The disadvantages are:

Stressing is not biaxial as for reactor pressure tubes.

Each specimen uses one reactor position, i.e., expensive on reactor space.

Pressure Tube Gauging

Diameters of pressure tubes are measured both on tubes installed in experimental reactors (NRX, NRU) and power reactors. Figure 6 shows photographs of a measuring head used for Canadian reactors.

— P.A. Ross-Ross and C.E.L. Hunt, *J. Nucl. Mat.* 26, 1968, p.2

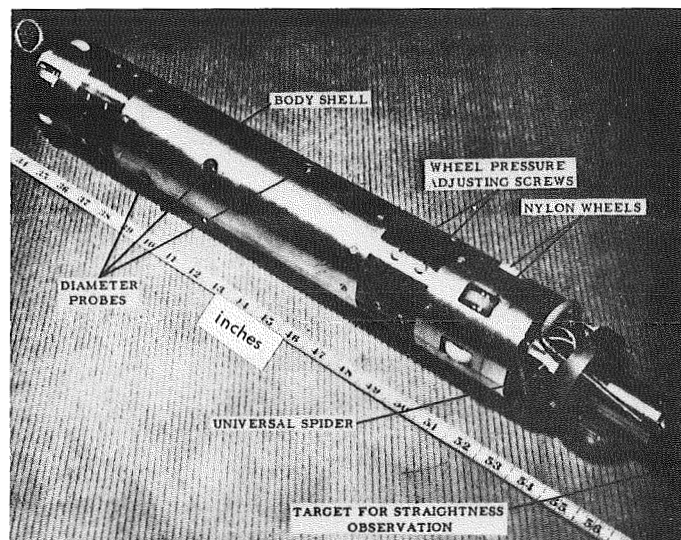
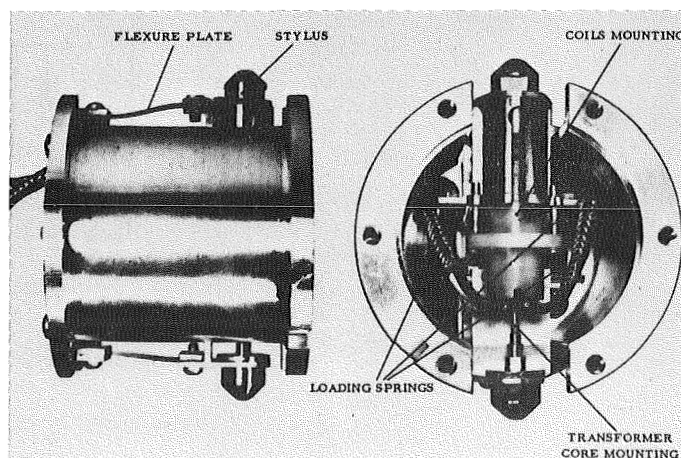


Figure 6 — Probe assembly for measuring diameters of pressure tubes.



The advantage of measuring pressure tubes is:

The data are directly applicable for reactor design because the operating conditions are similar to, or are the actual operating conditions of a power reactor.

The disadvantages are:

There is no experimental control of temperature or stress.

Material has to be in pressure tube form which does not allow easy changes of test material.

Measurements are intermittent at reactor shut-down.

Small Tube Experiments

Small diameter tubes (about 2.5 cm diameter) are brazed or welded together to form a continuous tube. Figure 7 shows a schematic of such an experiment,

— E.F. Ibrahim, *J. Nucl Mat.* 46, 1973, p. 169

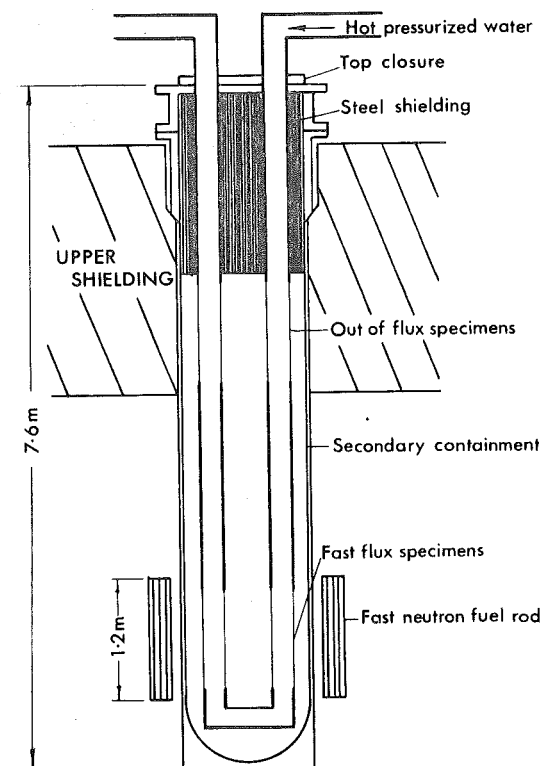


Figure 7 — Schematic diagram of an in-reactor tubular creep specimen assembly.

Internal diameters are measured intermittently, at reactor shut-down, with an air gauge.

— *E.F. Ibrahim and J.E. Winegar, J. Phys. E 6, 1973, p.884*

The advantages of these experiments are:

The biaxial stressing is the same as for pressure tubes, i.e., transverse stress is twice longitudinal.

Reactor space is used very economically, i.e., there are 12 specimens in-flux, which may be of different materials.

Out-of-flux controls have the same temperature and stress fluctuations as in-flux specimens.

The disadvantages are:

Small diameter specimens must be specially fabricated and hence they are not exactly the same as pressure tubes so data cannot be used directly for design.

Measurements are intermittent.

Temperature range is limited.

Stress-Relaxation Measurements

Strip specimens are pre-stressed in rigid holders and exposed to a neutron flux.

— *D.E. Fraser et al., J. Nucl. Mat. 46, 1973, p.281*

Figure 8 shows a photograph of such a holder with specimens. Specimen curvature is measured intermittently at reactor shut-down to measure change in stress, which can be related to a creep rate.

The advantages of stress-relaxation measurements are:

Large numbers of specimens can be tested in a single reactor hole.

New materials can be readily machined into specimens and inserted almost immediately in-reactor.

Measurements are probably unaffected by irradiation growth (to be discussed later).

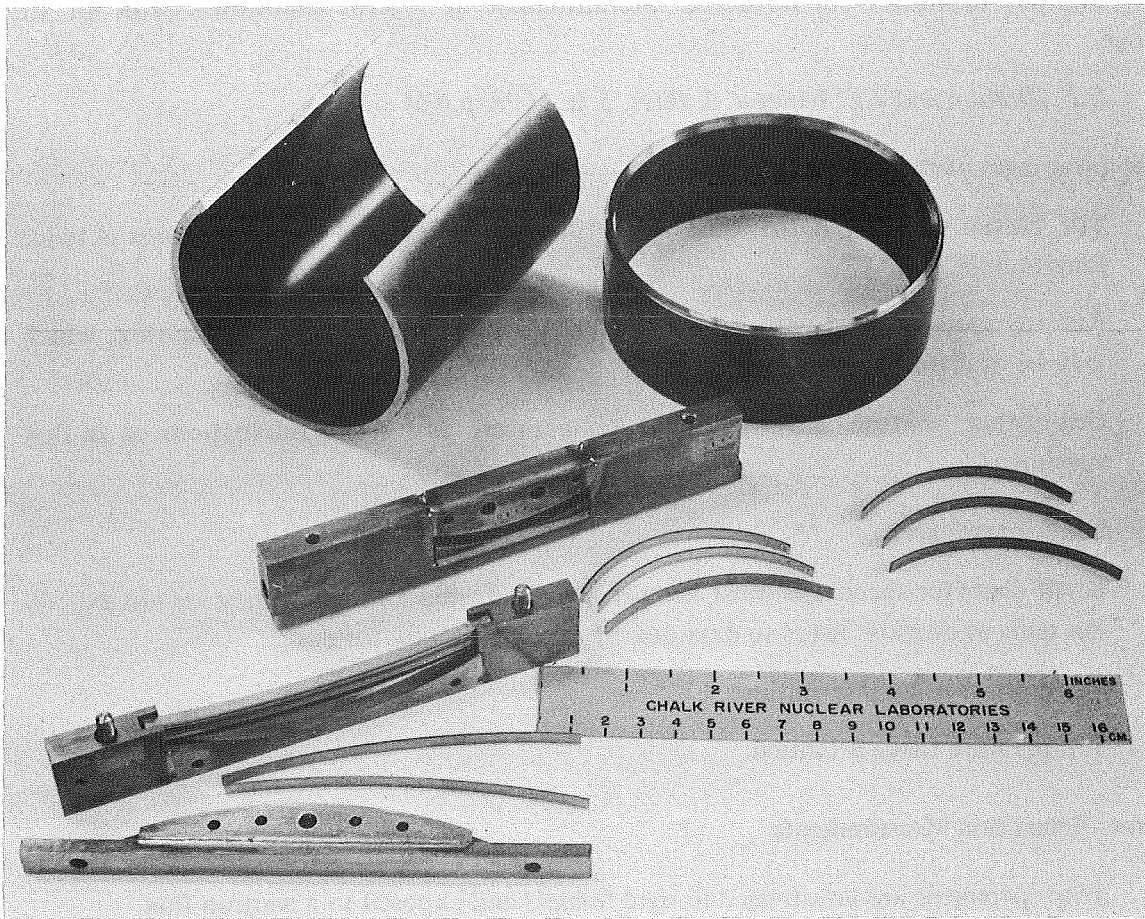


Figure 8 – Holder for stress-relaxation specimens

Disadvantages are:

Results are not creep measurements and have to be translated using some assumptions.

Stressing is not biaxial.

Measurement is intermittent.

Decrease of accuracy with test time is greater than for creep tests (because the stress is decreasing and thus also the strain rate is decreasing).

Stress is not readily controlled.

IN-REACTOR CREEP

OBSERVATIONS TO DATE

Effect of Alloy

The 2 alloys which have been tested extensively are Zircaloy-2 and Zr-2.5 wt% Nb. The results indicate that Zr-2.5 wt% Nb has better in-reactor creep properties than Zircaloy-2 in a similar metallurgical condition (creep rates about 1/2).

— *W. Evans et al., AECL-3982, 1971*

Effect of Material Condition

The most clearly defined effect is that increasing cold work increases creep rate. Figure 9 shows the effect of increasing cold work between quenching and aging Zr-2.5 wt% Nb. There are similar curves for Zr-2.5 wt% Nb cold-worked after extruding.

— *E.F. Ibrahim, ASTM-STP-551, 1974*

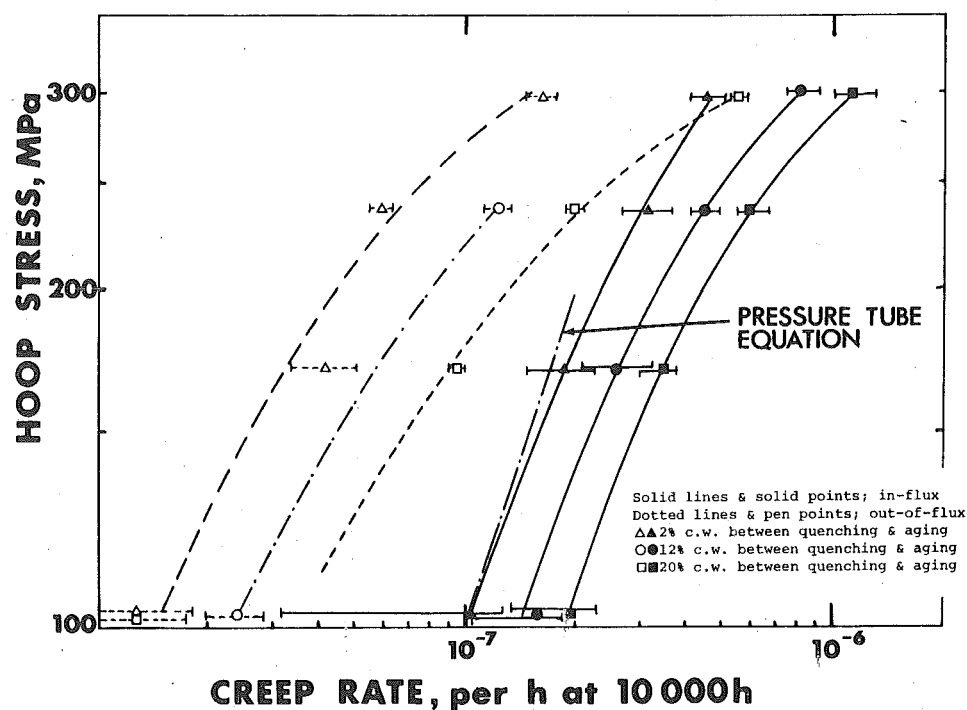


Figure 9 — Creep rates of quenched, cold worked and aged Zr-2.5 Nb tubular specimens in and out-of-neutron fluxes.

The results from stress-relaxation tests on a wide variety of Zr-base alloys in many conditions did not show any large differences for alloy or conditions.

— A.R. Causey, *ASTM-STP-551*, 1974

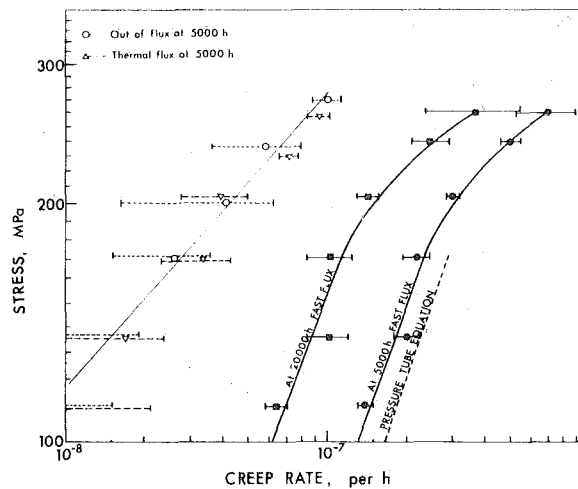
Effect of Stress

Below about 200 MPa (20 kg/mm²) the stress sensitivity (n) of the creep rate is close to 1, i.e., strain rate (ϵ) is directly proportional to stress (σ), $\epsilon \propto \sigma^n$.

Figure 10 demonstrates n close to 1 for both small tubes and pressure tubes.

— P.A. Ross-Ross and V. Fidleris, *Int. Conf. on Creep and Fatigue, Conf. Publication 13*, 1973, AECL-4626

Figure 10 — Creep rates of 20% cold-drawn Zircaloy-2 tubular specimens at 536 K in and out-of-neutron fluxes.



Effect of Time

Uniaxial tests, V. Fidleris, *J. Nucl. Mat.* **26**, 1968, p.51, and pressure tube measurements, P.A. Ross-Ross and C.E.L. Hunt, *J. Nucl. Mat.* **26**, 1968, p.2, show that after the 1st 1000 h creep rates did not change much for either Zircaloy-2 or Zr-2.5 wt% Nb up to 10 000 h. Longer-term tests on small tubes, E.F. Ibrahim, *J. Nucl. Mat.* **46**, 1973, p.169 and pressure tubes, D.S. Wood, *BNES, Conf. Proc.* 1972, p.34 show lower rates at longer times, the rates at 20 000 h being approximately 1/4 those at 5000 h, (see Figure 10).

Effect of Fast Neutron Flux

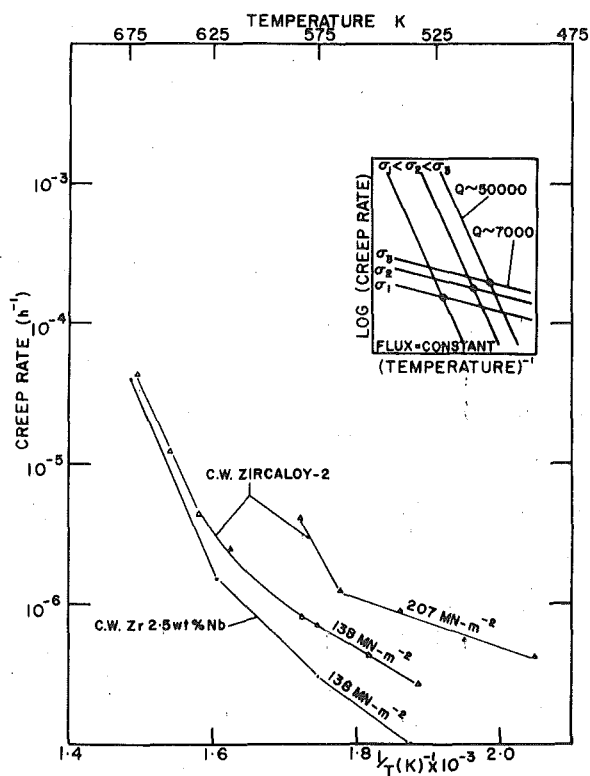
The results on pressure tubes, *P.A. Ross-Ross and C.E.L. Hunt, J. Nucl. Mat. 46, 1968, p.2* where the fast neutron flux differs along the tube, show that creep rate is about proportional to neutron flux. Another assessment in the UK, *D.S. Wood and B. Watkins, J. Nucl. Mat. 41, 1971, p.327* concluded that creep rate was proportional to neutron flux to the power 0.85.

Effect of Temperature

Most of the creep and stress-relaxation tests have been in the range 530 to 575K where creep rate is not very sensitive to temperature. Figure 11 shows results from some uniaxial tests over a much wider temperature range 475-675K. Above about 570K creep rates increase more rapidly with temperature as thermal creep becomes more important.

— *P.A. Ross-Ross and V. Fidleris, AECL-4626*

Figure 11 — Temperature dependence of in-reactor creep rate of zirconium alloys in a fast neutron flux of $6-9 \times 10^{16} \text{ n/m}^2 \text{ s}$.



CREEP DUCTILITY

Out of reactor creep ductility of zirconium alloys has been shown to increase with decreasing stress-sensitivity, as for many other alloys.

— *E.F. Ibrahim and C.E. Coleman, J. Nucl. Mat. 12, 1973, p.285*

Figure 12 shows the relationship between n and total elongation at rupture. Since n is about 1 for in-reactor tests very high ductility would be expected. Results so far indicate that this is so. Figure 13 shows an example of a Zircaloy-2 specimen which strained 9% without any signs of accelerating creep or fracture.

— D.S. Wood and B. Watkins, *J. Nucl. Mat.* 41, 1971, p.327

Figure 12 — Variation of the creep rupture ductility with the stress sensitivity of minimum creep rate for Zircaloy-2 and Zr-2.5 Nb: out-of-pile tests at 573 to 723 K. (Hatched band is for results plotted by Woodford for tests of many alloys.)

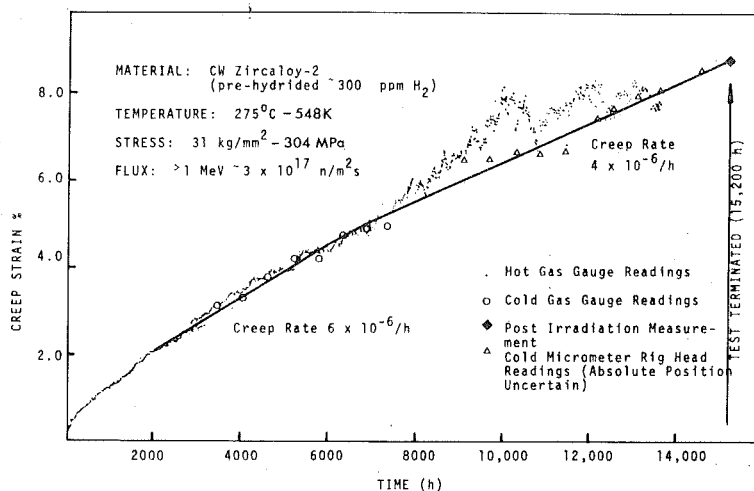
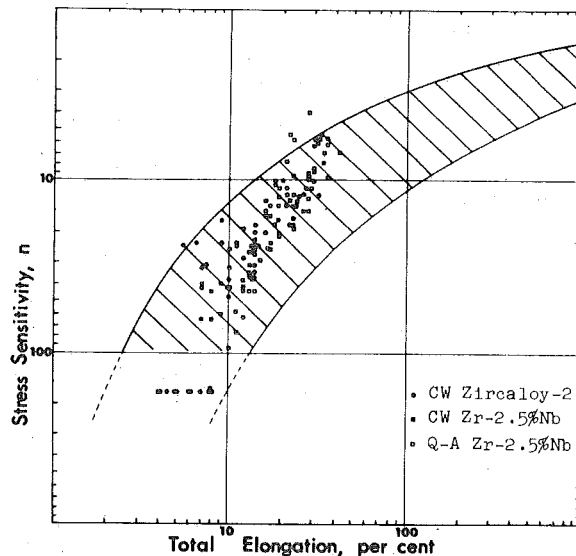


Figure 13 — In-reactor high strain test on uni-axial specimen of cold-worked Zircaloy-2.

MECHANISMS OF IRRADIATION CREEP

Many mechanisms have been proposed for the effect of irradiation on creep. More than one mechanism may be responsible and relative importance of a mechanism may depend on temperature, stress and neutron flux. *E.R. Gilbert, Reactor Tech. 14, 1971, p.258* has reviewed the mechanisms comprehensively.

Enhanced Climb

A fast neutron flux produces an excess of interstitials and vacancies over equilibrium thermal concentrations. If there is an imbalance in the rate of arrival of interstitials or vacancies at dislocations, then climb of dislocations will occur thus increasing the creep rate if climb is controlling creep rate. This mechanism is probably at least partly responsible for irradiation creep.

- *G.R. Piercy, J. Nucl. Mat. 26, 1968, p.18*
- *S.R. MacEwen, J. Nucl. Mat. to be published*

Yielding Creep

The yielding creep model was first applied to uranium, *A.C. Roberts and A.H. Cottrell, Phil. Mag. 1, 1956, p.711*, which has very high irradiation growth. *R.V. Hesketh, J. Nucl. Mat. 26, 1968, p.77* applied the yielding creep model to zirconium (which has much lower irradiation growth rate). Hesketh shows that if the stress sensitivity of creep rate is greater than 1 then summing the internal stresses between grains (from growth) plus the applied stress will give a higher creep rate than if the internal stresses are absent.

Loop Alignment

When point defects from neutron collisions condense into dislocation loops, the orientation of the loops may be biased by applied stress or there may be growth of favourably oriented loops resulting in strain. *F.A. Nichols, J. Nucl. Mat. 37, 1970, p.59* believes this mechanism to be important at low stresses.

Thermal Spike Relaxation

J.A. Brinkman and H. Wiedersich, ASTM-STP-380, 1965, p.3 proposed that in the region of a thermal spike from a fast neutron collision (where small regions up to 5.5 nm diameter may reach temperatures up to 3000K and may exist for up to 10^{-10} s) the applied stress may be relaxed or partly relaxed. The strain would be a sum of this relaxation. If the relaxation is from preferential condensation of dislocation loops, it is difficult to separate this theory from loop alignment theory.

IRRADIATION GROWTH

The first irradiation growth measurement on zirconium were by *S.N. Buckley*, *Properties of Reactor Materials*, Butterworths, 1962, p.13 who measured irradiation growth from fission fragments on a single crystal. He showed a contraction in the $[0001]$ and a growth in $[11\bar{2}0]$ direction. He proposed that (as with uranium) the growth was consistent with alignment of dislocation loops from the stresses resulting from anisotropic thermal expansion in a damage region. *E.F. Ibrahim and J.E. Winegar*, *J. Nucl. Mat.* **45**, 1972/73, p.335 and *J.E. Harbottle*, *ASTP-STP-484*, 1971, p.287 have shown that the growth of annealed polycrystalline zirconium alloys of known texture is as expected from single crystal data. *Ibrahim and Winegar and V. Fidleris*, *J. Nucl. Mat.* **46**, 1973, p.356 have shown that cold-worked specimens do not behave as expected from their texture. Since *S.N. Buckley*, *AERE-R-5944*, 1968, p.547 has shown irradiation growth to occur in cold-worked cubic metals this is not suprising. Growth then has 2 components:

- (1) that due to the crystallographic structure (probably because of anisotropic thermal expansion coefficients)
- (2) that due to dislocation arrangement.

SUMMARY

Design stresses for zirconium alloy components in-reactor are based on out-of-reactor properties, i.e., UTS. In-reactor, however, dimensional changes are induced by the high fast neutron flux, i.e., irradiation enhanced creep and growth. Creep and growth must therefore be investigated to evaluate behaviour of reactor components and to improve the materials used.

High creep rates in a fast neutron flux are probably wholly or partially due to enhanced climb of dislocations from point defects introduced by neutron collisions. The lower creep strength of material which has been cold-worked is consistent with this theory.

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LECTURE NO. 8*

PROPERTIES OF ZIRCONIUM ALLOY PRESSURE TUBES

by

W.J. Langford and C.E. Ells

Pressure tubes are the pressure vessels of Canadian designed CANDU (Canada Deuterium Uranium) nuclear reactors. They are about 10 cm in diameter, 0.3 to 0.5 cm thick by 6 m long and contain the fuel and cooling water operating at about 9.6 MPa (1400 psi) and 575K. A power reactor basically consists of many identical pressure tube assemblies similar to that shown in Figure 1.

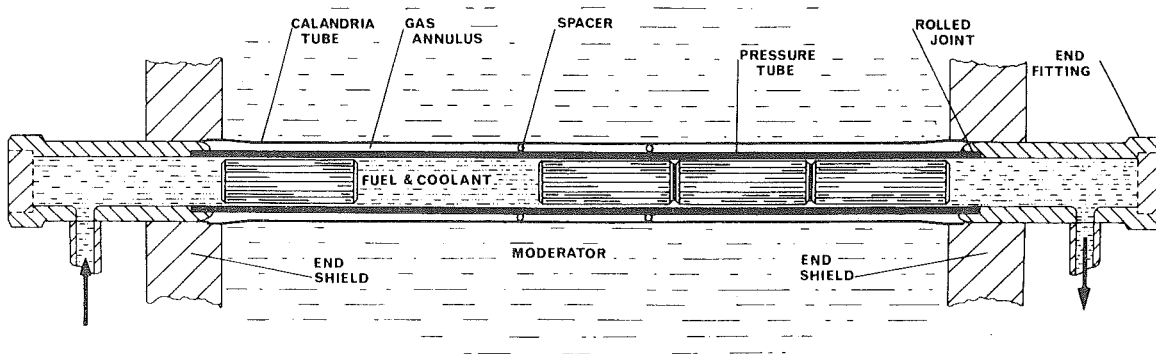


Figure 1 — Schematic of a Fuel Channel for a CANDU Reactor with Pressurized Water Coolant.

A pressure tube alloy must:

- a) be able to be fabricated into tubes,
- b) have adequate neutron economy,
- c) have adequate in-reactor creep strength,
- d) resist corrosion by the reactor coolant,
- e) have adequate tensile strength, and
- f) retain adequate ductility in the reactor.

This lecture is largely concerned with the two points e) and f), and with the effects of hydrogen picked up from the corrosion reaction.

Pressure tubes in the following alloys and metallurgical conditions are now in service in CANDU power reactors:

- a) Zircaloy-2 cold-worked
- b) Zr-2.5 wt% Nb quenched and aged
- c) Zr-2.5 wt% Nb cold-worked

Cold-worked Zr-2.5 wt% Nb is the current reference tube material. Tubes from a new alloy, Zr-3.5 Sn-0.8 Nb-0.8 Mo, are now being developed (Lecture 9), and the alloy Zr₃Al is being studied.

- C.E. Ells *et al.*, *Proc. BNES Conference on Irradiation Embrittlement and Creep in Fuel Cladding and Core Components*, Nov. 1972, p.43

The pressure tubes operate at about 575K in-reactor, and hence 575K becomes the general reference temperature for properties. The tensile properties for the three tube materials are listed in Table 1.

Table 1: Pressure Tube Tensile Properties at 575K

Material	Test ^a	0.2% Yield Strength		Ultimate Tensile Strength		Elongation (%)	Reduction in area (%)
		MPa	kpsi	MPa	kpsi		
Cold-worked Zircaloy-2	LT	320	45	380	54	26	55
	TT	350	50	370	52	23	54
Cold-worked Zr-2.5 wt% Nb	LT	370	53	530	76	15	50
	TT	540	77	570	81	23	54
Heat-treated Zr-2.5 wt% Nb	LT	480	69	600	86	19	61
	TT	670	95	690	98	12	50

^a Abbreviations — LT, longitudinal tensile; TT, transverse tensile.

- P.A. Ross-Ross *et al.*, *Proc. IIIrd Inter-American Conference on Materials Technology*, 1972

The effects of neutron irradiation on the tensile properties of the pressure tube material have been studied extensively. Most of this work has been with the temperature during irradiation in the range 375 – 575K. For this temperature range the response to irradiation can be summarized as:

- a) Yield and ultimate strengths increase, but approach saturation values at fluences of about 10^{25} n.m^{-2} ($E > 1.0 \text{ MeV}$);
- b) Uniform elongations decrease to values $\leq 1\%$;
- c) Total elongations decrease but remain significantly large;
- d) Reductions in area at fracture change very little.

Tensile load-elongation curves illustrating effects of irradiation are presented in Figure 2 for quenched and aged Zr-2.5 wt% Nb, and in Figure 3 for cold-worked Zr-2.5 wt% Nb. The approach to saturation exhibited by cold-worked Zircaloy-2 is illustrated in Figure 4.

— *J.E. Irvin, J. Electrochem., 4, 1966, p.240*

The effects of hydrogen have been discussed in a previous lecture. The maximum deuterium* concentrations expected in operating pressure tubes, $\leq 400 \text{ ppm}$, will have little effect on tensile properties when the hydride platelet orientation is properly controlled. Details of the combined effects of irradiation and hydrogen are presented in Table 2.

— *W. Evans and G.W. Parry, Trans. Electrochem. Soc. 4, 1966, p.225*

The response to irradiation is influenced by the crystallographic texture of the materials. The texture is very important in annealed materials, but when the material is hardened by cold-work it is more difficult to distinguish between different textures. Cold-worked Zr-2.5 wt% Nb tubes have a pronounced crystallographic texture and when a preponderance of basal plane normals are aligned with the tensile axis as in the transverse tensile test the uniform elongation after irradiation is low, Table 2.

— *G.W. Parry, AECL Report, AECL-2625, Nov. 1966*

* In a heavy water cooled reactor, the deuterium isotope is picked up in corrosion reactions. Due to the difference in mass, twice as much deuterium as hydrogen (by weight) is necessary to form a given amount of hydride. Thus 400 ppm D_2 is equivalent to a pickup of 200 ppm H_2 (by weight).

Table 2: The Combined Effect of Hydrogen and Irradiation on the Tensile Properties of Zr-2.5 Nb and Zircaloy-2 in Tests at 575K
Specimens were irradiated at about 555K to about $2.7 \times 10^{24} \text{ n.m}^{-2}$ ($E > 1.0 \text{ MeV}$)

Material	Hydrogen Concentration	Specimen Direction	Irradiation	0.2% Y.S. MPa	Y.S. kpsi	U.T.S. MPa	U.T.S. kpsi	% Uniform Elongation	% Total Elongation
Zr-2.5 wt% Nb water quenched from 880°C aged 54h at 773K	0	L	unirradiated	610	86.6	630	90.0	—	14.8
	0	L	irradiated	800	114.5	830	117.9	—	9.5
	220–290	L	unirradiated	580	82.7	660	93.6	—	13.2
	250–320	L	irradiated	830	117.4	840	119.0	—	5.5
Zircaloy-2 cold drawn 20%	0	L	unirradiated	300	42.2	340	47.8	—	12.8
	0	L	irradiated	450	63.7	450	63.7	—	5.8
	136–190	L	unirradiated	320	45.9	360	51.7	—	18.0
	162–216	L	irradiated	460	65.7	460	65.7	—	8.8
Zr-2.5 wt% Nb cold drawn 20%	0	L	unirradiated	390	54.9	490	69.5	4.7	8.5
	0	L	irradiated	530	75.3	640	91.6	4.1	7.5
	0	T	unirradiated	510	72.7	530	75.6	1.1	4.0
	0	T	irradiated	650	93.6	660	93.8	0.5	2.9

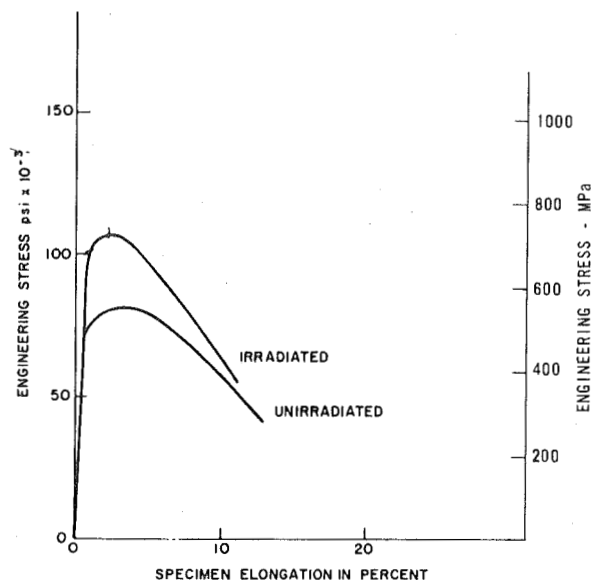


Figure 2 – Engineering Stress Strain Curves for Zr-2.5 wt% Nb Alloy Quenched from the $(\alpha + \beta)$ -Phase and Aged 24 h at 775K. Irradiation at 525 – 600K to $5.4 \times 10^{24} \text{ n.m}^{-2}$. Test at 575K; specimens from the longitudinal direction in rod.

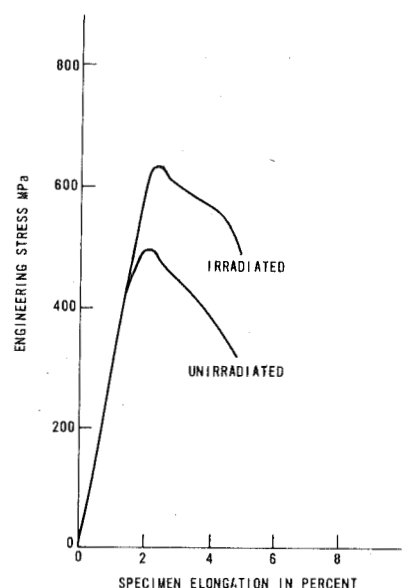


Figure 3 – Engineering Stress Strain Curves for Zr-2.5 wt% Nb Alloy in a Cold-Worked Condition. The Curves are for Transverse Specimens, taken from a Tube Cold Drawn 23%. Irradiation at 575K to 10^{24} n.m^{-2} . Tests at 575K.

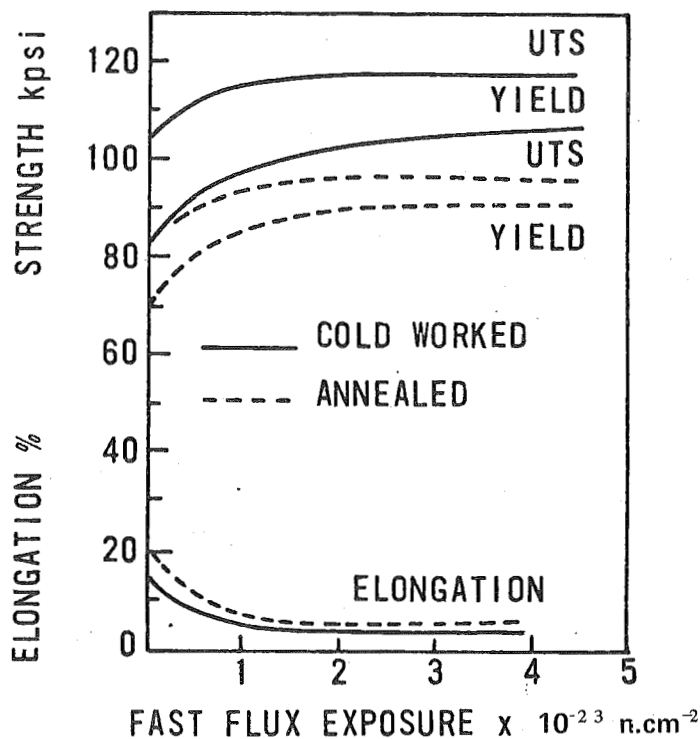


Figure 4 – The Effect of Neutron Irradiation on the Tensile Properties of Zircaloy.

The reduction in area at fracture of Zircaloy-2 remains high after irradiation for all the metallurgical conditions that have been examined. When Zr-2.5 wt% Nb is irradiated after quenching from the β -phase, irradiation induces a sharp drop in reduction in area, Figure 5. For this reason welds must be carefully designed.

— C.E. Ells and C.D. Williams, *Trans. AIME* 245, 1969, p.1321

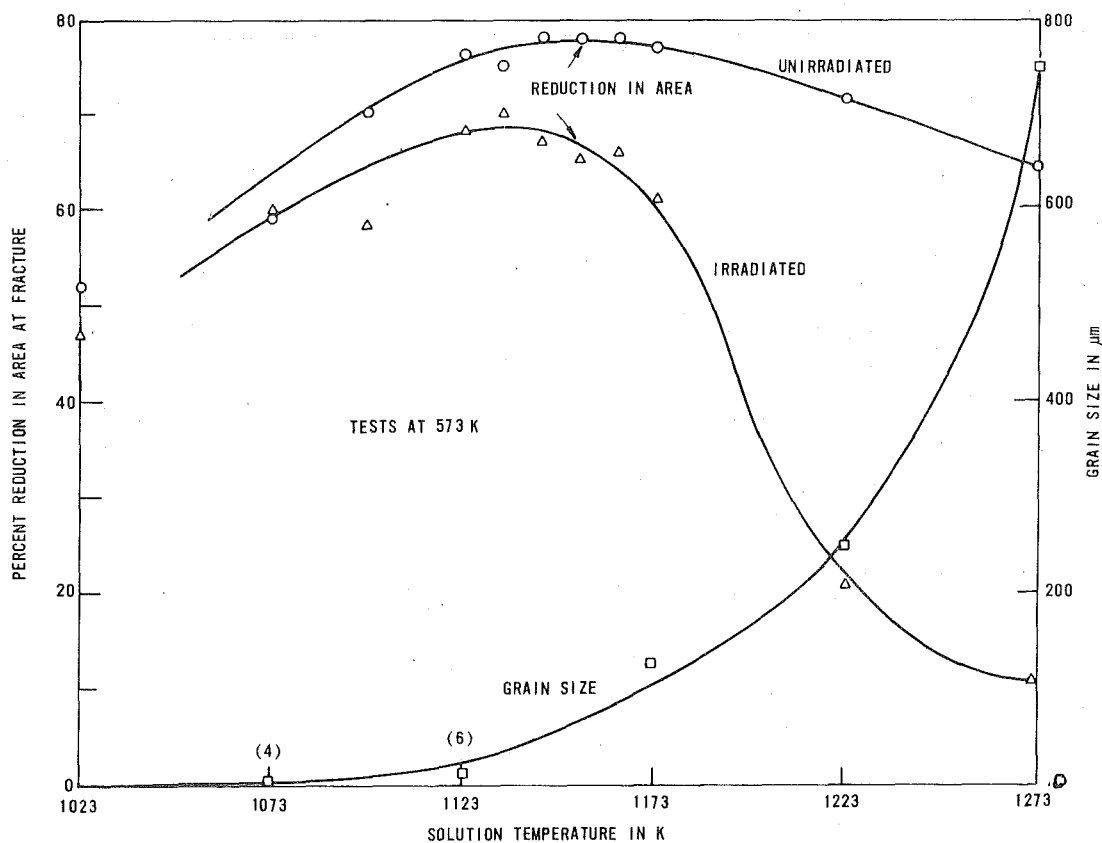


Figure 5 —The Effect of Solution Temperature on the Ductility of Zr-2.5 wt% Nb Alloy. The Specimens were Water Quenched from the Solution Temperatures Shown. Irradiation was at about 373K to a Fluence of about 4×10^{23} ($E > 1.0$ MeV).

Zirconium alloys, unlike steels, do not show a transition from ductile to brittle fracture with decreasing temperature in impact tests. Hydrogen and irradiation together reduce the impact energy absorbed at a given temperature, Figures 6 and 7. Impact properties cannot be quantitatively related to pressure tube fracture characteristics, and therefore play no part in safety evaluations.

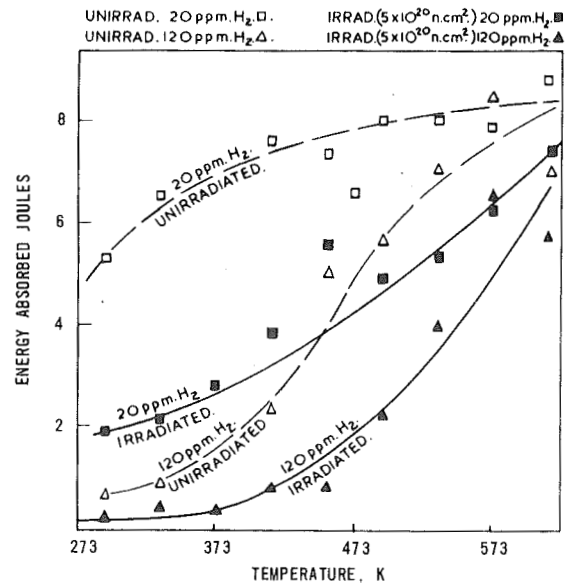


Figure 6 – The Impact Energy of Cold-Worked Zr-2.5 Nb. After Hydriding the Specimens were Cold Rolled 20%. Irradiation was at about 568K to a Fluence of about $5.3 \times 10^{24} \text{ n.m}^{-2}$ (Ni).

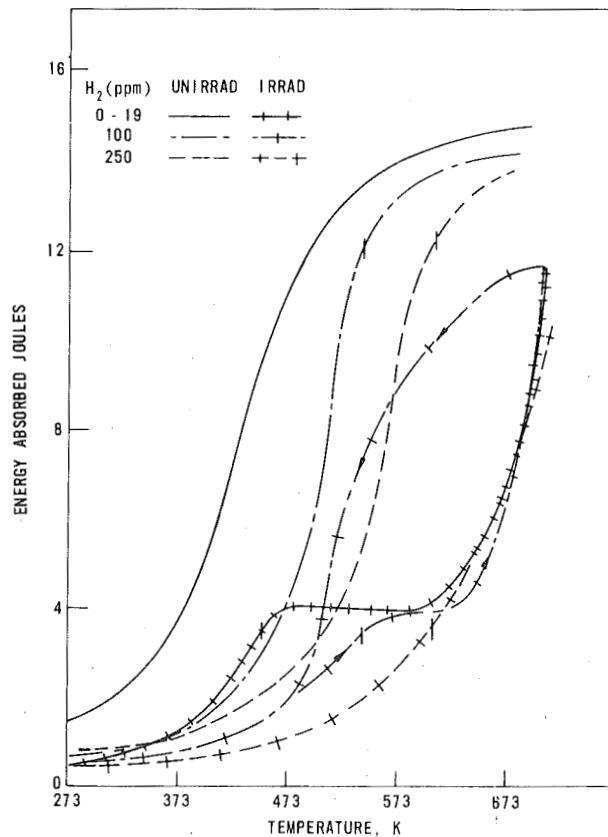


Figure 7 – The Impact Energy of Quenched and Aged Zr-2.5 Nb. After Hydriding the Specimens were Solution Treated 1 h at 1153K, Water Quenched, and Aged 24 h at 773K. Specimens were Irradiated at about 548K to a Fluence of about $3 \times 10^{24} \text{ n.m}^{-2}$ ($E > 1.0 \text{ MeV}$).

-- D.S. Wood et al., *Trans. Electrochem. Soc.* 4, 1966, p.250

There is limited information on the properties of the pressure tube alloys when the temperature during irradiation is $> 575\text{K}$. The effects from irradiation decrease with increasing temperature, which means that at any given fluence the ductility remains higher. The recovery of cold-work at 675K decreases the tensile yield strength more rapidly than neutron irradiation increases it, Figure 8.

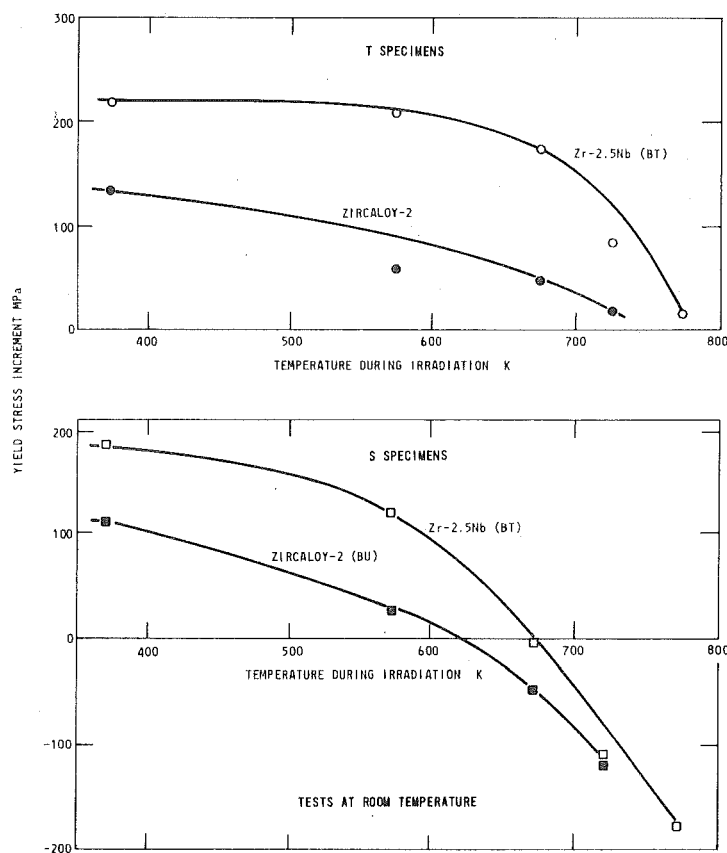


Figure 8 – Yield Stress Increments in Cold Worked Zr-2.5 wt% Nb and Zircaloy-2 as a Function of Crystallographic Texture and Temperature During Irradiation.

S – Specimens Textured Favourably for Slip.

T – Specimens Textured Unfavourably for Slip.

C.E. Ells et al., Proceedings at Conference on Mechanical Behaviour at Materials, Kyoto, Aug. 1974

POST-IRRADIATION TESTING OF PRESSURE TUBES

Testing of small specimens indicates alloys and metallurgical conditions which are worth developing for pressure tubes. A small number of development and pre-production pressure tubes is made, and tubes are irradiated *under full service conditions* in test reactors to determine their behaviour.

These development tubes are routinely monitored while in the reactor, and after a long irradiation the tube is removed and destructively examined. The location of test specimens can be selected depending on the neutron fluence, as shown in Figure 9.

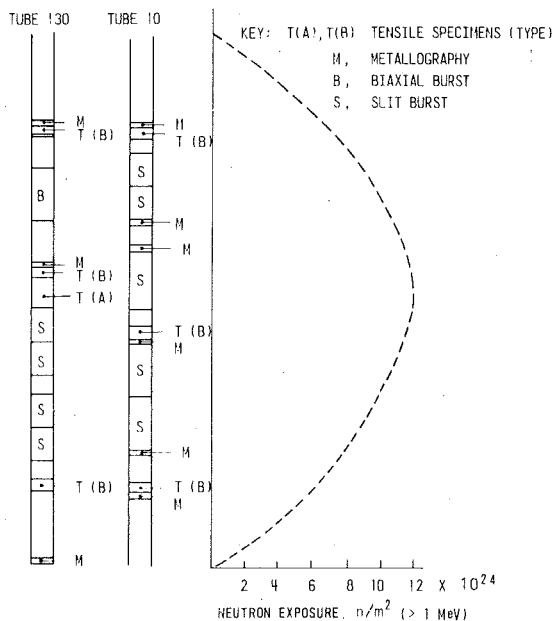


Figure 9 — Test Specimen Locations in Cold-Worked Zircaloy-2 Pressure Tubes.

Properties measured include uniaxial tensile strength, ductility, burst strength, oxide film thickness, hydrogen (or deuterium) concentration, and flaw tolerance. Diameter measurements are made for comparison with in-pile creep data.

EFFECTS OF IRRADIATION ON PRESSURE TUBE PROPERTIES

1 — Mechanical Strength and Ductility.

Irradiation increases uniaxial tensile strength and reduces ductility, agreeing with predictions based on irradiations of small specimens. Typical biaxial strength properties of irradiated tubes are given in Table 3, with unirradiated data for comparison. (Note that biaxial burst strength is typically up to 15% higher than uniaxial tensile strength in isotropic materials because plastic deformation is inhibited by the longitudinal stress (= 0.5 hoop stress). In zirconium alloy tubes, biaxial strength is up to 20% above uniaxial strength because of the additional influence of anisotropic deformation modes.)

Table 3: Burst Test Properties of Zirconium Alloy Pressure Tubes at 575K

Material	*	0.2% Yield Strength		Burst Strength		Elongation	Reduction in Area
		MPa	kpsi	MPa	kpsi	%	%
cold worked	U	420	60.0	450	63.0	28	35
Zircaloy-2	I	550	78.0	550	78.5	7.5	12-17
cold worked	U	530	75.0	600	85.0	3-7	30
Zr-2.5 wt% Nb	I	770	110.0	780	111.0	1	15-17
heat treated	U	650	92.0	770	109.0	2-5	20
Zr-2.5 wt% Nb	I	101.2	114.0	1100	157.0	1	14

U is unirradiated — I is irradiated

The reduction in ductility due to irradiation is shown in Table 3. Note the different behaviour of Zircaloy-2 compared with Zr-2.5 wt% Nb tubes. Zircaloy-2 bulges considerably during the 575K burst test, producing high transverse elongation, which is reduced by irradiation. This deformation behaviour has been explained using the following model, due to:

- A.L. Bement, *AIME Symposium on Irradiation Effects on Metals*, Asheville, North Carolina, September 1965

Irradiated cold-worked Zircaloy-2 with a texture oriented for $(10\bar{1}2)$ twinning in tension (i.e. the hoop direction in the pressure tube) generally shows an abrupt yield point

in uniaxial tension tests at 575K. This is attributed to mobile dislocations sweeping channels free of defects: the moving dislocations absorb defects and thus reduce the stress required to move following dislocations. The situation after yield is therefore unstable, since the stress to initiate plastic flow exceeds the stress necessary to maintain the flow. In the irradiated pressure tube under biaxial stress, plastic flow may commence if a local stress concentration (usually at the thinnest wall section) reaches yield, after which flow can continue unstably until the local stress is relieved. Failure would occur at this point while the remainder of the tube had barely yielded, as shown by the observed reduction in transverse elongation during burst tests of irradiated tubes. Under operating conditions, the stress in the tube is only one third of the unirradiated longitudinal tensile strength, and plastic instability is not a matter of concern. As will be discussed in the next section, pressure tubes are remarkably tolerant to severe stress-concentrating flaws, partly as a result of the plastic flow properties of these materials.

Zr-2.5 wt% Nb pressure tubes do not bulge during the burst test, and transverse elongation is relatively low: irradiation reduces it slightly. This behaviour is discussed by:

— C.E. Ells and B.A. Cheadle, *ASTM-STP-458, Philadelphia, 1969, p.68*

in terms of the greater restraints on deformation imposed by the higher strengths of the Zr-2.5 wt% Nb alloy.

In all three alloys, reduction in area at fracture is ample after irradiation: this localized yielding at stress concentrations is responsible for the very good flaw tolerance of the pressure tubes.

2 – Flaw Tolerance

The possibility of damage to a pressure vessel is always of concern. The pressure tube inspection program in operating CANDU reactors has shown that damage due to fuel movement is negligible. However, the ability of tubes to tolerate severe damage has been demonstrated. The tube irradiation program has been particularly valuable in providing highly irradiated tubes for such demonstration: only when the pressure vessel is a simple tube are replicate burst tests on full size components conceivable.

More than 120 specimens from pressure tubes have been burst after being artificially flawed. The technique employed was to spark machine through-wall longitudinal slits in pressure tube specimens 280 to 450 mm in length. The slits were about 0.15 mm (0.006 in) wide, of preselected lengths, and were sealed with a soft aluminum liner to prevent leakage during the test, Figure 10.

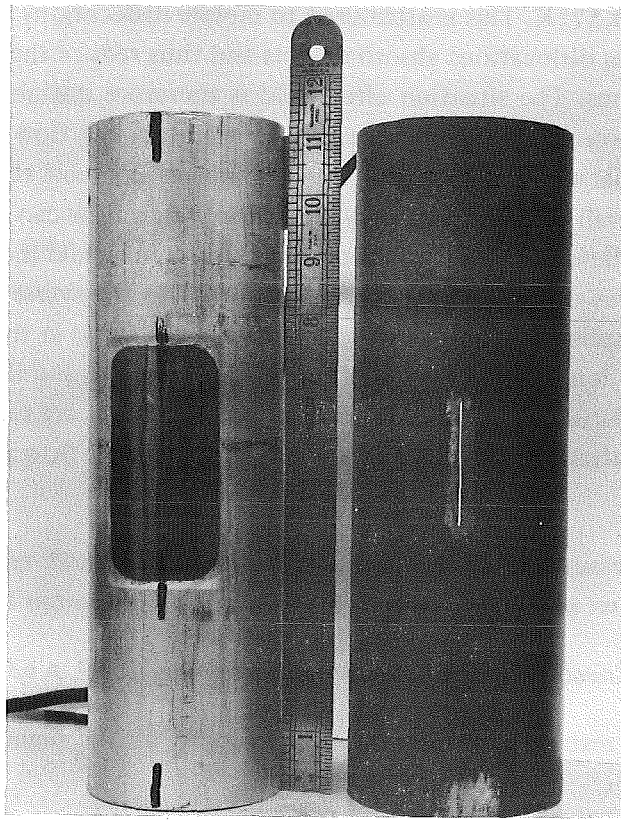


Figure 10 – Typical Assembly for Flaw Tolerance Test. Pressure Tube (Right) with Spark Machined Flaw, Soft Aluminum Liner on Left. Scale is in Inches.

Results are plotted in terms of failure stress as a function of slit length. On logarithmic scales the results produce reasonably straight-line plots. Figure 11 summarizes the Chalk River results for the three pressure tube materials of interest. The intercept between one of the curves, and reactor design stress (a horizontal line) gives the *critical crack length* for the material and temperature being considered.

Figure 11 shows that for present reactor design stresses (11.2-18.3 kg/mm², 16-26 kpsi) critical crack lengths at 575K exceed 50 mm for all three materials.

At 295K critical crack lengths are slightly smaller, particularly for the high-strength heat-treated Zr-2.5 wt% Nb alloy.

All critical crack lengths are large enough to ensure that a crack developing from a small defect will, if it grows at all, penetrate the tube wall, causing leakage of the pressurizing fluid. Detection of the leakage in the reactor system ensures that the reactor

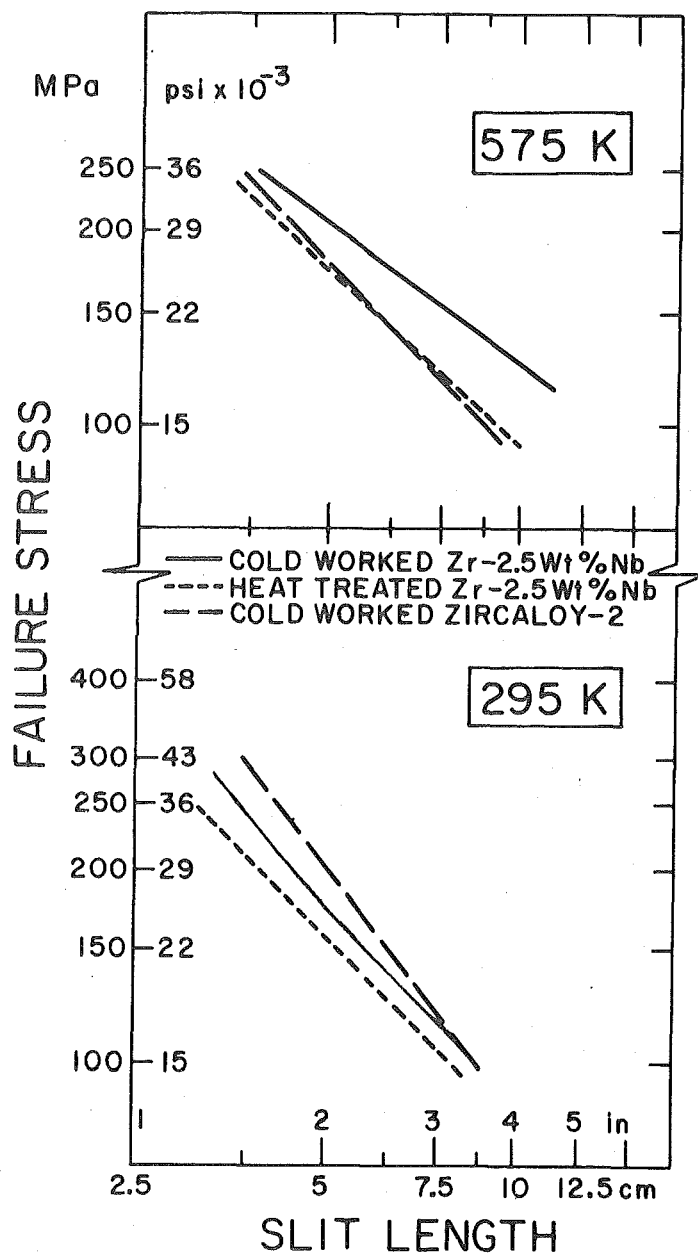


Figure 11 – Failure Stress of Zirconium Alloy Pressure Tubes Versus Slit Length.

can be shut down *before* the defect reaches a critical size. This is the “leak-before-break” philosophy of pressure vessel safety, and has been demonstrated to apply to pressure tubes in all conditions of practical interest. This conclusion is not altered by using sharper defects: recent tests have shown that “leak-before-break” occurs even when fatigue-sharp cracks are grown in tubes by pressure cycling.

3 – Effects of Hydrogen/Deuterium

This was the subject of an earlier lecture, and it will suffice to say that large hydrogen concentrations (up to 400 ppm) can be tolerated by all current pressure tube alloys with little effect on flaw tolerance at reactor operating temperature, 575K. At 295K, critical flaw sizes are reduced by high hydrogen concentrations, consistent with the observed interaction of temperature and hydride ductility.

Analyses of full size pressure tubes, irradiated under power reactor conditions for up to 29 000 h, have shown that deuterium/hydrogen pickup will not impair tube properties during the lifetime of a reactor.

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CRNL-1208

LECTURE NO. 9*

ZIRCONIUM ALLOY FUEL CLADDING

by

C.E. Coleman, R.A. Holt and B.A. Cheadle

In CANDU reactors natural UO_2 is clad in zirconium alloy tubes. This primary unit is called an element and several elements are held together in a bundle, Figure 1. The bundles are about 50 cm long and several bundles are placed end to end in the fuel channel, Figure 2.

Zircaloy-4 is the only fuel cladding alloy used in our current commercial power stations. Zr-1 wt% Nb, Zr-2.5 wt% Nb and Zr-1.15 wt% Cr-0.1 wt% Fe may be considered for future reactor designs.

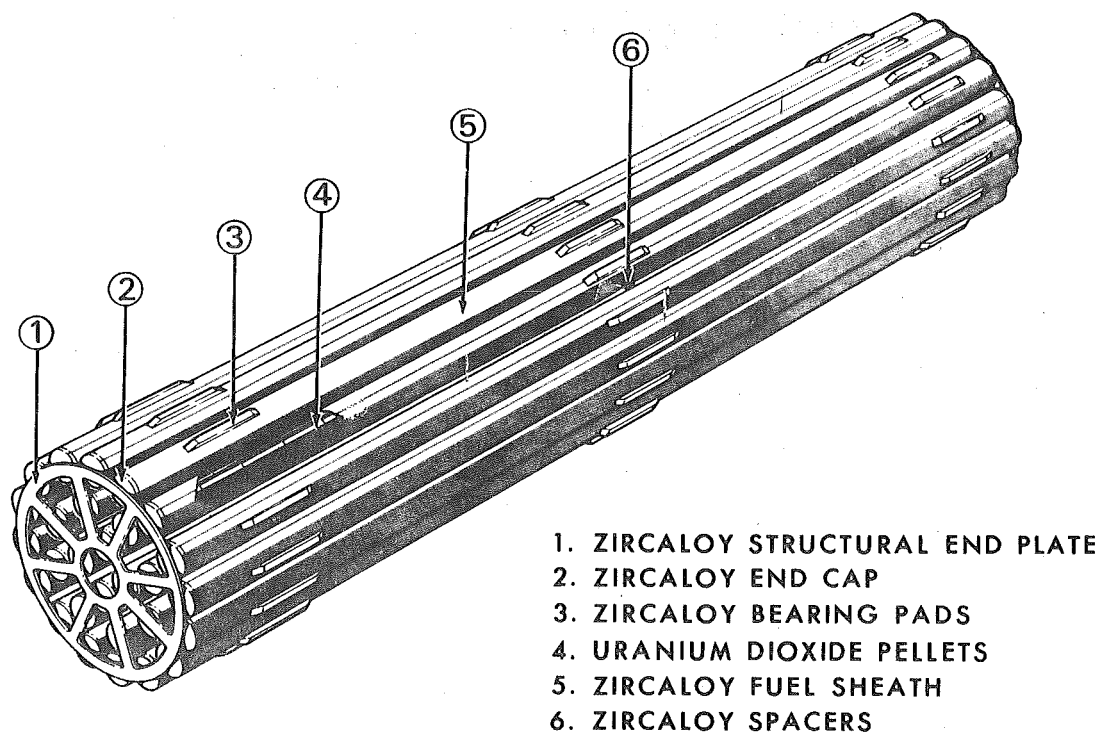


Figure 1 – CANDU reactor fuel bundle

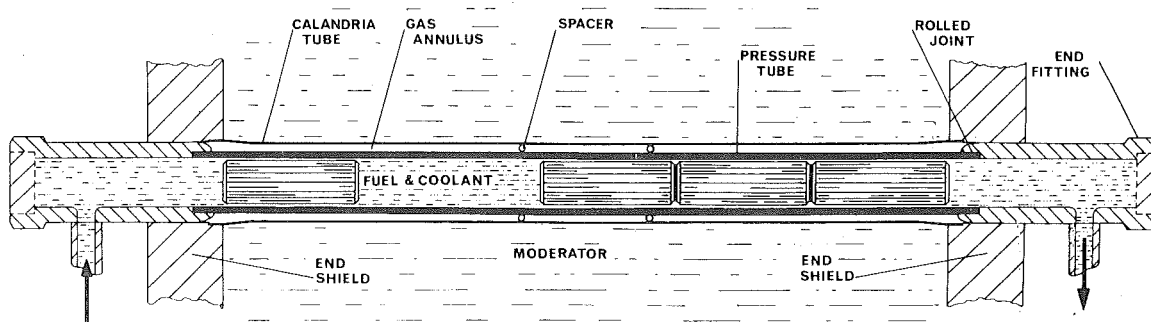


Figure 2 – Schematic of a fuel channel for a CANDU reactor with pressurized water coolant

1. MECHANICAL PROPERTIES

(a) Properties of Unirradiated Cladding

The strength of Zircaloy depends on chemical composition (within the permissible range, Table 1), microstructure and texture and decreases with temperature. Typical values are given in Table 2.

Fuel sheathing is made from hot-extruded tubes which are cold-worked to size by several stages with intermediate anneals. The cold-worked sheathing is then partially annealed to obtain the required compromise in strength and ductility.

Table 1: Typical Compositions for the Zircaloys

Element	Zircaloy-2	Zircaloy-4
Tin	1.20 – 1.70 wt%	1.20 – 1.70 wt%
Iron	0.07 – 0.20 wt%	0.18 – 0.24 wt%
Chromium	0.05 – 0.15 wt%	0.07 – 0.13 wt%
Nickel	0.03 – 0.08 wt%	—
Niobium	—	—
Oxygen	1400 ppm max.	1400 ppm max.
Balance	Zirconium plus impurities	

Cold-worked zirconium alloys start to recrystallize at about 725K (450°C) and their mechanical properties are sensitive to annealing temperature in the range 725-850K (450-525°C), Figure 3. *D. Lee, J. Nucl. Mat. 37, 1970, p. 159.*

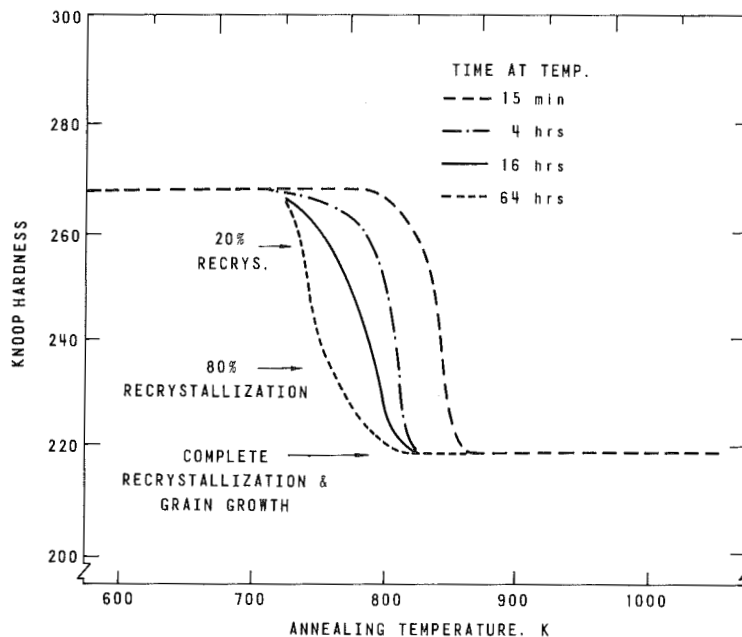


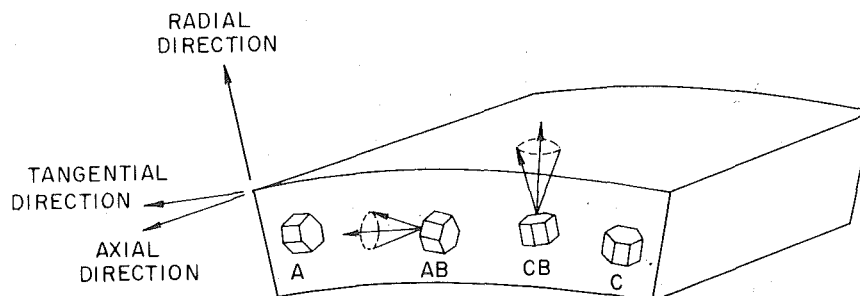
Figure 3 – The effect of annealing time and temperature on the hardness of 80% cold-worked Zircaloy.

During fabrication of fuel elements, appendages such as wear and spacer pads are brazed onto the cladding. In the region of the brazed joint the Zircaloy transforms to beta phase and then is cooled rapidly which produces a Widmanstätten structure, Figure 4. The strength of this material is similar to completely alpha recrystallized material but its ductility is similar to cold-worked material, Table 2.



Figure 4 – Widmanstätten structure in Zircaloy-2 slowly cooled from the β phase (500X)

Texture has a large effect on the mechanical properties of pressurized tubes because the biaxial stress system imposes additional restraints on existing anisotropic properties. This is shown in the properties of two batches of Zircaloy-2 tubes made by different fabrication routes so that they had different textures. Tubes from Batch 7 had the majority of the alpha grains in the C and CB orientations, Figure 5, and tubes from Batch 8 had the majority in the A and AB orientations.



Batch	Texture Coefficients	
	A + AB	C + CB
7	2.1	8.7
8	10.5	3.1

Figure 5 – The textures of two batches of Zircaloy-2 fuel sheathing

In longitudinal tensile tests all the grains are oriented for deformation by slip. The two batches had similar strengths, Table 3. The properties in the transverse ring test depend on the proportion of grains that will deform by twinning. Batch 8, which had the highest proportion, was the strongest, Table 3. In the closed end burst test the tube is under a biaxial stress of 2:1 in the hoop to longitudinal direction. For the tubes to bulge, the wall thickness must decrease. In Batch 7 this can occur only by compression twinning and hence Batch 7 tubes were the stronger, Table 3. In all the tests the tubes from Batch 7 were also more ductile than the tubes from Batch 8.

Table 3: The Effect of Texture and Irradiation on the Mechanical Properties of Zircaloy-2 Fuel Sheathing at 575K.

Batch Identity	Test	Unirradiated			Irradiated		
		0.2% Y.S. MPa	UTS MPa	% Elongation	0.2% Y.S. MPa	UTS MPa	% Elongation
7	Longitudinal tensile	360	430	11.8	450	660	11.3
8		350	430	5.4	460	670	1.4
7	Transverse ring	350	390	19.0	460	480	14.9
8		350	410	11.6	440	460	10.9
7	Closed end burst	410	450	21.5	590	590	2.9
8		400	410	14.8	500	500	0.8

Both batches of tubes show significant differences in their properties due to their different textures. The tubes from Batch 7 with grains in the C and CB orientations had the better combination of strength and ductility for fuel sheathing.

Hot-extruded tubes have a large proportion of their grains in the A and AB orientations. However if in the final cold-working stages the ratio of reduction in wall thickness to reduction in circumference is large then the majority of grains are in the C and CB orientations.

- K.P. Steward and B.A. Cheadle, "The Effect of Preferred Orientation on the Mechanical Properties and Deformation Behaviour of Zircaloy-2 Fuel Sheathing", AECL Report 2627, 1966

(b) Effect of Irradiation on the Properties of Cladding

Fuel cladding must have adequate ductility during irradiation to withstand the thermal expansion of the fuel. D.G. Hardy, *Irradiation Effects on Structural Materials for Nuclear Applications*, ASTM, STP 484 1970, p.215, has examined the effects of metallurgical variables on the post-irradiation ductility of Zircaloy fuel sheathing.

1) The effect of cold work:

Cold work is detrimental to the circumferential ductility of irradiated Zircaloy fuel cladding in both uniaxial and biaxial tests. This is shown by plotting axial tensile strength, which is proportional to cold work, against circumferential elongation, Figure 6. Therefore in order to maximize ductility sheathing should be used in the alpha-annealed condition.

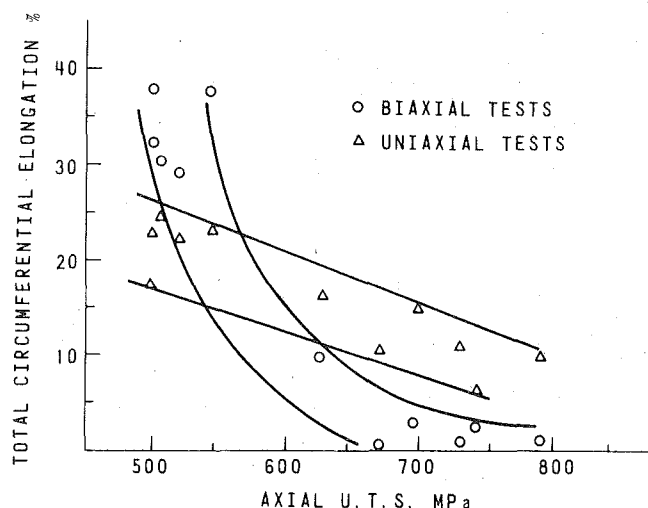


Figure 6 — Effect of cold work as measured by room temperature axial tensile strength on circumferential ductility of irradiated Zircaloy fuel sheaths at 575K

2) The effect of texture:

The effect of texture is small compared with the effect of cold work. However Batch 7 tubes which had the majority of grains in the C and CB orientations, Figure 5, were more ductile than Batch 8 tubes which had the majority of the grains in the A and AB orientations, Table 3.

3) The effect of grain size:

Large grain sizes tend to reduce the ductility of alpha-zirconium, *C.E. Coleman and D. Hardie, J. Inst. Met. 94, 1966, p.387*. Although fine alpha-grain sizes can be achieved easily in Zircaloy, beta heat-treatment can produce large "effective alpha-grains" (large areas of similarly oriented α -grains that behave as a large grain). *D.G. Hardy "Irradiation Effects on Structural Materials for Nuclear Applications", ASTM, STP 484, 1970, p.215*, found that beta-treated fuel sheathing had lower ductility than alpha-annealed sheathing and related this to the large "effective alpha-grain" size of the beta-treated material, Figure 7. A uniform dispersion of impurity second phase particles (ZrC or ZrP) help to refine the transformed beta structure and should minimize this effect, *G. Okvist and K. Kallstrom, J. Nucl. Mat. 35, 1970, p.316, R.A. Holt, J. Nucl. Mat. 47, 1973, p.262, 35, 1970, p.322*.

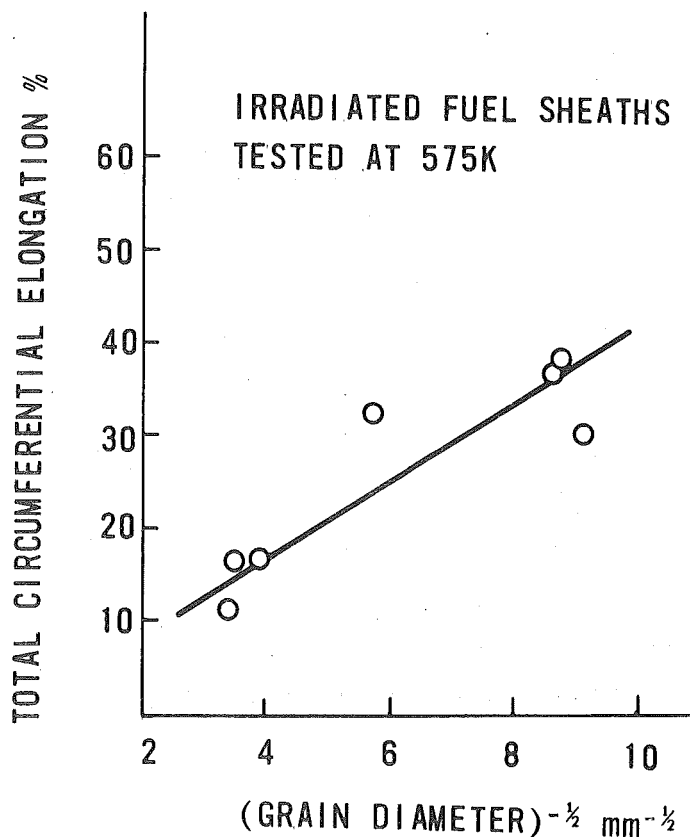
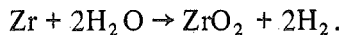


Figure 7 — Effect of α -grain size on the ductility of irradiated Zircaloy fuel sheaths at 575K (300°C)

In general, fabrication procedures which produce high as-fabricated ductility give the best post-irradiation ductility; therefore fuel sheath specifications can be based on pre-irradiation mechanical properties.

2. CORROSION RESISTANCE

When exposed to hot water, zirconium alloys oxidize



(In heavy-water cooled reactors H is replaced by D.)

In the initial oxidation period a thin, black protective film forms on the surface. The oxidation rate during this period is represented by a curve that approaches a parabolic or logarithmic form, Figure 8. After a time determined by temperature, pressure and chemistry of the coolant, as well as alloy composition, the corrosion rate increases sharply to be almost linear, extrapolating back through the origin. This point is the "breakaway" or "transition" and occurs when the zirconium oxide is about $2\text{ }\mu\text{m}$ thick.

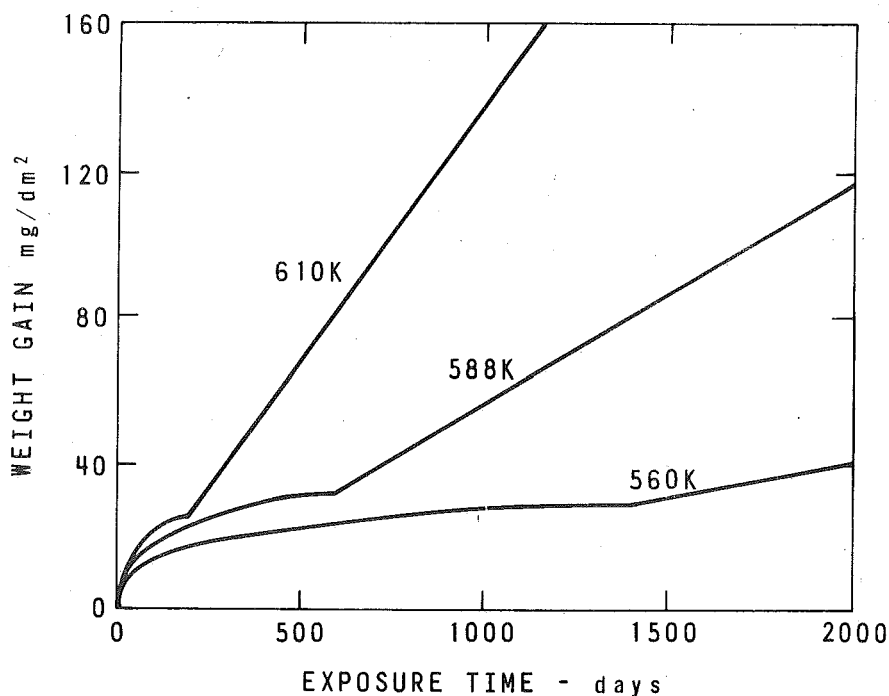


Figure 8 — Corrosion characteristics of Zircaloy-2 in water showing initial parabolic weight gain followed by linear weight gain

Oxidation of Zircaloy under reactor radiation conditions is increased only when oxygen or oxidizing free radicals are present in the coolant. To prevent this enhancement of corrosion, hydrogen is maintained in solution in the water, Figure 9.

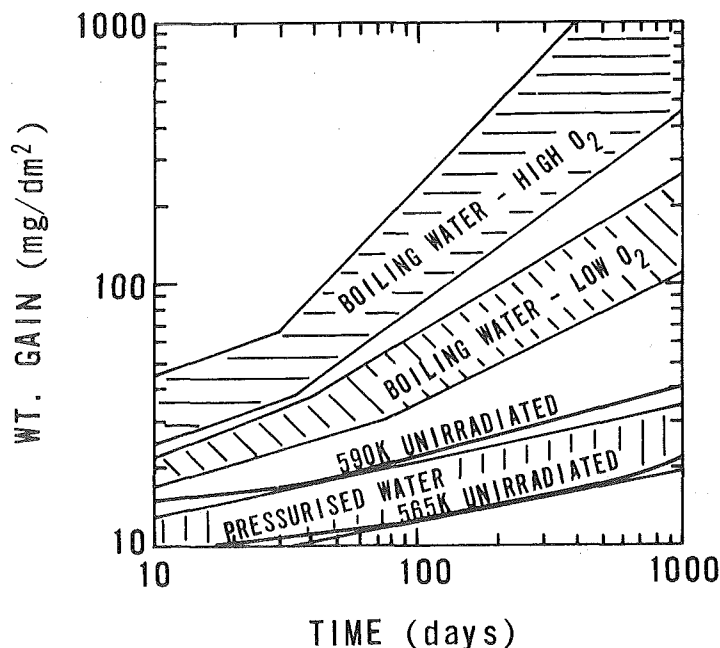


Figure 9 – Effect of oxygen on the in-reactor corrosion of Zircaloy 545-575K (270-300°C)

The corrosion resistance of Zircaloy is such that even if “breakaway” occurs the oxide is rarely more than 20 μm thick after service. Since fuel sheathing is nominally 380 μm thick the associated hydriding of the sheath could be more significant than any small reduction in wall thickness due to oxidation.

However, good control of water chemistry and reduction of the nickel content in the Zircaloy results in the hydrogen (or deuterium) pickup being less than 25 ppm after 4 year’s service, the maximum lifetime of the fuel, Figure 10. This quantity of hydrogen presents no problem since at operating temperatures it is all in solution and therefore innocuous.

- B. Lustman and F. Kerze, “Corrosion of Zirconium and its Alloys”, Chapter 11 in “The Metallurgy of Zirconium”, McGraw-Hill, New York, 1955
- D.L. Douglass “Corrosion” Chapter 11 in “The Metallurgy of Zirconium”, pp. 343-387, IAEA, Vienna, 1971
- B. Cox, “Effects of Irradiation on the Oxidation of Zirconium”, *J. Nucl. Mat.* 28, 1968, pp. 1-47
- A.S. Bain and J.E. LeSurf, “Oxidation and Hydriding of Zircaloy in NPD Reactor”, AECL-3065, 1969

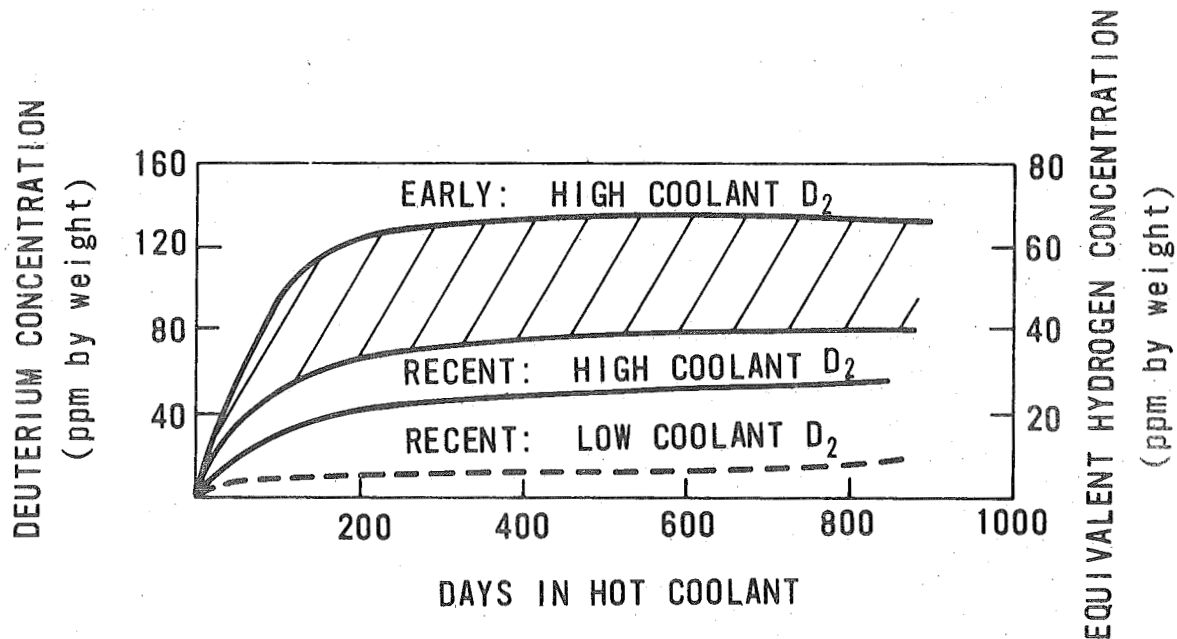


Figure 10 – Deuterium pick up by fuel sheathing in power reactors

3. FUEL ELEMENT BEHAVIOUR

In a fuel element, stress may be concentrated at fuel chips and at cracks in the UO_2 fuel as shown in Figure 11. During irradiation, radial cracks form in the outer annulus of the fuel pellet. When fuel bundle power is increased the fuel tends to expand radially which then stresses the sheathing. If the friction between the fuel pellets and sheath is high, the stress and therefore the deformation in the sheath is concentrated over the cracks in the fuel pellet, Figure 11.

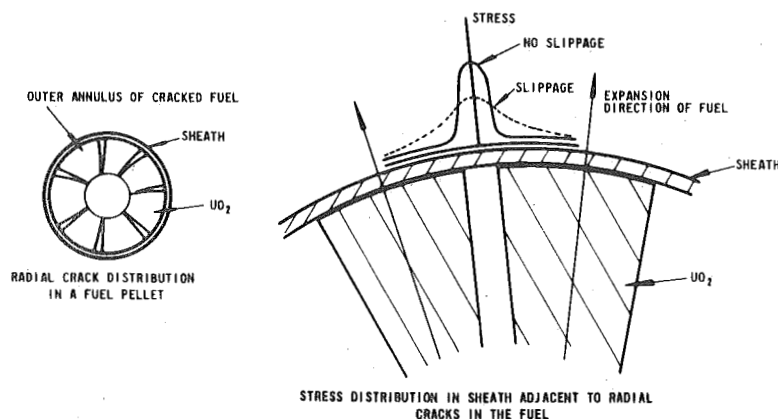


Figure 11 – Stress concentrations at radial cracks in UO_2

J. Gittus, *Nucl. Eng. and Design* 18, 1972, p.69, has shown that the strain concentration ϵ_c in the cladding over the crack in the fuel at the point of plastic instability is given by:

$$\epsilon_c \propto \frac{\mu}{Nm}$$

where μ = coefficient of friction between fuel and sheath
 N = number of radial cracks in fuel adjacent to sheath
 m = work hardening coefficient of sheathing material.

Tests at CRNL simulating fuel expansion have demonstrated that this relationship is valid. C.E. Coleman, *Conf. on Physical Metallurgy of Reactor Fuel Elements, Berkeley, Sept. 1973*. In the fuel expansion simulation test, Figure 12, when an aluminum core is compressed it expands radially and cracks the brittle ceramic liner. Further compression presses the cracked ceramic radially against the sheath which is then stressed to failure.

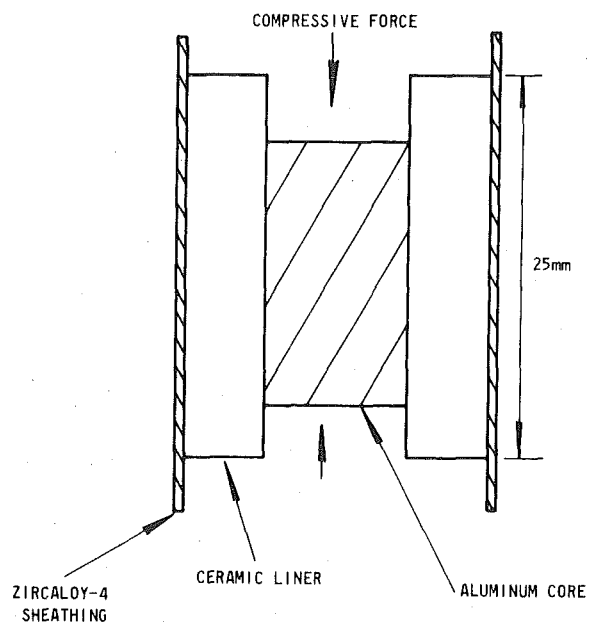


Figure 12 – The fuel expansion simulation test

The work hardening coefficient m is higher in annealed material than in cold-worked; annealing cold-worked Zircaloy-4 tubes increased the circumferential elongation.

	m	Circumferential Elongation %
Cold-worked material	0.02	5.6
Annealed 4 h at 875K	0.08	13.0

N was varied by replacing the ceramic annulus with 4, 8, 12 or 16 steel segments. The circumferential strain was increased by increasing the number of radial cracks, Figure 13.

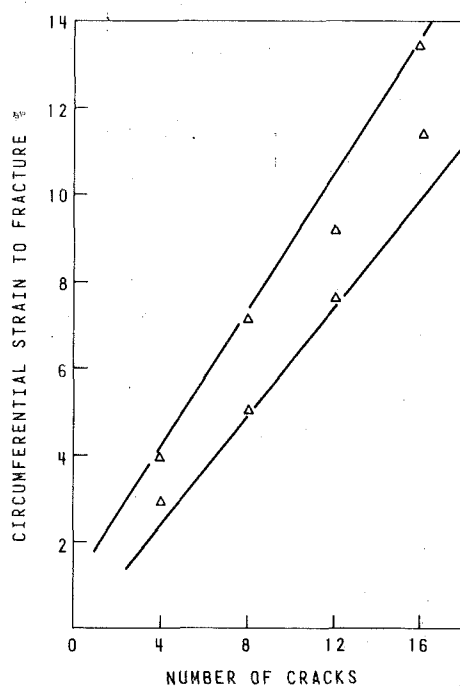


Figure 13 — Effect of number of cracks on strain to fracture at 300K

μ was reduced by placing graphite or siloxane on the inside surface of the sheath to act as a lubricant between the ceramic annulus and the cladding. Reducing μ increased the elongation.

	Circumferential Elongation %
No coating	4.8
Graphite coating	23
Siloxane coating	25

These results showed that the elongation could be increased by annealing the sheathing and coating the inside surface with graphite or siloxane.

4. ADVANCED FUEL SHEATH MATERIALS

Advances in reactor design will demand fuel sheathing materials with properties superior to the Zircalloys.

(a) Ductility:

More ductility may be required for fuel elements designed for higher power output or higher burnup than in present reactor designs.

B.A. Cheadle, C.E. Ells and J. van der Kuur, "Zirconium in Nuclear Applications", ASTM, STP 551, 1974, examined the effect of various alloying elements on the ductility of irradiated zirconium alloys, Figure 14a. They concluded that Zr-Nb alloys have higher initial work hardening rates after irradiation, which increases the uniform elongation and hence increases the strain before necking and plastic instability occur, Figure 14b. This may explain the success of Zr-1 wt% Nb alloy in the Russian reactors, A.D. Amaev et al, USAEC translation AEC-TR-6847, 1966.

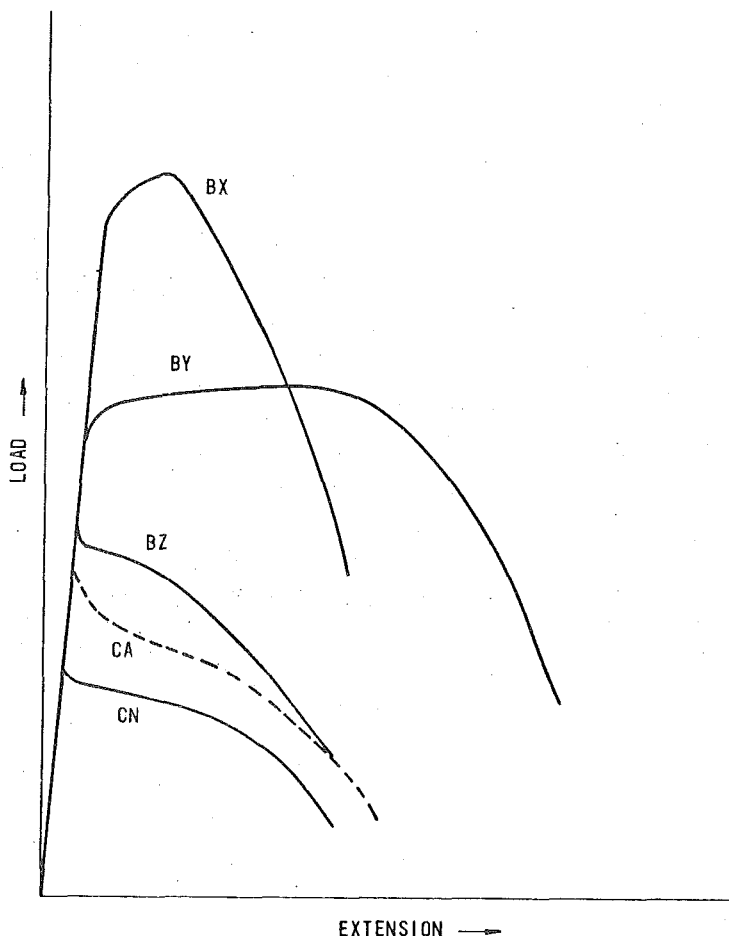


Figure 14(a) – The effect of alloy addition on the plastic stability of Zirconium alloys irradiated and tested at 575K (300°C)

CN Crystal bar Zirconium
 CA Zr-0.5 wt% Sn
 BZ Zr-0.1 wt% Nb
 BY Zr-0.6 wt% Nb
 BX Zr-2.35 wt% Nb

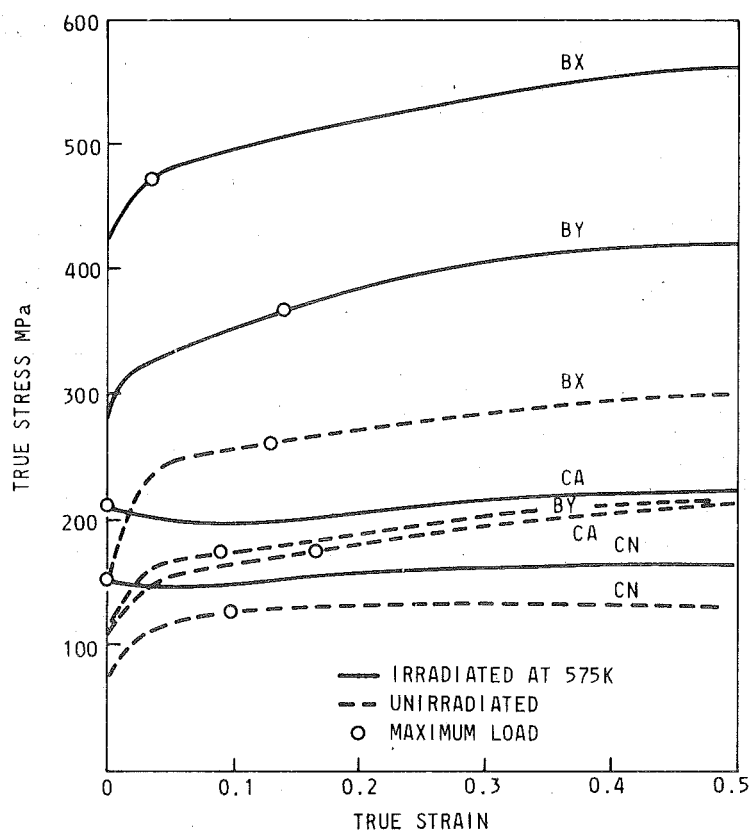


Figure 14(b) – The effect of alloy addition on true stress-true strain curves of zirconium alloys irradiated and tested at 575K (300°C)

Zr-2.5 wt% Nb and Zr-1 wt% Nb alloys are thus of interest for fuel sheathing where high uniform elongation may be advantageous. Zr-2.5 wt% Nb is however more difficult to weld or braze than the Zircalloys because of its susceptibility to beta embrittlement after irradiation, *C.E. Ells and C.D. Williams, Trans. Met. Soc. AIME 254, 1969, p.1321.*

(b) **Strength:**

More strength may be required to resist the circumferential expansion of metallic fuels. Candidate materials are Zr-2.5 wt% Nb and XL*. Table 4 shows the strengths of fuel sheaths made from these alloys compared with other alloys.

* Composition of XL is Zr-3.5 wt% Sn – 0.8 wt% Mo – 0.8 wt% Nb

Table 4: Tensile Properties of Fuel Sheath Materials at 575 K Demonstrating Potential of XL and Zr-2.5 wt% Nb Alloys for High Strength Fuel Sheathing.

Alloy	Metallurgical Condition	Ultimate Tensile Strength MPa	Total Elongation %
Zr-2.5 wt% Nb	Heat-Treated	605	22
	Annealed	275	30
XL	Heat-Treated	900	8
	Annealed	470	20
Zircaloy-2	Cold-Worked	356	12
	Annealed	124	40
Zr-1.15 wt% Cr-0.1 wt% Fe	Cold-Worked	407	26
	Annealed	208	34
Zr-1 wt% Nb	Annealed	276	30

(c) Improved high temperature corrosion resistance:

Allowing fuel to operate intermittently in dryout or using superheated steam as a coolant results in higher coolant temperatures and greater thermal efficiency. Therefore corrosion resistance for operation at temperatures up to 775K (500°C) in H₂O would be required.

Zr-1.15 wt% Cr-0.1 wt% Fe alloy was developed for this application by *H.H. Klepfer and S.S. Mehner, USA Report GEAP-10044, 1969*. Its mechanical properties appear comparable to Zircaloy-2 after irradiation, *R.A. Holt, J. Nucl. Mat. 50, 1974, p.207*, as shown in Table 5. Zr-2.5 wt% Nb may have adequate corrosion resistance for fuel sheathing applications at 775K (500°C) and its tensile properties also appear satisfactory, Table 5. The potential of both these alloys has been demonstrated by successful application as sheathing of experimental fuel irradiated in steam at 775K for 173 days, *J.L. Gray, AECL Report, 3913, 1971*.

Table 5: Axial Tensile Properties of Zr-1.15 wt% Cr-0.1 wt% Fe, Zircaloy-2 and Zr-2.5 wt% Nb after Irradiation at 575K.

Alloy	Metallurgical Condition	0.2% Ys MPa	U.T.S. MPa	U.E. %	T.E. %	R.A. %
Zr-1.15 wt% Cr-0.1 wt% Fe	α -annealed	343	345	0.4	14	80
	cold-worked	387	463	4.6	22	81
	β -heat-treated	354	374	1.5	17	70
Zircaloy-2	α -annealed	303	323	2	14.4	—
	cold-worked	427	435	0.5	9	—
Zr-2.5 wt% Nb	$(\alpha+\beta)$ -annealed	552	621	2	10	60
	cold-worked	696	800	1	3.5	26

SUMMARY AND CONCLUSIONS

Over 60,000 fuel bundles with Zircaloy cladding have been successfully irradiated in CANDU reactors. The metallurgical properties of zirconium alloys suitable for cladding tubes have been studied and excellent thin-walled cladding tubes developed. Cladding tubes made from new alloys are being developed and evaluated in our test reactors.

CRNL-1208

LECTURE NO. 10

DEVELOPMENT POTENTIAL OF ZIRCONIUM ALLOYS

by

R.A. Holt and B.A. Cheadle

CANDU reactors produce economic electrical power by utilizing natural uranium fuel and structural materials that have a low cross section for thermal neutrons. Zirconium alloys have far lower neutron absorption per unit strength than other commercially available structural materials, Table 1, with the exception of beryllium which is unsuitable for nuclear applications. Hence the CANDU reactor fuel channel components — fuel sheathing, pressure tube, garter spring and calandria tube — are all made from zirconium alloys.

Table 1: Neutron Economy of Various Metals Compared with Zirconium

Base Metal	Ultimate Tensile Strength of Alloy ^{a)} at 575K		Macroscopic Cross Section for Thermal Neutrons ^{b)} Σc , cm ² /cm ³	Relative Neutron Absorbtion for Given Design Stress
	MPa	kpsi		
Zirconium	900	130	.01	1
Iron	1100	160	.17	14
Nickel	1100	160	.31	25
Titanium	1000	145	.26	28
Aluminum	90	13	.014	14
Magnesium	90	13	.005	5
Beryllium	190–350 ^{c)}	25–50	.001 ^{c)}	.25–.5

a) Based on presently available high strength alloys

b) Probable value for high strength alloy designed to minimize neutron absorbtion

c) For unalloyed beryllium

The Chalk River Nuclear Laboratories continue to develop both alloys and improved components. This lecture will summarize the development potential of zirconium alloys relevant to CANDU reactors as improved alloys would allow:

- 1) Higher coolant temperatures
- 2) Higher power output per channel
- 3) Improved neutron economy, by reducing the thickness of the channel components.

A stronger more creep resistant alloy than Zr-2.5 wt% Nb would allow either higher coolant pressures and temperatures or reductions in the wall thickness of current pressure tubes. Stronger calandria tubes may also be attractive for future reactors. Current calandria tubes are fabricated from annealed Zircaloy-2 and hence there is considerable scope for increasing their tensile strengths.

STRENGTHENING MECHANISMS

The tensile strength of alloys at elevated temperatures can be broken down into components resulting from different strengthening mechanisms as shown by the equation:-

$$\sigma = \sigma_0 + f(G\rho^{1/2}) + f(d^{-1/2}) + f\left(C\frac{\partial a}{\partial C}\right) + f\left(C\frac{\partial G}{\partial C}\right) + \sigma_{\text{SRO}} + f\left(\frac{G}{\lambda}\right) + V_f \sigma_f$$

where $f(G\rho^{1/2}) + f(d^{-1/2})$ are structure strengthening components

$f\left(C\frac{\partial a}{\partial C}\right) + f\left(C\frac{\partial G}{\partial C}\right) + \sigma_{\text{SRO}}$ are solution strengthening components

$f\left(\frac{G}{\lambda}\right) + V_f \sigma_f$ are dispersion and fibre strengthening components.

σ = flow stress

σ_0 = basic high temperature flow stress

G = shear modulus

ρ = stable dislocation density

d = stable grain size

C	=	solute concentration
a	=	lattice parameter
σ_{SRO}	=	strengthening due to short-range order
λ	=	precipitate strengthening
V_f	=	volume fraction of fibres
σ_f	=	strength of fibres

An example of the extent of the different contributions to strength was shown by *C.D. Williams and R.W. Gilbert, Trans. JIM 9, 1968, p.18*, in their study of the strength of the martensitic α' in quenched Zr-2.5 wt% Nb. The effect of the initial cooling rate on the tensile strength and microstructure is shown in Table 2.

Table 2: The Effect of Cooling Rate on the Structure and Strength of Zr-2.5 wt% Nb

Material treatment	Initial cooling rate K/sec	0.2% Y.S.		U.T.S.		Hardness VPN	Structure
		MPa	kpsi	MPa	kpsi		
1.5 minutes at 1375K quenched into iced brine	>2000	720	105	870	124	262	Twinned α' needles 0.5–1.5 μm wide, 3–10 μm long.
15 minutes at 1275K quenched into oil	300	680	97	800	114	245	Large plates of untwinned α 3–10 μm long.
15 minutes at 1275K air cooled	25	490	70	560	80	225	Uniform α plates 0.25–0.5 μm wide, 5–10 μm long.

They attributed the maximum hardness to four strengthening factors:

	Hardness VPN
Annealed crystal bar zirconium (σ_0)	66
Interstitial oxygen (solution strengthening)	33
Substitutional niobium (solution strengthening)	35
Grain size of the martensitic needles (structure strengthening)	100
Substructure strengthening due to microtwins in the martensitic needles (structure strengthening)	30
Total	264

The strength of current cold-worked and stress-relieved Zr-2.5 wt% Nb pressure tubes can be broken down into its different components in a similar fashion, Figure 1.

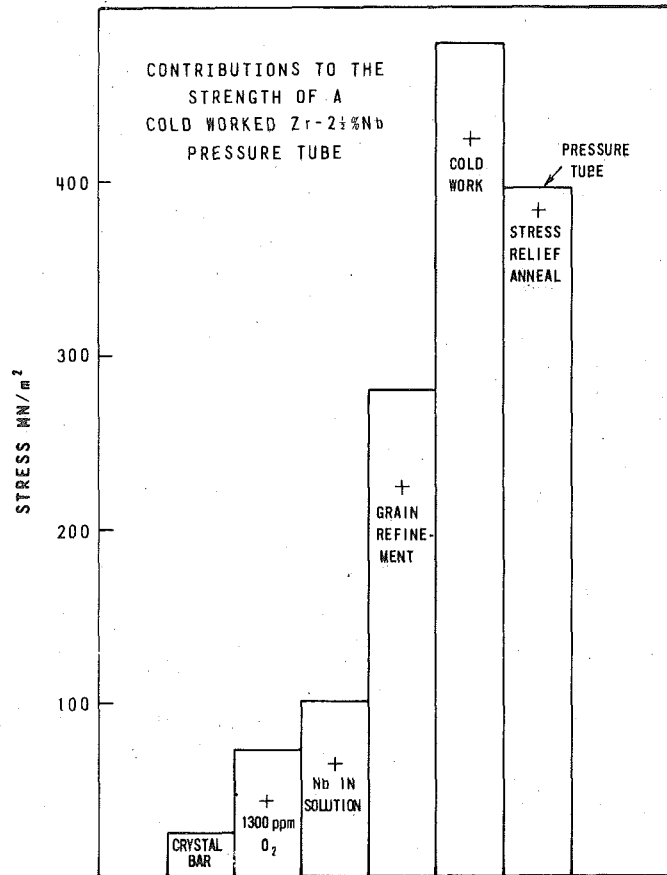


Figure 1 — Strengthening Mechanisms in Cold-Worked Zr-2.5 wt% Nb Pressure Tubes.

IMPROVING HIGH TEMPERATURE STRENGTH

An extensive review of the zirconium alloy literature and reference to titanium metallurgy, C.D. Williams, *Reactor Technology* 13, 1970, p. 147, has shown that several alloying elements, Table 3, are attractive in terms of strengthening potential and neutron absorption.

These alloying elements contribute to the last five terms in the equation. Alloys containing these elements can also be strengthened by thermal and mechanical processing techniques. Alloys containing β -stabilizing elements can be quenched from the β -phase or high in the $(\alpha + \beta)$ -phase field to produce a fine twinned α' structure, Figure 2, which is supersaturated in β -stabilizing elements and has a very fine effective grain size. This structure can be further hardened by aging to precipitate the β -stabilizing elements.

Table 3: Possible Alloying Additions for α -Zirconium Based Alloys for Nuclear Applications.

Element	Effect of 1 At% Addition on cross section	Effect of Addition on Phase Stability	Strengthening Mechanism
Tin	+1.7%		
Aluminum	+1.8%	Stabilize HCP α -Phase	Solution Strengthen α -Phase
Lead	-0.4%		
Molybdenum	+13%		
Niobium	+6.6%	Stabilize BCC β -Phase	Solution Strengthen β -Phase. Precipitation Strengthen α -Phase
Silicon	-0.1%	Very low Solubility	Solution Strengthening*

* Additions of silicon below the solubility limit improve the high temperature creep strength of α -titanium alloys.

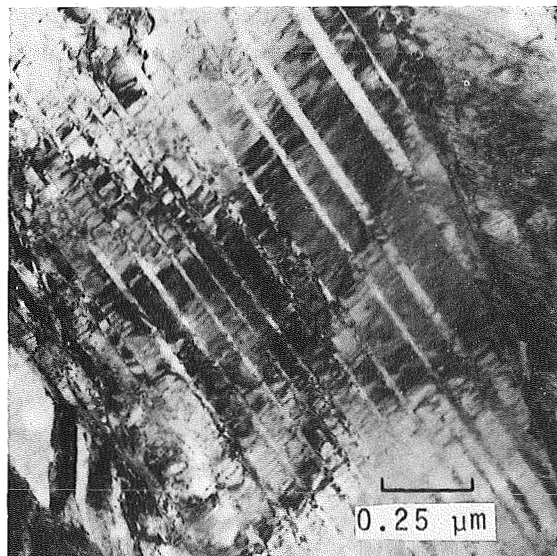


Figure 2 — Martensitic α' -Phase in XL Alloy Water Quenched from 1325K (1050°C).

Structures consisting of equilibrium α with a high concentration of α -stabilizing elements and retained β -Zr with a high concentration of β -stabilizing elements can also be produced by cooling more slowly from the β or $(\alpha + \beta)$ -phase fields. The α -grain size depends on the cooling rate and may be very fine, Figure 3. These structures can be strengthened by aging to decompose the retained β -phase or by cold-working.

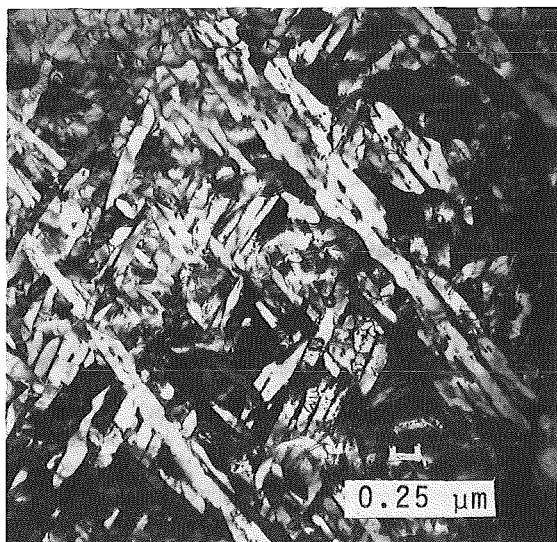


Figure 3 — Fine Acicular α Structure in XL Alloy Air Cooled from 1175K (900°C) and Aged 6 h at 800K (525°C).

The effects of combinations of these alloying elements have been studied by *C.D. Williams, C.E. Ells, and P.R. Dixon, Can. Met. Quart. 11, 1972, p.257*, and *E.F. Ibrahim, E. Price, and A. Wysikierski, Can. Met. Quart. 11, 1972, p.273*. Aluminum and lead, although effective α -solution strengtheners are very detrimental to the corrosion resistance of α -zirconium in water. Small additions of silicon had little effect on the properties; tin, niobium and molybdenum appeared to be the most promising alloying additions.

A new quaternary alloy of Zr-Sn-Mo-Nb called XL has been developed with the following composition:

Sn	3.0	—	3.5 wt%
Mo	0.8	—	1.0 wt%
Nb	0.8	—	1.0 wt%
O	800	—	1300 ppm
balance			Zr plus impurities.

The tensile properties of this alloy are compared with Zr-2.5 wt% Nb in Table 4 and their in-reactor creep behaviours are compared in Figure 4. XL has superior tensile strength for a given metallurgical condition and lower high temperature in-reactor creep rates.

Table 4 — Tensile Properties of Zr-2.5 wt% Nb and XL in Metallurgical Conditions Chosen to Show Practical Extremes in Strength.

Alloy	Condition	Test Temperature K	Ultimate Tensile Strength		Total Elongation %
			MPa	kpsi	
Zr-2.5 wt% Nb	quenched from $\alpha+\beta$ and aged	575	600	88	22
XL	"	575	910	130	8
Zr-2.5 wt% Nb	"	725	440	63	30
XL	"	725	770	110	10
Zr-2.5 wt% Nb	slow cooled from $\alpha+\beta$	575	280	40	30
XL	"	575	460	65	20
Zr-2.5 wt% Nb	"	725	250	36	38
XL	"	725	410	58	23

Another alloy presently under development is Zr-8.5 wt% Al which can be processed to single phase Zr_3Al which has a face-centered cubic ordered structure. This alloy can have a combination of ductility and strength superior to alloys based on α -zirconium, Table 5. The Zr_3Al compound has similar corrosion resistance to Zircaloy-2 in moist air at 575K unlike α -zirconium alloys containing aluminum which corrode very rapidly in the same environment, *E.M. Schulson, J. Nucl. Mat. 50, 1974, p.127.*

Because the glide dislocations in ordered solids must move in pairs, dislocation climb should be a more difficult process than in random solid solutions. In addition vacancy diffusion in ordered solids is difficult. Thus the alloy has potential for good high temperature and in-reactor creep resistance.

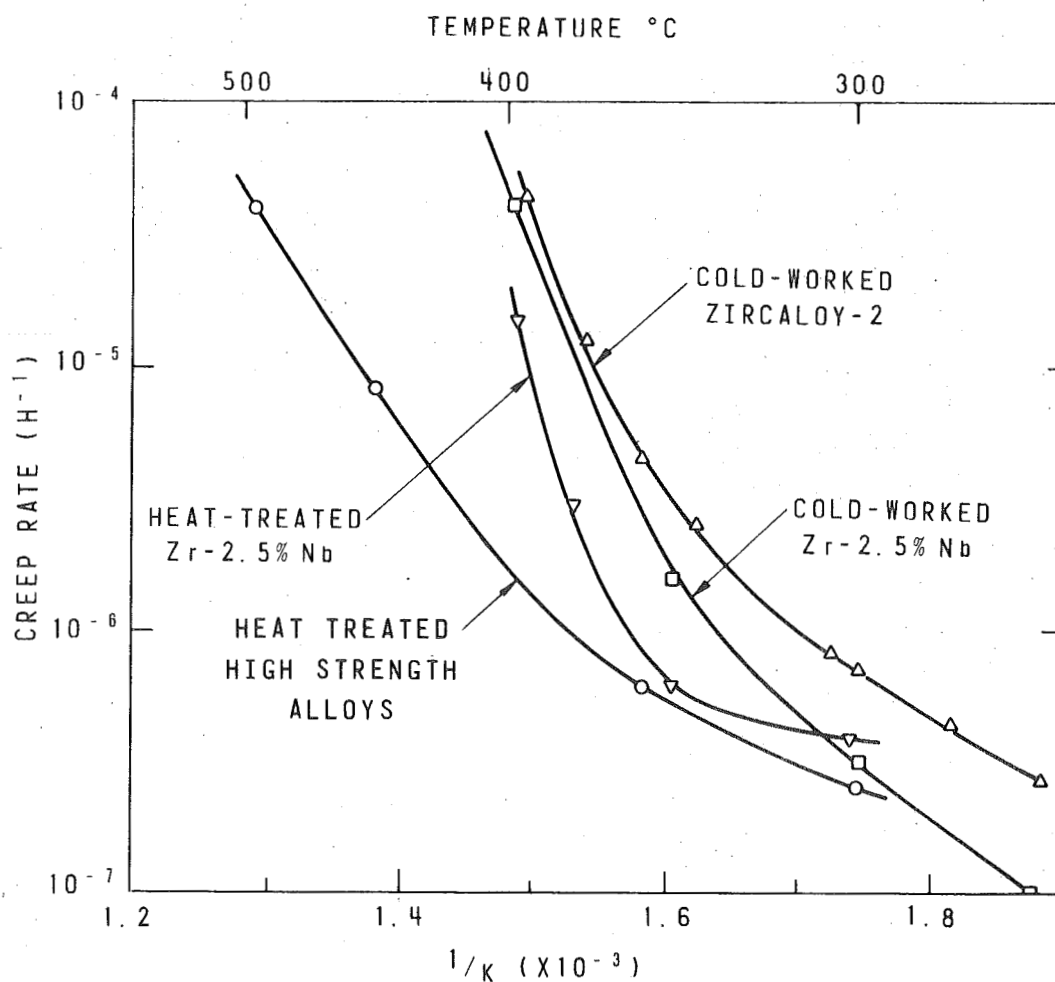


Figure 4 — In Reactor Creep of Zirconium Alloys at a Stress of 138 MPa and a Neutron Flux of $1 \times 10^{17} \text{ nm}^{-2} \text{ s}^{-1}$.

Table 5 — Tensile Properties of Zr_3Al ($\approx 8 \text{ wt}\% \text{ Al}$) and XL.

Alloy	Condition	Test Temperature K	Ultimate Tensile Strength		Total Elongation %
			MPa	kpsi	
XL	quenched from $\alpha + \beta$ and aged (Q & A)	575	910	130	8
Zr_3Al	as transformed	575	940	134	27
XL	Q & A	725	770	110	10
Zr_3Al	as transformed	725	820	116	27

IMPROVING CREEP RESISTANCE AT PRESENT OPERATING TEMPERATURES

Recent experimental observations have shown that cold work is detrimental to in-reactor creep, *C.E. Coleman, A.R. Causey and V. Fidleris to be submitted to J. Nucl. Mat. 1974*. Cold-working processes produce high dislocation densities and since about 15% of the short term strength of Zr-2.5 wt% Nb pressure tubes can be attributed to cold-work, reducing the dislocation density results in a significant decrease in short-term strength. In order for pressure tubes of low dislocation density to operate at the same stress, the strength lost by reducing the dislocation density must be replaced by other strengthening mechanisms.

Both the XL alloy and Zr_3Al have higher strength than Zr-2.5 wt% Nb in metallurgical conditions containing low dislocation densities and are candidates for this application.

The Zr-2.5 wt% Nb alloy itself may not yet have been developed to full potential however. We are at present investigating the effects of fabrication variables on grain size in an effort to replace the short-term strength produced by cold-working by strength due to fine grain size. Although the effect of grain size is usually small the Petch equation, Lecture 2, shows that at very fine grain sizes the strength increases rapidly with decreasing grain size. Thus in the grain size range of interest ($<1 \mu m$) a decrease in grain size by a factor of two gives a significant increase in strength. This has been shown experimentally for extruded Zr-2.5 wt% Nb tubes, Figure 5.

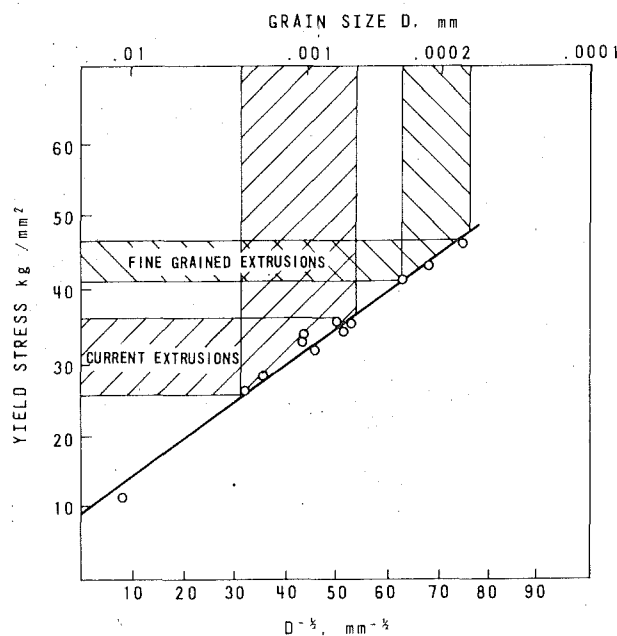


Figure 5 — Effect of α -Grain Size on the Strength of Zr-2.5 Wt% Nb.

HIGH STRENGTH PRESSURE TUBES

Experimental pressure tubes have been made from Zr-2.5 wt% Nb. The manufacturing process for the Zr-2.5 wt% Nb tubes was changed to reduce the α -grain size and the longitudinal tensile strengths were more than 10% greater than standard tubes, Table 6.

Table 6: Typical Longitudinal Tensile Properties of Experimental Pressure Tubes at 575K

Alloy	Identity and Condition	0.2% Y.S.		UTS		% El.
		MPa	kpsi	MPa	kpsi	
Zr-2.5 wt% Nb	current specification (minimum values)	330	48	480	69.5	12
	typical tube, 20% cold-worked	380	55	510	75	15
	fine grained tube, as-extruded	410	60	510	75	18
	fine grained tube, plus 20% cold-work	480	70	580	85	16
XL	as-extruded	410	50	580	85	15
	as-extruded plus 20% cold-worked	510	75	620	90	12
	heat-treated (quenched and aged)	620	90	860	125	5

Experimental pressure tubes have also been made from the XL alloy. In the as-extruded condition they were more than 10% stronger than standard cold-worked Zr-2.5 wt% Nb tubes, Table 6, but cold-working them did not increase the strength as much as in Zr-2.5 wt% Nb. The heat-treated tubes were very strong but had low ductility, Table 6.

HIGH STRENGTH CALANDRIA TUBES

The present seam welded calandria tubes are made of annealed Zircaloy-2. Either Zr-2.5 wt% Nb or XL alloy could be used and would be considerably stronger, Table 7. The selection will depend on the capability of fabricating a very thin-walled tube to the required dimensional tolerances. The most promising candidates are XL in the seam welded and annealed condition and Zr-2.5 wt% Nb in the extruded and cold-drawn condition.

Table 7: Room Temperature Tensile Properties of Zirconium Alloys in Metallurgical Conditions Suitable for Calandria Tubes

Alloy	Metallurgical Condition	0.2% Yield Stress		Ultimate Tensile Strength		Total Elongation %
		MPa	kpsi	MPa	kpsi	
Zircaloy-2	Annealed	32.0	45	460	65	30
Zircaloy-2	40% cold-worked	600	85	630	90	10
Zr-2.5 wt% Nb	Slow cooled from the ($\alpha + \beta$) phase	350	50	490	70	25
Zr-2.5 wt% Nb	Extruded +20% cold-worked	630	90	770	110	15
XL	Slow cooled from ($\alpha + \beta$)	670	95	770	110	15
XL	Extruded +20% cold-worked	700	100	880	125	10

SUMMARY

The development of the alloy Zr-2.5 wt% Nb gave the designers a structural material which had a design stress nearly 20% higher than Zircaloy-2. Recent work has demonstrated that Zr-2.5 wt% Nb can be developed further by refinements in thermal mechanical processing techniques. The alloy XL offers a further step in increased design strength. XL alloy pressure tubes, fuel sheathing and calandria tubes are now being made and evaluated. The Zr-Al alloys have very high tensile strengths and good tensile ductility and despite practical difficulties offer considerable potential.