ZIRAT-11 SPECIAL TOPIC REPORT

Manufacturing of Zr-Nb Alloys

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November, 2006

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ABBREVIATIONS

ANL	Argonne National Laboratory
ASTM	American Society for Testing and Materials
BOR	Research Fast Reactor
BWR	Boiling Water Reactor
CANDU	Canadian Deuterium Uranium
ChMP	Chepetsky Mechanical Plant
CSR	Contractile Strain Ratio
CWSR	Cold Work and Stress Relieved
DHC	Delayed Hydride Cracking
DW	Diffusion Welding
EBW	Electron Beam Welding
EDX	Energy Dispersive X-Ray Analyzer
FA	Fuel Assembly
FC	Fuel Channel
FCC	Face Centered Cubic
GAW	Gas Arc Welding
HAZ	Heat Affected Zone
HF	High Frequency
HPUF	Hydrogn PickUp Fraction
IAT	Intermediate Annealing Temperature
IIG	Impacting Irradiation Growth
IGSCC	Intergranular Stress Corrosion Cracking
IZNA	Information on Zirconium Alloys
KKG	KernKraftwerk Gösgen
LW	Laser Welding
LOCA	Loss of Coolant Accident
MDA	Mitsubishi Developed Alloy
MDW	Magnetic Discharge Welding
MHI	Mitsubishi Heavy Industries
MOX	Mixed OXide
NDA	New Developed Alloy
NFI	Nuclear Fuel Industries
PCMI	Pellet Cladding Mechanical Interaction
PET	Piezo Electric Transducer
PT	Pressure Tube
PWR	Pressurised Water Reactor
QC	Quality Control
R&D	Research & Development
RBMK	Russian type Boiling Water Reactor
RBW	Resistance Butt Welding
RSW	Resistance-Spot Welding
RT	Room Temperature
RX	Recrystallised

RXA	Recrystallised Annealed
SAC	System Automated Control
SCANUK	Scandinavian/U.K
SEM	Scanning Electron Microscopy
SGHWR	Steam Generating Heavy Water Reactor
SLAR	Spacer Location and Repositioning (är det här rätt?)
SNO	Sn, Nb, O
STR	Special Topic Report
SR	Stress Relieved
SRA	Stress Relieved Annealed
SPP	Second Phase Particle
TEM	Transmission Electron Microscopy
TM	Transition Metal
TMO	ThermoMechanical Treatment
TMT	ThermoMechanical Treatment
TSS	Terminal Solid Solubility
TTT	Time-Temperature-Transition
TVS	Fuel Assembley
VVER	Voda Voda Energo Reactor (Russian type *PWR*)
UT	Ultrasonic Testing
ZIRLO	Zirconium Low Oxidation

UNIT CONVERSION

TEMPERATURE $^{\circ}C + 273{,}15 = K$ $^{\circ}C * 1{,}8 + 32 = ^{\circ}F$		
T(K)	T ($^{\circ}$C)	T($^{\circ}$F)
273	**0**	32
289	16	61
298	25	**77**
373	**100**	212
473	**200**	392
573	**300**	572
633	360	680
673	**400**	752
773	**500**	932
783	510	950
793	520	968
823	550	1022
833	560	1040
873	**600**	1112
878	605	1121
893	620	1148
923	650	1202
973	**700**	1292
1023	750	1382
1053	780	1436
1073	**800**	1472
1136	863	1585
1143	870	1598
1173	**900**	1652
1273	**1000**	1832
1343	1070	1958
1478	1204	**2200**

DISTANCE	
x (µm)	x (mils)
0,6	0,02
1	0,04
5	0,20
10	0,39
20	0,79
25	0,98
25,4	**1,00**
100	3,94

PRESSURE		
bar	MPa	psi
1	0,1	14
10	1	142
70	**7**	995
70,4	7,04	**1000**
100	10	1421
130	13	1847
155	15,5	2203
704	70,4	**10000**
1000	100	14211

MASS	
kg	lbs
0,454	**1**
1	2,20

STRESS INTENSITY FACTOR	
MPa√m	ksi√inch
0,91	**1**
1	1,10

CONTENTS

1   HISTORICAL DEVELOPMENT OF ZR-NB ALLOYS

1.1   *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 Zircaloys, Kass, 1963, Lustman and Kerze actually made no mention of the composition of the Zircaloys!

At the next U.N. Conference on the Peaceful Uses of Atomic Energy (also in Geneva in 1958) the Russians presented extensive results on a range of Zr-Nb alloys. These ranged from the all α ozhennites, through the Zr-1%Nb (E110) alloy, to higher alloys with up to 5%Nb, 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 ozhennites (despite their apparently better corrosion resistance) were not being used, Table 1-1, IAEA-TECDOC-996, 1998.

Table 1-1:   Compositions of Zr-Nb Alloys.

| Composition | Ozhennite 0.5 | Zr-1%Nb | | Zr-2.5%Nb | | Zr-1%Nb/1%Sn/Fe | | |
		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	100	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. *PWR*s and *BWR*s 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, 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 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. Ultimately, although the Harwell studies, Cox, 1960 suggested 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 (*RBMK*s). Some years later a joint Scandinavian/U.K programme (*SCANUK*) studied a number of ternary and quaternary alloys 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, under *BWR* (*SGHWR*) conditions.

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 CO_2 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, LeSurf, 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 1-2, 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 alloy, 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 N_2 with some D_2 that diffuses through the stainless steel end-fittings-now changed to CO_2) have led to their progressive replacement with Incoloy 728 garter springs.

Table 1-2:   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 Zircaloys 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. The corrosion resistance of the ZrNb3Sn1 alloy was good both in- and out-reactor, but heat treatment of the welds was a problem (the corrosion rates of β-quenched alloys with ≥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, D$_2$O-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%. 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 service.

1.2 EVOLUTION HISTORY OF ZR-NB E110, E125 AND E635 ALLOYS (SLAVA SHISHOV AND ANTONINA NIKULINA)

Zirconium alloy developments proceeded almost concurrently with the setting up and evolution of zirconium production that was started in 1950s. For thermal reactor cores (*VVER* and *RBMK*) that were under design and construction in 1950 – 1960 binary zirconium-niobium alloys E110 (Zr–1Nb wt. %) and E125 (Zr–2.5 Nb wt. %) were chosen as the base structural material. The choice of those materials was primarily dictated by the following: to retain the low thermal neutron capture section characteristic of zirconium and to provide high corrosion resistance of components by alloying.

Those alloys were first used in cores of *VVER* having a relatively low power (up to 400 MW) viz., E110 alloy for the fuel cladding and E125 alloy for the fuel assembly outer channel, Ambartsumyan et al., 1958. The favourable results of their operation in relatively low power *VVER* were later corroborated in *VVER*-440 and *VVER*-1000 in which the alloys are currently in successful operation.

Thermal neutron pressurized water (*VVER*) and boiling water (*RBMK*) reactors that were under design in the USSR gave an impetus to thorough studies of zirconium and setting up the production of items thereof, Ambartsumyan et al., 1958. The structural materials of nuclear reactors serve to protect nuclear fuel against corrosion, to create a heat-exchange surface or supporting structures. These materials have to possess reliable mechanical properties and to be corrosion resistant to a coolant at high temperatures as well as not exhibiting gross neutron absorption.

In 1950 - 1960 the objective of the American and Soviet scientists was to search for alloying elements capable of providing items with required properties using zirconium produced by Kroll method in the USA and by molten salt electrolysis in the USSR. The gradually increased purity and uniformity of zirconium played a significant part in accomplishing the programs dedicated to designing alloys based on it. During those years intensive studies were made of issues pertaining to the influence of impurities and alloying elements on the corrosion and mechanical (tensile) properties of zirconium.

The choice of alloying elements was focused on: the thermal neutron absorption cross-section of elements so as not to lose this valuable property of zirconium; on the structure-phase states of zirconium alloys with the aim of providing alloys with technologically worthwhile corrosion resistant and mechanical properties; and on the feasibility of controlling the structure-phase state to acquire the required properties. The first results of the investigations of this type were published by B. Lustman and F. Kerze and reported by American and Soviet scientists at the International Conferences on Peaceful Uses of Atomic Energy (Geneva), 1955 and 1959, Ambartsumyan et al., 1958, Lustman & Kerze, 1955, Ivanov & Grigorovich, 1958 and Kiselev et al., 1958.

Unalloyed zirconium features an unstable corrosion behaviour in water and steam which stems from unavoidable variations in the contents of impurities. Zirconium of adequate purity is corrosion resistant in high temperature water. However, impurities such as nitrogen, carbon, aluminium, etc. if present in zirconium even in low quantities, – particularly when they are present together – noticeably degrade the corrosion resistance of zirconium, Zaimovsky & Nikulina, 1966, Amaev et al., 1964 and Amaev et al., 1971.

In the USSR zirconium base alloys were originally developed using semi-commercially produced adequately pure iodide zirconium and then electrolytic zirconium with the simultaneous setting up of its commercial production. The results of the investigations by O. Ivanov and V.Grigorovich to study the influence of alloying elements on the tensile properties of zirconium revealed that almost all additives increase its strength and reduce its ductility, Ivanov & Grigorovich, 1958.

Al, Ti, Sn, Nb and O were among the elements that increase the strength of zirconium. The strength increased with the contents of these elements. Fe, Cr, and Mo, added even in rather limited quantities, increased the strength of zirconium. As will be shown below the first group comprises the so-called "solid solution" elements forming solid solutions with zirconium in rather a wide range of concentrations. The other group being insignificantly dissolved in zirconium comprises the elements forming the "intermetallic type" alloys.

The first experiments on alloying zirconium with aluminium, titanium, tin and niobium demonstrated unexpected results. Even small additions of aluminium and titanium deteriorated zirconium corrosion resistance, Zaimovsky & Nikulina, 1966, Amaev et al., 1964 and Amaev et al., 1971.

Tin at < 0.8 weight % insignificantly affected the corrosion of iodide zirconium. However, with a further increase in Sn content the corrosion of zirconium deteriorated, particularly in steam at 400°C, and resulted in oxide spalling. These results acquired by the soviet scientists agreed with those of the American experts. An addition of niobium also degraded the corrosion properties of zirconium. However, this deterioration did not cause any oxide spalling in autoclave environments, Ambartsumyan et al., 1958, Zaimovsky & Nikulina, 1966 and Amaev et al., 1964.

Of all the studied elements that were introduced into binary zirconium alloys only iron added in a rather wide concentration range did not influence the corrosion properties of zirconium in water or steam. Actually, iron additions even resulted in lower corrosion rates. Simultaneously it was revealed that the uptake of hydrogen released during corrosion is significantly dependent on alloying, Zaimovsky & Nikulina, 1966 and Amaev et al., 1964. Niobium, chromium and iron containing Zr alloys showed the least uptake of hydrogen.

The results of the investigations carried out by Soviet scientists to study the influence of impurities and alloying elements on the properties of iodide zirconium were used to select alloys for the first nuclear reactors *VVER* and *RBMK*. Taking into account the requirements for the tensile and corrosion properties of cladding and pressure tubes, as well as fuel assembly shroud tubes, R. Ambartsumyan and colleagues gave priority to alloys containing 1.0 and 2.5% niobium (E110 and E125), Ambartsumyan et al., 1958, Yemelyanov et al., 1981, Grigoriev et al., 1990 and Ageenkova et al., 1977. So far, binary Zr-Nb alloys remain the basic commercial alloys for the *VVER* and *RBMK* cores. E110 alloy is the main cladding material of fuels in operating *VVER* and *RBMK*. E125 alloy is used in *RBMK* as a fuel channel material and in *VVER*-440 *VVER*-440 for the fuel assembly outer channel, Amaev et al., 1964.

Results of investigations of the influence of alloying elements and impurities on the properties of zirconium allowed the Soviet scientists to recommend an alloy containing niobium, tin and iron in the range of 1.0% Nb, 1.0-1.3 Sn and 0.3-0.5% Fe for further studies and subsequent use, Amaev et al., 1971, Zaimovsky, 1978, Zaimovsky & Nikulina, 1981 and Markelov et al., 1978.

When creating a multicomponent alloy the Soviet scientists took advantage of the favourable effects of tin, niobium and iron on the corrosion properties in water and steam; each of them making its own special contribution to improving the corrosion resistance of zirconium. Niobium enhances corrosion resistance and reduces hydrogen pickup during corrosion under irradiation. Tin stabilizes the corrosion resistance of zirconium via reducing its sensitivity to some deleterious impurities. Iron improves the water/steam corrosion resistance by reducing its temperature dependence.

The multicomponent alloy that was designated E635 has the adequate properties inherent in the binary Zr-Nb and Zircaloy type alloys, but does not have their limitations. E635 is primarily used for fuel claddings and other fuel assembly structural components both in *VVER*s and *RBMK*s. Its low creep and irradiation growth rate as well as high corrosion resistance behaviour were verified in *VVER*-1000 fuel assemblies as guide thimbles and angles of rigid frame and in boiling *RBMK* pressure tubes, Amaev et al., 1971.

Fuel assemblies with E635 alloy guide thimbles and central tubes as well as spacer grids have been successfully operated in *VVER*-1000 since 1999.

1.3   DEVELOPMENT OF ZR-NB ALLOYS FOR PWRS (FRIEDRICH GARZAROLLI)

The Zircaloy-2 and -4 selected for *BWR* and *PWR*s, respectively, behaved so well that no major incentive existed to replace these materials with better Zr-alloys for many years. However, the target burnup and fuel duty increased over the years, Figure 1-1 and in the mid 1980s it became evident that even the Zry-4 material with the best corrosion properties will limit the burnup in modern *PWR*s. Therefore, almost all fuel vendors initiated large programs to develop a more *PWR* corrosion resistant alloy. This included studies of the binary Zr-Nb alloys (such as Zr1Nb and Zr2.5Nb) as well as ZrNbFe and ZrNbSnFe alloys.
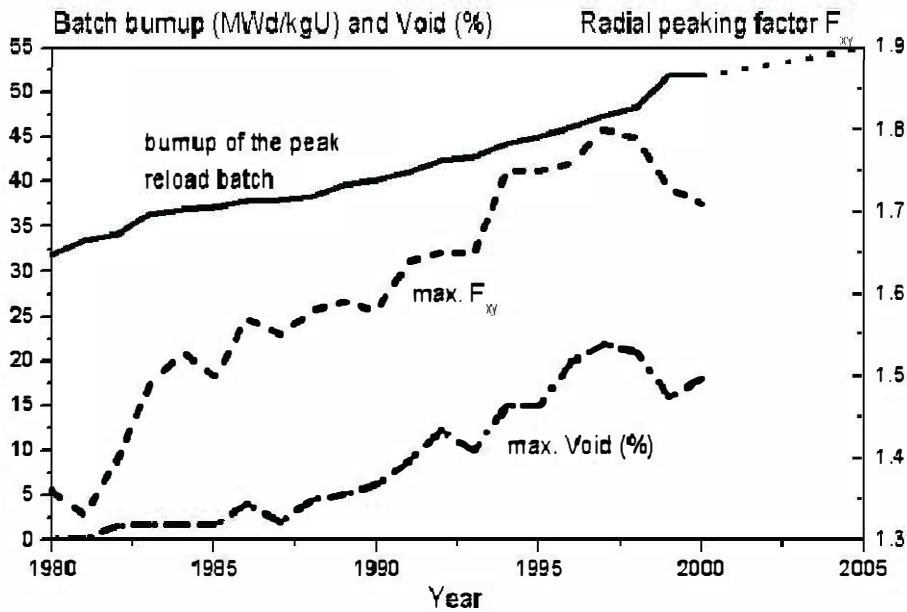

Figure 1-1:   Evolution of fuel assembly discharge burnup and operating conditions in *PWR*s built by Siemens, Seibold et al., 2001.

In the following the different *PWR* development programs are summarised. Table 1-3 provides the chemical composition of the more recent commercial Zr-Nb alloys.

Table 1-3: Chemical composition of Nb alloyed Zr alloys for *PWR/VVER* application.

Alloy	Sn (%)	Nb (%)	Fe (%)	Cr (%)	V (%)	Others
Zry-4	1.2-1.7		0.18 - 0.24	0.1		1000-1400 ppm O_2
NDA	1	0.1	0.3	0.2		1200 ppm O_2
E635	1.3	1	0.4			900 ppm O_2
ZIRLO	1	1	0.1			1200 ppm O_2
MDA	0.8	0.5	0.2	0.1		1200 ppm O_2
E635M	0.8	0.8	0.35			700 ppm O_2
Optim. *ZIRLO*	0.75	1	0.1			1200 ppm O_2
E110		1	0.01			600 ppm O_2, F- impurity
M5		1	0.04			1200 ppm O_2, 20 ppm S

1.3.1   Corrosion

Already in 1976 *Westinghouse* started a development program including irradiation of several Zr-Nb alloys, such as Zr1Nb, Zr2.5Nb and Zr1Sn1Nb0.1Fe in the experimental BR-3 *PWR* reactor in Mol. Maximum burnups of 70-80 MWd/kgU were reached in this irradiation program lasting up to 1985. In spite of the high burnup, the oxide thickness values were rather low even for Zircaloy-4, due to the low system pressure (139 bar) and low maximum cladding surface temperature (335°C), Sabol et al., 1989. The reference Zircaloy-4 rods showed an oxide layer thickness of only ≤30 μm and Zr1Sn1Nb0.1Fe a corresponding value of only ≤20 μm. The two Zr-Nb binary alloys showed an even lower uniform oxide layer thickness but quite heavy nodular corrosion due to a rather high oxygen and a low hydrogen coolant concentration during the 2nd and 3rd irradiation cycles. Based on these results Westinghouse selected Zr1Sn1Nb0.1Fe, which was called *ZIRLO*, for demonstration rods in 1987 and for its first reload in 1991.

The Nb content in ZrSnNbFe alloys, such as *ZIRLO*, provides a quite high creep resistance. Due to the lower Sn content in *ZIRLO* compared to that in Zry-4, the former alloy had a lower irradiation growth rate. *ZIRLO* is used today as material for fuel cladding as well as fuel assembly structural parts such as guide tubes and spacer grids in several *PWR*s. *ZIRLO* exhibits a lower irradiation creep and irradiation growth rate, as well as better corrosion resistance, compared to that of Zircaloy-4.

The corrosion resistance of *ZIRLO* with 1% Sn is, however, not sufficient for the most demanding duty cycles (e.g. high enriched fuel exposed under full low leakage loading). Thus efforts were initiated to improve the corrosion performance of the *ZIRLO* alloy starting in the mid 1990s. The improvement of corrosion resistance was obtained by reducing the tin alloy content. In a first step Sn was limited to a maximum 1.0%, Comstock et al., 1996.

Later low Sn variants were tested out-of-pile showing a continuous improvement of uniform corrosion resistance in high temperature water with reduced Sn content. However, Westinghouse concluded that the Sn content in the binary Zr-Nb and ZrNbSnFe alloys should exceed 0.5% to maintain good corrosion resistance in a coolant enriched in Li[1]. This conclusion was based upon out-of-reactor high temperature water corrosion tests in 70 ppm Li, Hallstadius et al., 2002. In 2003 the first result for a low-Sn *ZIRLO* with about 0.7% Sn were reported for a burnup of 50 MWd/kgU, Limbäck et al., 2003. In Figure 1-2 the burnup dependency of oxide layer thickness of *ZIRLO* fuel rods in Vandellos II is shown together with data for *ZIRLO* and optimized (Low Sn) *ZIRLO* from Byron. Figure 1-2 shows that the corrosion behaviour of *ZIRLO* with 1%Sn is somewhat better than that of low-Sn Zry-4. However, at burnups in excess of 60 MWd/kg, *ZIRLO* has formed quite thick oxide layers. The oxide thickness growth versus burnup of *ZIRLO* varies from reactor to reactor depending on fuel duty, as was observed previously for Zry-4. The fuel duty in Byron is obviously more moderate than the fuel duty in Vandellos-II. Comparing the 1%Sn *ZIRLO* with low Sn *ZIRLO* irradiated in the Byron reactor, the latter has better corrosion resistance.

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[1] The normal maximum Li coolant concentration ranges from 2.2 to 3.5 ppm. However, due to subcooled boiling in *PWR*s with high surface heat fluxes/high coolant inlet temperatures much higher Li concentrations can result in porous oxide close to the corroding Zircaloy surface.
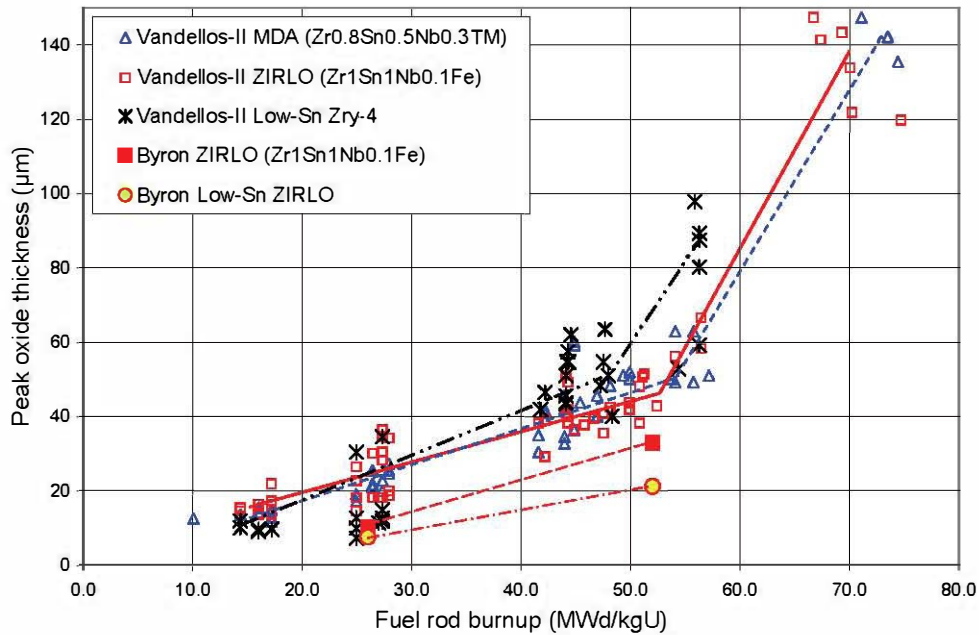
Figure 1-2:   Corrosion behaviour of different ZrNbSnTrM alloy claddings in Vandellos II and Byron, Tsukuda et al., 2003, Yueh et al., 2004, and Watanabe et al., 2005.

Mitsubishi Heavy Industries (*MHI*) developed the *MDA* alloy (Zr0.8Sn0.5Nb0.2Fe0.1Cr) for the Japanese market. The *MDA* material shows somewhat better corrosion resistance, reduced creep and growth rate compared to that of Low-Sn Zry-4, Figure 1-2. *MDA* is being extensively tested in Japanese *PWR*s but is still not used for full reloads as of today, Kitagawa et al., 2005.

Nuclear Fuel Industries (NFI) developed the *NDA* alloy (Zr1Sn0.1Nb0.3Fe0.2Cr) for the Japanese market. This Zr alloy has a Nb addition of 0.1%, a reduced Sn and an increased Fe+Cr content in comparison with Zry-4. Out-of-pile tests, e.g. Isobe & Matsu, 1991, indicated that increased corrosion resistance may be obtained by:

1)   small additions of Nb (0.1-0.2%),

2)   reduced Sn content and,

3)   increased Fe+Cr content.

However, in *PWR*s, the *NDA* alloy show only slightly better corrosion behaviour compared to that of Low-Sn Zry-4. *These results indicate that conclusions from out-of-pile tests are not always valid for in-PWR behaviour.*

The largest test program with alternative Zr alloys has probably been performed by *Siemens (today AREVA NP)*, Garzarolli, 2001. Figure 1-3 summarises the behaviour of several Zr-Nb alloys with/without Sn and transition metals (*TM*), such as Fe, Cr, and V obtained in the corrosion demanding *PWR* Gösgen (*KKG*g) plant. The figure shows that properly heat-treated Zr2.5Nb has the best corrosion behaviour and that the behaviour of the other alloys depends primarily on the Sn content.

For most alloys an increase in oxidation rate can be seen at a threshold oxide layer thickness between 40 and 50 μm, Figure 1-3. This increase is probably due to solid hydride rim formation at the fuel clad outer surface. This rim will form under high heat flux conditions, as is the case in *KKG*g plant, and at hydrogen clad contents in excess of 300 ppm, Garzarolli et al., 2001. The late increase of oxide layer growth rate of Zr1Nb-"Process A" material at burnups >70 MWd/kgU cannot be due to a dense hydride rim because of the low Hydrogen PickUp Fraction, *HPUF*, and must have other reasons. The only alloys that did not show any increased oxidation rate up to max burnups of 70-85 MWd/kgU are properly heat-treated Zr2.5Nb and Zr1Nb-"Process-B" materials.

Based upon its large test program, Siemens selected at first a DUPLEX cladding with an extra low Sn and an enhanced Fe and Cr content in the outer part of the fuel clad wall. Reloads with such an cladding are introduced since 1990. Siemens did, however, also continue to explore binary ZrNb alloys in several *PWR*s under high duty operating conditions for later development steps.
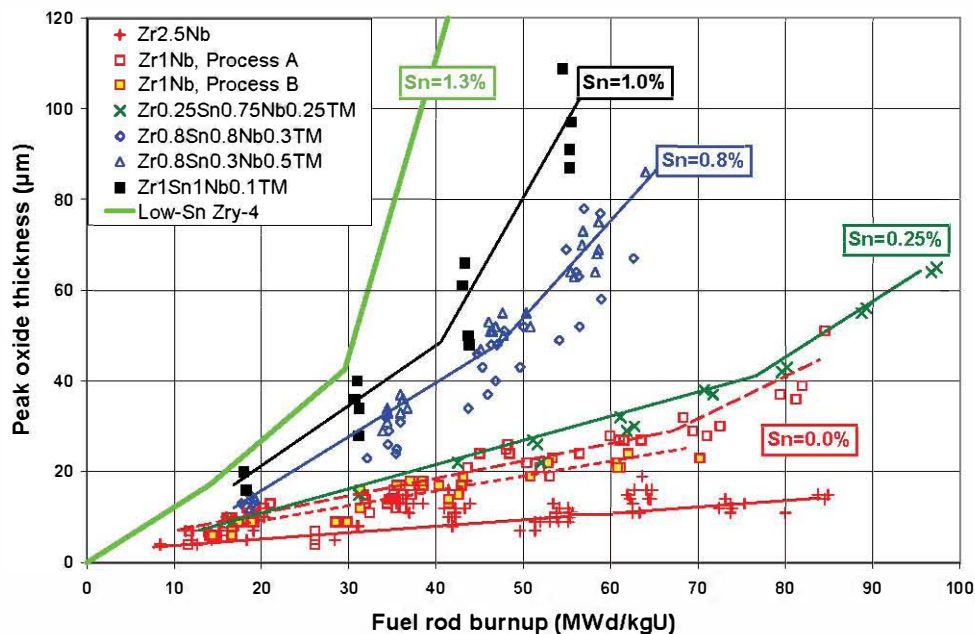

Figure 1-3:   Corrosion behaviour of experimental fuel rods with different ZrNbSnTrM alloy claddings in *KKG*g, Seibold et al., 2000, Seibold & Garzarolli, 2002, Seibold & Mardon, 2002.

Framatome (today AREVA NP) performed a cladding development program in the early 1990s. This program included several types of Zr alloys with an extra low Sn content, and the Zr-Nb alloys M3 (Zr0.5Sn0.5Nb0.25Fe) and M5 (Zr1Nb). M5 is fully recrystallized ternary Zr1Nb0.125O alloy, similar to the Russian Zr alloy E110. The results showed a very low corrosion rate for M5 and surprisingly a rather poor corrosion behaviour of M3, Mardon et al., 1994. In 1996 the M5 alloy was introduced on a commercial basis by Framatome.

Oxide data from fuel rods with M5 cladding demonstrate excellent corrosion behaviour up to a burnup of 80 GWd/tU, Figure 1-4. These oxide thickness data come from about 6000 rods from 20 plants and covering a wide range of different operating conditions and all fuel assembly arrays used in *PWR*s, i.e. 14x14 through 18x18. The data shown in Figure 1-4 includes cladding with different wall thicknesses, UO_2 as well as *MOX* fuel pellets, different coolant chemistry regimes including Li contents up to 3.5 ppm, different cycle lengths and different fuel duties. However there are some recent cases of atypical increased corrosion of M5 fuel rods, which are not yet fully understood, Thomazet et al., 2005.
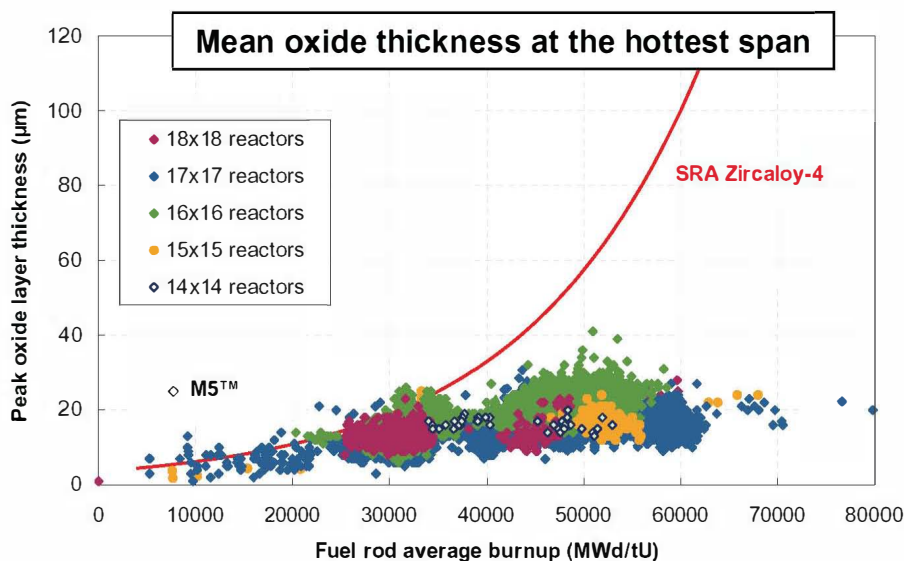

Figure 1-4:   Oxide thickness on fuel rods with M5 cladding, Chabretou & Mardon, 2006.

Today, M5 is proven to have a high corrosion resistance, a low *HPUF*, and low creep rate due to its fully recrystallized condition. The material has also shown a lower irradiation growth rate. However, the fuel rod axial elongation[2] is larger than expected indicating that anisotropic creep-down (before pellet–cladding contact) contributes more to the length increase than in the case of the stress-relieved materials such as Zircaloy-4, *ZIRLO*, *NDA* and *MDA*.

An extensive program has also shown that the *LOCA* behaviour of M5 is similar to that of Zircaloy-4, e.g. Mardon et al., 1999.

1.3.2   Hydrogen pickup

Pickup of corrosion hydrogen is another crucial material property that has to be considered for fuel elements. In Table 1-4 different reported *HPUF* values are summarized for different Zr-Nb and Low-Sn-Zry-4 materials with thick oxide layers.

In general the *HPUF* of *ZIRLO* and *MDA* is similar as that of Low-Sn Zry-4 whereas the *HPUF* of M5/*Zr1Nb*[3] is lower, but the absolute values can vary from *PWR* to *PWR*. Sabol et al., 1997 reported for *ZIRLO* a *HPUF* between 10 and 20% at a burnup of 45 MWd/kgU. Quite similar numbers were found later in Vandellos-2 and Ohi-1/4.

On the other hand, *Zr1Nb* and M5 show a significantly lower *HPUF* than that of Zry-4, *MDA*, and *ZIRLO*. Thomazet et al., 2005 reported a *HPUF* between 10 and 11%. This value is slightly higher than the value reported by Goll & Hoffmann, 2002 for *Zr1Nb*. E110, the Russian Zr1Nb alloy, with a different impurity content (Hf, O, Fe, and F) shows also a very low oxide build up rate in *VVER*s. The reported hydrogen content[4] in E110 is also low (10-110 wtppm) but the calculated *HPUF* is relatively high due to the very low oxide layer thickness values specifically at burnups in excess of 45 MWd/kgU.

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[2] Fuel fuel rod axial elongation is a function of several processes, as follows: irradiation growth, hydrogen pickup, anisotropic creep (before pellet-cladding contact) and, *PCMI* (after pellet-cladding contact) where pellet axial swelling will result in additional clad elongation.

[3] The designations of the various Zr1Nb alloys are: M5 (developed by Framatome), Zr1Nb alloy developed by Siemens and E110 (the original material from which both M5 and Zr1Nb were developed from) developed in Russia.

[4] The hydrogen content in the material is the product of corrosion rate and *HPUF*

Table 1-4:   Reported hydrogen pickup fraction for different materials at high oxide layer thicknesses, Sabol et al., 1989, Sabol et al., 1997, Seibold et al., 2000, Goll & Hoffmann, 2002, Watanabe et al., 2005 and Kitagawa et al., 2005 and Markov et al., 2005.

PWR	Low-Sn Zty-4	ZIRLO	MDA	Zr1Nb/M5	E110	Reference
Siemens *PWR*s	(20%)*			6%		Goll & Hoffmann, 2002, Seibold et al., 2000
BR-3**		11%				Sabol et al., 1989
V.C. Summer	18%	10-20%				Sabol et al., 1997
Vandellos-2	16%	14%	15%			Watanabe et al., 2005
Ohi-1/4	14%	16%	19%			Kitagawa et al., 2005
Several	15-16%			10-11%		Thomazet et al., 2005
*VVER*s					(10-30%)	Markov et al., 2005

*   estimated number by comparing the relative data published by Seibold et al., 2000, with absolute data from Goll & Hoffmann, 2002.

**   Irradiation occurred during cycles 3B, 4A, 4B, and 4D. Oxygen was 44 ppb during cycle 4A and 30 ppb during cycle 4B. Hydrogen was 7-9 cc/kg during cycle 4B and probably higher during cycle 3B and 4D, Lippens et al., 1981.

The *HPUF* of structural Zr-alloy components (e.g. grids and guide tubes) is usually quite similar as that of fuel rod claddings, but minor variations are sometimes observed due to different operational temperatures. However, the total hydrogen pickup in structural components may be larger than that in fuel rods since all the structural material surfaces are corroding while for a fuel rod only the fuel rod outer surface is corroding. Thus, the hydrogen generation and absorbtion is larger for structural materials than that of fuel rods.

2 ALLOYING ELEMENTS AND IMPORTANT IMPURITITES IN ZIRCONIUM ALLOYS (SLAVA SHISHOV AND ANTONINA NIKULINA)

2.1 IMPACT OF VARYING ALLOYING ELEMENTS AND IMPURITIES ON IN-PILE MATERIAL PERFORMANCE

The choice of zirconium materials for components of each reactor type requires a versatile approach with due account for specific designs of cores, fuel assemblies, fuel elements and their operation conditions.

2.1.1 Alloying Elements

The need to retain the low thermal neutron absorption coefficient of zirconium substantially limits the number of possible alloying elements. Taking this consideration into account, the most suitable alloying elements are Al, Si, Sn, Nb and V, Table 2-1.

Table 2-1: Thermal neutron absorption of alloying elements and impurities in zirconium.

Element	σ_a(barn) [a]	ΔE (wt.%) [b]	Element	σ_a barn) [a]	ΔE (wt.%) [b]
Zr	0.18	-	Nb	1.1	14.1
Al	0.23	17.0	Mo	2.5	6.3
Si	0.13	30.2	Sn	0.6	25.6
Ti	5.8	1.4	Sb	5.5	3.7
V	5.1	1.8	Te	4.5	4.6
Cr	2.9	2.9	Hf	105	0.29
Fe	2.53	3.9	Ta	21.3	1.4
Co	37	0.23	W	19.2	1.8
Ni	4.6	2.2			
Cu	3.69	2.9			
Ge	2.35	5.2			
Y	1.3	10.6			

Note a): σ_a – macroscopic cross section of thermal neutron absorption cross section
   b): ΔE – quantity of alloying element in binary Zr alloy at which an extra 0.05% U^{235} enrichment of fuel is needed

The influence of some of the elements on thermal neutron absorption by zirconium are discussed in the following.

The chemical composition and structure of a zirconium alloy are critical factors that ensure its proper function in a reactor. The choice of a zirconium material is governed by a set of material requirements for a specific fuel component and its operation conditions.

When choosing a material its microstructure is of crucial importance. The microstructure is in turn a function of the material chemistry and the thermomechanical manufacturing processes. The zirconium material microstructure is dictated by the material property requirements for a specific component and its operation conditions. Thus, both successful selection of alloying elements and of the manufacturing process conditions are needed to enable the production of the material microstructure resulting in the required properties.

The alloying process conditions are based on the results of studying zirconium alloying element systems, Hansen & Anderko, 1962, Ivanov et al., 1973, Domagala & McPherson, 1954 and the relationship between microstructure and properties.

The principal advantage of zirconium as a structural material for thermal reactors is its specific nuclear properties, in particular, low thermal neutron absorption. The preservation of this advantage substantially limits the number of alloying elements:

1)   thermal neutron absorption coefficient of alloying elements has to be low and their irradiation has not to result in long-lived radioactive species (e.g., cobalt);

2)   alloying has to provide an alloy with high corrosion resistance and low hydrogen uptake during interaction with an aggressive environment;

3)   alloying elements have to ensure mechanical properties required by a design and to retain good technological properties inherent in zirconium, including weldability;

4)   alloying has to ensure stable properties and dimensional stability of fuel assembly components during operation.

Selection of alloying elements and assessment of alloying concentrations intended to reduce zirconium corrosion were for the most part done empirically, i.e., on the basis of results from autoclave testing without irradiation and, some theoretical considerations, Thomas, 1955 and Ambartsumyan et al., 1958.

According to one of the theories, zirconium corrodes via anion vacancy diffusion of oxygen ions through the oxide layer at the metal-oxide interface where the corrosion process occurs.

According to this theory, the alloying of zirconium with the elements of VA, VIA and VIIIA group Elements of the Periodic System (V, Nb, Ta, Cr, Mo, W, Fe, Ni) should increase the electron concentration and consequently a decrease in the oxide anion vacancy concentration would result which in turn would reduce the corrosion rate. Among the elements mentioned above, Ta and W having a high neutron capture cross-sections are not suitable for zirconium alloying. Ni enhances the hydrogen pickup in the zirconium corrosion process and Ni is therefore not an appropriate alloying element.

Sn appears to be the alloying element that is most useful for suppressing the deterioration of the corrosion properties by impurities. However, while Sn suppresses the harmful effect of impurities, nitrogen in particular, Sn in itself will substantially reduce the zirconium corrosion resistance. A beneficial effect of Sn additions on zirconium corrosion may only be seen if Sn is added simultaneously with other elements (Fe, Cr, Ni). Thus, only Sn, Nb, Fe and small concentrations of Cr, Ni, V, Cu and Mo might be added to zirconium to obtain corrosion resistance in high temperature water or steam. Autoclave tests of zirconium alloys containing the above elements essentially corroborated this alloying concept.

Zirconium with the above alloying elements in combination with an appropriate thermomechanical manufacturing process might provide fuel assembly components with high mechanical strength and creep resistance. This is primarily achieved via elements of high solubility in α-Zr(Sn, O), the ones promoting precipitation hardening (V, Mo) as well as the ones (Fe, Cr, Ni, Cu) that form intermetallic phases with zirconium.

In the 1950s soviet scientists selected Nb, Sn, O and Fe as the basic elements for alloying zirconium. Up to the present time those elements in various combinations have been used to design corrosion and irradiation resistant zirconium materials. Figure 2-1 to Figure 2-7 show the impact of impurities and alloying elements on corrosion and hydrogen uptake in out-of-reactor autoclave tests as well as tensile properties of unirradiated zirconium alloys.
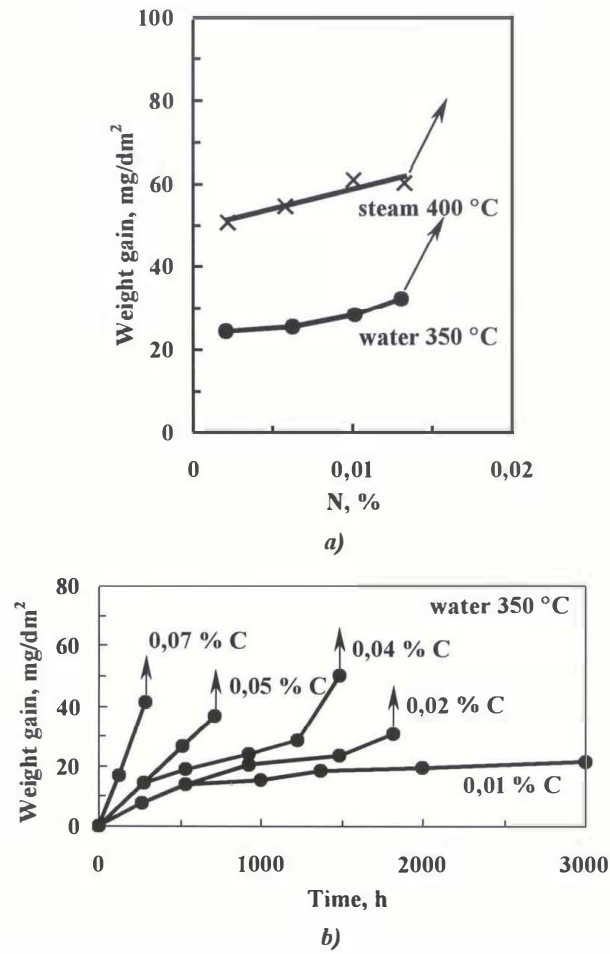
Figure 2-1:   Influence of nitrogen (a) and carbon (b) on out-of-reactor corrosion of zirconium in water and steam, Abriata & Bolcich, 1982.
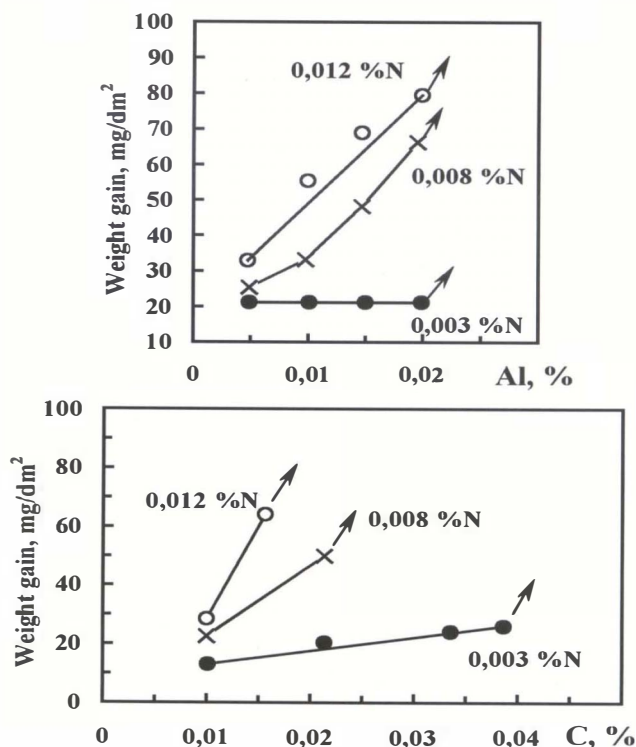
Figure 2-2: Influence of nitrogen, carbon and aluminum impurities on out-of-reactor corrosion of zirconium in water (350°C, 17 MPa), Abriata & Bolcich, 1982.
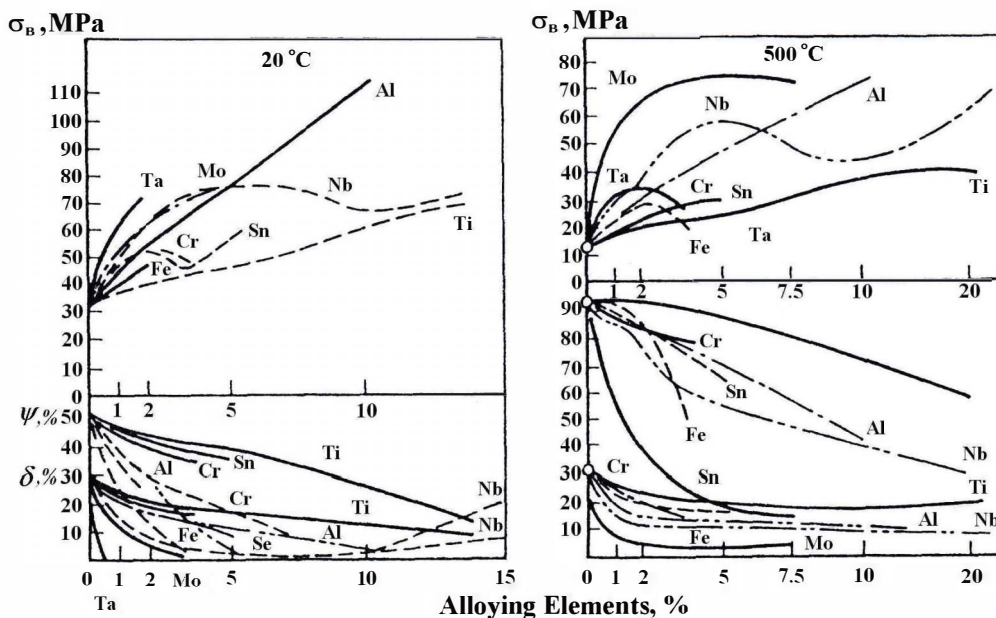

Figure 2-3: Influence of alloying elements on tensile properties of unirradiated zirconium, Lustman & Kerze, 1955.
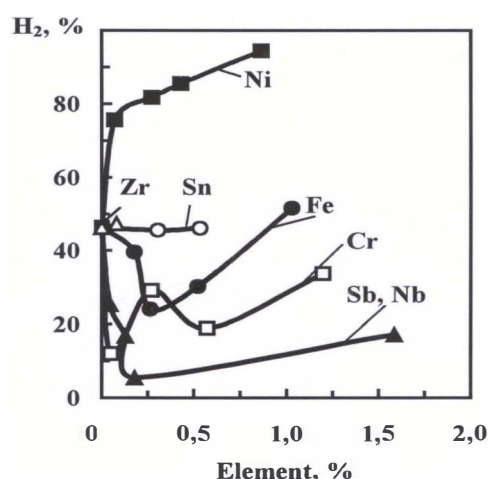
Figure 2-4:   Hydrogen pickup fraction during out-of-reactor zirconium corrosion in 350°C water as a function of alloying elements, Amaev et al., 1964.

To develop zirconium alloys for long-term in-pile operation is a complex challenge that, in addition to laboratory investigations, requires in-reactor tests. Neutron irradiation results in significant changes not only in coolant and fuel compositions but also in the zirconium microstructure and properties of the fuel assembly structural components. Experience shows that alloys having an equilibrium microstructure, that does not change significantly during irradiation, have the most stable in-reactor properties (corrosion, tensile properties). As a rule, high strength alloys having a supersaturated solid solution microstructure may lose their original mechanical strength and corrosion resistance due to irradiation assisted partial or complete microstuctural decomposition. That is why zirconium materials designed for long-term in-pile operation should have a stable equilibrium microstructure, preferably that of α-Zr.

2.1.2   Impurities in Zirconium

Impurities existing in zirconium and its alloys as a result of the methods used to produce zirconium, its alloys and fuel assembly structural parts thereof may strongly influence their properties. In the majority of cases impurities will degrade the properties and characteristics of materials, therefore their contents are restricted by the standards and specifications for zirconium, its alloys and fuel assembly structural parts.

The basis for these restrictions is the requirements to preserve low neutron capture, high corrosion resistance, processability and crack resistance during manufacturing as well as reliable operation in reactors. Among the impurities that are most important in this respect are C, N, Al, H, Cl, P, Hf, F, as follows:

- N, Al and C impurities are most harmful for corrosion of zirconium, Figure 2-1 and Figure 2-2.

- C, H, Si, Cl, P and F impurities decrease the ductility of zirconium and its alloys, thus, degrading processability and crack resistance,Figure **2-5**, Figure **2-6** and Figure **2-7**.

- Cd, B, Hf and Co are elements that increase the neutron capture.

- O increases strength and affects corrosion and ductility to some degree.

- Fe and Cr favourably influence the corrosion of zirconium, for this reason their allowable contents are much higher.

The typical requirements specified for impurity contents of zirconium and its alloys are summarized in Table **2-2**.

Table **2-2**:   *ASTM* Standard B353 for Zr and its alloys used in nuclear industry (content of impurities).

| Element	Pure Zr	Zry-2	Zry-4	Zr-Nb (2.4-2.8%Nb)	Zr-Nb (2.5-2.8%Nb)
Impurity, max (ppm)					
Al	75	75	75	75	75
B	0.5	0.5	0.5	0.5	0.5
Cd	0.5	0.5	0.5	0.5	0.5
C	270	270	270	270	150
Cr	200	-	-	200	200
Co	20	20	20	20	20
Cu	50	50	50	50	50
Hf	100	100	100	100	100
H	25	25	25	25	25
Fe	1500	-	-	1500	650
Mg	20	20	20	20	20
Mn	50	50	50	50	50
Mo	50	50	50	50	50
Ni	70	-	70	70	35
N	80	80	80	80	65
Pb	-	-	-	-	50
Si	120	120	120	120	120
Sn	50	-	-	50	100
Ta	-	-	-	-	100
Ti	50	50	50	50	50
U	3.5	3.5	3.5	3.5	3.5
V	-	-	-	-	50
W	100	100	100	100	100
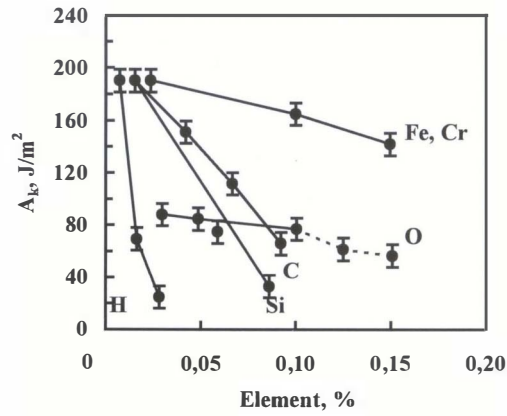
Figure 2-5: Influence of impurity content on impact toughness of unirradiated Zr-1%Nb alloy, Zaimovsky et al., 1994.
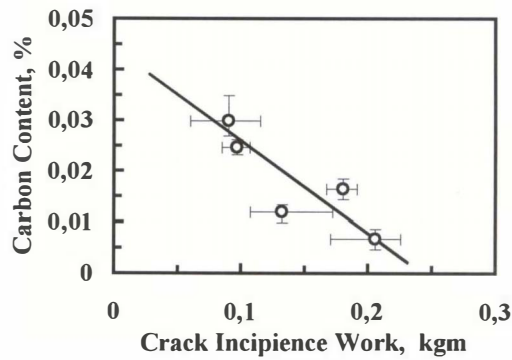

Figure 2-6: Influence of carbon (mass content) on crack incipience work in unirradiated Zr-2.5%Nb alloy, Zaimovsky et al., 1994.

3   PRESSURE TUBES (ZR2.5NB)

3.1   *CANDU REACTORS (BRIAN COX)*

3.1.1   Pressure tube design

The *CANDU* reactor is a heavy water moderated and cooled natural uranium fuelled reactor in which the fuel bundles (50 cm long and usually 12 per fuel channel) are contained in individual pressure tubes through which the heavy water coolant flows. The number of pressure tubes varies according to the power output of the reactor (e.g. 380 in the *CANDU*-6 design). Reactor outlet temperatures vary somewhat in the range 310-315°C. The pressure tubes are separated from the "cold" (60-80°C) heavy water moderator contained in a large, horizontal, cylindrical Calandria Vessel. Each individual Calandria Tube in the Calandria Vessel contains a smaller diameter Pressure Tube, and the two are separated by an insulating gas gap, maintained by spacers ("Garter Springs"). There were initially 2 per pressure tube, but this was increased to 4 per tube in all reactors after the failure of the G8 pressure tube in Pickering-2 as a result of the pressure tube sagging into contact with the calandria tube, Hart, 1997.

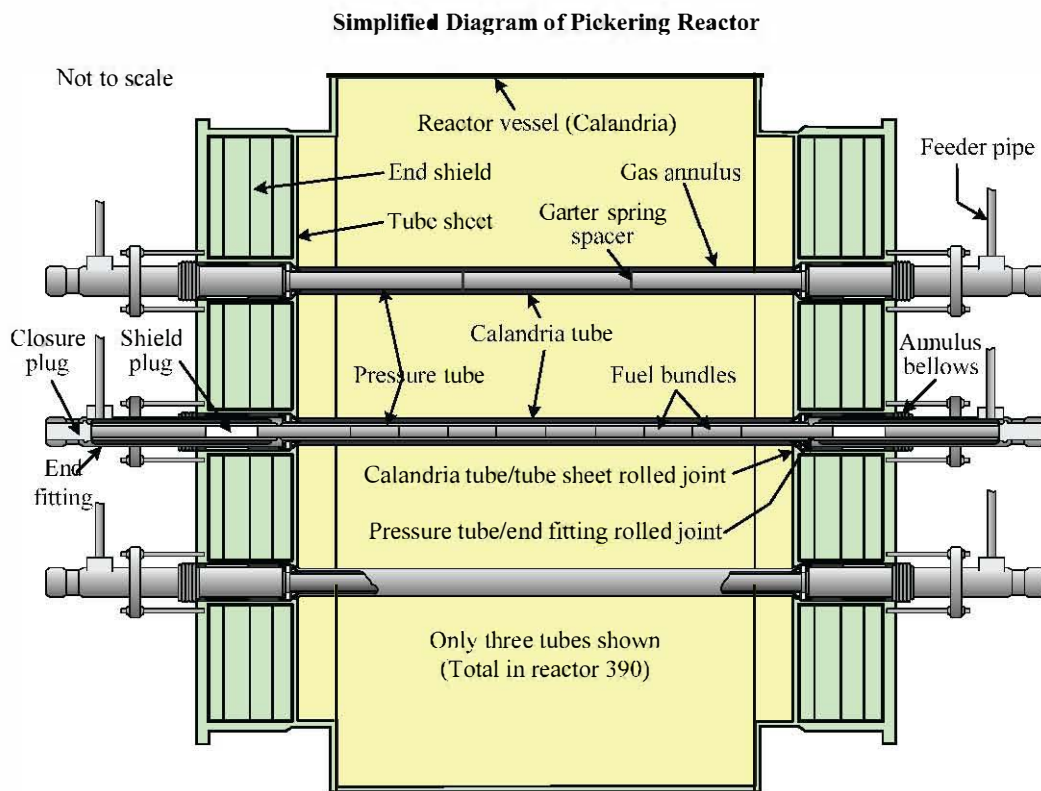A simplified diagram of the Calandria Vessel, end shields and fuel channels is shown in Figure 3-1.

Figure 3-1:   Simplified diagram of Pickering reactor showing fuel channels and garter springs.

Details of an individual fuel channel showing the end fittings that the fuelling machines latch onto during on-power refuelling operations are shown in Figure 3-2. The typical appearance of the pressure tube-calandria tube spacers (garter springs) is shown in Figure 3-3. These garter springs were initially of Zr-2.5Nb-0.5Cu alloy, and were a tight fit on the pressure tube. They were subsequently changed to a loose fit, which allowed vibrations to cause spacers to move out of place during reactor construction. This movement was a major contributor to the P2-G8 pressure tube failure. A subsequent change to tight fitting Inconel 728 spacers (4 in number) resulted from this. The gas annulus between the pressure tube and the calandria tube was initially filled with nitrogen, but this was changed to carbon dioxide to reduce deuterium uptake in the pressure tube from deuterium diffusing into the gas annulus from the stainless steel end fitting.
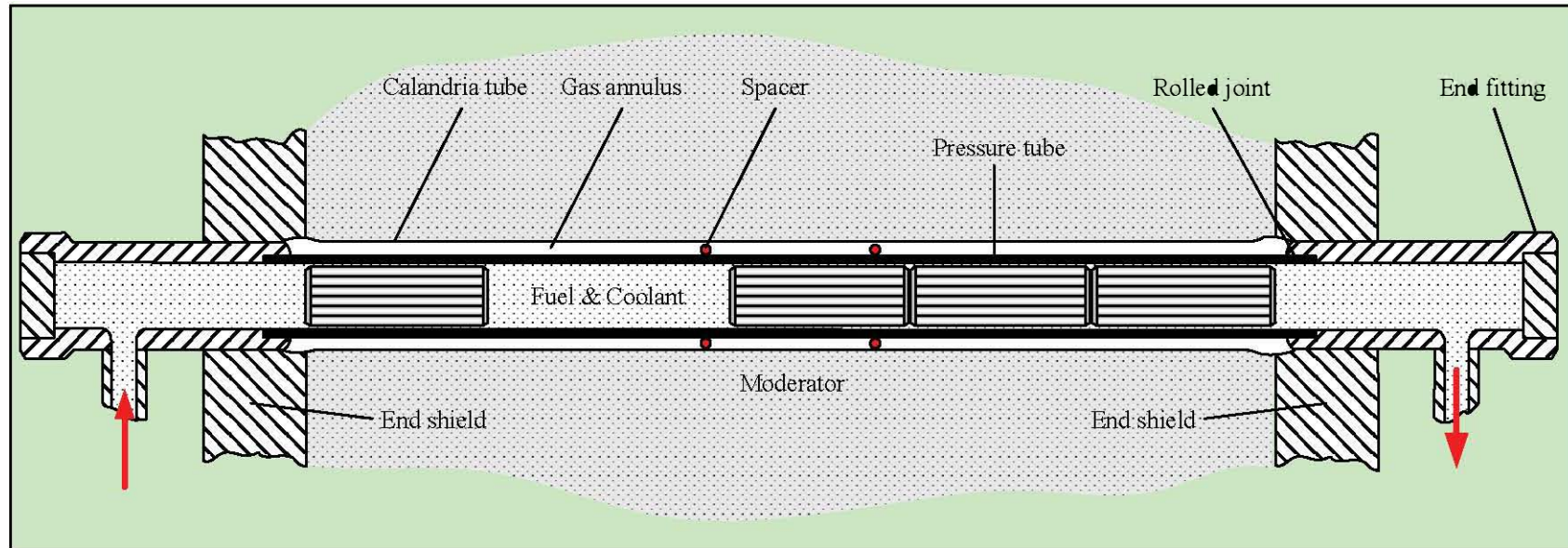
Figure 3-2: Schematic of a fuel channel for a *CANDU* reactor with pressurized water coolant.

4   FUEL RODS, GUIDE TUBES, SPACER GRIDS

4.1   M5, ZIRLO, MDA, NDA FOR PWRS

4.1.1   Fuel Design (Peter Rudling)

There is a wide variety of different types of fuel assemblies for *PWR*s. Over the years there has been a trend to greater subdivision of fuel rods, e.g. from Westinghouse 15x15 to 17x17 design, however to accomplish this required a new reactor design. This is because the *PWR*s do not have the same flexibility with core internals and control rods as is the case for *BWR*s. Figure 4-1 shows the current *PWR* fuel rod array designs.
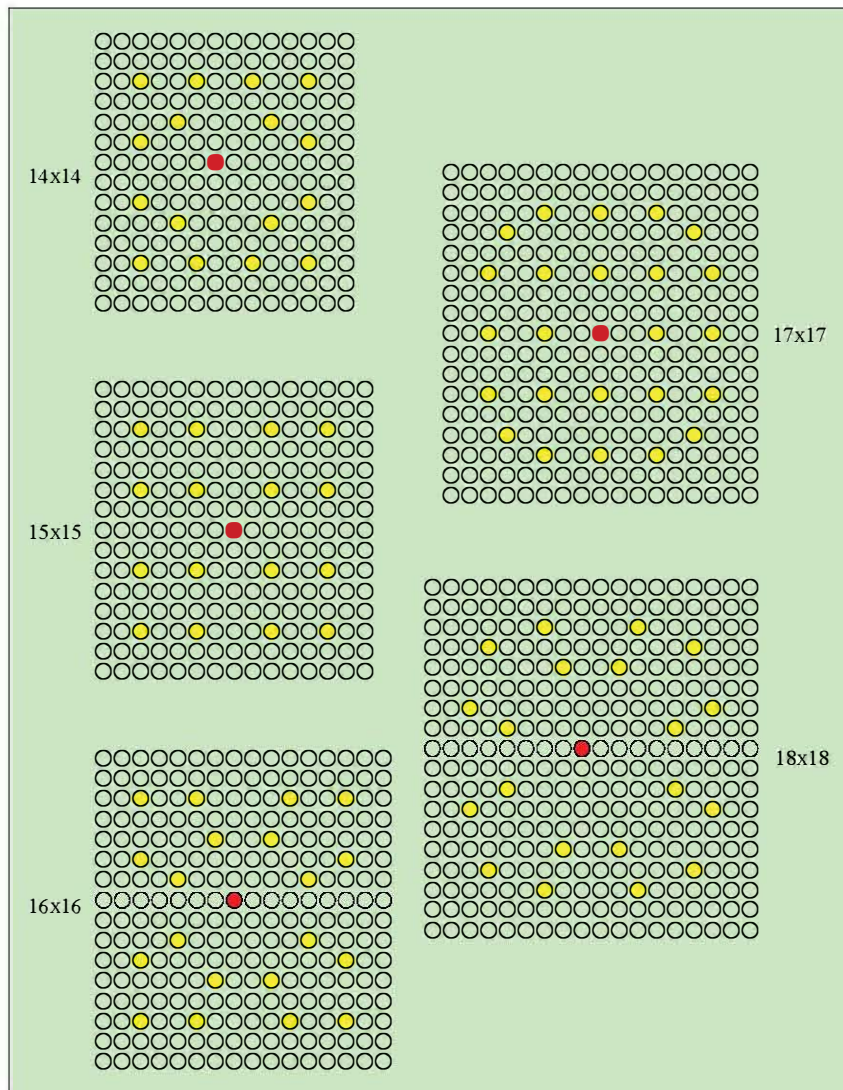
Figure 4-1:   Layouts of different *PWR* fuel assembly design. Rods marked with yellow colour are guide tubes into which the control rod cluster is inserted. The position marked by a red filled circle is the instrument tube position.

In most *PWR*s, the assemblies are positioned in the core by bottom and top fittings, and the lateral clearances are restricted by the assembly-to-assembly contacts at the spacer-grid levels. Figure 4-2 shows a typical *PWR* Fuel Assembly, *FA*. Also, the different fuel assembly components are shown and the material selections for these components are provided. The reason for the difference in structural material selection is that in general the most inexpensive material is chosen for a specific component that yields the lowest cost to produce the component while ensuring adequate performance during normal operation and accidents.
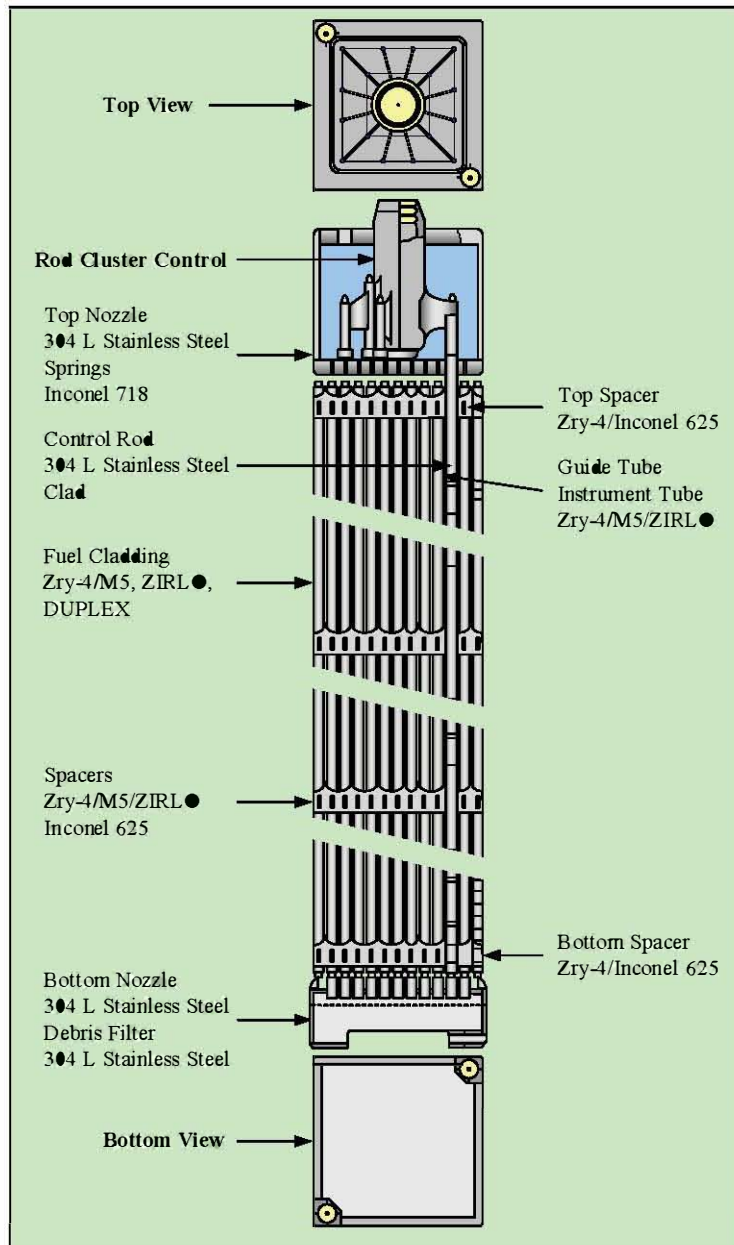
Figure 4-2:   Typical *PWR FA*.

4.1.2 Fabrication of ZrNb materials for *PWR*s (Peter Rudling)

For M5, *ZIRLO*, *MDA* and *NDA* manufacturing the zirconium sponge, recycle material from earlier manufacturing, and alloying elements are put together into an electrode.

The subsequent melting of the electrode is normally done in vacuum to prevent oxygen and nitrogen pickup from the air. The consumable electrode is melted into a water cooled copper mould slightly larger than the ingot diameter. As the arc melts the metal, a fraction is solidified and forms a solid layer of the zirconium alloy in between the mould and the molten metal. Only a small fraction of the whole ingot is molten at any time during the continuous consumption of the electrode. To increase the homogeneity of the ingot, the zirconium alloy electrode is melted three or four times.

An overview of the tube (used for fuel cladding and guide tube manufacturing), and sheet (for the spacer grid strip manufacturing) manufacturing process is shown in Figure 4-3.

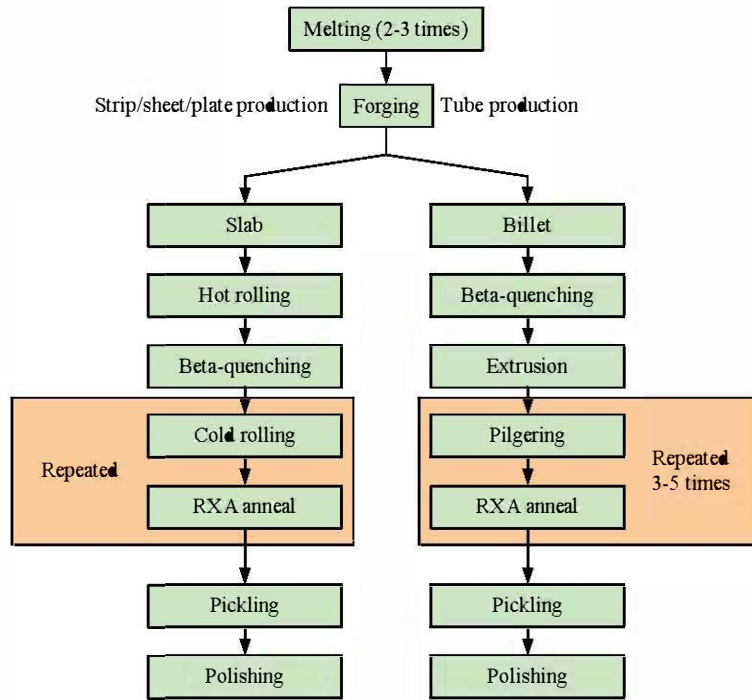Figure 4-3:   Outline of manufacturing of Zr-Nb materials from the ingot stage.

The forging (and hot rolling for flat products) is done in the β phase (1070 to 900°C). The material is heated to about 1100°C and the forging is performed in a number of steps bringing down the size of the workpiece. Before each forging step, the workpiece needs to be reheated several times to increase its plasticity.

5 WELDING AND WELD PROCESS CONTROL AND QC OF ZR-NB ALLOYS (SLAVA SHISHOV)

5.1 *DESCRIPTION OF VARIOUS SUITABLE WELDING TECHNIQUES FOR ZR-NB ALLOYS AND THE REASON WHY*

In many respects the operational reliability of fuels depends on the quality of welded joints, Zaimovsky et al., 1994 and Reshetnikov et al., 1995. This weld quality is directly related to the weldability of the employed structural materials, design of joints, the processes used to implement them, as well as to variability of weld material properties affected by temperature, neutron flux, stresses and environment (coolant and within a fuel element). The main objective of sealing the rod with a weld is to have a leak-tight rod throughout the lifetime in reactor and subsequent storage and transportation up to the moment of rod destruction in conjunction with final waste storage. Sealing is one of the basic processes that govern the fuel reliability. In the mass production of fuel rods each of them must be manufactured with adequate quality. Fuel rods must have guaranteed integrity and not contain defects that might show up during operation. In Russia the requirements placed on integrity are adequately rigid. In the majority of cases the maximum leakage of the fill gas (for the most part it is helium) from a fuel rod must not exceed 6.05×10^{-9} Pa/s (10^{-5} litre·μm/s) at a testing temperature equal or close to the operating temperature.

Adequate quality of a fuel assembly component under automated production conditions can only be obtained if the weld joint is adequately designed, the materials are weldable and the welding process has been optimized for the particular fuel assembly.

The feasibility of producing a weld joint with adequate quality depends on a number of factors:

1) Design of the fuel assembly component, its weld joints, materials used, fuel pellet composition (specifically if the pellet moisture content is too large);

2) Selection of manufacturing processes for weld joint preparation, as well as selection of subsequent mechanical processing techniques for welded joints;

3) Welding equipment and its instrumentation for system automated control, *SAC*, (for the automated mode);

4) Degree of optimization of the automated welding technique and workers' qualification;

5) Quality control of the welding equipment, the control equipment (to assess the quality of the weld) and the weld itself;

6) Conditions of access to items during process implementation by using manipulator.

Various methods of welding are used for zirconium fuel assembly components: fusion-gas-arc non-consumable electrode welding (*GAW*), laser (*LW*) and electron beam welding (*EBW*); resistance-spot (*RSW*) and seam resistance (*SPW*); with intensive plastic strain (*RPW*), specifically, resistance butt welding (*RBW*), magnetic discharge (*MDW*), solid state diffusion welding (*DW*); as well as brazing with high temperature solders.

The major problems with fusion welding are to produce welded joints without discontinuities, i. e., without microcracks; defects similar to cracks; poor penetration; different kinds of inclusions (e.g. fuel) in the weld; hair-line non-metallic inclusions in rods used for plugs; coarse pores in welds, weld overhang and gas pockets.

One of the major problems of welding low-alloyed zirconium alloys (E110, E635, E125) is to prevent the metal heated to above 350-400° being exposed to atmospheric air, primarily, nitrogen. It is well known that this situation will result in nitrogen contamination of the weld significantly reducing the corrosion resistance of the welded joints and the cladding metal. Another disadvantage of fusion welding is a greater tendency to form high porosity in the solidified weld metal. At the same time weld joints of low alloyed zirconium are not prone to formation of cracks.

The standard technical requirements for unacceptable defects cover cracks of any extent, lack of penetration, channel and planar type defects, non-metallic inclusions in the weld zone and other defects that may result in gas leakage during fuel rod fabrication or defect deterioration during reactor operation resulting in gas leakage. In seam welds individual pores are acceptable if their sizes do not make up more than 20% of a cladding thickness, or if the distance between adjacent pores exceeds the critical value (tripled sum of diameters of adjacent pores). The probability of forming unacceptable defects during welding, viz. cracks, relates primarily to the weldability of the cladding material, the weld joint design, the selected welding process and welding operations.

5.1.1   Design of joints sealing fuel elements clad in Zr-Nb alloys

To achieve a reliable sealing of the fuel rod it is very important to choose an adequate weld join design, Reshetnikov et al., 1995. Examples of different weld joint designs are illustrated in Figure 5-1. A butt-seam weld joint is primarily used for fuel rods that are sealed by fusion welding, Figure 5-1(a). A butt weld joint, Figure 5-1(b), or an end-face weld joint are used less often, Figure 5-1(c).

In recent years cladding-plug co-melting weld seam joints for fabricating zirconium alloy fuel rods are being used, Figure 5-1(d). End-face fuel rod weld joints with annular fuel pellets are more often used when the pellet diameter exceeds 10-12 mm.
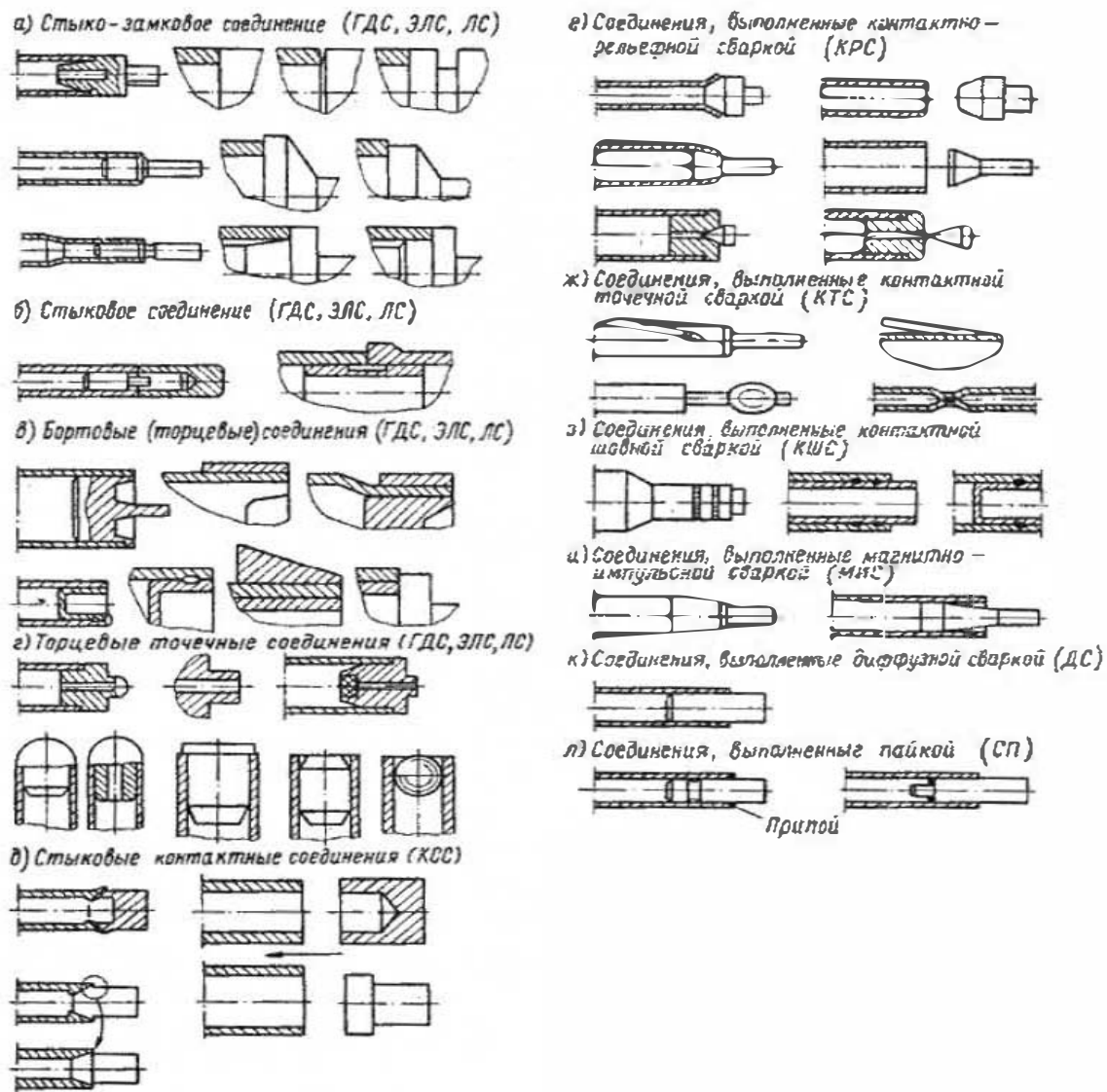
Figure 5-1:   (a) (edge) butt-seam joint (*GAW, EBW, LW*), (b) butt joint (*GAW, EBW, LW*), (c) end-face joints (*GAW, EBW, LW*), (d) end-face spot joints (*GAW, EBW, LW*), (e) resistance butt welding joints (*RBW*), (f) resistance projection joints (*RBW*), (g) resistance spot welding joints (*RSW*), (h) resistance seam welding joints (*RSW*), (i) magnetic discharge welding joints (*MDW*), (j) diffusion welding joints (*DW*), (k) brazed joints.

The designs of joints produced by resistance butt, Figure 5-1(e), resistance projection, Figure 5-1(f), and magnetic impulse welding, Figure 5-1(i) are similar in shape.

The choice of the weld joint type and its method takes into account the way of fixing a fuel element in a fuel assembly.

6   DISCUSSION AND SUMMARY (ALL)

The developments of Nb alloyed Zr alloys started in Russia in the late 1950s and resulted in the selection of the alloys Zr1Nb (E110) and Zr2.5Nb (E125) for the *VVER* and *RBMK* reactors in the early 1970s. Later on a Zr1.2Sn1Nb0.4Fe (E635) was developed as an alternate alloy. Recently, an optimized E635M alloy with a reduced Sn and Nb content is under development and E110 is also being improved. The alloys E110, E125 and E635 show excellent in-reactor performance and are used for fuel cladding and other structural components of *VVER* and *RBMK* cores.

In USA, Canada, UK, and Germany several studies with Zr-Nb-(Sn-Fe) alloys were performed in the late 1950s and early 1960s. Attention to these alloys was given again in the mid of 1980, when it became evident that even the best Zry-4 will not permit the anticipated burnup target in modern *PWR*s to be achieved. Binary Zr-Nb alloys (such as Zr1Nb and Zr2.5Nb) as well as ZrNbFe- and ZrNbSnFe-alloys were tested in *PWR* by several fuel vendors.

Westinghouse started an experimental fuel rod irradiation program with several Zr-Nb alloys in 1976 and selected from this *ZIRLO* (Zr1Sn1Nb0.1Fe) for a first reload in 1991. *ZIRLO* has a quite high creep resistance, a better irradiation growth behaviour and a somewhat higher corrosion resistance than Zry-4. Today *ZIRLO* is used for fuel rod cladding and structural components in many *PWR*s. A low-Sn (0.7%) *ZIRLO* version is being explored.

Mitsubishi Heavy Industries (*MHI*) developed the *MDA* alloy (Zr0.8Sn0.5Nb0.2Fe0.1Cr) for the Japanese market which also exhibits a reduced creep and growth rate and a somewhat improved corrosion behaviour compared with Low-Sn Zry-4. *MDA* has been extensively tested in Japanese *PWR*s but is still not used for full reloads today.

Probably the largest test program with alternative Zr alloys was performed by *Siemens* (today AREVA NP). Their results showed that properly heat treated Zr2.5Nb has the best corrosion behaviour and that the corrosion behaviour of the other Zr-Nb-Sn-FeCrV alloys depends primarily on the Sn content. Siemens selected from their large test program a DUPLEX cladding with an extra low Sn content and an enhanced Fe and Cr content in a thin outer clad layer for reloads, but continued to explore binary ZrNb alloys in several *PWR*s under high duty operating conditions.

Framatome (today AREVA NP) started an in-*PWR* cladding material development program in the late 1980s and selected M5 (a fully recrystallized ternary Zr1Nb0.125O alloy), exhibiting a very high corrosion resistance, a very low uptake of corrosion hydrogen, a good creep strength, and equivalent or even better *LOCA* behaviour compared to that of Zircaloy-4.

Pressure tube fabrication. Zr-2.5%Nb alloy pressure tubes are used in three different countries' reactors (Canada; Russia; and India). Although all pressure tubes are manufactured by a sequence of extrusion in the alpha + beta phase field, followed by cold working to the desired dimensions and a final stress relief anneal, the details are different for each of the three countries using them.

Pressure tubes for CANDU reactors are fabricated from quadruple melted ingots to reduce initial impurity concentrations. Billets are quenched from the beta phase before extrusion at a ratio of 10.5:1. They are then cold drawn about 25% to final size to give the desired uniformity to the grain structure. The final stress relieving is at 400°C in steam and reduces the dislocation density without modifying the structure, and provides a thin protective oxide during handling. Figures showing the desired grain structure; the initial hydrogen contents that are achieved; the improved fracture toughness resulting from impurity reduction; and the tube textures and in-reactor creep and growth data have been presented. Some of the problems that resulted from creep-sag of the pressure tubes due to spacer misplacement have been discussed together with techniques for restoring spacers to their correct locations.

Russian Zr-Nb pressure tubes are fabricated by a similar extrusion process to that used for *CANDU* pressure tubes, but cold working is introduced by pilgering rather than by cold-drawing, and the final annealing is at a higher temperature. These differences result in significant structural and textural differences from *CANDU* tubes.

India uses a lower extrusion ratio for their tubes. A much larger cold working stage by pilgering follows, and the final annealing temperature is higher still, resulting in a very different structure. Full details of the Russian and Indian fabrication routes are not available.

In Russia the specified requirements of the E110 (*RXA*), E125 (*CWSR*) and E635 (*RXA* and *CWSR*) alloys related to:

- the chemical compositions,

- the microstructures of the materials and the fuel assembly components,

- the surface conditions- and manufacturing process parameters and,

- the set up for commercial production

These factors have contributed to excellent in-reactor performance and in a potential for further alloy improvements based upon a scientific approach to meet future demands with higher discharge burnups with retained safety margins.

The E110 alloy is a basic material for fuel cladding and spacer grids in *VVER* and *RBMK* reactors. It is highly ductile and corrosion resistant with a low *HPUF* in high temperature pressurized water (*VVER*s). In boiling coolant conditions with higher oxygen contents in the coolant (*RBMK*) the alloy may experience nodular corrosion.

The E125 alloy is a basic material for *RBMK* pressure tubes. Pressure tubes made of this alloy are characterised by high corrosion resistance and toughness.

The E635 alloy is a basic material for guide thimble tubes, grid straps and central tubes in the *VVER*. This alloy is also being tested as fuel cladding in some fuel assemblies in both *VVER* and *RBMK* reactors to higher fuel discharge burnups. In addition, this alloy is promising for *PWR*.

In *VVER* conditions, the E635 fuel cladding forms thicker oxides than form on the E110 alloy.

The E635 alloy shows, however, high corrosion resistance under boiling conditions (*RBMK*) and also high strength and low irradiation induced creep and growth rates in a fast neutron field.

Current development of the E635 alloy will result in higher corrosion resistance in *VVER* conditions.

The promising characteristics of the E365-type alloys of the Zr-Nb-Sn-Fe alloy system were later verified by researchers in other countries.

The parameters that affect the microstructure of Zr-Nb alloys are:

- β-quenching

- Hot rolling or extrusion (especially temperature)

- Degree of cold rolling or rocking

- Intermediate annealing temperatures

- Final annealing temperature (degree of recrystallization)

These parameters affect homogeneity, precipitate size, grain size and texture. Nb alloyed Zr alloys have the advantage that lower β-quenching rates are necessary for an optimum material homogeneity than for Zircaloy-type alloys, due to the fact that Nb lowers the phase transition temperatures significantly.

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