

ZIRAT-9 SPECIAL TOPICS REPORT

Corrosion of Zr-Nb Alloys

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1 DEVELOPMENT OF ZR-NB ALLOYS

1.1 HISTORICAL INTRODUCTION (BRIAN COX)

The first information of the use of zirconium alloys in nuclear reactor environments appeared with the U.S. publication of some of their development work on Zr-Sn based alloys at the First U.N. Conference on the Peaceful Uses of Atomic Energy in Geneva during August 1955. Although little was said during the actual conference sessions, the simultaneous publication of “The Metallurgy of Zirconium”, Lustman & Kerze, 1955, presented data on these alloys; and remained the “reference text” for many years. Although it took sometime to get details of the development of the Zircalloys, Kass, 1963, Lustman and Kerze actually made no mention of the composition of the Zircalloys!^{°C}

The Russians had been “caught napping” by this U.S. publication of previously classified data so, at the next U.N. Conference on the Peaceful Uses of Atomic Energy (also in Geneva in 1958) they presented extensive results on a range of Zr-Nb alloys. These ranged from the all α zirconites, through the Zr-1%Nb (E110) alloy, to higher alloys with up to 5%Nb, Figure 1-1, Ambartsumyan, et al., 1958; Ivanov & Grigorovich, 1958 and Korobkov, et al., 1958. It was quite sometime after this before it was evident that only the Zr-1%Nb (E110) and the Zr-2.5%Nb (E125) alloys were being used commercially in Russian reactors, and that the zirconites (despite their apparently better corrosion resistance) were not being used, Table 1-1, IAEA TECDOC-996, 1998(a).

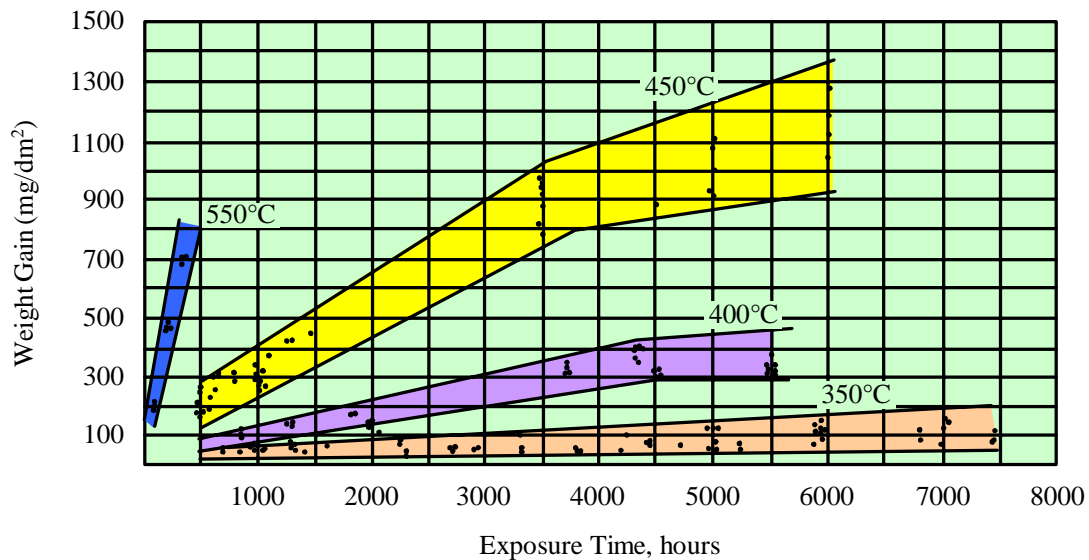


Figure 1-1(a): Corrosion of zirconium alloy with 1% niobium in water and superheated steam at various temperatures.

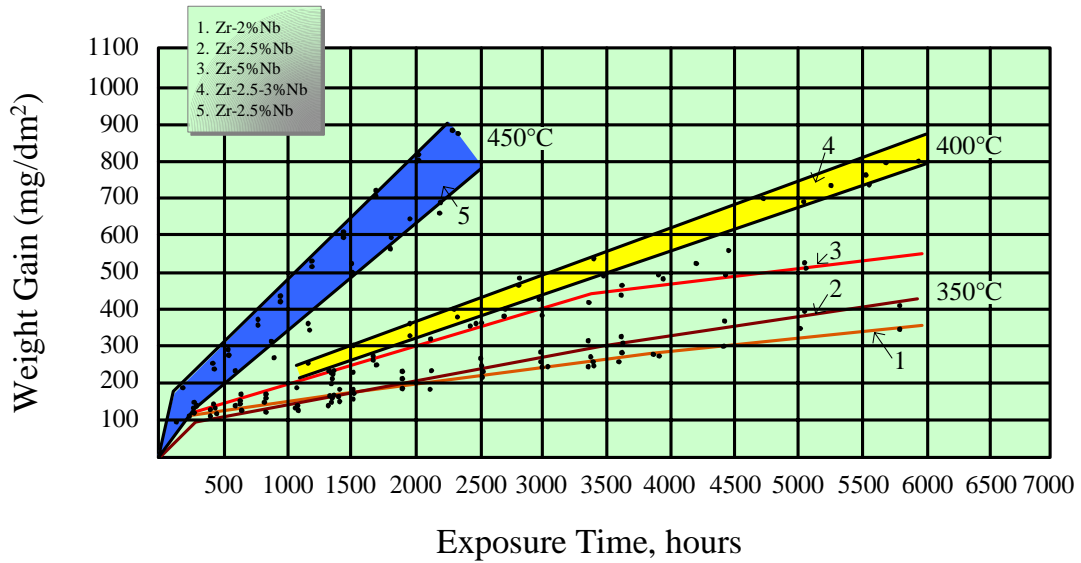


Figure 1-1(b): Corrosion of alloys with 2.5% niobium in water and superheated steam at various temperatures.

Table 1-1: Compositions of Zr-Nb Alloys

Composition	Zr-1%Nb			Zr-2.5%Nb		Zr-1%Nb/1%Sn/Fe		
	Ozhennite 0.5	E110	M5	E125	CANDU	E635	ZIRLO	Otto Hahn
Nb %	0.1	1.0	1.0	2.4-2.8	2.5-2.7	1.0	1.0	3.0
Sn %	0.2			0.005	0.01	1.2	0.7-0.9	1.0
Fe %	0.1		300-650	300-650	<650	0.4	0.1	0.06
O ppm		600-700	1400	900-1300	1200-1500			
C ppm			50-100	<270	<100		<270	
H ppm	25	25	25	25	<5	25	25	25
S ppm	-	-	25	-	-	-	-	-
Ni ppm	0.1%	<70	<70	<70	<70	<70	<70	<70
Hf ppm	<100	<100	<100	<100		<100	<100	<100

The Russian revelations at the 1958 Geneva Conference started a “Bonanza” of studies of the corrosion of Zr-Nb alloys elsewhere, especially where reactor designs other than the U.S. PWRs and BWRs were under development. In the U.K.A.E.A at Harwell a study of the corrosion of the whole range of Zr-Nb alloys from Zr-0.5%Nb to 100%Nb, Figure 1-2, was started, Cox, 1960; Cox, et al., 1960; Cox, et al., 1961; Cox, et al., 1962; Cox, 1963; Cox & Johnston 1963 and Cox & Read 1963. Meanwhile in the Industrial

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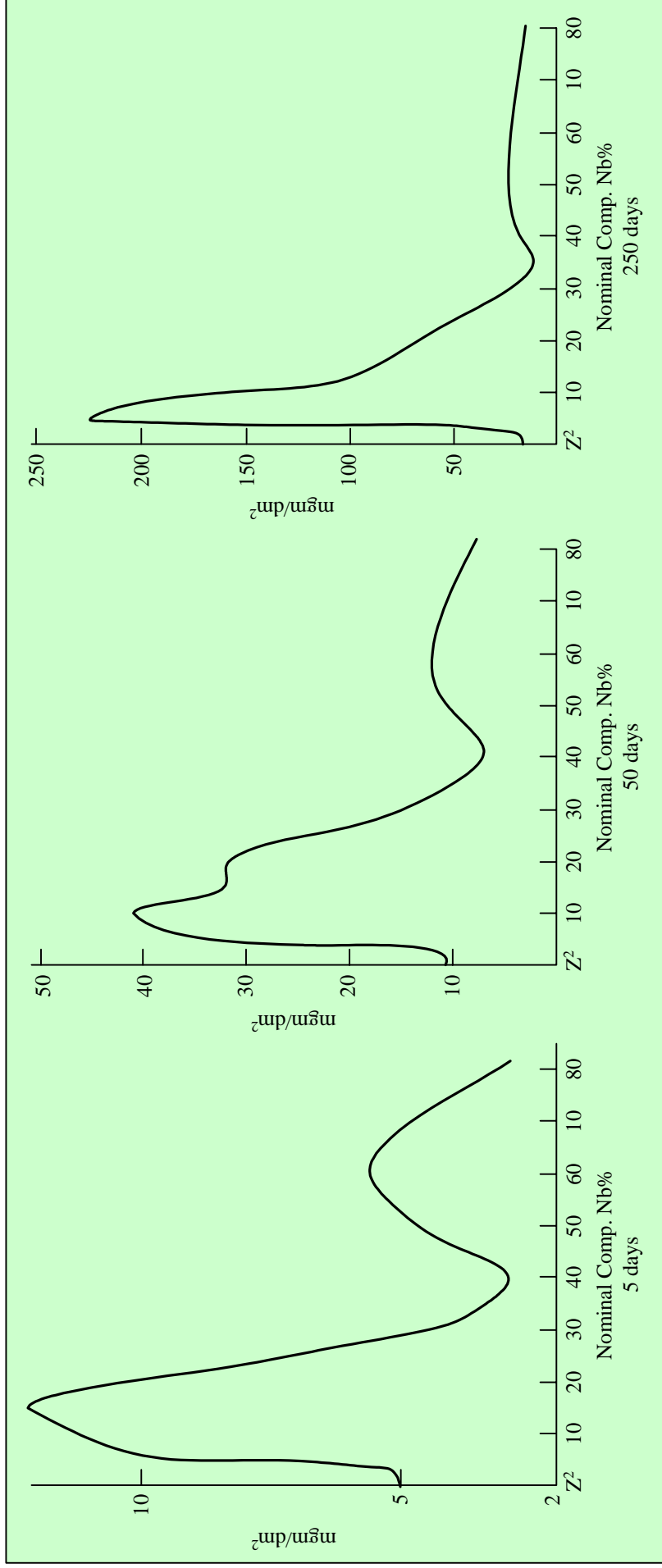


Figure 1-2: Variation of weight gain with alloy composition at 300°C and 1, 50 and 250 days.

Group of the U.K.A.E.A at Culcheth work focused particularly on the Zr-2.5%Nb alloy as an alternative to Zircaloy-2 for the pressure tubes of the proposed Steam Generating Heavy Water Reactor (SGHWR), Perryman, et al., 1963 and Allen, et al., 1966, Figure 1-3. Ultimately, although the Harwell studies, Cox, 1960 suggested

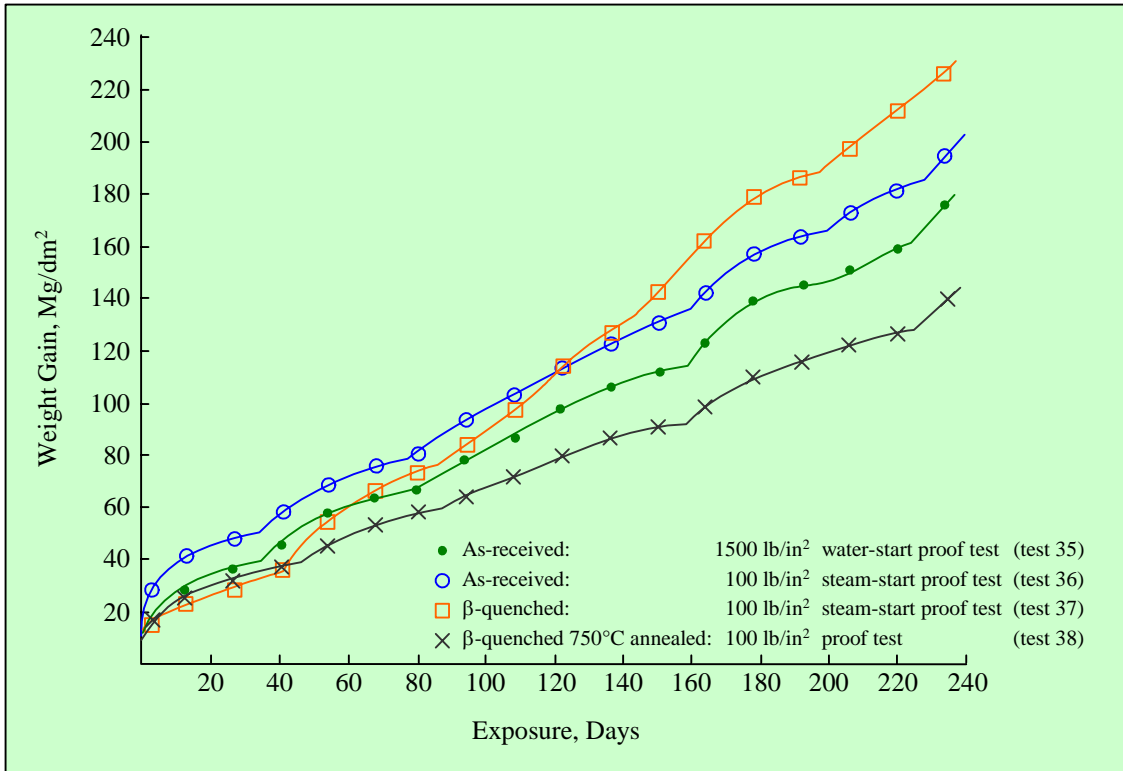


Figure 1-3(a): Corrosion of Zircaloy-2 at 400°C, effect of heat treatment of pressure tube.

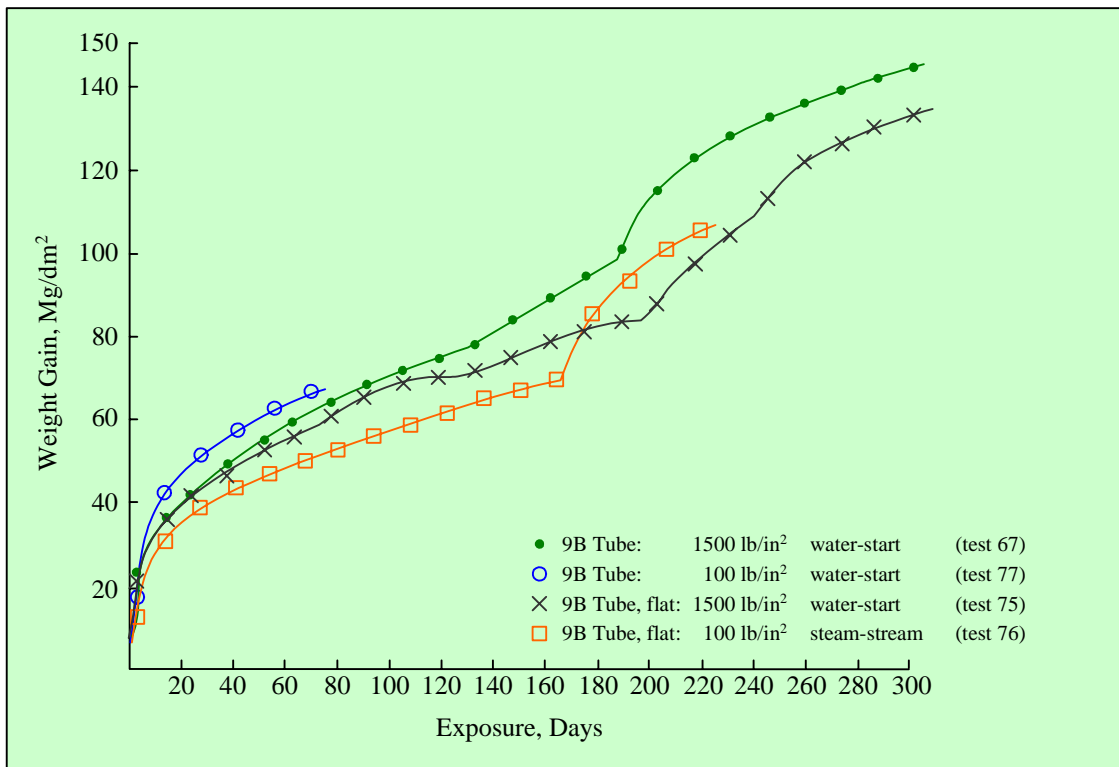


Figure 1-3(b): Corrosion of Zr2.5%Nb at 400°C, effect of proof-test pressure.

that an alloy with a composition close to Zr-2%Nb-0.5%Sn offered the best corrosion resistance among the higher strength Zr-Nb alloys, the U.K. programme focussed on the Zr-2.5%Nb alloy, once it became clear that this was the pressure tube alloy adopted by the Russians for their boiling water reactors (RBMKs). Some years later a joint Scandinavian/U.K programme (SCANUK) studied a number of ternary and quaternary alloys, Table 1-2 aimed at improved fuel cladding with the ability to withstand short, high-temperature excursions, Tyzack, et al., 1977. None of these alloys were significantly better than Zircaloy-2 either in- or out-reactor, however, Table 1-2 under BWR (SGHWR) conditions.

Table 1-2: Scanuk Alloy Compositions

Alloy	Nb	Fe	Sn	Cr	Mo	Ni	Oxygen
1	0.91	0.026	-	<0.01	<0.005	<0.005	0.100
2	0.93	0.038	0.073	<0.01	<0.005	<0.005	0.096
3	1.12	0.046	0.060	0.49	<0.005	<0.005	0.126
4	0.52	0.036	0.060	0.49	0.004	0.005	0.134
5	0.49	0.037	0.047	<0.01	0.280	<0.005	0.097
6	0.58	0.044	0.060	0.32	0.220	0.005	0.125
Valloy	0.014	0.101	<0.001	1.29	0.004	0.005	0.135
Ozhennite 0.5	0.100	0.059	0.091	<0.01	<0.004	0.052	0.117

All compositions in weight %

A similar trend occurred in the Canadian programme, where, once again, an alloy for pressure tubes was required. There, however, the desire to maximise the mechanical properties of an alloy that was heat-treatable led to CO₂ extensive work in heat-treated Zr-2.5%Nb, after some studies of a range of Zr-Nb-Sn alloys, Dalgaard, 1960 and Dalgaard, 1961. Typically the alloy was first water-quenched from the ($\alpha+\beta$) phase field (~880°C) or the β -phase (~960°C), given a pre-determined amount of cold-work to accelerate the approach to an equilibrium structure, and then annealed at the temperature (480-500°C) below the monotectoid temperature (590-610°C depending on the oxygen content). In the β -quenched condition the corrosion resistance was very poor, and this improved with both the amount of cold-work and the annealing time, Figure 1-4 and Figure 1-5,

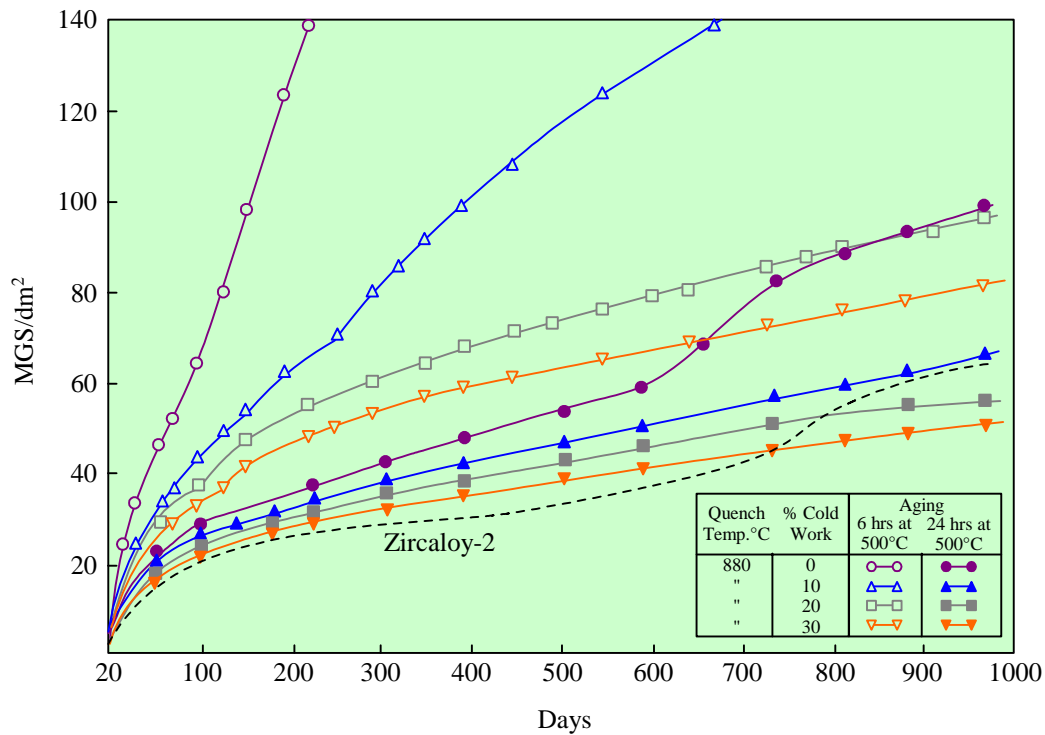


Figure 1-4: Effect of cold work and aging time on corrosion of 2.5Nb zirconium in water at 316°C, 1500 Psig.

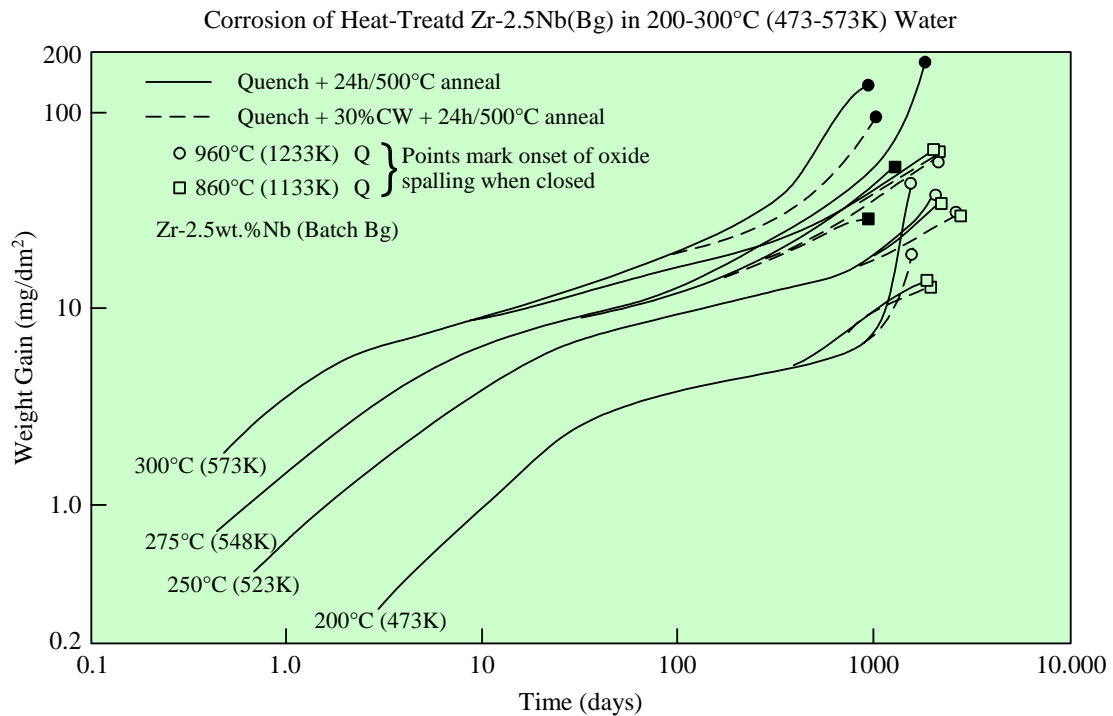


Figure 1-5: Corrosion of heat-treated Zr-2.5wt%Nb in 200-300°C (473-573 K) water.

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Le Surf, 1969 and Cox, 1976(a). Again the knowledge that the Russians were already using the Zr-2.5%Nb alloy for pressure tubes in the extruded (in the $\alpha+\beta$ phase field) and annealed condition, Table 1-3, led to a change to a similar fabrication route, but with 25-30% cold-work. And only a 400°C/24 hr stress-relief. Subsequent comparisons have shown that, although the Russian and Canadian fabrication routes are similar, the Russian tubes have slightly better mechanical properties than the Canadian tubes. The Canadians also developed a higher strength Zr-2.5%Nb-0.5%Cu alloys, which behaved reasonably well in high temperature water, Dalgaard, 1960, but was mainly of interest for situations where strength was more important than corrosion resistance, such as for the “garter springs” that separate the pressure and calandria tubes in CANDU reactors. Concerns about the long-term effects of hydrogen embrittlement by the annulus gas (originally N₂ with some D₂ that diffuses through the stainless steel end-fittings-now changed to CO₂) have led to their progressive replacement with Incoloy 728 garter springs.

Table 1-3: Pressure Tubes – Material and Operational Conditions

Reactor	Material	Finished ready condition	Configuration and moderator	Outlet temp., °C	Hoop stress, MPa	Fast neutron flux, 10 ¹⁷ n/cm ² s
CANDU	Zr-2.5%Nb	Cold worked	Horizontal, D ₂ O	308	135	3.7
FUGEN	Zr-2.5%Nb	Solution heat treated	Vertical, D ₂ O	280-286	96	2.7
RBMK	Zr-2.5%Nb	Annealed	Vertical, Graphite	288	86	1.7

The German studies of Zr-Nb alloys started at Metallgesellschaft AG, where a higher strength alloy than the Zircalloys was sought for the fuel cladding in the “Otto Hahn” nuclear ship reactor, Richter & Wilhelm, 1975 and Matucha, et al., 1978. Extensive early corrosion results were presented for a range of Zr-Nb alloys, Rösler, 1961; Jangg, et al., 1971; Anderko, et al., 1962; Beyer, et al., 1967 and Rückdeschel & Wincierz, 1967, and led to the selection of a Zr-3%Nb-1%Sn alloy for the Otto Hahn cladding. Corrosion results for this alloy, and some of the other alloys investigated are shown in Figure 1-6 and Figure 1-7. The corrosion resistance of the ZrNb3Sn1 alloy was good both in- and out-reactor, but

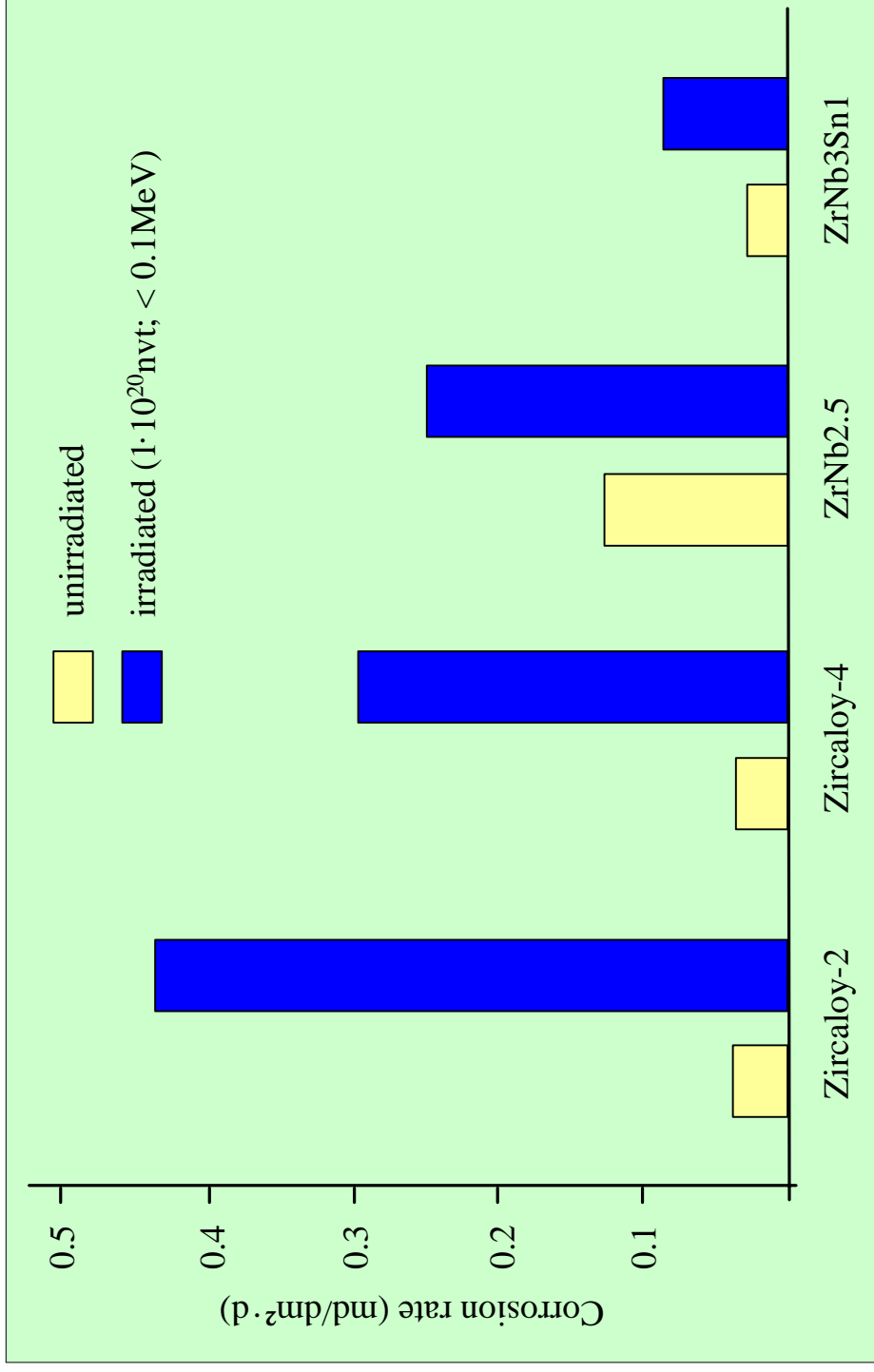


Figure 1-6: Corrosion behaviour of Zr alloys in water at 320 C and 115 bar.

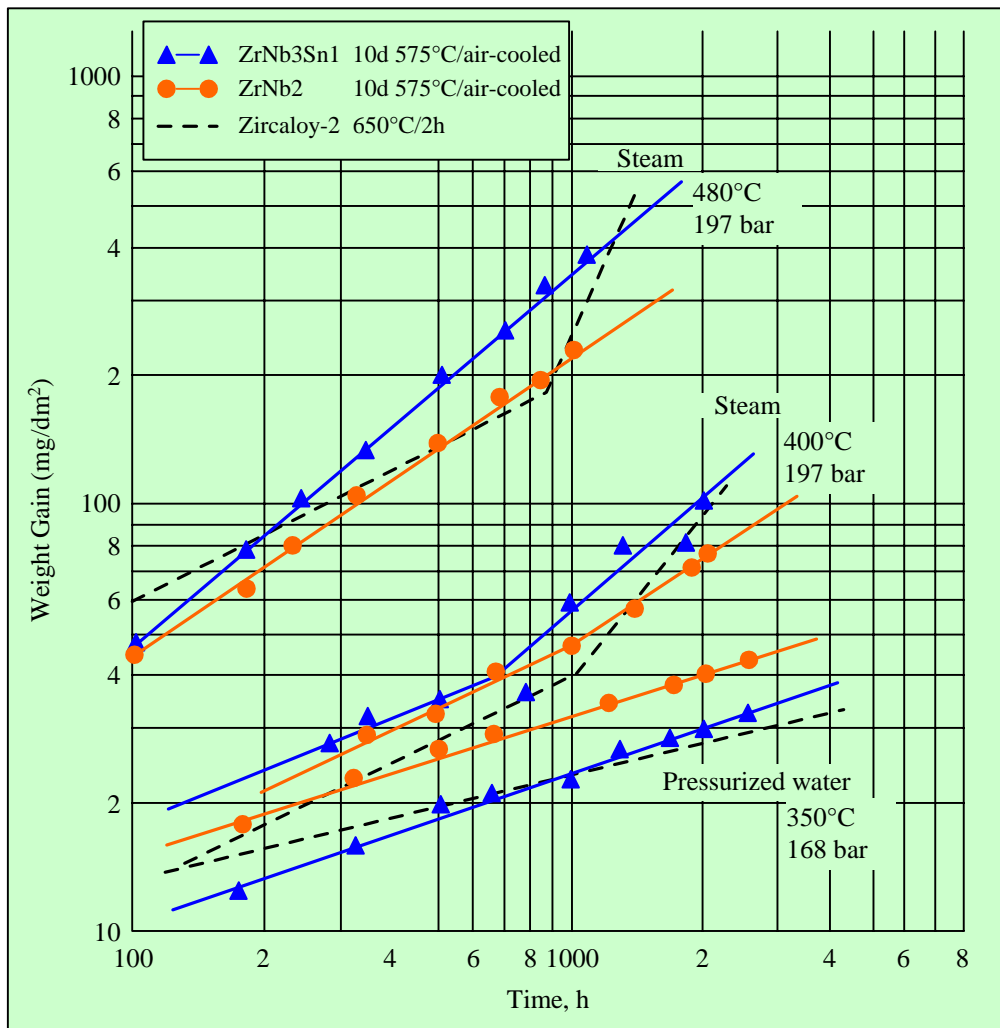


Figure 1-7: Corrosion behaviour of Zr3%Nb1%Sn, Zr2%Nb and Zircaloy-2 at 350, 400 and 480°C.

heat treatment of the welds was a problem (the corrosion rates of β -quenched alloys with $\geq 2\%$ Nb, and sensitivity of these welds to delayed hydride cracking were known problems).

In Canada the same problem faced the proposed use of Zr-2.5%Nb cladding in the organic-cooled, D₂O-moderated WR-1 prototype reactor. Cracking of unannealed welds in stored fuel elements for this reactor provided the first direct observations of DHC (Delayed Hydride Cracking) in a commercial situation, Simpson & Ells, 1974. These results came just too late to allow remedial action before the first in service DHC cracking of pressure tubes in Pickering A^{#3} on August 10th 1974, Cox 1976(b) and Perryman, 1978.

In the U.S. investigations of Zr-Nb alloys by Naval Reactors Branch at the Knolls Atomic Power Laboratory centred on a Zr-2 at %Nb-2 at %Sn alloy, Bibb, et al., 1960 and Fish, 1961. The alloy generally oxidised somewhat faster than Zircaloy-2 in both 360°C water and 400°C steam, but hydrogen uptakes were lower at ~10-15%, Figure 1-8 and Figure 1-9. There is no evidence of whether this alloy was used by Naval Reactors Branch, however, it is suspected that a Zr-3%Nb alloy may have seen some services.

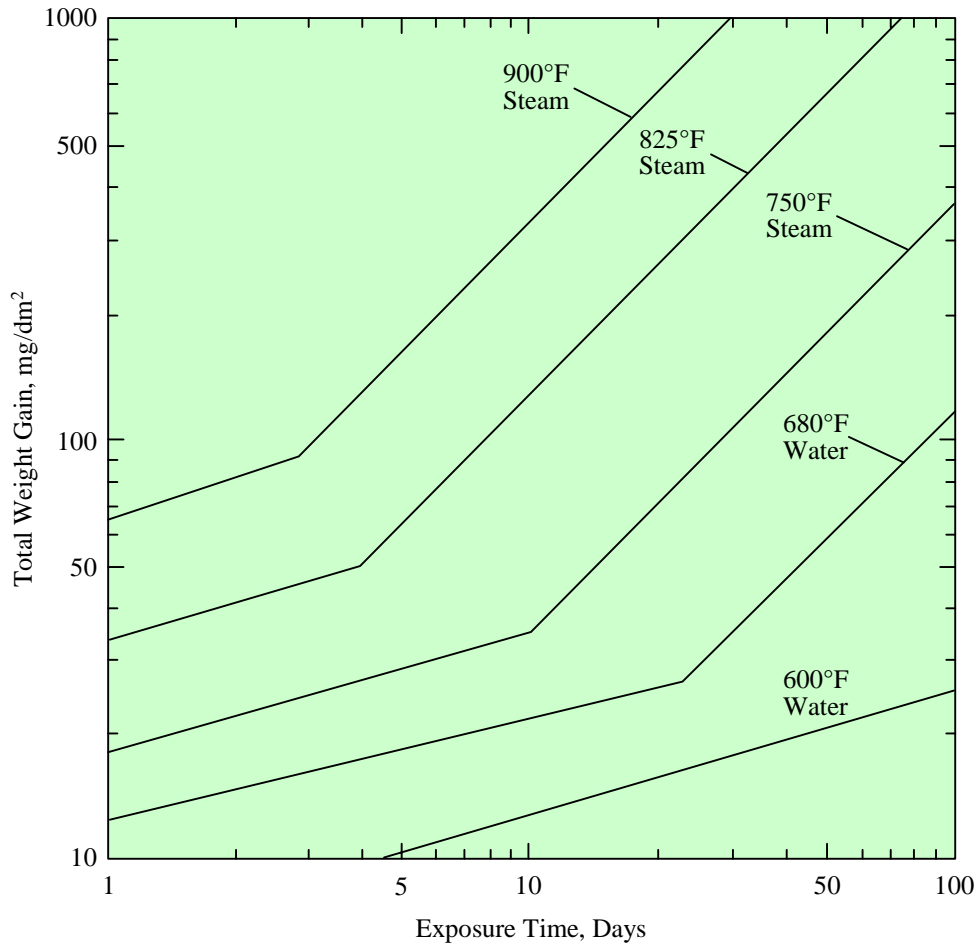


Figure 1-8: Corrosion of Zirconium-2 at % Tin-2 at % Niobium alloy in water steam.

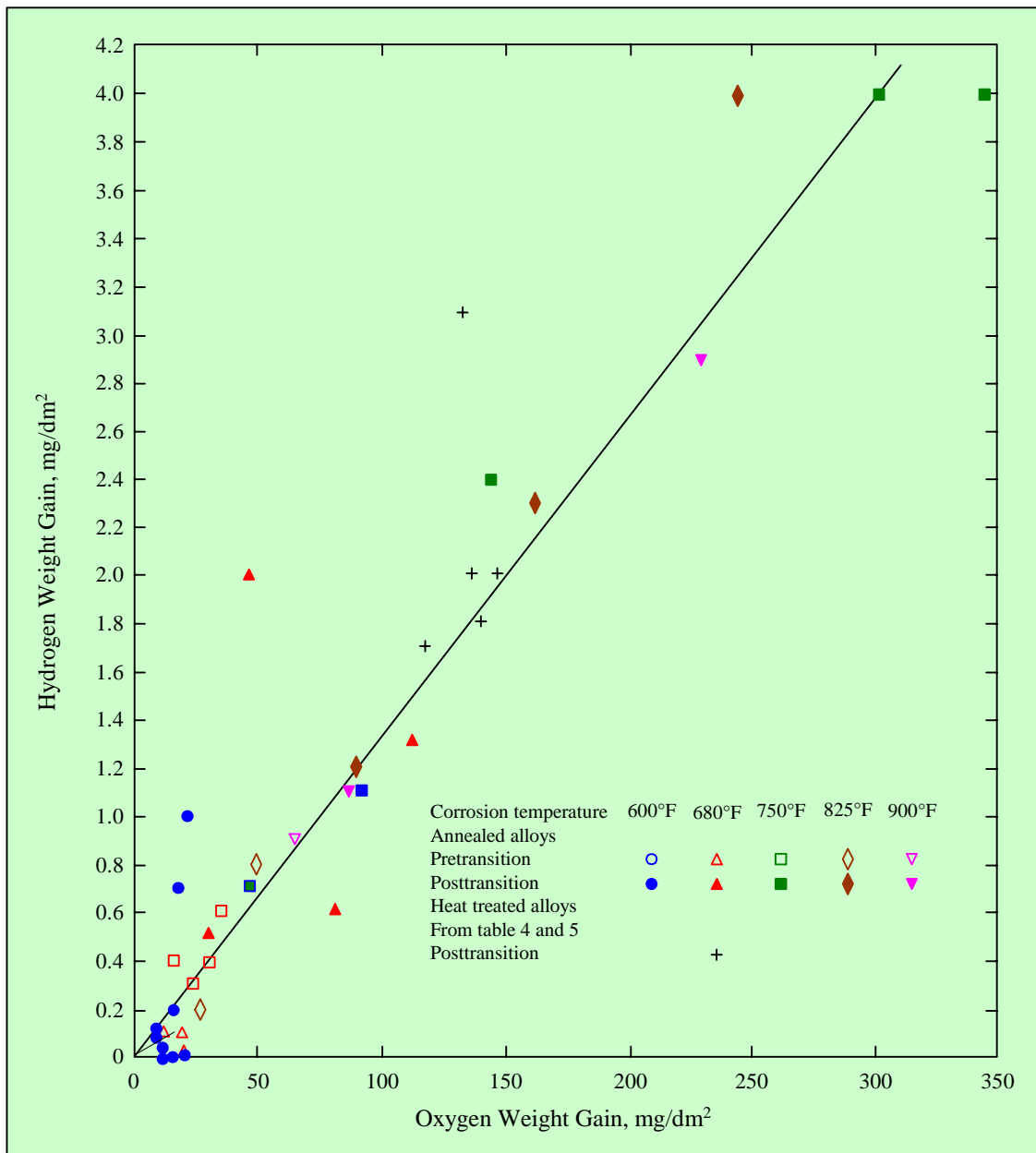


Figure 1-9: Relationship between absorbed hydrogen and oxygen weight gains.

The Russians seem to have been happy with the performance of their E110 fuel cladding in VVERs, but both it and the E125 Pressure Tubes in RBMKs suffered a severe form of “nodular corrosion” (although it clearly has very different origins than does nodular corrosion of Zircalloys in BWRs – see later). They never pursued the use of ozhennites which appeared to give better corrosion and lower hydrogen uptake, but had inadequate mechanical strength. However, the all- α Zr-Nb alloys (<0.6%Nb) still show the best corrosion resistance among Zr-Nb binary alloys in recent studies, Figure 1-10, Jeong, et al., 2003.

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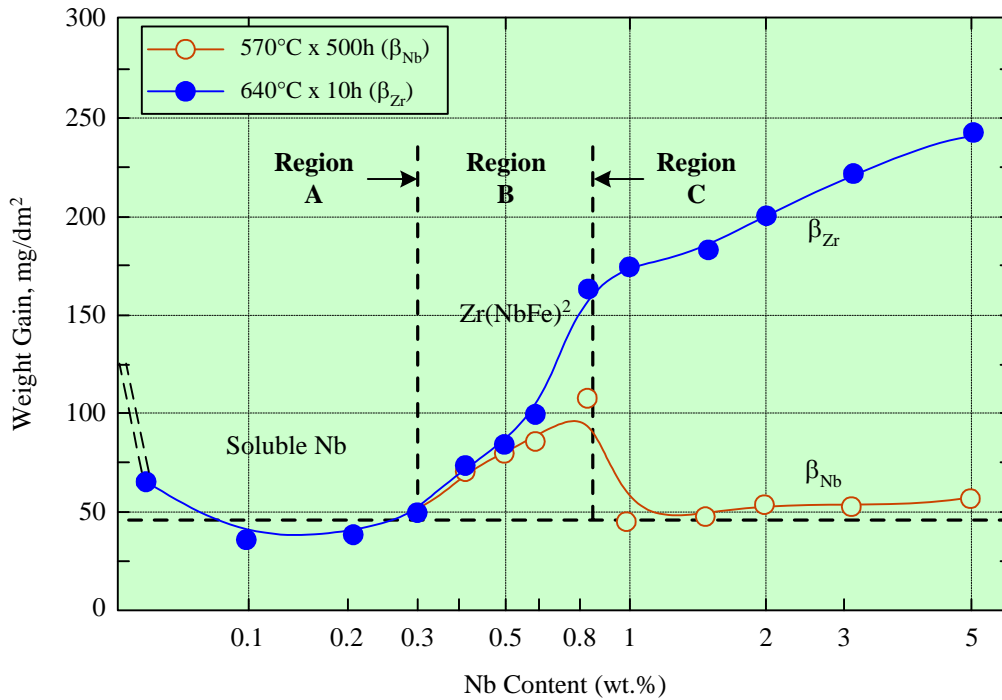


Figure 1-10: Corrosion behaviours of Zr-xNb alloys with variation of Nb-content at 360°C for 60 days.

However, in the late 60's and early 70's a group led by Amaev, Nikulina and Zaimovskii began to advocate a Zr-1Nb-1Sn-0.4Fe alloy (E635) for use in both VVER and RBMK conditions where higher strength, and freedom from the type of “nodular corrosion” that was prevalent, was needed, Amaev, et al., 1971; Zaimovskii, et al., 1975 and Zaimovskii, 1978. By adjusting the alloy composition to suite PWR water chemistry Westinghouse developed ZIRLO (Zr-1%Nb-1%Sn-0.1%Fe), and this has become the Westinghouse replacement for Zircaloy-4 (adjusted) in high performance plants, Sabol, et al., 1994(b) and Comstock, et al., 1996. Over time it has been necessary to adjust the tin content downwards to get good behaviour in high-performance PWRs. So we now have low-tin ZIRLO, just as at an earlier stage low-tin Zircaloy-4 was developed, IAEA TECDOC-996, 1998(a). So far E635 has seen little or no commercial use in Russia, even though it would appear to offer reduced “nodular corrosion” thicknesses in both VVERs and RBMKs. At present M5 (Framatome’s variant of E110) and ZIRLO (Westinghouse variant of E635) comprise the major fraction of reloads for Western high-performance PWRs, rendering standard Zircaloy-4 almost extinct, and reducing the number of the reactors that can still use low-Sn “adjusted” Zircaloy-4.

1.2 *LESSONS LEARNED FROM EARLY STUDIES OF ZR-NB ALLOYS*
(BRIAN COX)

It is difficult to compare the results presented in these early reports and papers with current experimental data because the metallurgical conditions and impurity levels in the alloys reported were not as carefully described as in recent work. The large variations in both corrosion rates and hydrogen uptake rates with relatively small differences in fabrication route and impurity content serve to confound comparisons with early data. Wherever, possible, therefore, plots that include comparative curves for Zircalloys have been used, since the corrosion rates of the Zircalloys do not seem to be as sensitive to the same variables, with the exception of β -quenching which results in poor corrosion resistance and hydrogen uptake for both Zircaloy and Zr-Nb alloys.

a) *Enhanced Corrosion in Oxygenated Water*

Unlike the Zircalloys, most Zr-Nb alloys show enhanced corrosion when there is dissolved oxygen in the water during out-reactor tests, or in steam tests. Russian data show that the corrosion rates in oxygenated water in out-reactor loop or autoclave tests are the same as in RBMKs (or in boiling loops in test reactors such as MR), IAEA TECDOC-996, 1998(a). This enhanced corrosion takes the form of white oxide “nodules”, although the cause cannot be the same as for the nodular corrosion of Zircaloy-2 in BWRs, since this occurs only in-reactor, whereas the so-called “nodular corrosion” of Zr-Nb alloys occurs equally in- and out- of reactor and is, therefore, the result of the alloys sensitivity to oxygen in the environment and not to any effect of the radiation fields in-reactor.

The sensitivity of Zr-Nb alloys to oxygen in the water was evident in early out-reactor autoclave tests, Le Surf, 1969, and persisted in in-reactor loop tests, Johnson, 1969. A possible explanation of this sensitivity to oxygen came from early studies of the oxidation of unalloyed niobium, Cox & Johnston 1963, which shows even bigger enhancements in oxidation rate in oxygen or air compared with oxygen free steam. It was observed that, in oxygen free low pressure steam, pure Nb followed a normal parabolic oxide growth curve without any transition. X-ray analysis showed that the protective oxide formed was NbO/NbO₂. When small quantities of oxygen were added to the steam an immediate breakaway occurred, producing a porous white surface oxide at a rate identical to the oxidation rate in pure oxygen. X-ray analysis showed this oxide to be Nb₂O₅. When the weight gain following the oxygen addition equalled the weight of oxygen added the oxidation rate reverted to the oxidation rate in pure steam, Figure 1-11. The addition of

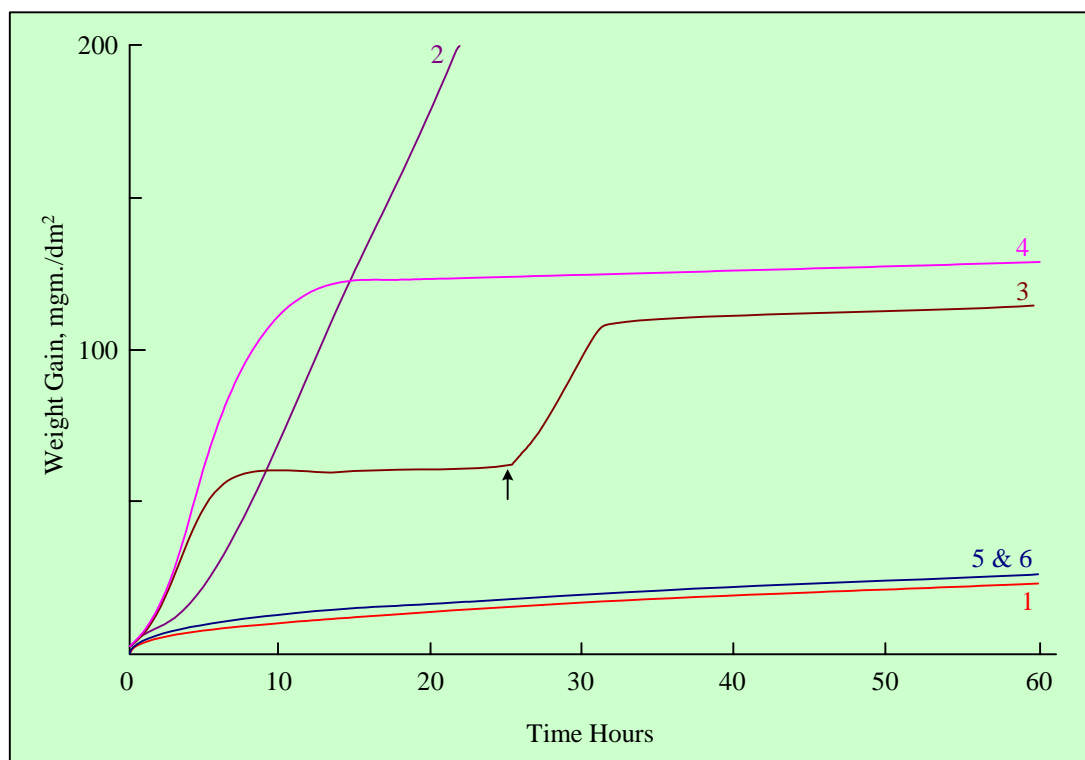


Figure 1-11: The effect of additions of oxygen and nitrogen on the oxidation of niobium in water vapour at 400°C. Curve 1: Water vapour at ~1.5 cm pressure. Curve 2: Oxygen at 7.6 cm pressure. Curve 3: Water vapour + 1 mm Hg oxygen, with the addition of a further 1 mm Hg of oxygen at 25 hr (arrow). Curve 4: Water vapour + 2 mm Hg oxygen. Curves 5 and 6: Water vapour + 1 and 2 mm Hg nitrogen, respectively.

oxygen; the acceleration in oxidation rate; and the reversion to the steam oxidation rate when all the added oxygen had reacted could be repeated. Thus the formation of the porous Nb₂O₅ oxide from the protective NbO/NbO₂ film gettered the molecular oxygen in the environment and the kinetics then reverted to the lower rate due to the reformation of a protective NbO/NbO₂ film at the oxide/metal interface. The conversion of the NbO/NbO₂ film to Nb₂O₅ caused the breakdown of the protective oxide, probably as a result of the large volume increase on converting NbO₂ to Nb₂O₅. In oxygen free steam at high pressure a small amount of Nb₂O₅ was found on the surface of the NbO₂, and oxidation rates were higher than at low pressure, but the change was not significant enough to cause a complete breakdown of the protective NbO/NbO₂ film. Oxidation rates in high pressure steam were not, therefore, as high as in air or oxygen at the same temperature.

The same sequence of events occurred when oxygen was added to a low pressure steam test of Zr-2.5%Nb specimens. This suggests that the Nb in this alloy also forms some NbO₂ crystallites during oxidation and that the volume change on converting these to Nb₂O₅ might be sufficient to damage the protective nature of the oxide film. Some evidence for “high Nb” oxide crystallites was found during the STM analysis of oxides on Zr-2.5Nb as follow-up to similar studies on Zircaloy-2 oxides, Cox & Sheikh, 1997. However, this investigation could not be pursued.

Because of the small Nb containing particles in both E110 and E125 the effect of oxygen in the water may cause local oxide breakdown that has the appearance of “nodular corrosion” when observed both in- and out-reactor, IAEA TECDOC-996, 1998(a).

b) “Nodular Corrosion” of Zr-Nb Alloys

Early batches of Zr-2.5%Nb alloy commonly exhibited white oxide spots following oxidation in high temperature water, Cox, 1964. These were thought to have resulted from large Fe containing intermetallic particles that were present in these batches, Figure 1-12. Fe analyses as high as 800-1000 ppm were measured both in early batches of the Zr-2.5Nb sheet and in some of the Pickering 3 and 4 reactor pressure tubes. No white oxide spots were seen on the pressure tubes after service; so perhaps the autoclave tests were not degassed as well as they

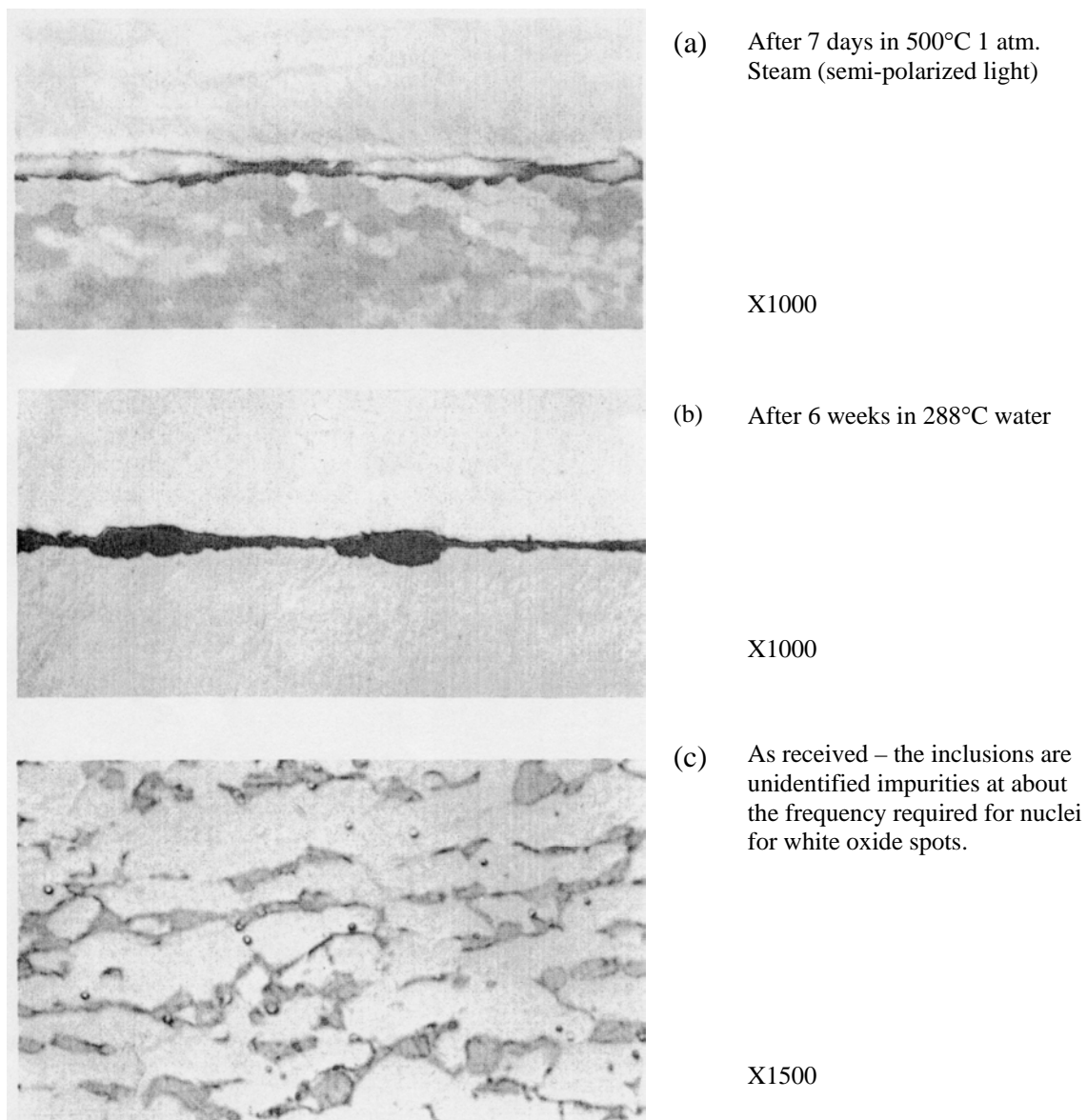


Figure 1-12: “White oxide spots” formed on early batches of Zr-2.5%Nb.

might have been. The two phenomena-Fe containing intermetallics and sensitivity to oxygen in the environment – may therefore be synergistic, leading to the “nodular” corrosion observed both in- and out-reactor in oxygenated water.

In early days electron microprobe analysis did not have the resolution necessary to characterise these intermetallics. Using modern techniques, however, Barberis, et al., 2004, it has been shown that variants of Zr_2Fe and $ZrFe_2$ are the common SPPs in Zr-1%Nb, in addition to β -Nb. These variants – $(Zr_1Nb)_4Fe_2$; $Zr(Nb_1Fe)_2$ – contain both Nb and Fe in a single intermetallic and so may give both high Nb and high Fe oxide crystallites adjacent to each other following oxidation. Thus, we may get a localised form of oxide breakdown that requires both oxygen to convert NbO_2 to Nb_2O_5 and perhaps Fe_3O_4 crystallites that are converted to Fe_2O_3 in oxygenated water.

The current hypothesis for nodular corrosion in BWRs requires the presence of redox potential differences between the intermetallics and the Zr matrix and a large reduction in the electrical resistance of the oxide as a result of irradiation. Thus, it is seen as a micro-version of “shadow corrosion”, where the adjacent grid (Ni alloy, stainless steel) provides the cathode; the water chemistry under irradiation allows the persistence of potential difference between these alloys and Zircaloy, and the radiation field enhances conductivities in the other components of the circuit, Cox, 2003. If the presence of “high Nb” oxide crystallites in the oxide formed on Zr-Nb alloys make the oxide sufficiently electrically conducting that irradiation is not needed to allow these electrochemical currents to flow, then the Russian observation that the “nodular corrosion” of E110 is the same in both in-reactor and out-reactor loops becomes understandable, IAEA TECDOC-996, 1998(a).

c) “Powdering-Off” of the Oxide on Zr-Nb Alloys

From the early days of studies of the oxidation of the Zr-Nb alloys it was suspected that, unlike Zircalloys where thick oxides spall in large pieces, the oxide on Zr-Nb alloys could be lost as small particles of powder in a semi-continuous manner, Rosenfel’d, et al., 1962. Such a mechanism for losing oxide was confirmed for commercial grade titanium, which was used for both in-reactor and out-reactor autoclaves at Harwell, Cox & Alcock, 1959. The titanium autoclaves, and control specimens included with the zirconium alloy specimens, developed a first order blue interference coloured oxide film that was protective, and remained the same colour without evidence of thickening no matter how long the exposure of the titanium. However, the blue colour became cloudy because of the formation of a thin white, powdery oxide on top of it. The blue colour, and the formation of the outer powdery layer were the same whether the test was in-reactor or out-reactor. Weight change measurements on control specimens showed a continuous, linear, loss of weight during test, Figure 1-13, indicating that powdery layer was being gradually lost, Cox et al., 1957 and Cox et al., 1961. A similar steady weight loss of an outer powdery oxide, with some rather pale interference coloured oxide underneath, was also observed with pure tantalum, which was being tested as

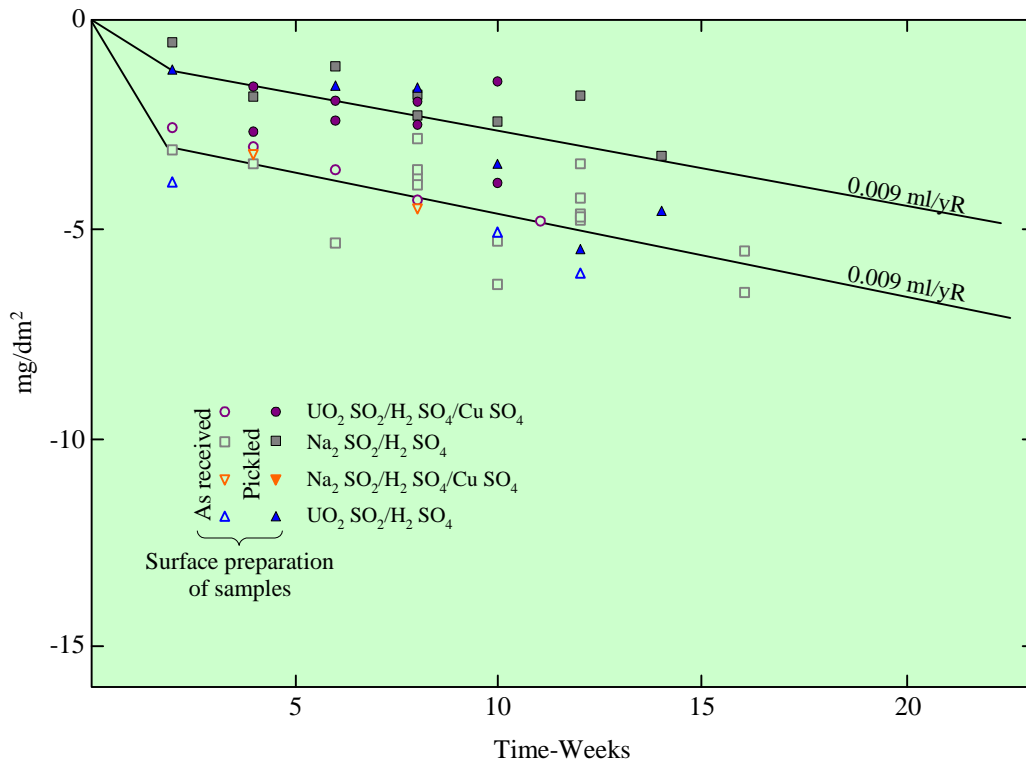


Figure 1-13: Titanium 130 corrosion at 300°C.

an alternative autoclave material to titanium. A similar process was suspected for Zr-Nb alloys under some conditions because of irregular weight gains and small weight losses especially in test in low temperature ($\leq 300^{\circ}\text{C}$) water. This effect was never proved, Cox, 1976(a).

In an in-reactor water loop test in the RPT reactor the Russians, Amaev, et al., 1964, tested prehydrided (0.002 to 0.1% H) E110 specimens at 290°C, 100 atm. And a flow rate of 4.5 m.s⁻¹ for 4000 hr. They observed a factor of 8 increase in the corrosion of the in-flux specimens compared with the out-of-flux specimens with the lowest hydrogen content (0.002%), but little or no effect for the other specimens with higher hydrogen contents. However, with higher initial hydrogen contents they reported that “a certain decrease in weight gains is traced. This may be supposed to be connected with deterioration of oxide film adhesion, which results in extensive washdown of the oxide film due to erosion by the water steam”. They did not see a similar loss of oxide in static autoclave tests at 350°C. This appears to be a similar observation to ours; that the loss of powdery oxide was more prevalent a low water temperatures, and did not result in any major flaking of the oxide until very long times (>1000 days), Cox, 1976(a). It is tempting to conclude that the loss of oxide powder from Zr-Nb alloy specimens is restricted to early batches of alloy, with high Fe and H contents, tested at <300°C in water – particularly at high water flow rates. However, no specific study of either M5 or Zr-2.5Nb surface topography before and after exposure in-reactor, and designed to detect small losses of oxide has been attempted. This powdering-off of oxide is suspected of being the explanation of the apparently constant thickness of the oxide formed on E110 in both VVER-440 and VVER-1000 reactors, Figure 1-14, IAEA TECDOC-996, 1998(a) and IAEA TECDOC-997, 1998(b).

In autoclave tests it was not uncommon to find significant time periods where the weight gain plateaued, or showed erratic decreases, especially during tests at 280°C or 250°C. This may be indicative of some powdering-off of oxide. Technicians did report “dust” left on the balance pan for some specimens, but the records of these tests have been destroyed. Thus, the reports of plateaux in the oxide thickness for E110 in VVERs immediately suggested a powdering-off of oxide from the cladding. This has never been investigated.

d) Low Hydrogen Uptake

Initial results for hydrogen uptake by Zr-Nb alloy specimens in 360°C or 400°C autoclave tests did not indicate a particularly low hydrogen uptake percentage, Figure 1-9, and the same applied to early studies on Zr-2.5%Nb, Figure 1-15, Dalgaard, 1961. In the latter instance these were primarily heat-

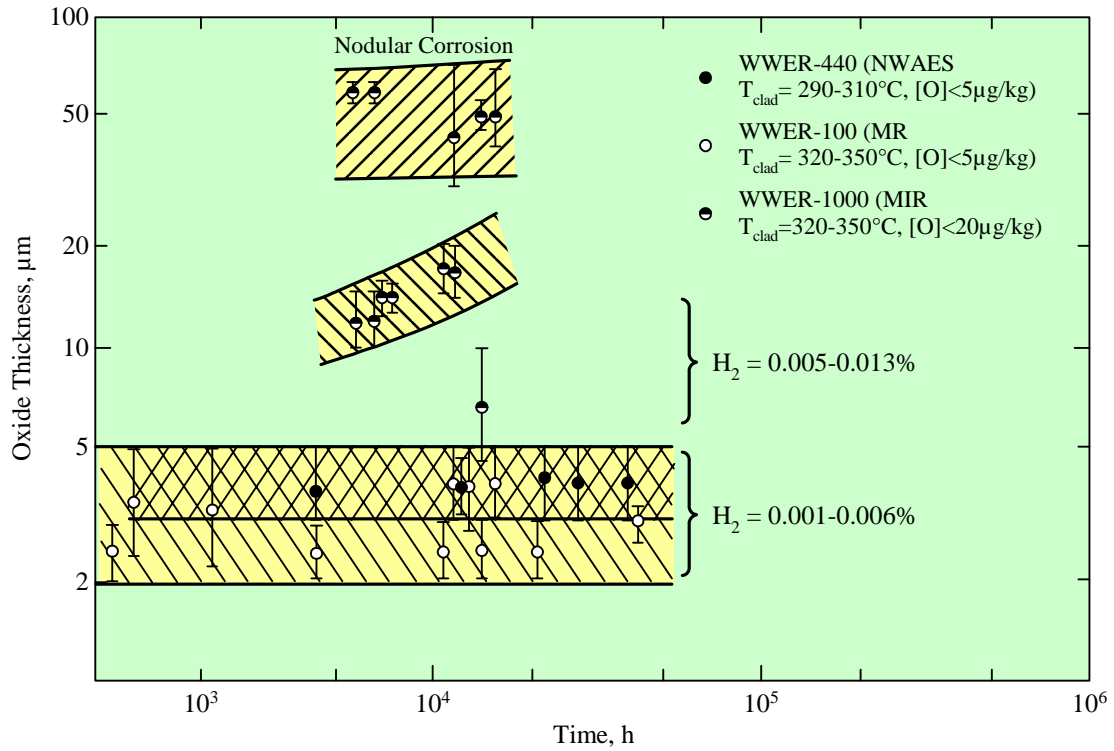


Figure 1-14: Corrosion of Zr-1%Nb cladding.

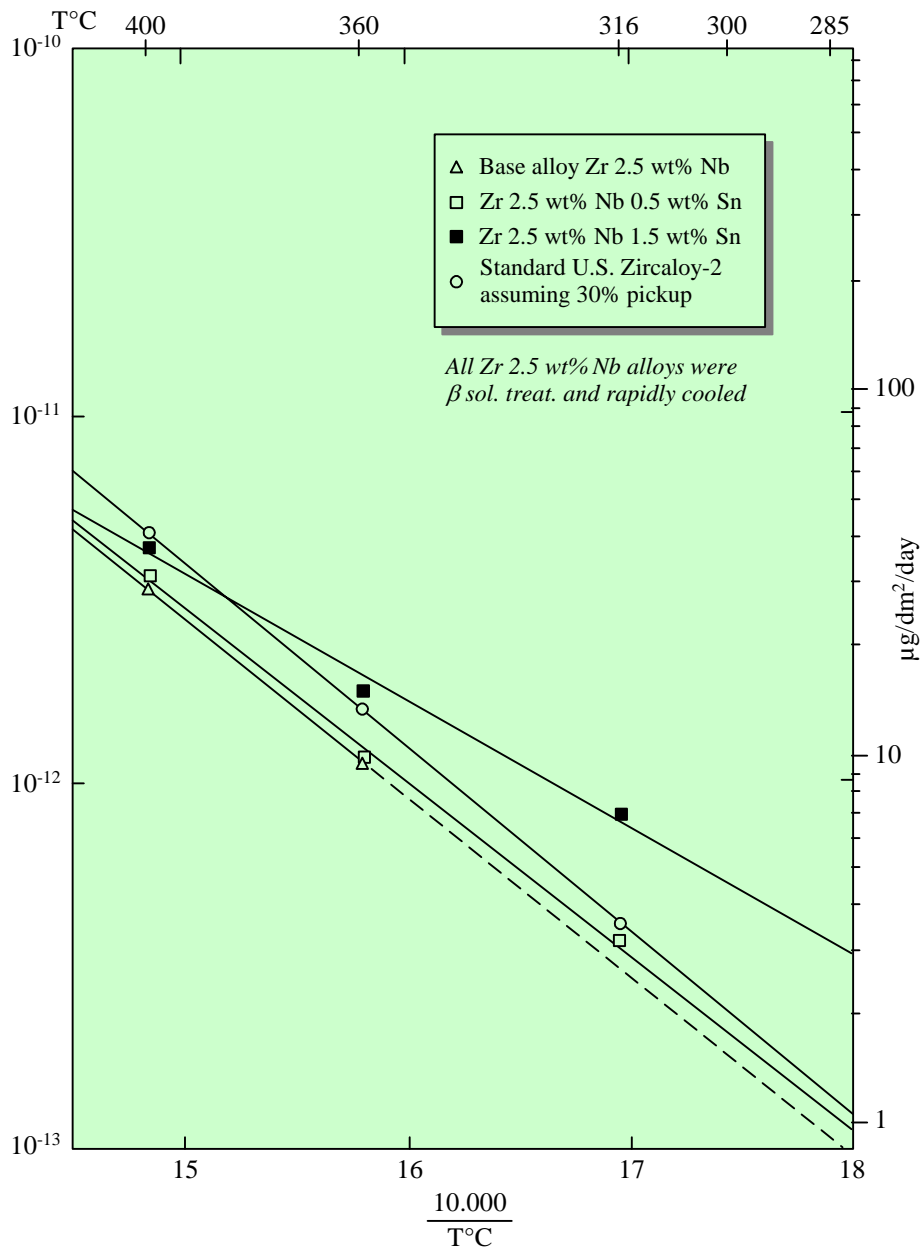


Figure 1-15: Effect of Tin on hydrogen pickup in the Zr-2.5wt%Nb alloy.

treated specimens. Other results showed that hydrogen uptakes of 10% or less could be obtained, but only for heat treatments that resulted in poor corrosion resistance, Cox & Read 1963. The Russians had not reported hydrogen uptake figures for their RBMK pressure tubes at that time, so when the decision was made to change to an ($\alpha+\beta$) phase extrusion ($\sim 760^\circ\text{C}$) with 25-30% cold-work and a 400°C stress-relief (24 hr. in steam) the low hydrogen uptake sales ($\sim 5\%$) came as a welcome surprise. By that time DHC (Delayed Hydride Cracking) was seen as the major problem for Zr-2.5Nb pressure tubes. The Russians did not publish hydrogen uptakes for their e110 cladding, but Vrtilkova, et al., 2000 did, and did not find low values for E110 in autoclave tests, Table 1-4. So the low hydrogen uptakes by M5

Table 1-4: Fraction of the Hydrogen Pickup in %

Environment	Zr1Nb	ZIRLO™	Zry-4W	Zry-4S
360°C VVER water	33	10	15	12
360°C water + 43 O ₂	32	24	25	15
360°C water + 70 lithium	5	5	23	25
360°C water + 210 lithium	<45	<35	38	45
360°C water + 450 lithium + 17.5B	<5	<4	42	54
400°C steam	45	30	60	26

were again a welcome surprise once they became known.

e) Reduction of Corrosion Rates Under Irradiation

When studying the in-reactor corrosion of the Zircaloy, most researchers approached the topic with the expectation of finding an in-reactor enhancement of the corrosion rate, IAEA TECDOC-996, 1998(a). It was surprising, therefore, to find that there was a well established irradiation induced reduction in the corrosion of the Zr-2.5%Nb alloy, Figure 1-16, Urbanic, 1974 and Urbanic et al., 1975. For the heat treated specimens being studied it was known that corrosion rates decreased with

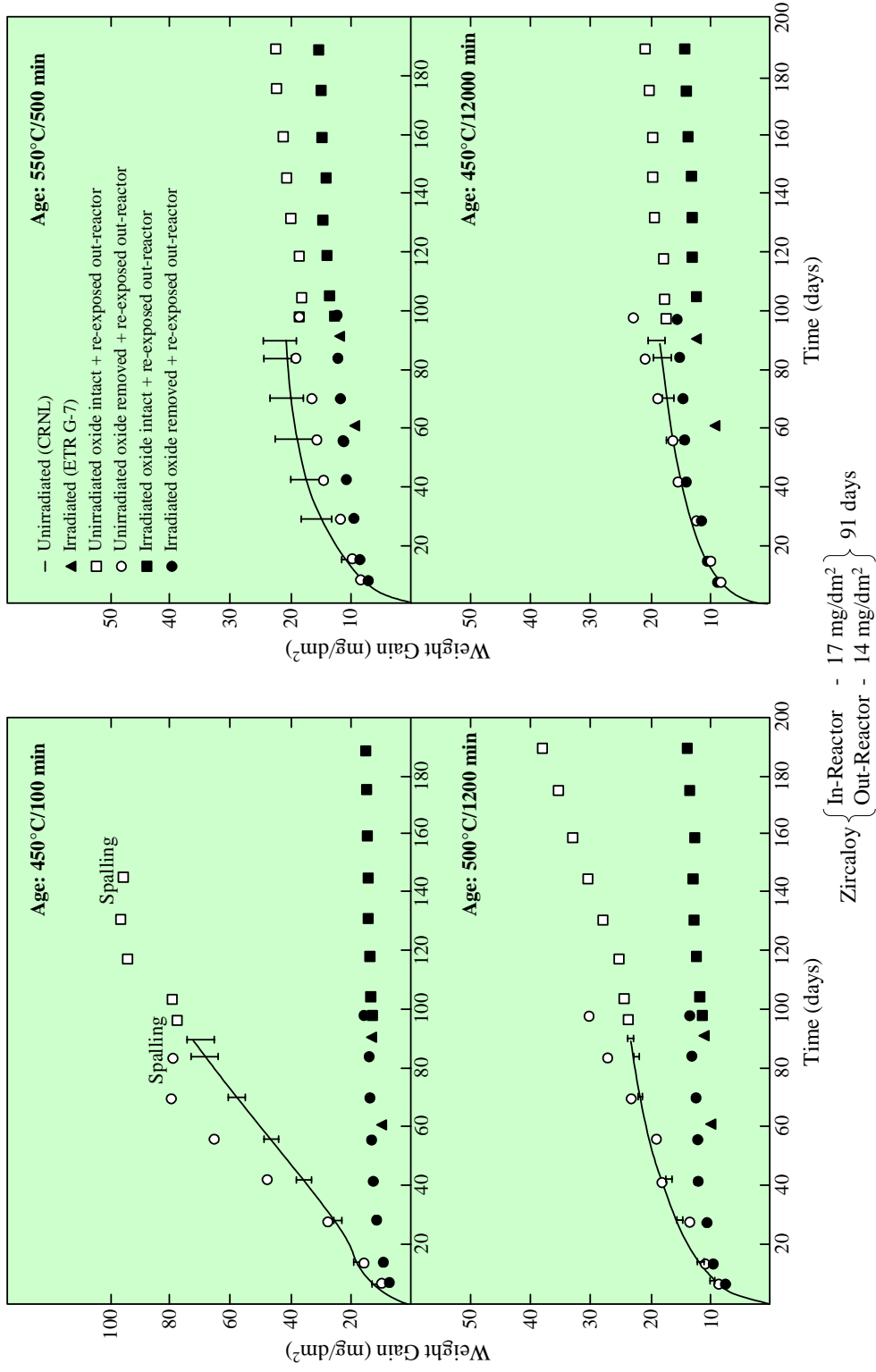


Figure I-16: The effect of irradiation and descaling on subsequent corrosion of heat-treated Zr-2.5wt%Nb in 280°C ammoniated water.

increasing annealing times after the quench, and that increasing the intermediate cold-working percentages speeded up approach to an annealed structure. It was thus evident that irradiation was behaving like cold-working to speed up the annealing process. This gave lower corrosion rates than could be achieved by thermal annealing treatments alone, Figure 1-17. However, the effects are more complicated than this simple picture. Under irradiation there are several processes operating. The amount of niobium in solid solution in the metal decreases under irradiation as it approaches the equilibrium solubility at the irradiation temperature. There is an increase in β -Nb as the niobium coming out of solid solution precipitates in this form. The volume fraction of β -Zr decreases as it decomposes under irradiation and the composition of β -enriched Zr increases except this increase in the niobium concentration of β -Zr is inhibited at the highest fluxes, Urbanic & Griffith, 2000, Figure 1-18. The net effect is a corrosion rate in-flux that is lower than that achieved with very high (80%) cold-work, and little dependence under irradiation on the amount of cold-work.

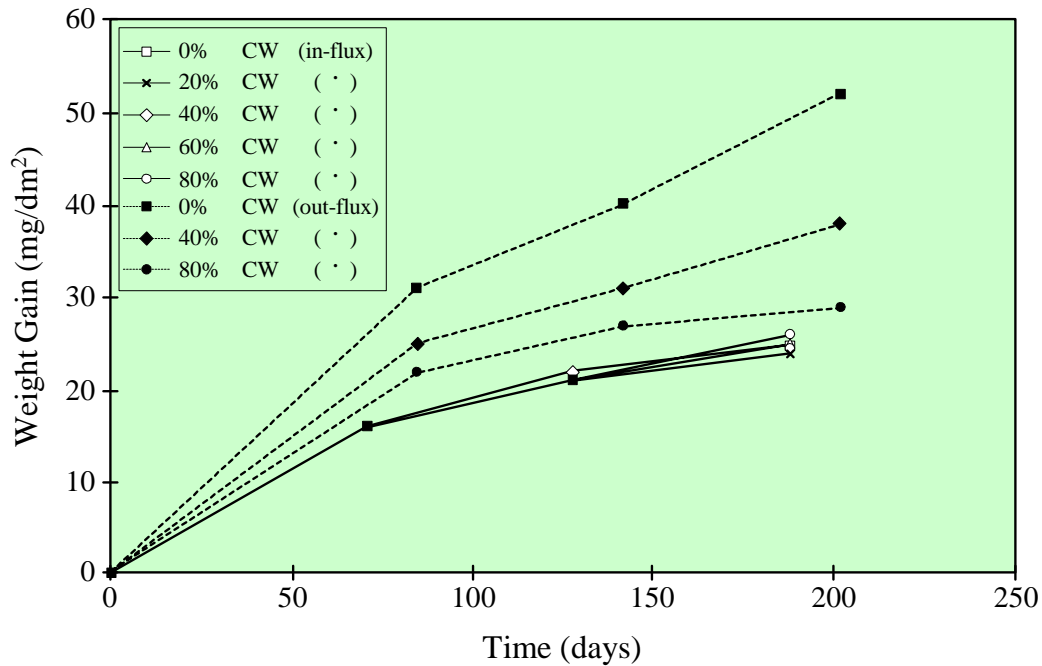


Figure 1-17: Effect of cold work on corrosion of Zr-2.5Nb pressure tube material.

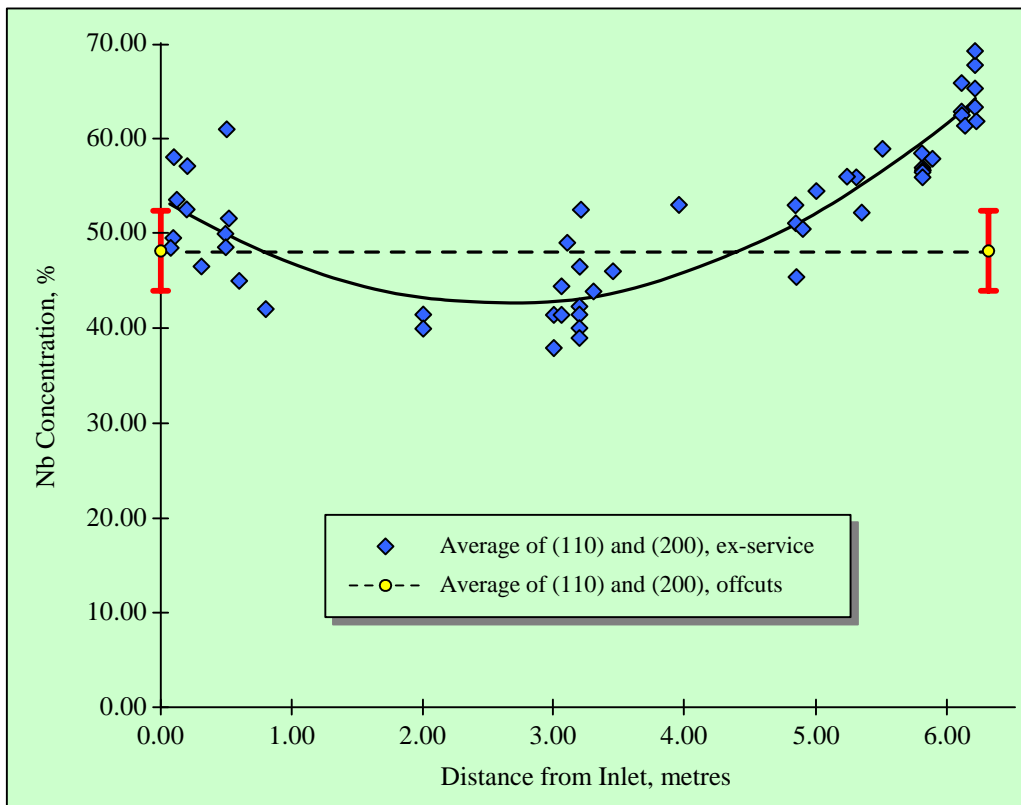


Figure 1-18: Nb concentration in the β -phase of Zr-2.5Nb pressure tubes as a function of position relative to the inlet in CANDU reactors.

1.3 EARLY IN-REACTOR EXPERIENCE WITH ZR-NB ALLOYS

1.3.1 Russian and Canadian reactor types (Brian Cox)

Apart from the Zr₃Nb₁Sn alloy fuel cladding in the Otto Hahn ship reactor, only Zr-1%Nb (E110/M5), Zr-1%Nb-1%Sn-0.1-0.4%Fe (E635/ZIRLO) and Zr-2.5%Nb (E125) have seen extensive operational exposure in nuclear reactors. Several other alloys in which niobium is a minor addition, and which are basically modified Zircalloys have seen some exposure LTA's (Lead Test Assemblies), but have generally not shown any notable improvement over the Zircalloys – with compositions adjusted to get the best corrosion behaviour. The three commonly used Zr-Nb alloys will be considered here. The Zr-2.5%Nb-0.5%Cu alloy has seen extensive service in the annulus gas atmospheres of CANDU reactors, but this experience is not seen as being relevant to the main aim of this report.

1.3.1.1 RBMKs

RBMKs are basically vertical channel-type boiling water reactors. They use E110 (Zr-1%Nb) fuel cladding in the fully recrystallised conditions. The fuel assembly consists of two fuel bundles of 18 rods supported on a central stainless steel rod, Figure 1-19, with 11 stainless steel grids on each bundle. The overall length of the assembly is 10.01 metres, Kupalov-Yaropolk, et al., 1998. The fuel channels are 88 mm I.D. and are Zr-2.5%Nb. Both the E110 cladding and the E125 pressure tubes show extensive “nodular corrosion” and evidence of “shadow corrosion” adjacent to the stainless steel grids. Since the alloys also show nodular corrosion in out-reactor, boiling, oxygenated water-loop tests there is clearly no necessity for there to be an irradiation field to get “nodular corrosion” in these alloys. The effect of irradiation and the galvanic couples with stainless steel giving “shadow corrosion” may be to enhance the severity of these processes. Amaev, et al., 1971 showed the extent of the sensitivity of E110, E125, Zr-2.5%Nb-0.5%Cu and E635 to oxygen in the water in the absence of irradiation, Figure 1-20. Their sensitivity decreases in the order in which the alloys are listed. Irradiation had little or no effect on the corrosion of these alloys. Micrographs of irradiated material

2 BASIC METALLURGY (BRIAN COX)

The Zr-Nb phase diagram is shown in Figure 2-1. It differs significantly from that of unalloyed zirconium because of the β -stabilising effects on Nb. Thus, the solubility of Nb in α -Zr is a maximum of ~0.6 wt% at the, monotectoid temperature of ~610°C. The monotectoid temperature varies according to the concentration of α - or β -stabilising impurities in the alloy. Thus, oxygen (an α - stabilising

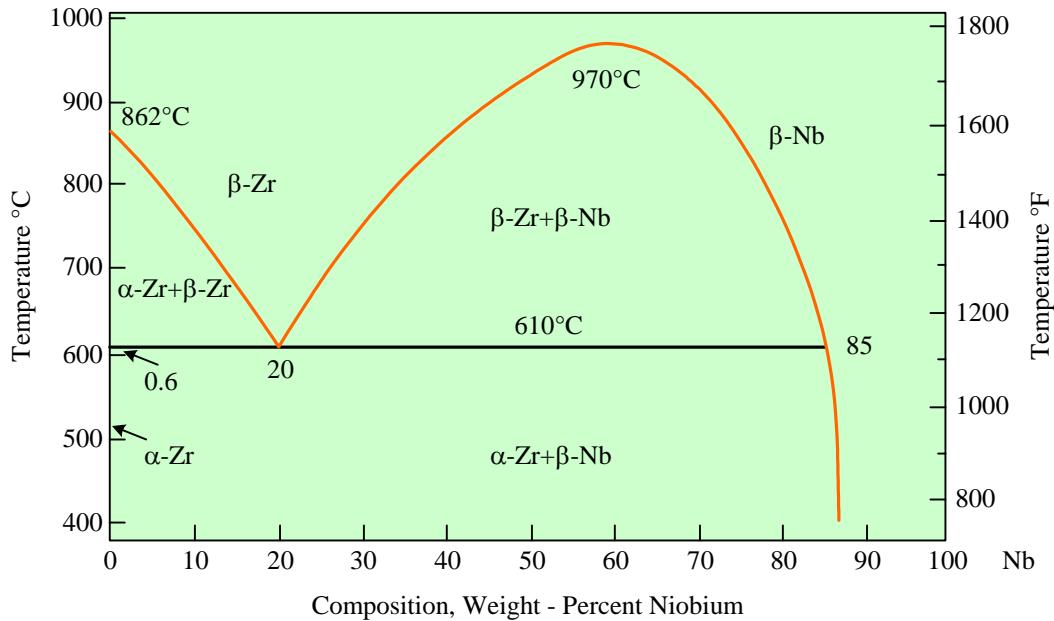


Figure 2-1: The zirconium-niobium equilibrium phase diagram determined by Lundin & Cox, 1962.

impurity) whose concentration varies significantly in Kroll sponge Zr, and whose concentration may be deliberately increased to improve the mechanical properties of the alloy, is probably the major impurity that affects the monotectoid temperature. With very low oxygen concentrations the monotectoid temperature may be as low as 590°C, whereas, with high oxygen concentrations (>1500 ppm) it may be as high as 620°C. Other impurities that may affect the monotectoid temperature, such as Fe which is a β -stabiliser, may depress the monotectoid temperature. It will probably be necessary to measure the monotectoid temperature in any particular batch of alloy if an accurate value is needed.

Quenching from the β -phase does not result in a metastable β -Zr alloy because of the martensitic nature of the $\beta \rightarrow \alpha$ transformation. The product of β -quenching is an α' (alpha prime) Zr phase with high Nb will precipitate as (β -Nb depending of the speed with which it is cooled through the ($\alpha+\beta$) region, and the length of the time spent in the high α -Zr region. Quenching from the ($\alpha+\beta$) phase field will result in a mixture of α -Zr plus β -Zr. The composition of the β -Zr will depend on the actual ($\alpha+\beta$) temperature it is held at and the time it is held there prior to quenching.

Reactors that use Zr-2.5Nb alloy pressure tubes have adopted a variety of fabrication routes, Table 1-3. A typical fabrication route for CANDU-PHWR pressure tubes uses an $\alpha+\beta$ ($\sim 760^\circ\text{C}$) extrusion (in recent tubes a prior β -quench is given before the extrusion) followed by cold-working 25-30% to final size, with a final stress-relief at 400°C in steam for 24 hr which also produces an $\sim 2\ \mu\text{m}$ black oxide layer that protects the surfaces. Variables such as the length of time the extrusion billet is held in the furnace prior to extrusion (which allow Nb diffusion into the β -Zr and oxygen diffusion into the α -Zr) and the extrusion ratio (determined by the ratio of the billet size and the final tube size) can affect the microstructure of the final tube, and its mechanical properties, Cheadle, et al., 1972 and Cheadle, 1974. For instance it is usual in commercial practice, for a series of extrusion billets to be put in the preheating furnace together at the start of an extrusion run. The billets are taken out one at a time for extrusion so that there can be a big range of ($\alpha+\beta$) hold-times from the first to the last billet extruded (and a range of properties is shown in Figure 2-2 and for the fracture toughness in Figure 2-3. A typical product of such a process would have very elongated and

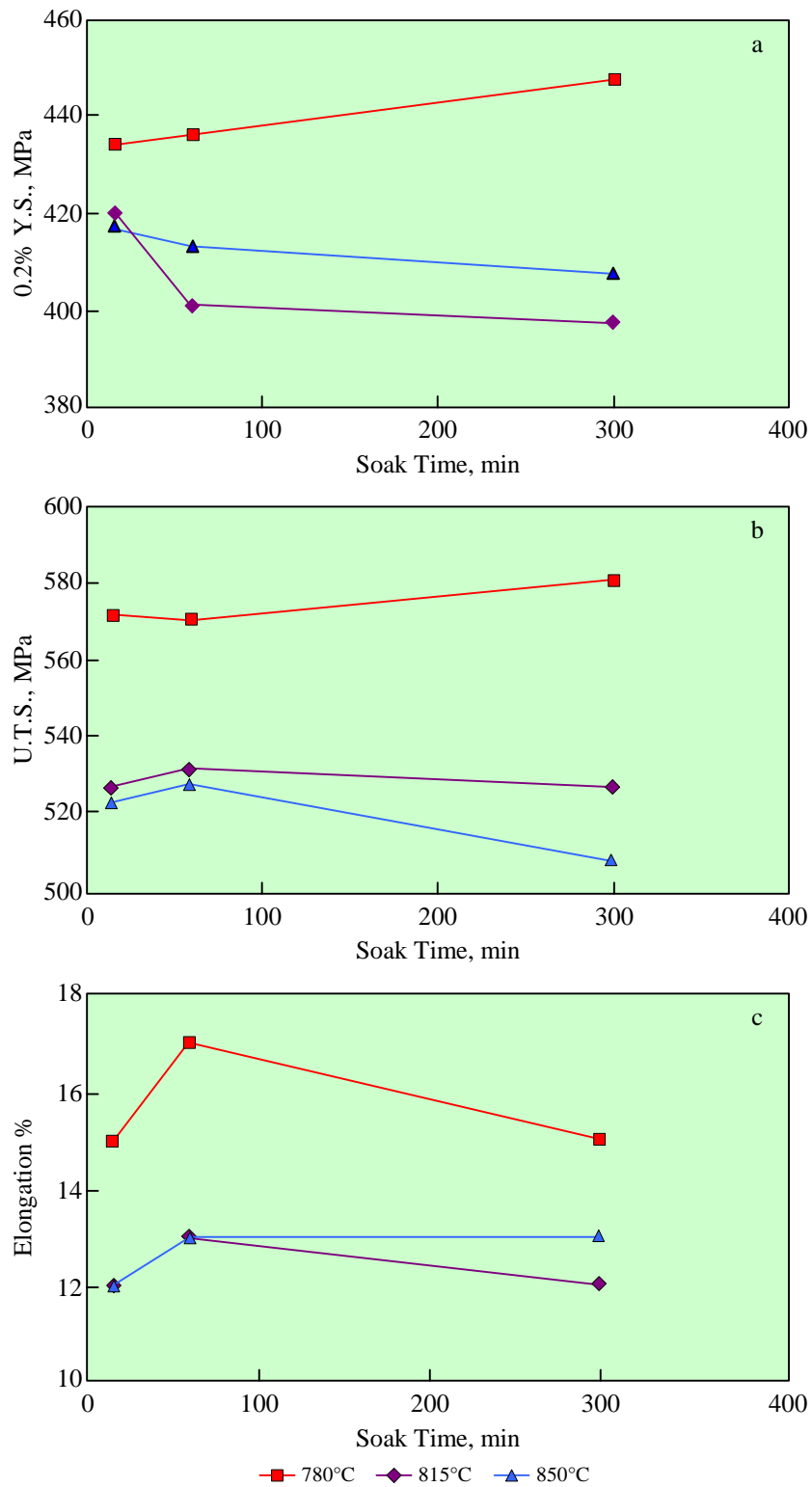


Figure 2-2: Effects of billet pre-heated temperature and soak time on the longitudinal tensile properties of Zr-2.5Nb pressure tubes (front ends) tested at 300°C: (a) Yield stress, (b) UTS, and (c) elongation %.

3 FABRICATION (BRIAN COX)

3.1 FABRICATION OF ZR-2.5NB PRESSURE TUBES

Although initial studies focussed on ($\alpha+\beta$) quenching ($\sim 880^{\circ}\text{C}$) or β -quenching ($\sim 960^{\circ}\text{C}$) of the already extruded tubes, the use of “heat-treated” tubes was ultimately not pursued either in Russia or in Canada. However, several reactors were built with heat-treated tubes. These were the Japanese prototype reactor “Fugen”; the CANDU-BLW prototype in Gentilly-1 and the 180 MWe Karachi Nuclear Power Plant (KANUPP). Of these only the last is still operating. In addition a few heat-treated Zr-2.5Nb tubes were installed in other prototype reactors – 4 in SGHWR; (1 heat-treated + 1 cold-worked tube) in the 25 MWe CANDU prototype NPD. Three in-reactor loop tubes were also exposed in test reactors NRX and NRU. The tubes in Gentilly-1 saw very little irradiation exposure, but comparisons of the properties of the others have been published, Chow et al., 1996, Koike & Asada, 1988 and Koike et al., 1994. For present purposes only the comparison of the corrosion behaviour is appropriate, Figure 3-1. Although the corrosion of heat-treated tubes appears to be better than that of cold-worked tubes (base on this limited evidence), the hydrogen uptakes all appear to fall in the same scatter band, Figure 3-2. The low deuterium contents of the NPD tubes may reflect the comparatively low temperatures and fluences in this reactor.

The Russian and Canadian fabrication routes for cold-worked Zr-2.5Nb pressure tubes are very similar. Both comprise an initial β -quench of the billet prior to extrusion in the ($\alpha+\beta$) phase field ($780\text{-}850^{\circ}\text{C}$), Figure 3-3, Cheadle et al., 1972, followed by a similar cold-working to final size (typically 25-28% recrystallised, Shishov et al., 1996. Only small differences in billet shapes and sizes and extrusion ratios distinguish the two products. The Canadian ingots are now quadruple melted compared to double melting for the Russians. The quadruple melting reduces impurities such as H, C and Cl in the initial ingot. This has resulted in a major improvement in fracture toughness, Figure 3-4, Coleman et al., 1996, and has reduced the average initial hydrogen content

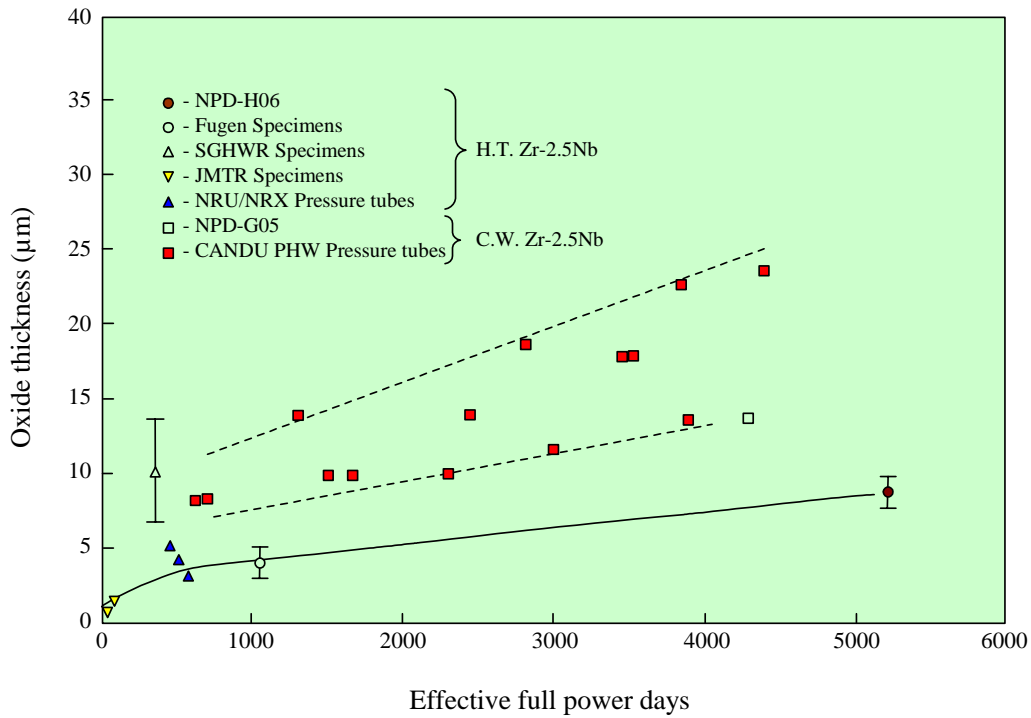


Figure 3-1: The maximum oxide thickness measured on the inside surface of Tube 589 is compared with other Zr-2.5Nb tubes and specimens as a function of time.

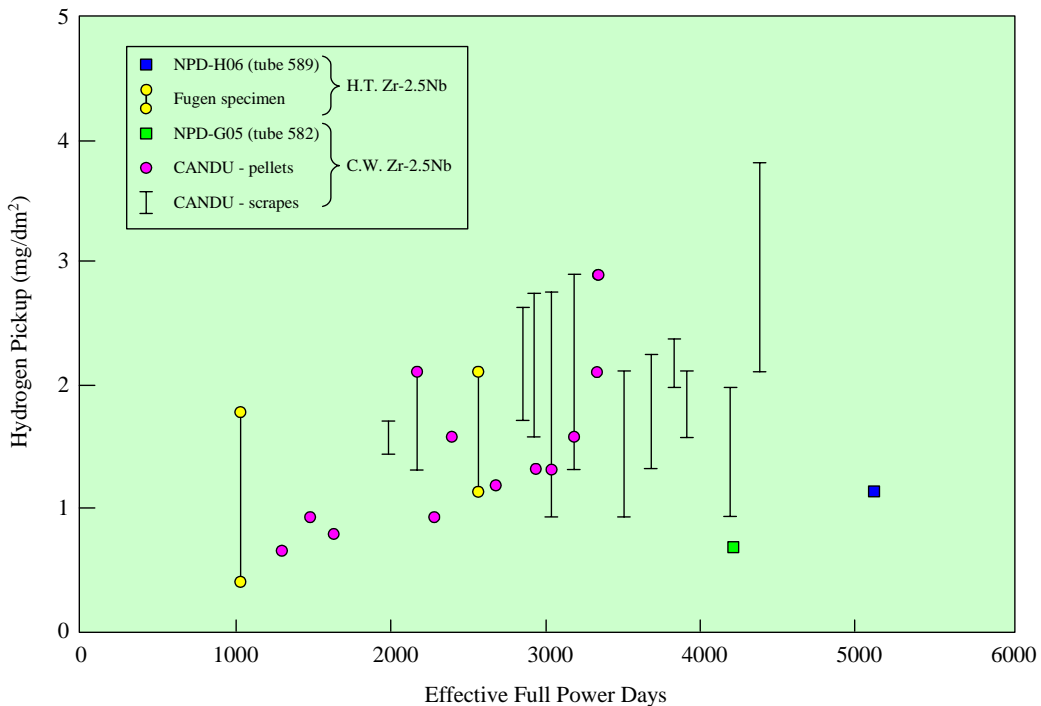


Figure 3-2: The maximum deuterium pickup measured in Tube 589 is compared, with terms of equivalent hydrogen, with other Zr-2.5Nb tubes and specimens as a function of time.

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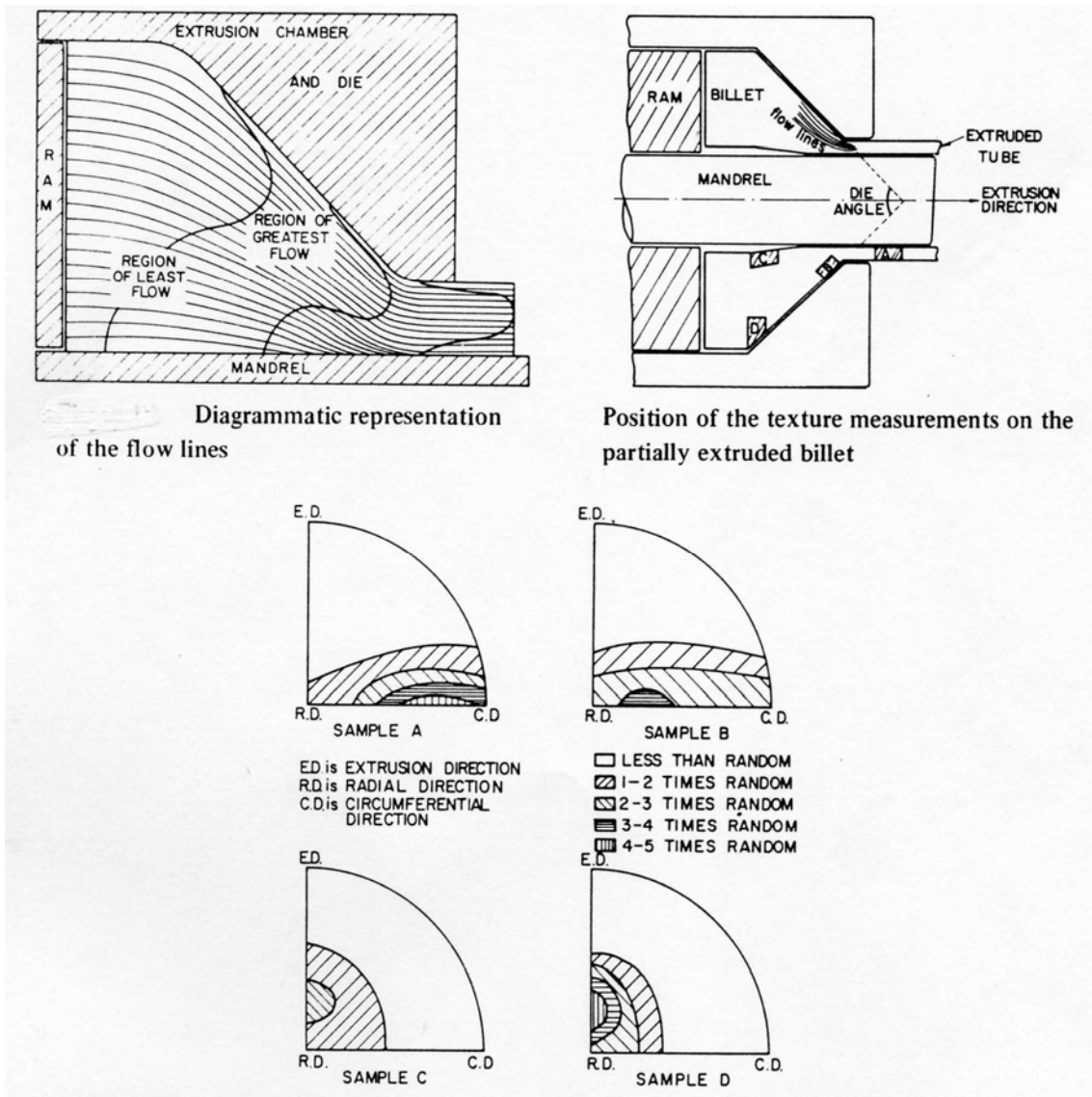


Figure 3-3: The (0002) pole figures of samples A, B, C and D from the partially extruded billet.

4 OUT-REACTOR CORROSION AND HYDRIDING (BRIAN COX)

As we have seen in Section 1.1 (Historical Introduction), there was a lot of variability in the early results for both corrosion and hydrogen uptake, largely as a result of much variability in impurity concentrations, and the sensitivity of corrosion and hydrogen uptake to metallurgical condition of the early materials. Zr-Nb alloys are more sensitive to these variables than the Zircalloys. Since the specimens in these early tests were not well enough characterised to permit comparison with current commercial alloys, the discussion here will be restricted to recent results of tests where adequate characterisation of the materials was performed. The three principal alloys in commercial use are: Zr-1wt%Nb (E110, M5), Zr-2.5wt%Nb (125) and a Zr-1%Nb-1%Sn-0.1-0.4%Fe alloy (E635, ZIRLO). These will be dealt with in three separate sections, with comparative data for all three presented at the end; although much of the data in the literature compares one Zr-Nb alloy with Zircaloy-4.

4.1 ZR-1WT%NB (E110, M5)

Kiselev, et al., 1962, presented more extensive data on the corrosion of E110 in water and steam than did Ambartsumyan et al., 1958. Kiselev's results extend to 22,000 hrs, but with much wider scatter than for Ambartsumyan's data, and without any explanation for this. Was this variability a function of variations in the dissolved oxygen content of the water? In a recent paper Nikulina et al., 1996 presented comparative autoclave data for E110 and E635 with both Zircaloy-4 and ZIRLO, using published Westinghouse data for the last two alloys. This is a convenient set of comparisons since, in their original papers Westinghouse compare ZIRLO only with various grades of Zircaloy-4. Thus, we now have comparisons in 350°C water, Figure 4-1, 360°C, Figure 4-2, 360°C dilute LiOH (70 ppm Li) in Figure 4-3, 400°C steam in Figure 4-4 and 500°C steam in Figure 4-5. In all these tests, except for LiOH, E110 gives the lowest weight gains. A similar set of data was presented at Park City, Vrtilkova et al., 2000, and here the comparisons differ from those of Nikulina et al., 1996. For instance, data in VVER chemistry water at 360°C, Figure 4-6 and 360° water +O₂, Figure 4-7 are not included in the Nikulina et al., 1996 comparisons, and Vrtilkova's 400°C steam results, Figure 4-8 show marked differences from Nikulina's. The corresponding hydrogen uptake data are presented in Figure 4-9. Interestingly the poor corrosion resistance of E110 in dilute LiOH solutions

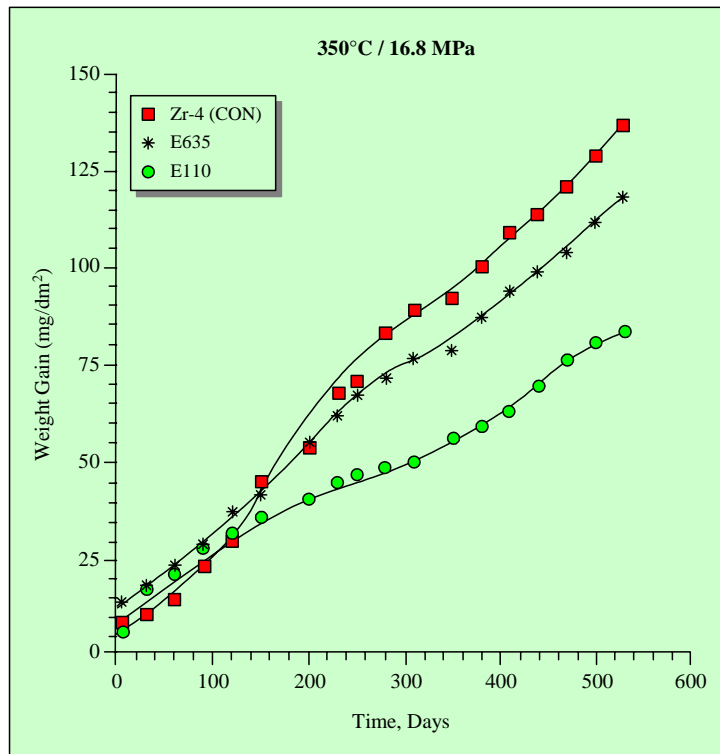


Figure 4-1: Autoclave corrosion of alloys in deionised water at 350°C, 16.8 MPa.

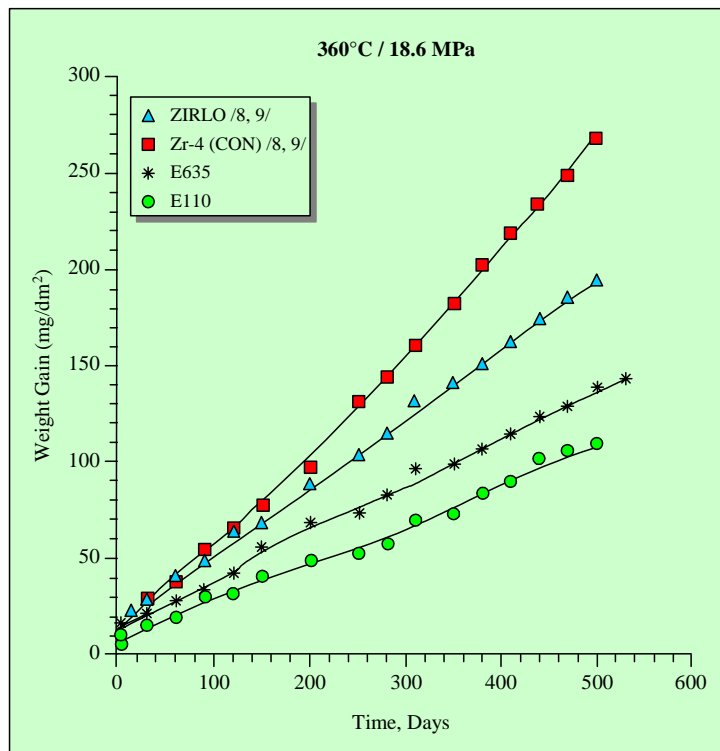


Figure 4-2: Autoclave corrosion of alloys in deionised water at 360°C, 18.6 MPa.

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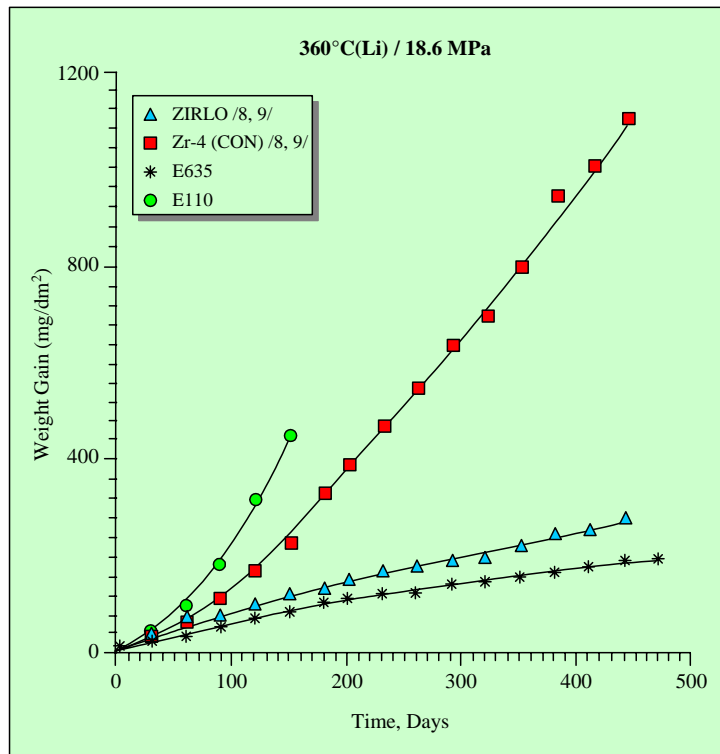


Figure 4-3: Autoclave corrosion of alloys in water containing 70 ppm lithium at 360°C, 18.6 MPa.

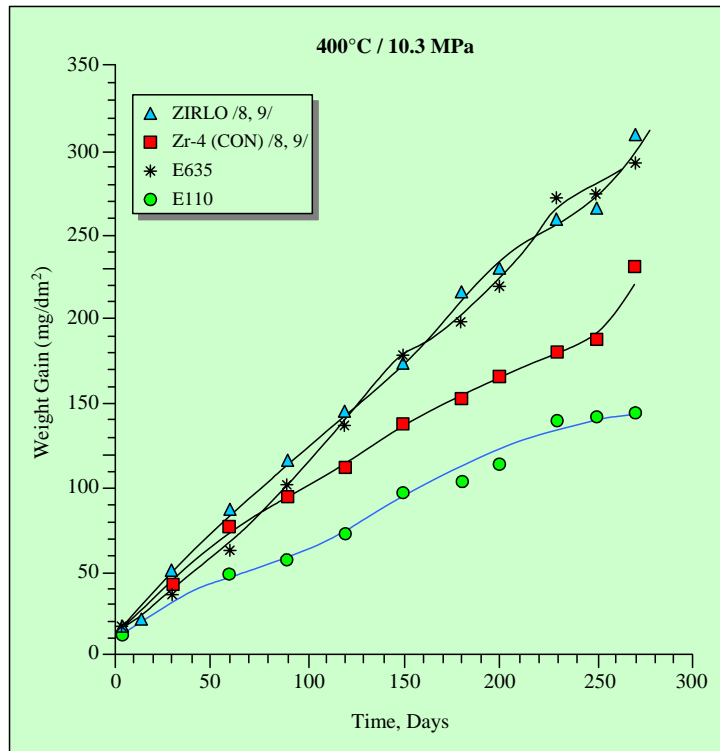


Figure 4-4: Autoclave corrosion of alloys in steam at 400°C, 10.3 MPa.

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5 IN-PILE CORROSION AND HYDRIDING PERFORMANCE (FRIEDRICH GARZAROLI)

As far as the alloying elements are concerned the in-pile corrosion behavior of Nb containing Zr alloys depends not only on the Nb content but also to the content of other alloying elements. Furthermore, the material condition plays an important role probably even a larger one than in case of the Zircalloys. In addition, a very important factor for in-pile corrosion is the water chemistry. The oxygen content and the impurity content may have a large effect especially in case of the Sn-free binary Zr-Nb alloys.

5.1 EFFECT OF COOLANT CONDITION

The corrosion behavior of Nb containing Zr alloys differs from the Zircalloys, in showing a marked dependence on oxygen in the corrosion environment even in the absence of irradiation. Such observations have been reported especially for binary Zr-Nb alloys, e.g. Urbanic, et al., 1991. Furthermore, Nb containing Zr alloys differ from the Zircalloys also with respect to the effect of irradiation on corrosion under oxygenated coolant conditions as well as under hydrogenated coolant (low oxygen) conditions. This is especially pronounced for Nb containing Zr alloys with low or no Sn such as binary Zr-Nb alloys. Whereas Zircalloys exhibits a strong increase of corrosion under oxygenated conditions compared to samples exposed in the same environment out-of-flux, Zr2.5Nb shows a slight reduction of the oxygen enhanced corrosion by irradiation as can be seen from Figure 5-1.

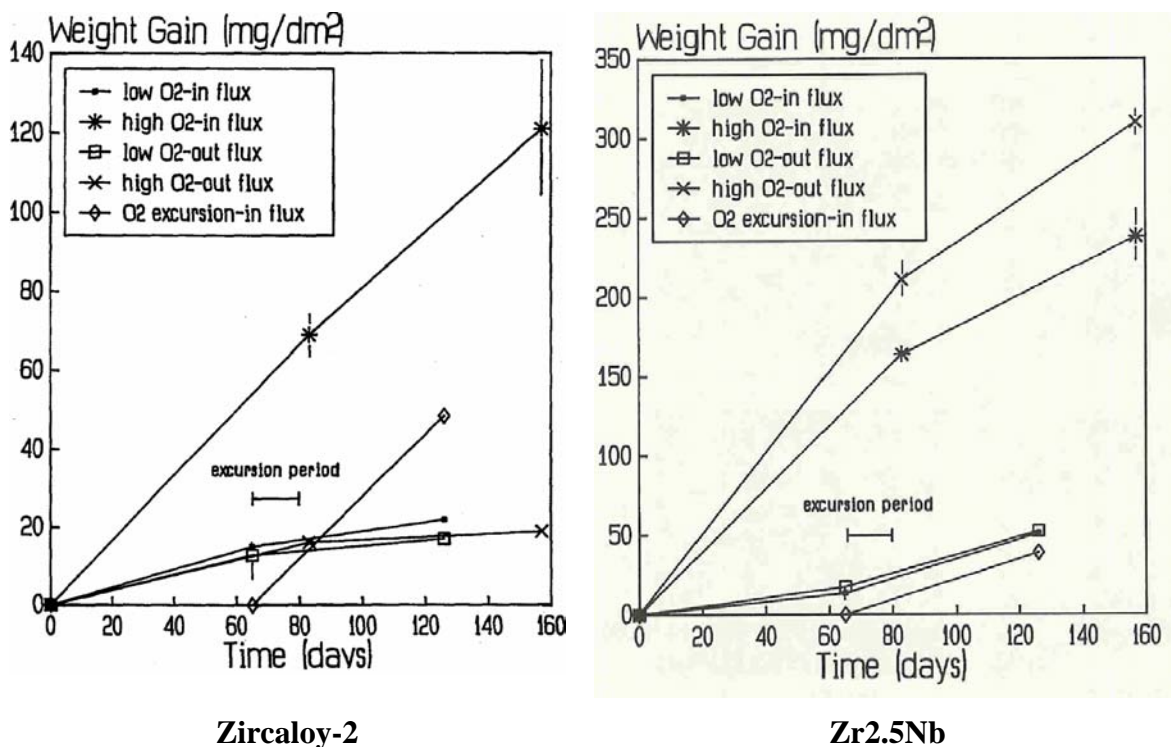


Figure 5-1: Corrosion of Zircaloy-2 and Zr2.5Nb in the U2 loop of NRU in low and high oxygen water at 295°C, Urbanic, et al., 1991.

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In a hydrogenated (low oxygen) environment, Zircaloy exhibits in-pile up to about 5 μm the same corrosion behavior as out-of-pile. At higher oxide layer thickness, the corrosion is enhanced by about a factor of 4, as can be seen from Figure 5-2. The figure shows the weight gain of Zircaloy and Zr2.5Nb by corrosion under PWR and BWR conditions versus the normalized time, which is calculated from the time (t) in hours and temperature (T) in K of the individual exposure steps (i) applying the equation: Normalized time = $\sum t_i * \exp(Q/(R*T))$, where Q/R is the activation temperature describing the temperature dependency of corrosion which was set as 14200 K. Zr2.5Nb exhibits in-pile under hydrogenated conditions a deviation from out-of-pile corrosion behavior at a twice as high exposure time and a significantly lower enhancement at higher exposure times. Under BWR (high oxygen) conditions corrosion of Zircaloy is enhanced from begin of exposure. Zr2.5 Nb shows in-BWR a significant higher enhancement of corrosion compared to out-of-pile corrosion in a low oxygen environment.

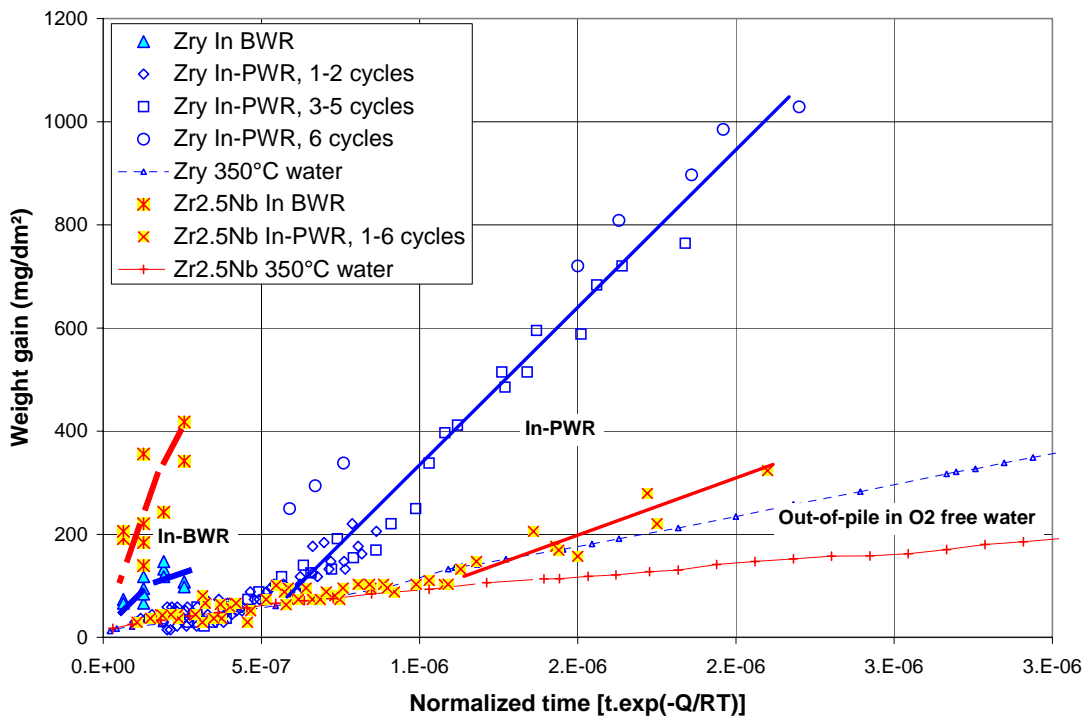


Figure 5-2: Corrosion behavior of Zry and Zr2.5Nb in-BWR, in-PWR, and out-of-pile in oxygen free water. Data from Garzarolli, et al., 1996.

Figure 5-3 shows the influence of the oxygen content of the water on the factor between in-pile corrosion and out-of-pile corrosion in low oxygen pressurized water. The shown data are collected from the following references: Johnson, et al., 1974, Pyecha, et al., 1985, Urbanic, et al., 1979, Urbanic, et al., 1991, Nikulina, et al., 2002, Seibold, et al., 2000, Garzarolli & Manzel, 1977, Garzarolli, et al., 1985, 1996, 2002(a), Sell, et al., 2004. In low oxygen coolant Zircaloy exhibits at the long exposure times, considered for Figure 5-3, an enhancement of about 4. At higher oxygen contents in the water uniform corrosion exhibits only a slightly higher enhancement, however, nodular corrosion (that appears at ≥ 30 ppb) can result in a much higher corrosion enhancement (up to 30). Binary Zr-Nb alloys exhibit under oxygen free conditions only very little irradiation induced corrosion enhancement and often even a slightly lower corrosion than out-of-pile in oxygen free water. At oxygen contents above ≥ 15 ppb the enhancement, compared to out-of-pile corrosion in oxygen free water, increases significantly mostly due to nodular corrosion. β -quenched and aged Zr2.5Nb is much more resistant to oxygenated coolant conditions and does usually not experience nodular corrosion.

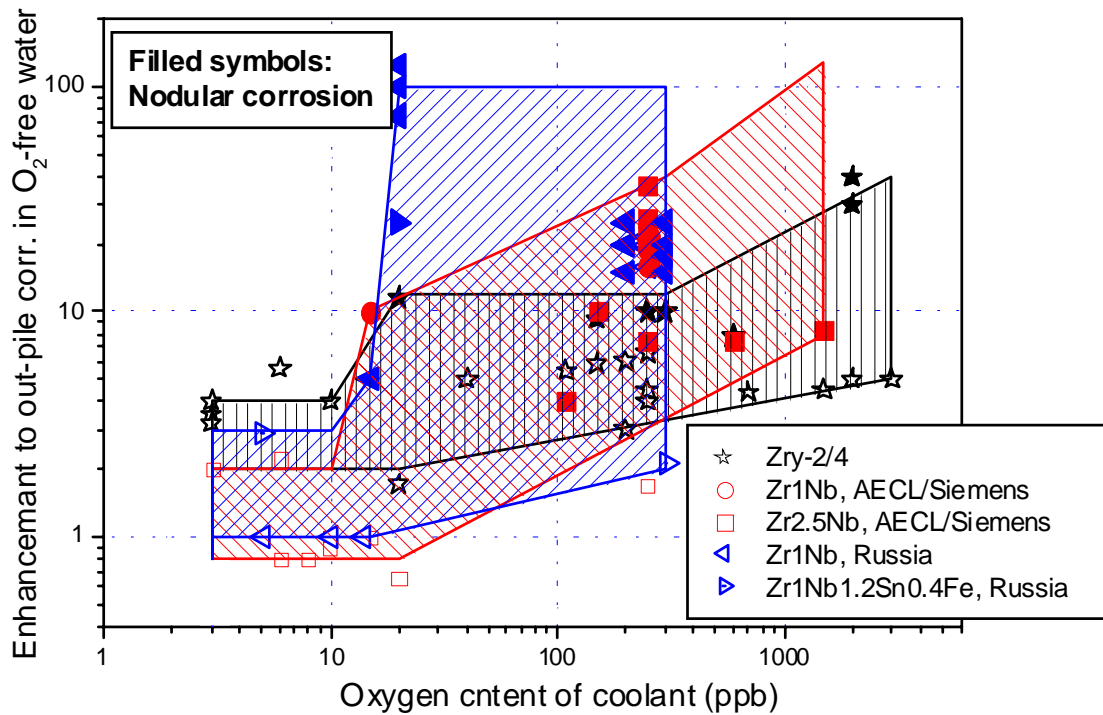


Figure 5-3: Influence of the oxygen content of the water on the factor between in-pile and out-of-pile corrosion in low oxygen pressurized water. Filled symbols indicate nodular corrosion.

6 SUMMARY

An extensive study of the corrosion of the whole range of Zr/Nb alloys (from almost pure Zr to pure Nb) was triggered by the publication of the Russian corrosion data at the 2nd. U.N. Conference on the Peaceful Uses of Atomic Energy in 1958. Apart from the Zr-3%Nb-1%Sn alloy used as fuel cladding in the Otto Hahn ship reactor, only three alloys ;- zr-1%Nb (E110, M5), Zr-2.5%Nb (E125), and Zr-1%Sn-1%Nb-0.1to0.4%Fe (E635, ZIRLO) have seen extensive use in reactor.

Zr/Nb alloys are heat-treatable and after extrusion, cold working and heat treatment may contain distributions of the beta-Zr phase. This phase has poor corrosion resistance, and may be decomposed, ultimately, by heat treatment below the monotectoid temperature (590-610°C, depending on the oxygen content). The best corrosion resistance for Zr/Nb alloys is usually achieved in the fully annealed condition. Because of the sensitivity of corrosion rates to metallurgical structure, and the generally incomplete knowledge of the structures of the specimens used in early studies, it is difficult to compare corrosion data for the many alloys investigated in the early studies conducted in a large number of laboratories in different countries. However, a few of the lessons learned from these studies are still valid.

- The enhanced corrosion observed for Zr/Nb alloys in oxygenated water may result from the volume expansion resulting
- from the conversion of crystallites of NbO_2 to Nb_2O_5 in the oxide film causing oxide cracking. Some crystallites high in Nb are probably present because of the uneven distribution of the Nb in the Zr matrix.
- Zr/Nb alloys were susceptible to the formation of white spots (like nodular corrosion) in laboratory autoclave tests. These were thought to initiate at SPP sites that were high in Fe. Thus susceptible batches of Zr/Nb alloys can appear to show "nodular corrosion" in both out-reactor and in-reactor tests.
- There is evidence that some Zr/Nb alloys can lose oxide as a fine powder when oxide films are thick.
- Zr/Nb alloys typically show lower hydrogen uptakes than the Zircalloys, and appear to show lower percentage uptakes in-reactor than out-reactor.
- Out-reactor autoclave testing shows a generally higher sensitivity to enhanced corrosion in LiOH solutions than for the Zircalloys.

Because irradiation accelerates the approach to the fully annealed condition, in-reactor corrosion rates are often lower than out-reactor corrosion rates. Zr/Nb alloys (E110, E125) show "nodular corrosion" in both RBMK and VVER reactors, although it is much less severe in VVERs than in RBMKs. E635 (ZIRLO) is said to be resistant to this type of corrosion, perhaps because of a more radiation resistant SPP structure. The hydrogen content of the water in CANDUs (3-10 cc/kg) appears to be sufficient to prevent this "nodular corrosion".

6.1 SUMMARY ON IN-PILE CORROSION

- The water chemistry, especially the oxygen content of the coolant, plays a large role on the corrosion behavior of Nb containing Zr alloys. The following conclusion that can be drawn:
 - Corrosion of Nb containing alloys can accelerate at coolant oxygen contents of ≥ 15 ppb.
 - The corrosion of Nb containing Zr alloys increases with increasing oxygen in the corrosion environment out-of-pile and somewhat less in-pile, whereas the Zircaloy-type materials are affected only in-pile.
 - In-PWR, irradiation increases after an initial un-effected period the corrosion rate of binary Zr-Nb alloys slightly, but much less than in case of Zircalloys. The irradiation induced increase of Zr-Nb-Sn-TM alloys depends on the Sn content.
 - In-BWR, irradiation decreases the corrosion rate of most Nb containing Zr alloys in comparison to the out-of-pile behavior in the same environment, but shows a much larger corrosion rate if compared with the out-of-pile corrosion in oxygen free water.
 - For PWR fuel application, the high sensitivity of Nb containing Zr alloys against oxygen needs much attention to the minimum hydrogen level in the coolant, in-leaking oxygen, and remaining oxygen after start up.
 - The effect of the Sn alloying content on the sensitivity of Nb containing Zr alloys in environments with LiOH additions, such as used for PWRs, are discussed contradictory in the literature. On the one side Sn increases the oxide thickness that forms in-PWR and as consequence the possibility to concentrate LiOH in the outer oxide layer but on the other side Sn contents of $>0.5\%$ decreases the sensitivity in environments with high LiOH concentrations.
 - Data are missing on the potential effect of off-normal water chemistries, such as resin intrusions, graphite intrusions, and periods with low hydrogen (e.g. before shut down) on corrosion behavior of binary Zr-Nb alloys, such as M5 and Zr1Nb.

- For PWR fuel Nb containing Zr alloys will be the most important alloys in the future and will push away the Zircalloys. The following conclusion that can be drawn:
 - Several Nb containing Zr alloys were exposed under demanding conditions to quite high burnups. Properly treated Zr_{2.5}Nb has the highest corrosion resistance in-PWR.
 - At oxide thickness values between 35 and 45 μm most Nb containing Zr alloys exhibits a rate increase probably preferentially due to formation of a dense hydride rim.
 - Nb reduces in-PWR corrosion of Zr-Nb alloys. The Nb alloying content should be $\geq 0.5\%$ for binary alloys. In Zr alloys with a TM content of $>0.25\%$, Nb does not further improve in-PWR corrosion.
 - Sn in excess of 0.2-0.3% increases the in-PWR corrosion of Nb containing Zr alloys significantly.
 - Not much is known on the optimum Fe respectively TM content of ZrNbSnTM alloys. Fe and TM additions lead to quite large Zr(NbFe)₂ SPP, which decompose under irradiation to β -Nb. The very large (ZrNb)₂Fe SPP, that form at very high Fe contents, are resistant against irradiation dissolution but seem to increase in-PWR corrosion. Probably the TM content should be rather low in Nb containing Zr alloys for optimum in-PWR corrosion resistance.
 - Application of a β -quenching step during fabrication and rather low process temperatures improve significantly out-of-pile corrosion but have much less influence on in-PWR corrosion.
 - Not enough information is available on the effect of final cold deformation and final annealing on in-PWR corrosion. Especially, for Nb containing Zr alloys containing also Sn and TM a quite large influence can be expected from the experience with Zircaloy type materials. Out-of-pile tests can not give relevant information on this question, because the effect may be in-PWR even opposite.
 - The hydrogen pickup fraction of Zr-Nb-Sn-TM alloys is similar as that of Low-Sn-Zircaloy-4, whereas binary Zr-Nb alloys pickup less corrosion hydrogen.

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