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**Zr-Alloys, the Nuclear Material for Water Reactor Fuel.
A Survey and Update with Focus on Fuel for Pressurized Water Reactor Systems**

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Introduction

This paper is not given primarily for the perfect material specialist in Zirconium alloys. It is intended to provide a solid overview on the development of the requirements and the respective answers found as far as water cooled fuel rods and assemblies are concerned. It shall be a help as well for designers and manufacturers as also for users of this fuel, because only a broad and consistent knowledge on all aspects of the application of this material in nuclear fuel can guarantee a successful operation under the still increasing requirements in water cooled reactor cores.

Zr-Materials Development

The Early Beginnings

In the West the history of nuclear use of Zr-alloys started in the US in the early 1950's with the Naval Nuclear Propulsion Program under Admiral Rickover. Zircaloy-2 became the cladding material in the submarine Nautilus' water cooled (PWR) reactor core. Originally the work was mainly focused on tubular material. In the cores of early US power reactors (BWR and PWR) austenitic stainless steel was used as fuel rod cladding material. But chloride stress corrosion cracking and problems with corrosion in the trans-passive region of these materials forced reactor engineers to switch to Zry-2 [1].

It was also adopted in Canada for the development of the first reactor cores with natural uranium, called CANDU-reactors [2].

Zircaloy-4 was the first modification of Zr-alloys for commercial use to reduce the hydrogen pick-up from the PWR coolant [3].

During the "nuclear gold rush" in the US during the 1960'ies, Zircaloy became the standard material for cladding materials in Light water reactors (LWR), Zircaloy-2 in BWR cores and Zircaloy-4 (both Table I a + b) in PWR cores. However, besides the BWR FA-channels, the structural components remained to be made from stainless steel or Ni-alloys. The use of Zircaloy for other fuel components occurred slowly and step by step, mainly in the 1980'ies. In the early days the BWR channels were made of Zircloy-2, but due to the lower hydrogen uptake, later the standard material became Zircaloy-4 – up to today.

In Russia an alloy with 1%Nb in zirconium, today known as E 110 material, was used from the very beginning of the nuclear energy technology both for naval and for commercial reactors. It is the standard cladding tube material up to today in Russian water cooled reactor cores (Table II).

Alloy / Element	Zircaloy-2 wt %	Zircaloy-4 wt %
Tin	1.20 - 1.70	1.20 - 1.70
Iron	0.07 - 0.20	0.18 - 0.24
Chromium	0.05 - 0.15	0.07 - 0.13
Nickel	0.03 - 0.08	-
Fe+Cr+Ni	0.18 - 0.38	-
Fe+Cr	0.28 - 0.37	-
Oxygen	0.09 - 0.16	0.09 - 0.1
Silicon	0.005-0.012	0.005-0.012

Table Ia
Nominal Chemical Composition of
Zircaloy-2 and -4 (ASTM)

Element	Zry-2 ppm	Zry-4 ppm	Element	Zry-2 ppm	Zry-4 ppm
Al	75	75	Mg	20	20
B	5	5	Mn	50	50
Cd	5	5	N	80	80
Hf	100	100	Ti	50	50
C	270	270	H	25	25
Co	20	20	W	10	10
Cu	50	50	U (total)	35	35
Ni	-	70			

Table Ib
Impurities in Zircaloy-2 and -4 (ASTM)

Element	Tolerable wt%	Typical wt%
Niobium	0.9 - 1.1	0.95 - 1.10
Tin	≤ 0.05	< 0.001
Iron	≤ 0.05	0.014
Oxygen	≤ 0.1	0.05 - 0.07
Nitrogen	≤ 0.006	0.003 - 0.004
Hydrogen	≤ 0.0015	0.0004 - 0.0007
Carbon	≤ 0.02	0.03 - 0.007
Silicon	≤ 0.02	0.040.004 - 0.009
Hafnium	≤ 0.05 (0.01)	0.03 - 0.04 (< 0.008)

Table II
Chemical Composition and Major Impurities of E 110 (Russian Zr-1Nb) [4]

As next new Zr-alloy Zr -2.5Nb was developed in the 1950'ies for nuclear core components where higher strength at operation temperatures was needed as for the Canadian and the Russian pressure tubes and for the Russian fuel assembly shrouds in VVER-440 [5, 6].

Progress with Zr-Alloy Development

In the 1960'ies, besides Zircaloy, many other Zr-alloys were investigated [7] for its use in water-cooled reactor cores. In the West such alloys for example were: Zircaloy-1 (Zr-2.5Sn) and Zircaloy-3 (Zr-0.25Sn-0.25Fe), Valloy (Zr-1.15Cr-0.10Fe), Valloy S (Zr-1.2Cu-0.28Fe). Valloy S was especially developed for the use in superheated steam. But none of the mentioned alloys became of commercial importance.

In Russia in about the same time various alloys of the Ozhenite type were investigated containing Sn, Fe, Ni, and Nb with a total alloy content of 0.5 to 1.5 %. First they were

investigated in boiling reactor water environment [8], later also for WWER application [9].

In the early 1970'ies this resulted in the development of an alloy with the nominal composition Zr-1Nb-1.3Sn-0.35Fe. It was developed as potential cladding as well as structural material for WWER end for RBMK fuel. This type of material today is known under the commercial name E 635 with the nominal composition Zr-1Nb-1.2Sn-0.4Fe [10, 11] (Table III).

<i>ALLOY</i>	<i>Component Content in Alloy, mass%</i>				
	Tin	Iron	Niobium	Zirconium	
<u>E 635</u>	0.9-1.2	0.3-0.6	0.1-1.1	Balance	
	<i>Ultimate Tensile Strength, at Temperature, °C</i> kg/mm ²		<i>YIELD STRENGTH at Temperature, °C</i> kg/mm ²		
	20	350	20	350	
	50-60	38-37	35-40	19-25	
	<i>Elongation, at Temperature, °C</i> %		<i>Corrosion Resistance, after h</i> mg/cm ²		<i>Creep Rate, %/h</i>
	20	350	3400	7840	
	24-27	25-30	0.3-0.4	0.8-0.95	(1.3-3.6) x 10 ⁻⁵

Table III
Range of Chemical Composition and Properties of E 635 in Russian Patent of 1970 [12]

Besides these experimental alloys in the West Zircaloy-2 and -4 were exclusively in control of the market of fuel components for the light water reactor types BWR (Boiling Water Reactor) and PWR (Pressurized Water Reactor) for the time between the 1950'ies to the 1980'ies.

In the same time and up to today Zircloy-4 is in use for the cladding tubes and structural material of the CANDU fuel type as well as the Atucha-type fuel, besides Zr-2.5Nb for the pressure tubes of the CANDU pressure tubes [13]

In CANDU reactors the ternary Zr-2.5% Nb-0.5% Cu alloy is used as spring material to separate pressure and calandria tubes [14].

In Russia, up to today Zr-1Nb, with the alloy Zr-1Nb, now commercial name E 110 continued to be in use as unique material for cladding tubes and fuel structures (WWER and RBMK), with the exception that Zr-2.5Nb is used for (WWER) fuel channels (wrappers) and (RBMK) pressure tubes.

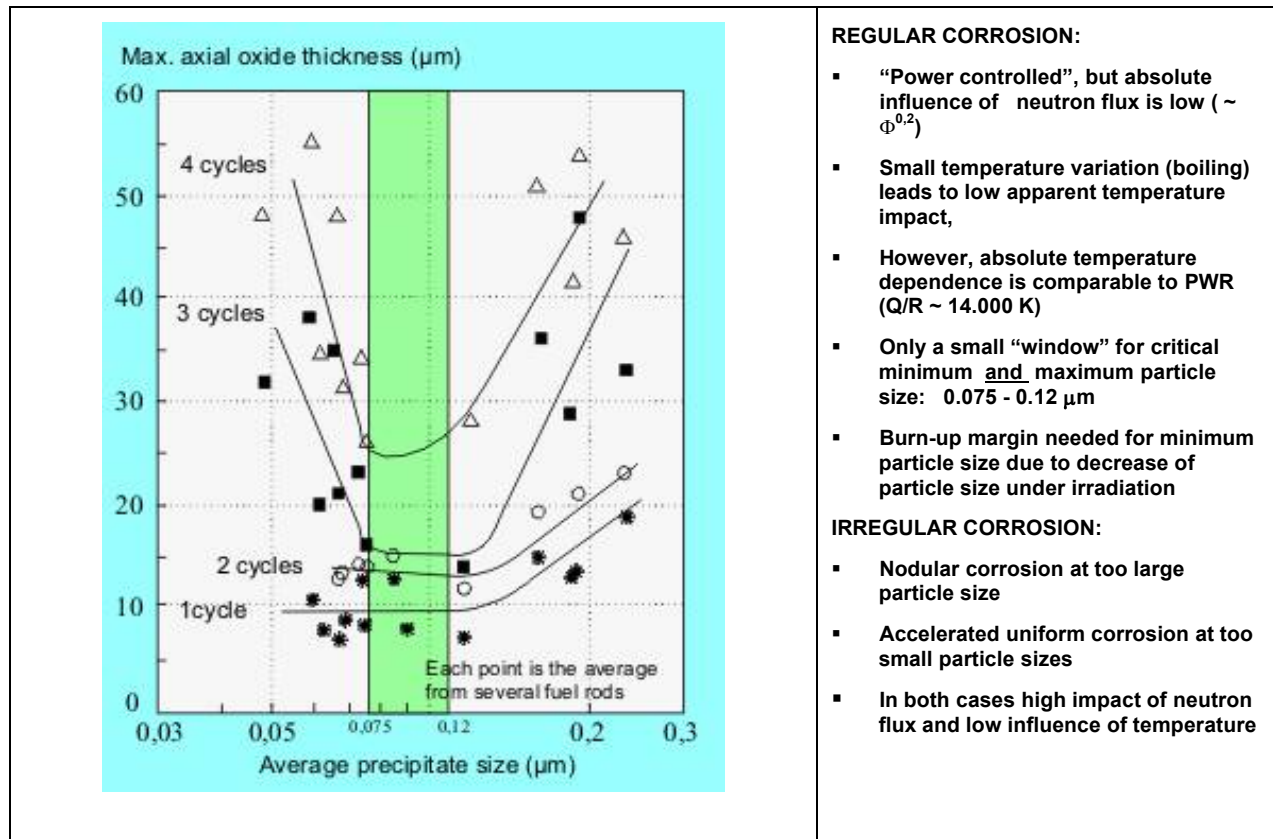
On the request of customers a modified version of E110 (with the commercial name E110K) was developed in the 1980'ies. It contains 900 – 1300 ppm oxygen [15].

Up to the end of the 1970'ies the reactor core operation conditions (linear heat generation, cladding temperature and burn-up) were so moderate, that not much attention was given to the details of the chemical composition and the microstructure of

Zircaloy-2 and -4 as material for cladding tubes and structural fuel components. Therefore the fabrication parameters for both materials and for the application in BWRs and PWRs were mainly the same.

This changed significantly in the late 1970'ies and early 1980'ies, when in BWRs nodular corrosion and in PWR accelerated uniform corrosion became a problem with Zircaloy materials. Therefore different ways to optimize Zircaloy-2 and -4 for BWR and PWR application had to be developed.

For BWR a so called LTP-Zircloy-2 (LTP: "Low Temperature Process") was developed [16] with strict limits for the particle size of the intermetallic precipitates (figure 1).



REGULAR CORROSION:

- "Power controlled", but absolute influence of neutron flux is low ($\sim \Phi^{0.2}$)
- Small temperature variation (boiling) leads to low apparent temperature impact,
- However, absolute temperature dependence is comparable to PWR (Q/R \sim 14.000 K)
- Only a small "window" for critical minimum and maximum particle size: 0.075 - 0.12 µm
- Burn-up margin needed for minimum particle size due to decrease of particle size under irradiation

IRREGULAR CORROSION:

- Nodular corrosion at too large particle size
- Accelerated uniform corrosion at too small particle sizes
- In both cases high impact of neutron flux and low influence of temperature

Figure 1 Dependence of In-BWR Corrosion of Zircaloy-2 on Precipitate Size [16]

For PWR application an optimized Zircaloy-4 was developed, e.g. at Siemens called PCA- Zircaloy (with PCA for "Prime Candidate Alloy") [17]. For that purpose the fabrication had to be optimized to stay above a lower limit for the particle size of the intermetallic precipitates by using a so called "Annealing Parameter" ΣA (figure 2), controlling all thermal processes (deformation and annealing) after beta-quenching [18, 19, 20].

Other designers were following with adequately improved Zircaloy-4 cladding material, like

- OPTIN™ by ABB [21, 22]
- AFA 2G-Cladding by Framatome/Fragema [23], and
- "Improved Zircaloy-4" by Westinghouse [24]

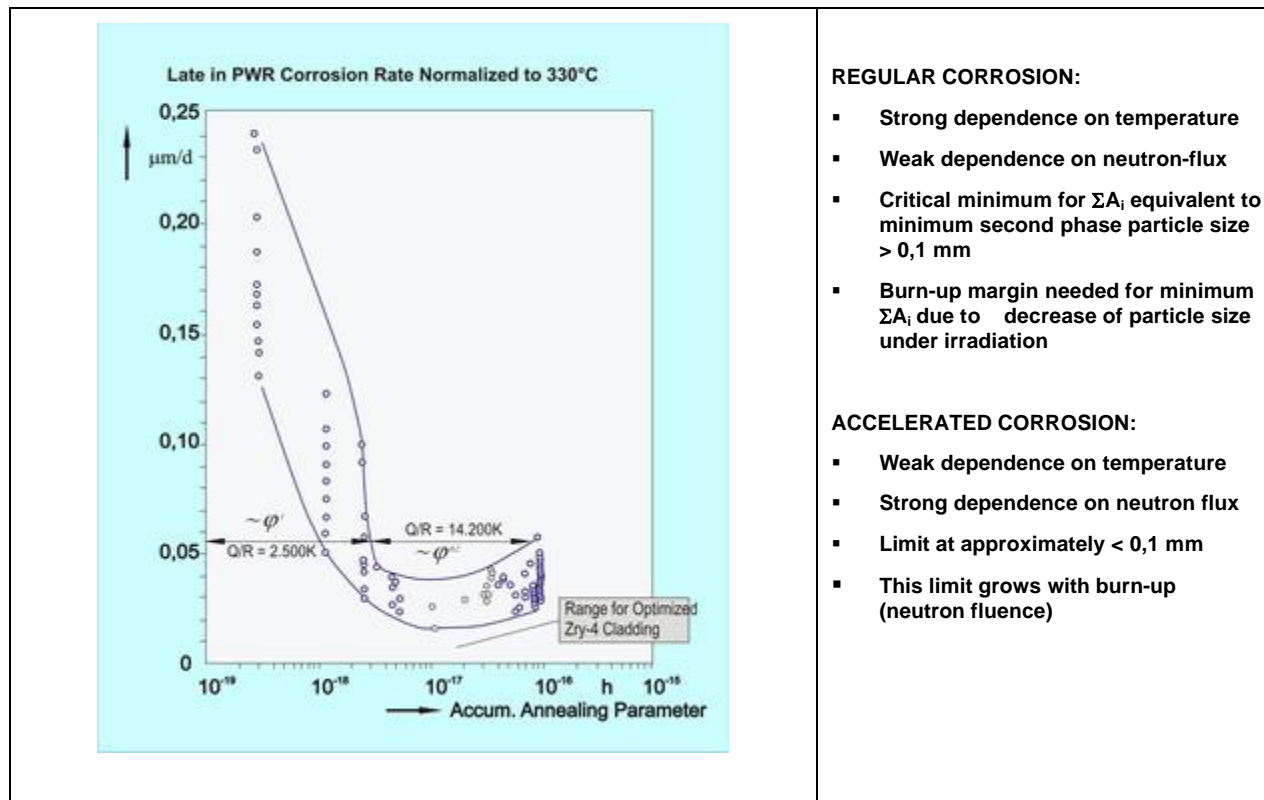


Figure 2 Dependence of In-PWR Corrosion of Zircaloy-4 on the Annealing Parameter [18]

REGULAR CORROSION:

- Strong dependence on temperature
- Weak dependence on neutron-flux
- Critical minimum for ΣA_i ; equivalent to minimum second phase particle size $> 0,1$ mm
- Burn-up margin needed for minimum ΣA_i ; due to decrease of particle size under irradiation

ACCELERATED CORROSION:

- Weak dependence on temperature
- Strong dependence on neutron flux
- Limit at approximately $< 0,1$ mm
- This limit grows with burn-up (neutron fluence)

While the taken improvements on these materials for BWR application turned out to be sufficient for the corrosion resistance under BWR conditions up to today, it became clear very soon, that the increasing operation requirements in PWRs made it necessary to look for new solutions for further improved corrosion resistance in particular of the fuel rod cladding tubes.

On the other hand another performance problem with Zircaloy claddings under BWR operating conditions became known in laboratory tests already in the 1960'ies. This is the susceptibility of Zircaloy to stress corrosion cracking under the influence of gaseous iodine. In the early 1970'ies it became clear that this sensitivity of Zircaloy can lead to serious fuel operating problems due a so called "pellet-clad-interaction" (PCI) mechanism, already at burn-up in the range of 10 – 15 MWd/kg_U. In order to overcome this problem a so called zirconium-fuel-barrier cladding was developed, where an internal liner of pure zirconium acts as a protective layer against stress-corrosion under the combined influence of fission-iodine and circumferential stress from pellets expanding during power ramps [25].

Interestingly the same measure was never necessary for cladding tubes in PWR cores due to another, more moderate power-versus-time history in PWR fuel as compared with BWR fuel.

Later, in the 1990'ies it turned out that pure zirconium as internal liner can, under certain conditions, lead to severe secondary fuel failures due to secondary hydriding from the inside after a small primary cladding defect, e.g. by fretting (for more details see chapter "Inpile Behavior of Zr-based materials").

Therefore various modifications of the chemical composition of the liner material were developed by different fuel designers.

- ”.
- Siemens changed to a Zr-Liner with addition of “about 0.4 Fe. [26]
- ABB developed a barrier cladding with “moderate”¹ Sn addition to the Zr-liner . [27, 28]
- GE changed to “Classical Barrier”, i.e. pure Zr, containing 400 ppm Fe and < 600 ppm O. GE also developed a “Tri-Clad”-solution with two different material-layers for the internal liner: 1st internal liner made of Zircaloy-2, 2nd internal liner = “Classical Barrier [29]

Since no internal liner was ever used in PWR fuel claddings, this type of severe secondary hydriding and splitting of the cladding was never observed with PWR fuel.

Advanced Zr-alloys

From the knowledge obtained during the optimization of Zircaloy-4 as PCA-material, it was possible to develop a new generation Zr-material cladding for PWR, called “Duplex Cladding” [30]. The material of the outside liner of this duplex tube was developed from Zircaloy-4 by leaving the limits for the chemical composition according to the ASTM specification. In a first step the Sn content was decreased below this limit of 1.2% down to 0.8%. Therefore e.g. the name of this duplex tube at Siemens was “DX ELS 0.8” (from “Duplex tube with Extra Low Sn Content of 0.8 % in the Liner”). This solution worked successful in many European PWRs with high thermal load on the fuel assembly during the 1990’ies.

Nevertheless new solutions with other materials were sought to meet the still increasing requirements on the corrosion resistance of PWR fuel rod claddings.

Such alloys are:

- M5TM, the French version of the Zr-1Nb alloy, [31]
- M4TM, a French development of a Zr-0.5Sn-0.6Fe-0.4V alloy [32]
- HPA-4, a Siemens development of the Zr-0.6SnNbV-type (with HPA for “High Performance Alloy”) [33],
- Zr-2.5Nb, a Siemens development with a special heat treatment [33].
- ZIRLOTM, a Westinghouse development of a Zr-1.0Sn-1.0Nb-0.1Fe alloy [24, 34, 35].

These are the alloys where up to now substantial experience in commercial PWRs or by extended in-pile tests has been collected.

There are various other investigations under way in an earlier stage of development – mainly in Far East which are also aiming at improved corrosion resistance.

¹ No Sn contents are given in the literature

One example is the experimental alloy NDA from Japan (Table IV) [36].

	Sn wt%	Fe wt%	Cr wt%	Ni wt%	Nb wt%
NDA	1.01	0.27	0.16	0.01	0.1
Zry-4	1.30	0.21	0.10	0.001	-

Table IV Chemical Composition of Japanese NDA vs. Zircaloy-4 [36]

Another group of experimental alloys, called HANA High Performance Alloy for Nuclear Application (Table V) is under investigation in Korea [37].

Alloy	Chemical Composition, wt%
HANA-3	Zr-1.5Nb-0.4Sn-0.1Fe-0.1Cu
HANA-4	Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr
HANA-3	Zr-1.1Nb-0.05Cu
Zircaloy-4	Zr-1.3Sn-0.2Fe-0.1Cr

Table V Chemical Composition of Korean HANA Alloys vs. Zircaloy-4 [37]

Out of this various possible cladding materials, for the time being, the winner in the market is the French M5TM, a Zr-1Nb alloy (Table VI) with a special fabrication route and an addition of traces of sulphur. The special fabrication route is a low temperature cycle where all intermediate and final anneals are performed at temperatures below 600°C [37]. This leads to a fully recrystallized microstructure with fine grains. The most recent overview on reactor operating results is given in [39]

ALLOYING ELEMENTS	COMMERCIAL PRODUCT COMPOSITION
Nb (%)	0.8 - 1.2
O (ppm)	1100 - 1600
Fe (ppm)	< 500
S (ppm)	10 - 35
C (ppm)	<200

Table VI Chemical Composition of Commercially used M5TM Material [38].

Westinghouse started rather early with developing ZIRLOTTM as an alternative advanced alloy [33, 34]. However, for a long period of time various problems with fabrication and in-pile behavior postponed a broad introduction of this material into the

market. In the meanwhile Westinghouse developed an improved modification of ZIRLO™ which is now called “Low-Tin –ZIRLO” [40]. The precise composition so far has not been published. But it is understood that this material now is fully commercially mature.

In Russian water cooled reactors corrosion never was a design limiting factor, due to different water chemistry. The focus of the design efforts is on mechanical stability. This may be the reason that the fuel designer still work with the classical Russian version of Zr-1Nb, called E-110, and Zr-2.5Nb.

However, it appears that development work is under way to optimize the chemical composition and the fabrication of this E-110 material. A fully commercial use of the material E-635 so far has not been announced.

In-pile Performance Experience

Fuel Failure Aspects

As already mentioned, in the early days of Zr-material in water-cooled reactors there were no problems that could be related to the regular operation, since burn-up of and thermal load on the fuel was rather low.

However, there were some behaviour problems even under those low operation requirements. But the causes for those problems were the rather limited experience with Zr-materials under reactor conditions.

The one type of problems was fuel rod failures caused by pellet-cladding interaction (PCI) in BWR fuel rods under certain power ramping conditions. This pellet-cladding-interaction lead to stress-corrosion cracking, starting at the inside of the cladding, due to a chemically attack by iodine in combination with a circumferential stress peak caused by the extension of the fuel pellet diameter during the power ramp. The iodine was produced as fission product in the pellet matrix and suddenly released to the fuel-to-cladding gap as a result of pellet cracking during the power ramp. It took a long time until this mechanisms was consistently understood and adequate mitigation was developed [27, 28, 29, 41, 42, 43].

Another type of generic failure was the development of cracks in special areas of the CANDU-pressure tubes made of Zr-2.5 Nb. In CANDU reactors, the pressure tubes are joined to the reactor at their ends by a mechanical joint to thick-walled tube of ANSI-403 stainless steel by a special rolling process. This rolling may induce high residual tensile stresses in the joint. Consequently, cracks may initiate.

The interpretation was that the cracks grew at low temperatures by “Delayed Hydrogen Cracking” (DHC), but once the reactor was at power and the pressure tubes were at a high temperature, i.e. above 250°C, cracking stopped because the low hydrogen concentration, i.e. below 15 ppm, was all in solution. The crack surface oxidized. However, cracking continued during subsequent reactor shutdowns and the stopped crack continued to oxidize during operation. Corresponding with the number reactor shut-downs the cracking proceeded stepwise. To prevent further occurrences of such cracking the residual stresses were minimized by stress-relief or redesign of the rolled-joint.

Much R&D effort was paid – and is still being paid – to mitigate this problem by improved material conditions, in particular to achieve a sufficient margin of fracture

toughness (>250 MPa at 25 °C) to make Zr-2.5 Nb resistant to delayed hydride cracking during a long-term contact with heavy water. Regardless of the progress made up to today it is understood that further work is needed to ensure the in-pile design lifetime of CANDU pressure tubes for 30 years and longer [44]

Cracking in the pressure tubes in RBMK reactors had a similar cause. Therefore respective investigations have been performed up to recently to find adequate materials conditions in Russia [45, 46, 47].

Recently a survey was given on the state of the art in Russia and in the West, by the IAEA in 2004 [48]. Although no new cracks have been observed in CANDU or RBMK reactors since the mid of the 1980'ies, it was necessary to continue the studies on this phenomenon as the reactors age, the spectrum of DHC looms because of increasing hydrogen concentration from corrosion and potential mechanical damage to the surfaces of the pressure tubes. Today the results of those extensive investigations can be used to determine the life of the pressure tubes due to both crack initiation and subsequent DHC propagation.

The step by step collected knowledge on the DHC-phenomenon helped to clarify the mechanism that caused very severe long split cracking in Zircaloy cladding of BWR fuel rods during the mid of the 1990'ies. These long splits (figure 3a) caused a very high release of fission products and even of Uranium to the coolant and thus gave a big problem to the respective reactor operators. It was clear rather soon that these long splits were the result of a secondary failure mechanisms (figure 3b) after the occurrence of small of small defects in the cladding that allowed the coolant to enter the fuel rod, developing there steam that oxidized the internal liner of the cladding, thus generating high amounts of hydrogen entering into the bulk of the Zircaloy-2 cladding. In combination with high stresses in the cladding a DHC mechanism finally led to the long splits in the cladding.

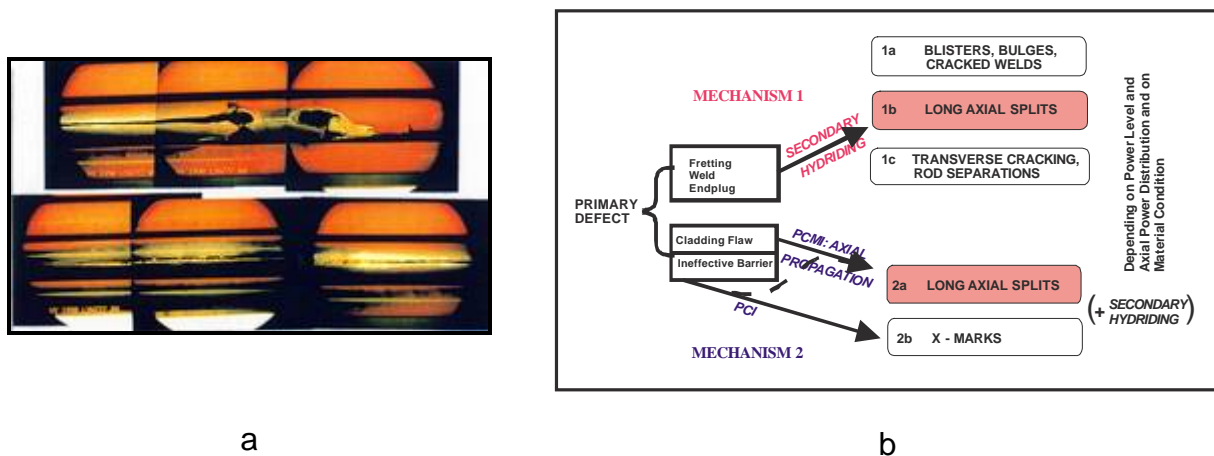


Figure 3 Severe Secondary Degradation of Zry-2 Cladding in BWR [49]

- a Long Axial Splits[49],
- b Mechanisms of Secondary Degradation [50]

It took considerable international efforts to fully understand the conditions that finally led to the severe cracking in the cladding [51]. While the DHC occurring in pressure tubes could be clarified and remedies were realized without substantial changes of the material chemistry of Zr-2.5 Nb, the DHC that caused secondary degradation in BWR

Of course several performance criteria have to be observed in fuel design to reach the performance requirements reliably. However, the long experience available for the application of Zr-materials in nuclear fuel has shown that only very few performance requirements are limiting the fuel design to reach the required performance targets as burn-up, thermal and nuclear efficiency. For example under PWR conditions all the time only the corrosion resistance of the cladding material and the corrosion dependant hydrogen uptake in fuel components, like spacer grids, limited the fuel burn-up under a given thermal load, expressed e.g. by the liner heat generation rate (LHGR) of the fuel rods.

Therefore, for the following consideration it is distinguished between

- design relevant aspects, and
- design limiting aspects.

Design Relevant Aspects

With regard to the use of Zr-materials, in any nuclear fuel design the following performance criteria have to be regarded at regular operating and at shut-down conditions :

- mechanical performance, i.e. strength and ductility,
- dimensional behavior, i.e. creep and growth,
- chemical interaction with the coolant, i.e. corrosion and hydrogen uptake,
- mechanical and chemical interaction with the fuel, in particular the pellet-to-clad interaction (PCI).

There are also performance criteria under off-normal condition to be considered. They will be discussed in a separate chapter later (“Safety aspects”).

Of course for all mentioned performance criteria the respective material properties have to be well known (see figure 4), and how they depend on the fabrication process parameters.

This review is restricted to a gross overview on the operation experience only, in terms of the above mentioned performance criteria.

The performance experience with nuclear fuel has shown, that, with some few exceptions, the mechanical behavior parameters, as reflected by the classical material properties strength and ductility, mainly play a formal role for licensing rather than for the operation behavior of the fuel components. The best proof for this statement is the fact that several fuel rod designs with different strength and ductility properties of the cladding material Zircaloy-4 (stress relieved, partially recrystallized and fully recrystallized) have worked fully satisfactorily in PWRs over decades.

In some cases derived mechanical properties, like fracture toughness, play a role. One example is the pressure tube cracking as a result of delayed hydrogen cracking (DHC), as discussed shortly in the chapter “Fuel Failure Aspects”.

More important for adequate performance is the dimensional behavior of Zr-materials in nuclear fuel. This dimensional behavior includes creep and growth under the respective operation condition. For creep an external stress on the fuel component is necessary, in addition to the operation temperature and the flux and fluence of fast neutrons. Growth basically occurs without external stress under the impact of the fast neutron flux.

Experience has shown that the in-pile creep behavior of Zr-alloys is significantly different from out-of-pile creep under comparable temperatures. While out-of pile the thermal activation of micro-structural processes after a short period of primary creep leads to a range of secondary creep that is constant with time until in the ternary range

a rapid dysfunction or rupture of the component occurs. Different from this well known out of pile creep characteristics in-pile only a primary creep type develops within the time history relevant for the material exposure in the reactor. Most important in-pile and out-of-pile creep resistance depends in a different way on the material condition. The optimum for (secondary) out-of pile-creep is observed with partially recrystallized material. The best in-pile creep resistance is obtained with fully recrystallized material.

Most important for nuclear fuel design is the diametric creep down of cladding tubes in the fuel rod. Today the in-pile creep-down behavior is well known for most commercially important Zr-materials up to the high burn-up ranges of modern fuel design.

In figure 5 the in-pile creep-down of commercial M5TM cladding tubes is depicted versus the in-pile creep-down of improved (low Sn) Zircaloy in the SRA condition (which is not the optimal material condition for in-pile creep) [39].

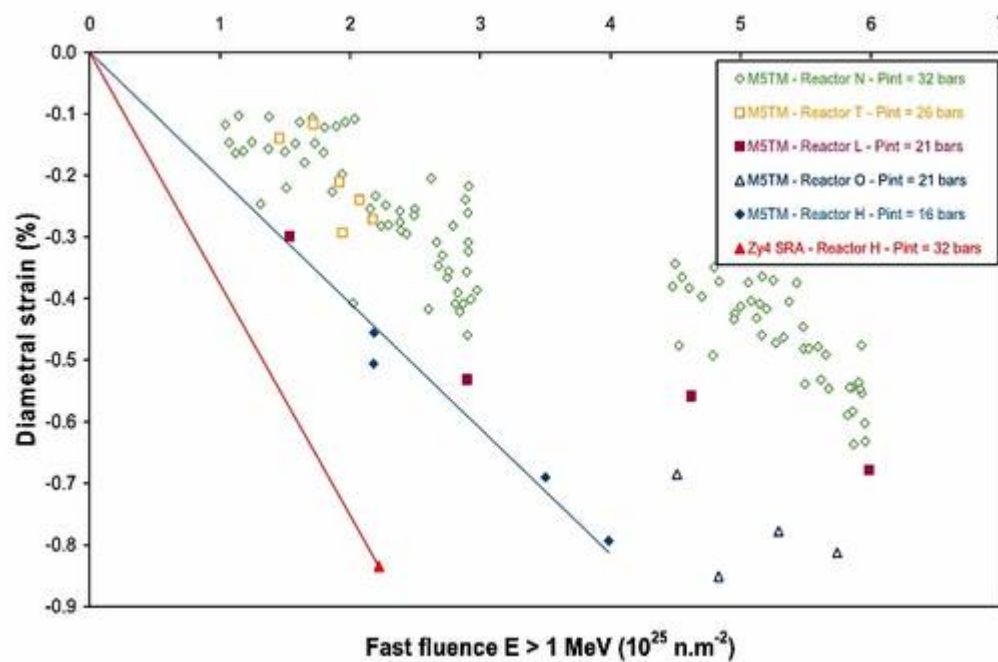


Figure 5
Diametric Fuel Rod Creep vs. Fast Fluence ($E > 1 \text{ MeV}$)
For SRA Low-Tin Zircaloy-4 and M5TM [35]

There is no recent data in the literature on the creep-down of the recently reported [40] optimized “Low-SN ZIRLOTM”-material. In a recently published overview of Sabol [53] on the development of ZIRLOTM there is a figure given from a more previous publication [54], depicting the creep-down of ZIRLOTM and Zircaloy-4 fuel rod cladding after one cycle of irradiation in a commercial PWR (figure 6). This is the only information available in the open literature.

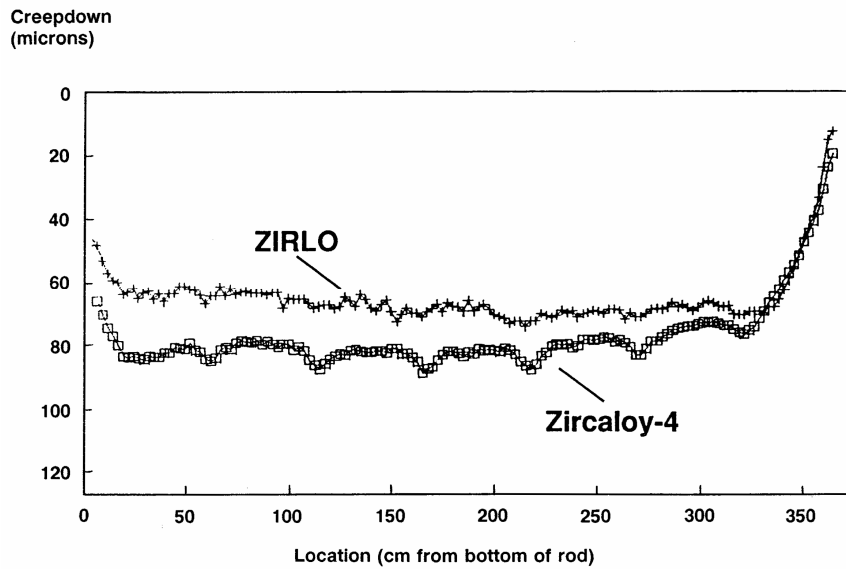


Figure 6

Comparison of the Creep-Down of ZIRLO and Zircaloy-4 Fuel Rod Cladding after one Cycle of Irradiation in a Commercial PWR [54]

Due to the consistent use of E-110 material in Russia in the meanwhile there exists a long experience with in-pile creep-down of cladding tubes made from this material. Recent PIE data are available [55] for burn-up of over 55 MWd/kg_U, as shown in figure 7.

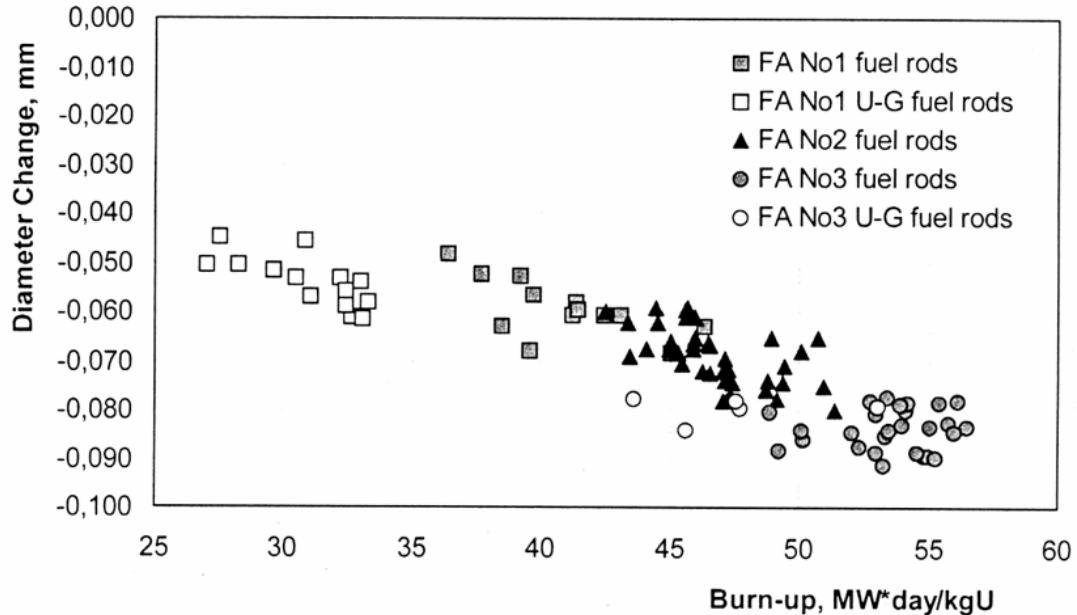


Figure 7

Dependence of Diameter Change of Fuel Rod and U-Gd Fuel Rod Claddings to Fuel Burn-Up [55].

Additional PIE data have been published recently [56] on the diameter change of cladding tubes made of E-110 and E-635 in a burn-up range of up to 55 MWd/kg_U, as shown in figure 8.

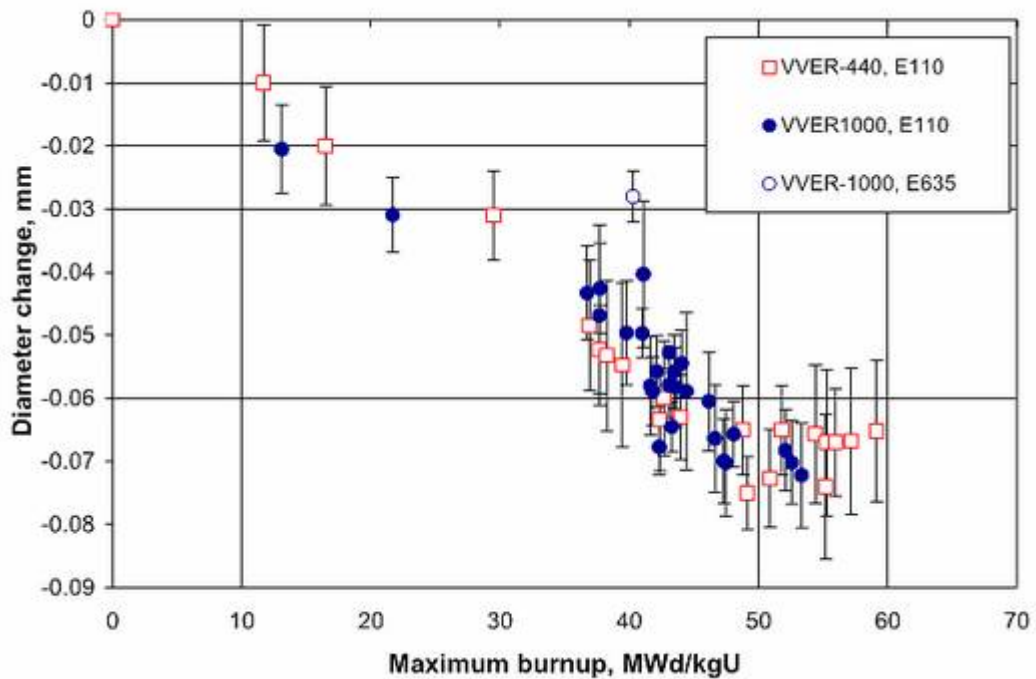


Figure 8

Maximum Diameter Change as a Function of Fuel Burn-up [56]

In figure 8 there is only one data point representing creep-down of cladding tubes made of E-635. From this data-point it could be concluded that E-635 shows significantly higher creep resistance as compared with E-110. This conclusion is supported by creep down profiles from the same paper as shown in figure 9. These findings are also in agreement with earlier published data [57].

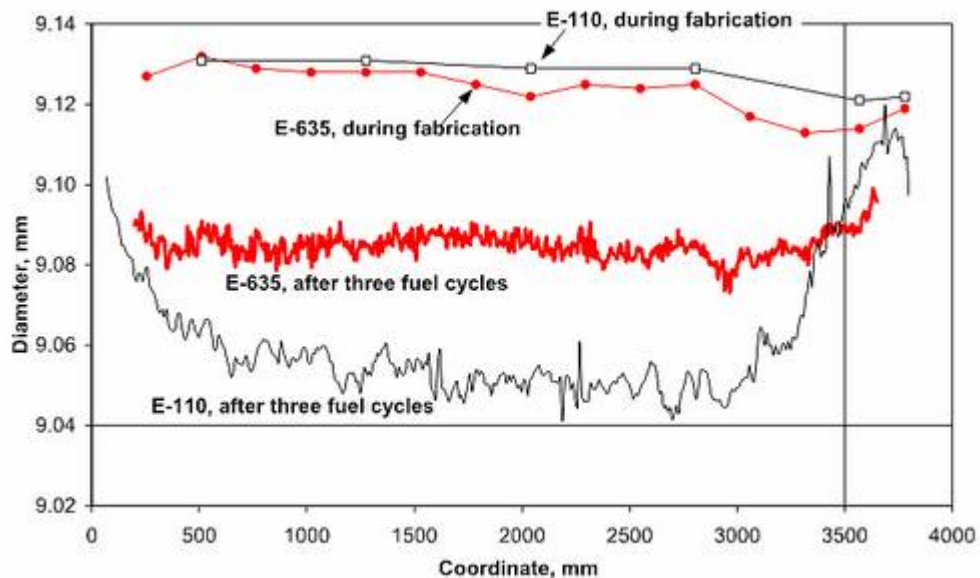


Figure 9

Distribution of Diameter in VVER-1000 Fuel Rods [56]

While under comparable fluences there is no significant difference of the creep behavior of Zr-materials in pressurized and in boiling water reactors, a more differentiated consideration is necessary for the in-pile growth of Zr-materials. This holds for different material conditions as well as for different micro-structural characteristics as the type and the size of precipitates.

Already 30 years ago a qualitatively different growth behavior was found for cold-worked and for recrystallized Zircaloy [58] as shown in figure 10. Twelve years later a more detailed study [59] showed a broad spectrum of different growth behavior depending on different material condition. In particular a very low or even partially negative growth rate in as beta-quenched condition became important for the choice of Zircaloy as material for guide tubes in PWR fuel assemblies (figure 11).

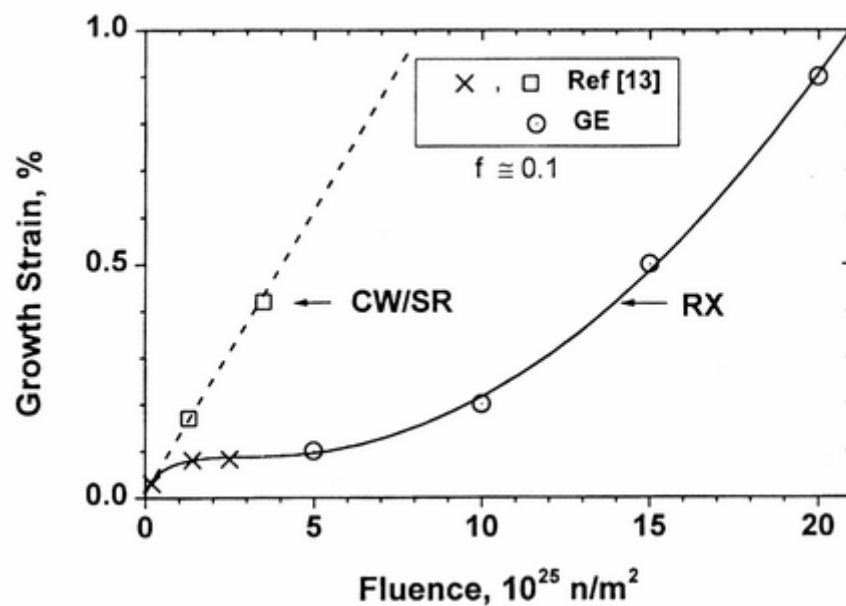


Figure 10
Irradiation Induced Growth of Zircaloy-2 at about 565K [58]

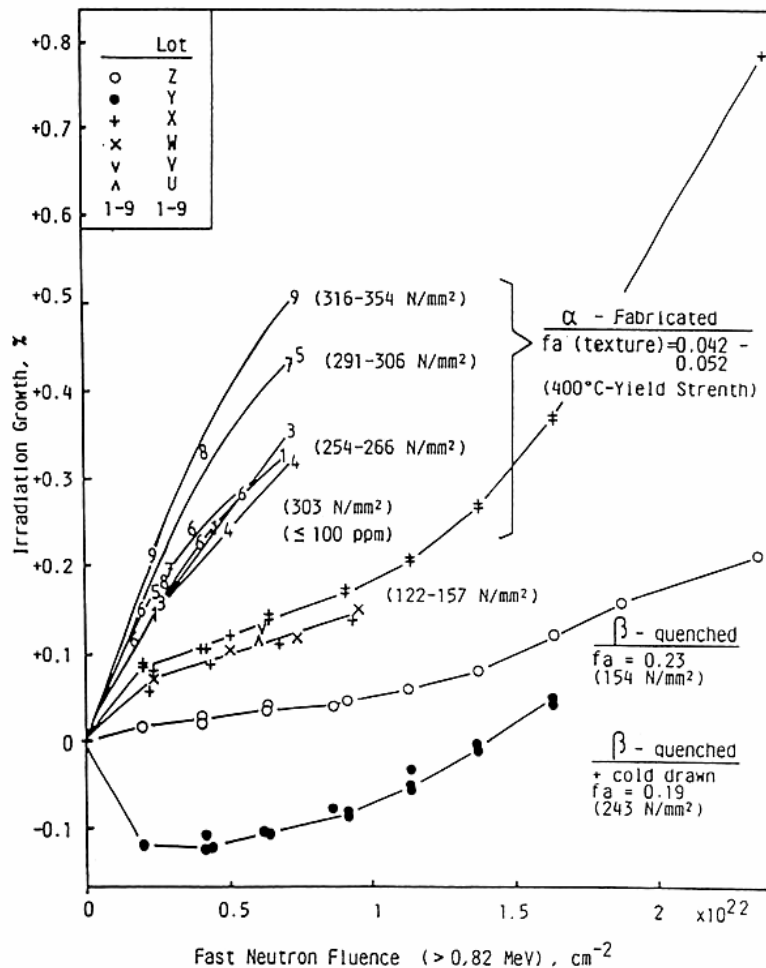
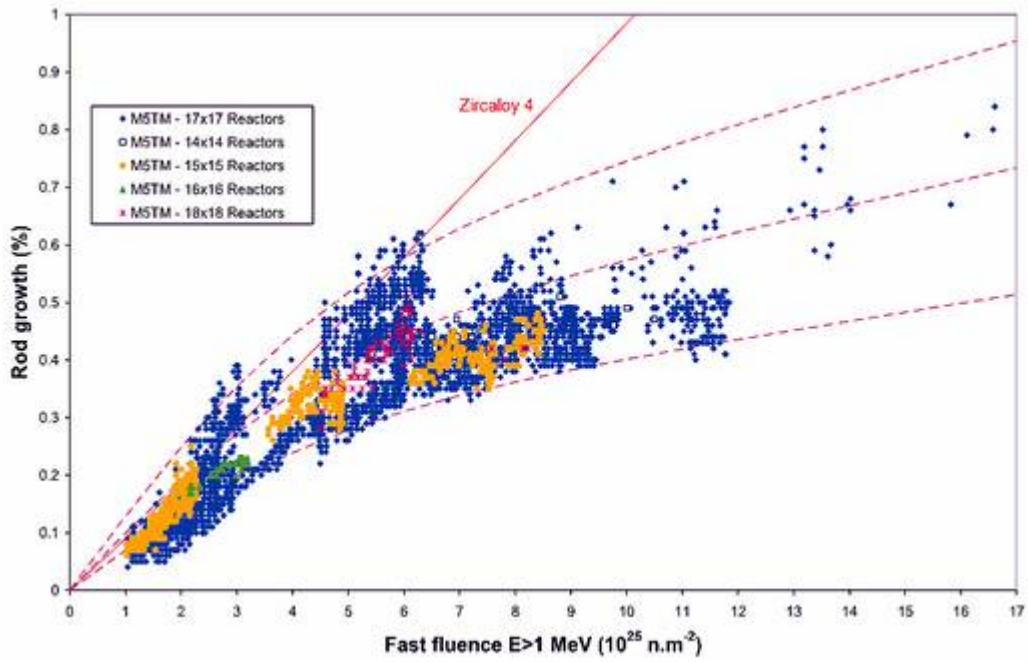


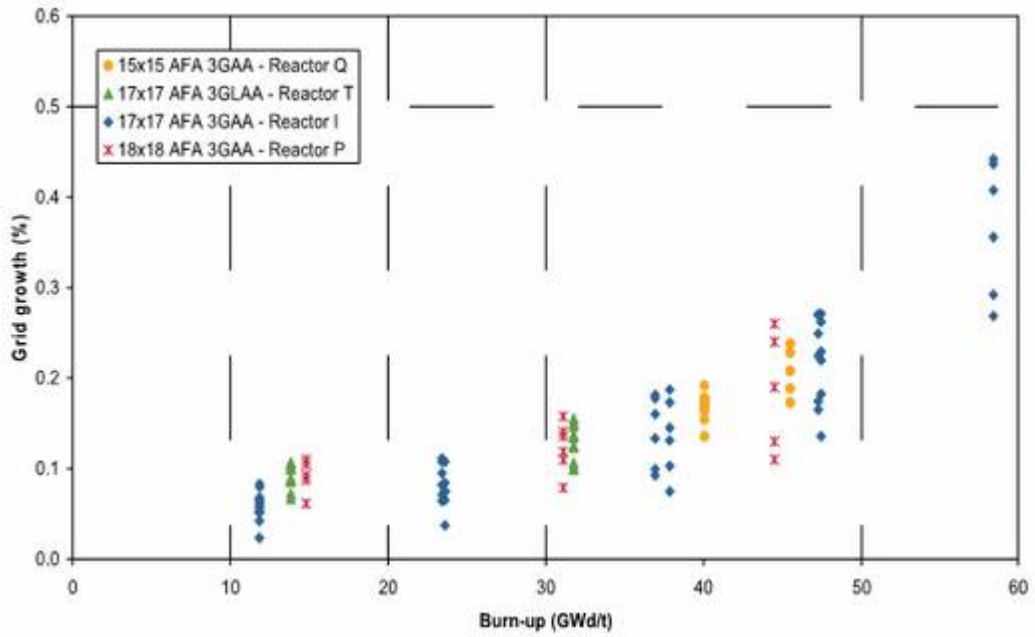
Figure 11
Effect of Various Material Conditions on Growth of Zry-4 [59]

In these times there were more and more indications that growth of Zircaloy increased dramatically with higher temperatures, i.e. above 643 K [60] and differences between cold-worked and recrystallized materials disappeared. Also there were first indications that higher fluences itself increased the growth rate. This was confirmed by the experiments of Rogerson et al., summarized in [61]. It was shown that growth rates at LWR temperatures increased significantly for fluences above about 5×10^{25} n/m². The precise growth mechanism is not fully understood up to now, however a clear correlation of growth to microstructure evolution could be evaluated by Adamson et al. as summarized in [62]. According to this work there are indications that different growth mechanisms are occurring at different growth rates, depending on whether or not <c> component dislocations are present. These <c> component dislocations appear to nucleate near precipitates that have released Fe to the matrix by irradiation-induced dissolution [63, 64].

Today of more technical interest is the growth behavior of the advanced alloys M5TM and ZIRLOTM. In figure 12 the most recent information [39] for M5TM is depicted. In figure 12a fuel rod growth develops a margin to Zircaloy-4 that increase with burn-up. In the meanwhile there is also substantial experience available with M5TM as sheet material used in PWR spacer grids of AFA3G fuel assemblies (figure 12b). Noticeably there is a slight increase of the growth rate at burn-up above 50 MWd/kg_U.



a



b

Figure 12

a Fuel Rod Growth vs. Fast Fluence ($E > 1 \text{ MeV}$) for M5 and SRA Low-Tin Zircaloy-4 [39]

b M5TM Grid Growth vs. Fuel Assembly Burn-up [39]

From figure 13, showing the respective growth data for ZIRLOTM [65] it can be concluded, that the in-PWR growth rate is about the same for both alloys M5TM and ZIRLOTM up the fluences of at least $10 \times 10^{25} \text{ n/m}^2$.

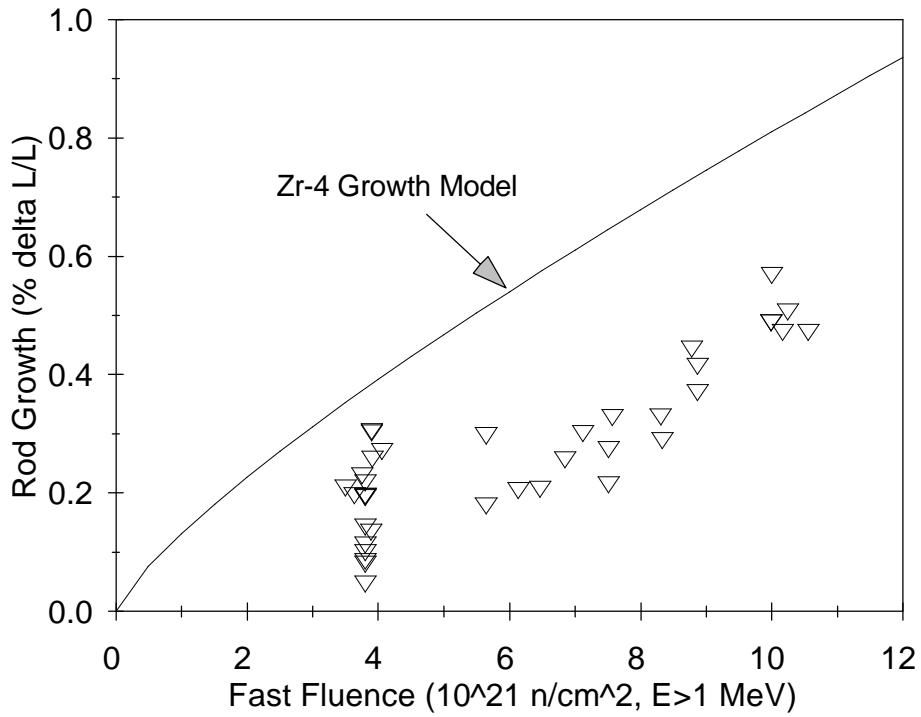


Figure 13
 Fuel Rod Growth Data for ZIRLO and Comparison to Zircaloy-4 [65]

Recently published data [55] show (figure 14) that the elongation of fuel rods with E-110 as cladding material as found from commercial WWER 1000 reactors is comparable with the data shown for M5™ and ZIRLO™ in figures 12 and 13 respectively. Typically all these materials do not show the second increase as found for Zircaloy after medium burn-up.

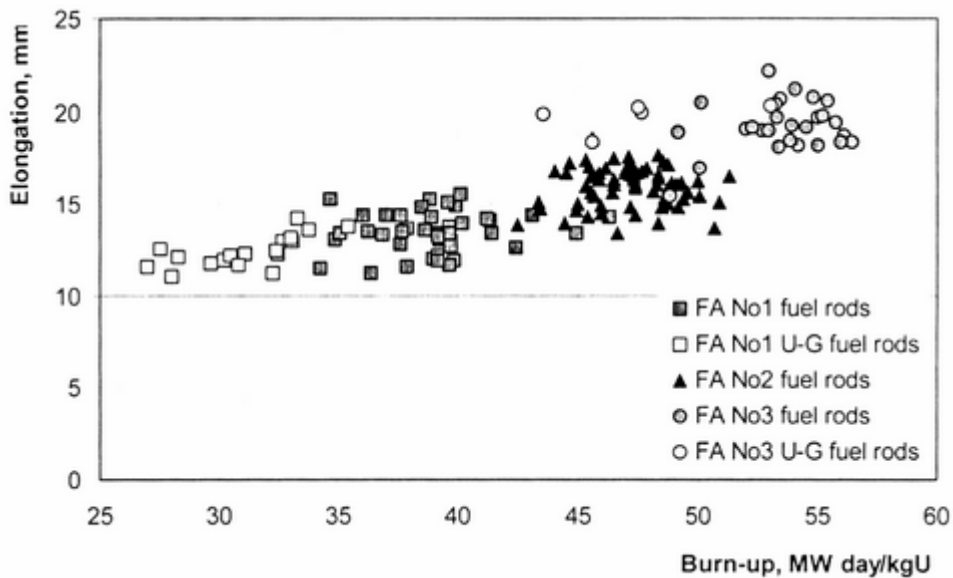
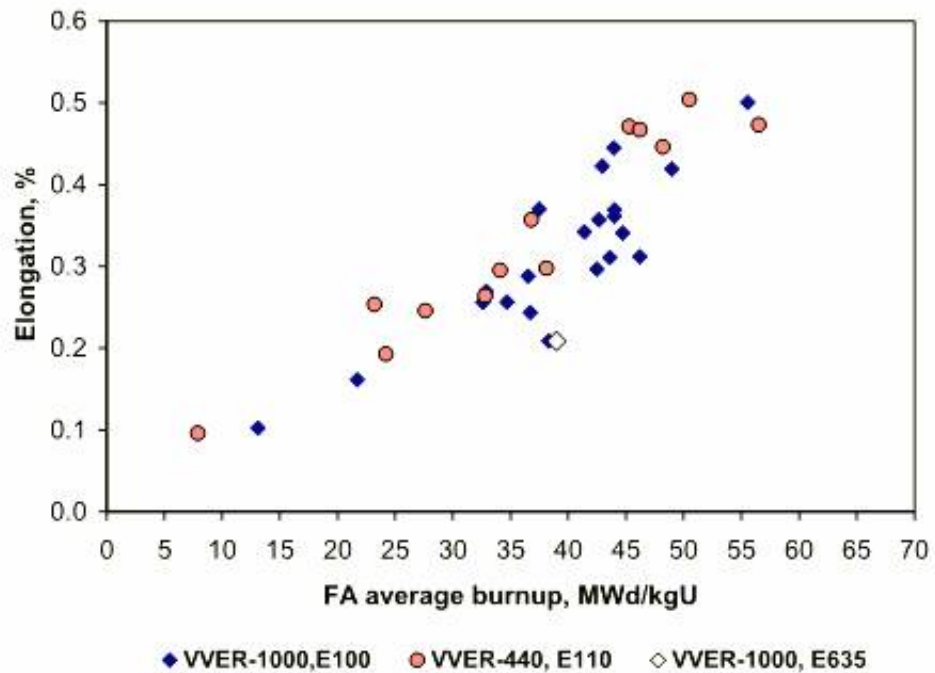
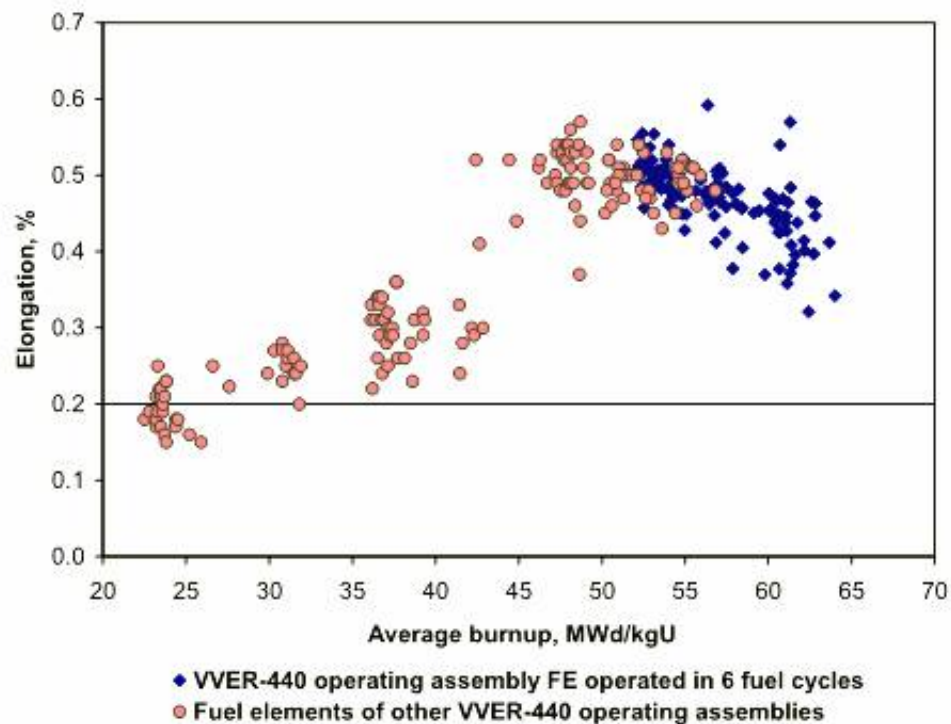


Figure 14
 Dependence of Elongation of WWER Fuel Rods and U-Gd Fuel Rods to Burn-Up [55]

Some data on growth of E-635 as published [56] indicate some lower growth rate as compared with E-110 (figure 15). However the given data are on the lower end of the band width of the E-110 data.



a



b

Figure 15 Elongation of VVER Fuel Rods as a Function of Fuel Burnup [56]

According to earlier published [66] data there should be much more margin for growth of E-635 (figure 16).

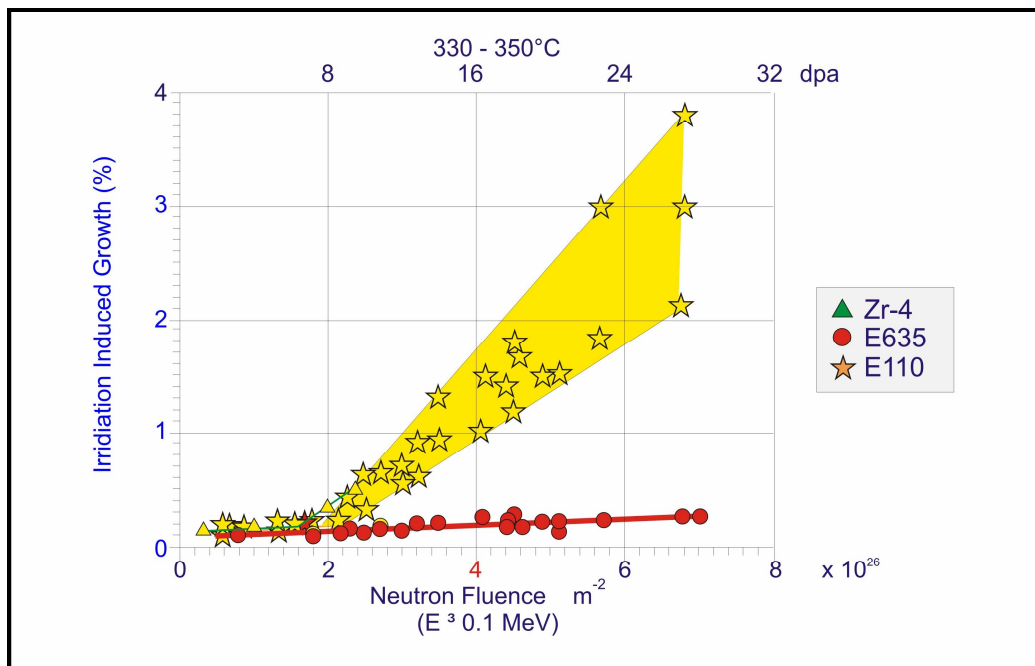


Figure 16
Irradiation Induced Growth (IIG) of Tubes vs.
Neutron Fluence at 330 - 350°C [66]

Design Limiting Aspects

Different from fuel in Russian water cooled reactors, in Western PWR fuel design the regular uniform corrosion of cladding tubes and corrosion induced hydrogen uptake in fuel structures played the most important role since the last three decades.

The reason for this basic difference mainly is the different water chemistry used in Russian and in Western light water reactors, in particular in PWRs. To compensate the pH shift caused by the addition of boron to the reactor water for reactivity control, in Russia KOH+NH₄OH is used, while in the West LiOH is used which has a deteriorating impact on the corrosion of Zr-alloys. With increasing thermal load and burn-up the very soon the corrosion resistance of Zircaloy-4 became the design limiting performance criteria for PWR fuel rod claddings.

Consequently the choice of the right Zr-material and the optimization of its properties was the key-topic in nuclear fuel material technology and it will continue to be so in the foreseeable future, because there is no chance to change the water PWR chemistry due to the high risks for the primary reactor systems materials.

As already shown years ago (figure 17), many material- and operation-parameters have to be considered jointly to end up with a corrosion behavior that allows fuel operation under optimal technical and economic condition.

	■		■		■					STRENGTH	■			■	■													
	■		■		■					DUCTILITY	■	■		■	■							■						
	■		■		■					CREEP	■			■	■	■												
	■		■		■					Growth	■			■	■	■												
	■	■	■	■	■	■				CORROSION	■	■	■	■	■	■						■						
		■	■	■	■	■				HYDROGEN UPTAKE	■											■						
	■	■	■							STRESS CORROSION CRACKING	■			■						■		■						
					■					LOCA	■			■	■	■												
NEUTRON FLUX	NEUTRON FLUENCE	POWER HISTORY	EXPOSURE	HEAT TRANSFER	CLADDING TEMPERATURE	WATER CHEMISTRY				Operation Parameters																		
										<i>In-Pile Behavior</i>																		
										Material Properties																		
										<i>Fabrication Procedures</i>																		
										CHEM. COMPOSITION																		
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<div style="border: 1px solid black; padding: 5px; width: fit-content;"> <p>PWR CORROSION INFLUENCES</p> <p>STRONG</p> <p>MEDIUM</p> <p>WEAK</p> </div>																MELTING	■	■										
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Figure 17
Complex Influence of Fabrication, Material Properties and Operation on the In-PWR Corrosion of Zircaloy-4 [52]

For a while it was sufficient to optimize the chemical composition and microstructure of Zircaloy-4 as shown at that time in many publications and already discussed in the previous chapter “Materials Development”.

However, already early in the 1980-ties it became clear that all efforts to improve the classical Zircaloy-4 material would not be sufficient to meet the rapidly further increasing requirements of thermal and nuclear efficiency and of more and more increasing burn-up targets.

With the knowledge obtained during the optimization of Zircaloy-4, it was only a logical consequence as a next step to develop the so called “Duplex Cladding”. The material of the outside liner of this duplex tube was developed by leaving the ASTM specification limits for the chemical composition. In a first step the Sn content was decreased below this limit of 1.2% down to 0.8%. Therefore the name of this duplex tube at Siemens was “DX ELS 0.8” for “Duplex tube with Extra Low Sn Content of 0.8 % in the Liner”.

It could be shown that with this duplex-cladding not only the corrosion rate was drastically decreased, but also the hydrogen uptake was improved and the cladding showed less sensitivity to the impact of LiOH on the corrosion [67]. Also all other requirements of the high duty and high burn-up design of this time could be met [33]. Additional studies [68] showed that the corrosion resistance of the duplex liner material could be further improved by increasing the Fe and Cr content. This cladding material then was called “DX ELS 0.8b”. A material with even further increased Fe+Cr content was called “DX D4”.

In figure 18 the broad corrosion experience with different duplex cladding variants is shown as it was collected in commercial PWRs already around the year 2000.

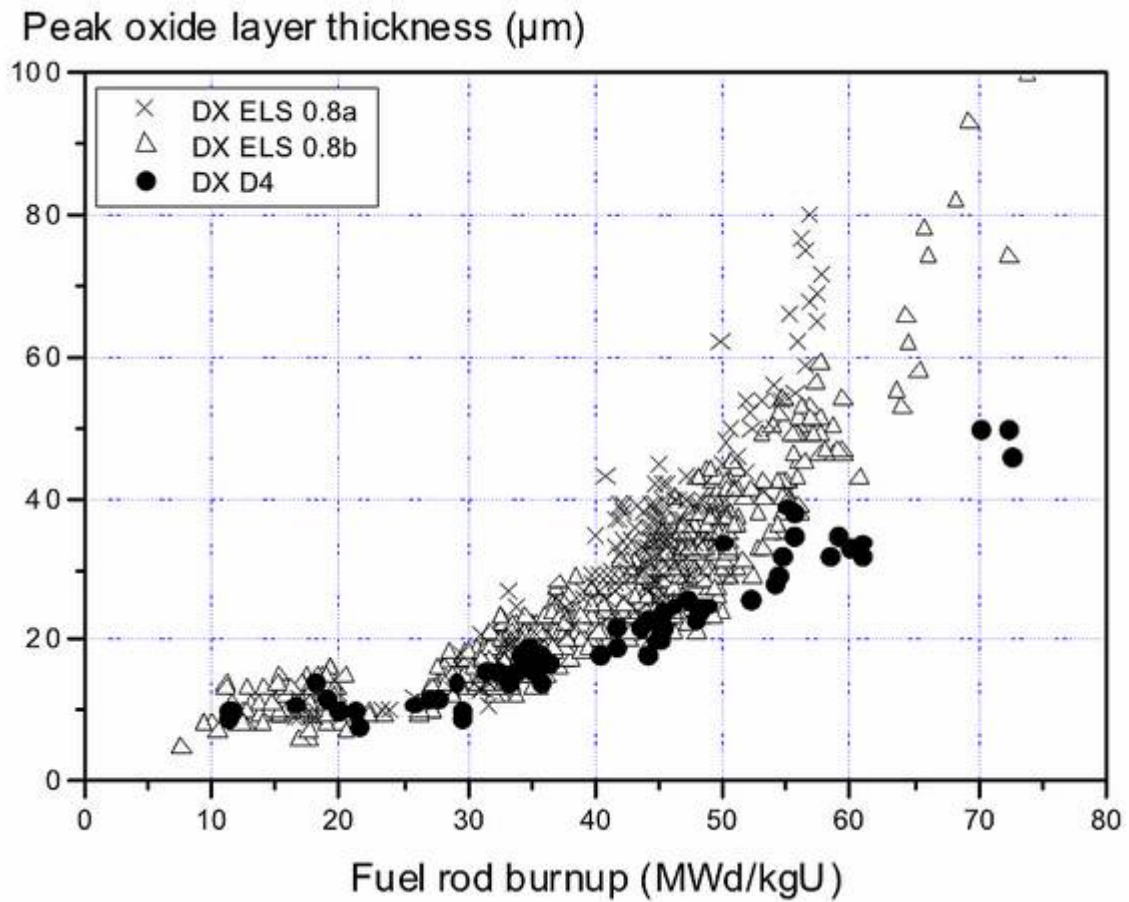


Figure 18
Corrosion Behavior of Several DX ELS Cladding Materials
at High Heat Fluxes [67]

In figure 19 the improved resistance of the duplex claddings against corrosion enhancement by LiOH is shown in terms of Li-content that ingressed the Zr-oxide of the cladding tube during PWR operation.

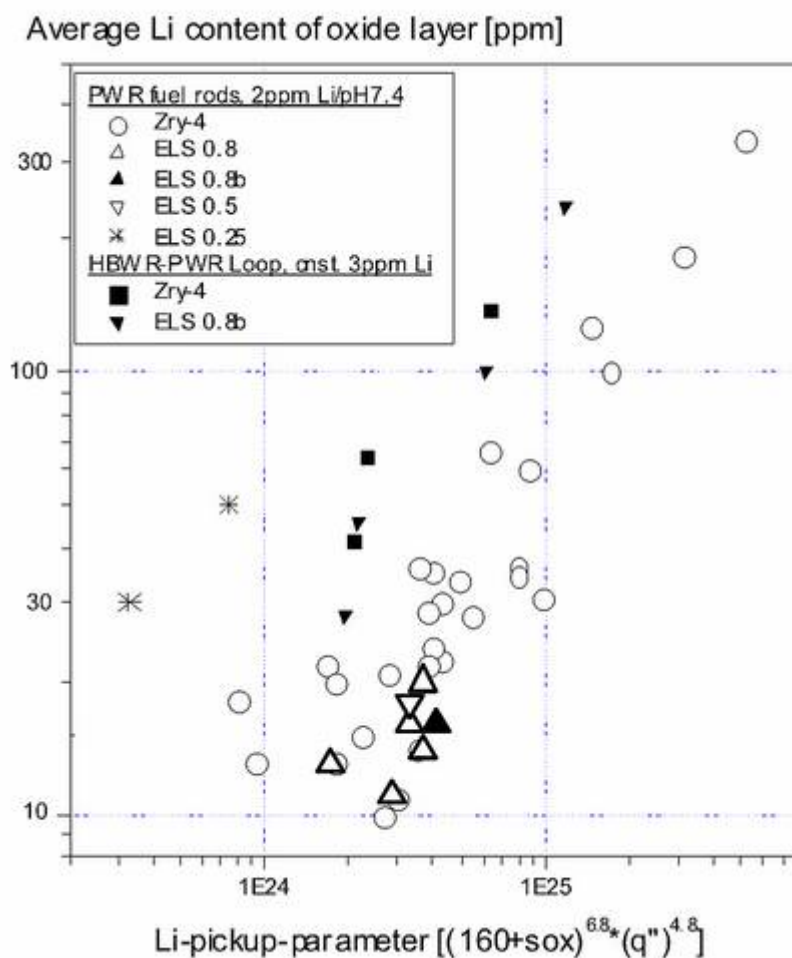


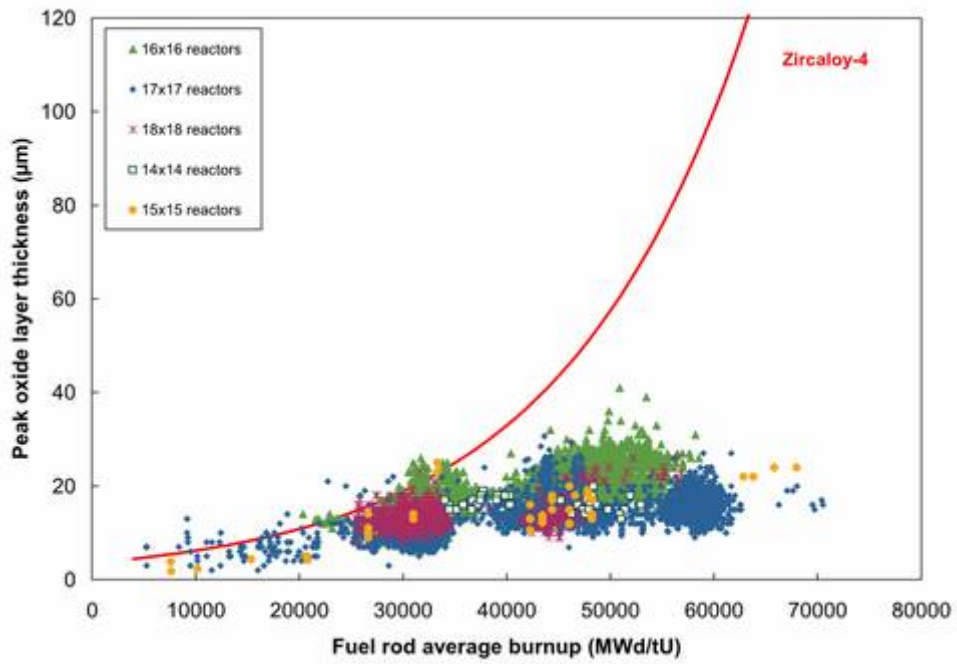
Figure 19
Li-pickup in the oxide layer of PWR Cladding Tubes
Made from Different Zr-Materials [67]

However, as already mentioned in a previous chapter (Zr-Materials Development), in that time it was foreseeable that the further and further increasing burn-up targets will soon call for more advanced materials with further increased corrosion resistance. Also the duplex cladding could not solve the increasing problem with high hydride contents in the FA spacers which in the meanwhile all were made of Zircaloy.

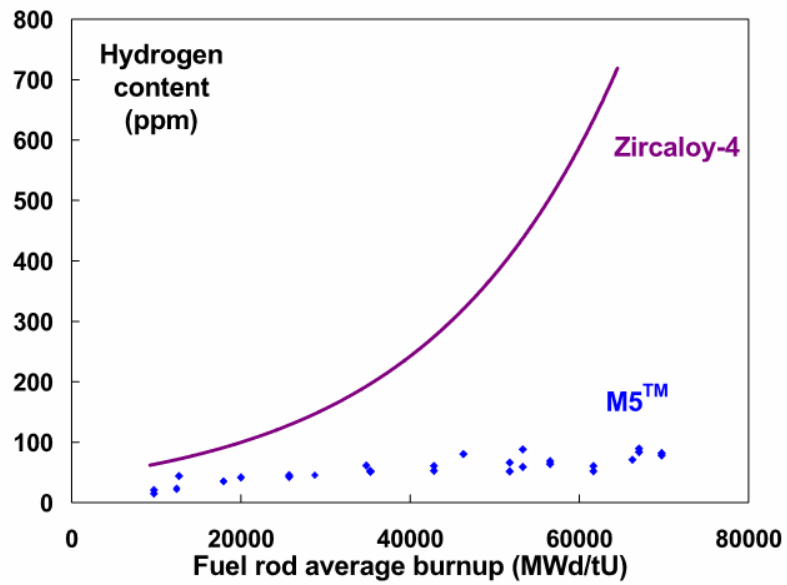
Therefore Zr-materials were needed that were basically different from the Zircaloy-type. This demand led to various research and development activities of different fuel designers in the West.

In France these efforts finally led to the development of a French variant of the in Russia well known Zr-1Nb material which was called M5™. It has been broadly and successfully introduced into the commercial fuel market Figure, as well as cladding material as also as structural material [39].

High corrosion resistance, low hydrogen up-take and good creep and growth behavior could be shown in many PWRs with burn-up of up to 60 MWd/kg_U and above (figures 5, 12, 20).



a



b

Figure 20

Corrosion (a) and Hydrogen Uptake Performance (b) of M5™ Fuel Rods in PWR, Compared with Zircaloy-4 [39]

All together the corrosion (and hydrogen uptake) behavior of M5™ appears to be very satisfactory in fuel rods and FA structures.

However, very recently some strange accelerated corrosion was observed with M5 cladding in a German PWR [69] In figure 21 the deviating corrosion behavior is depicted. Despite immediately started comprehensive investigations a final explanation for this unexpected result is not yet available.

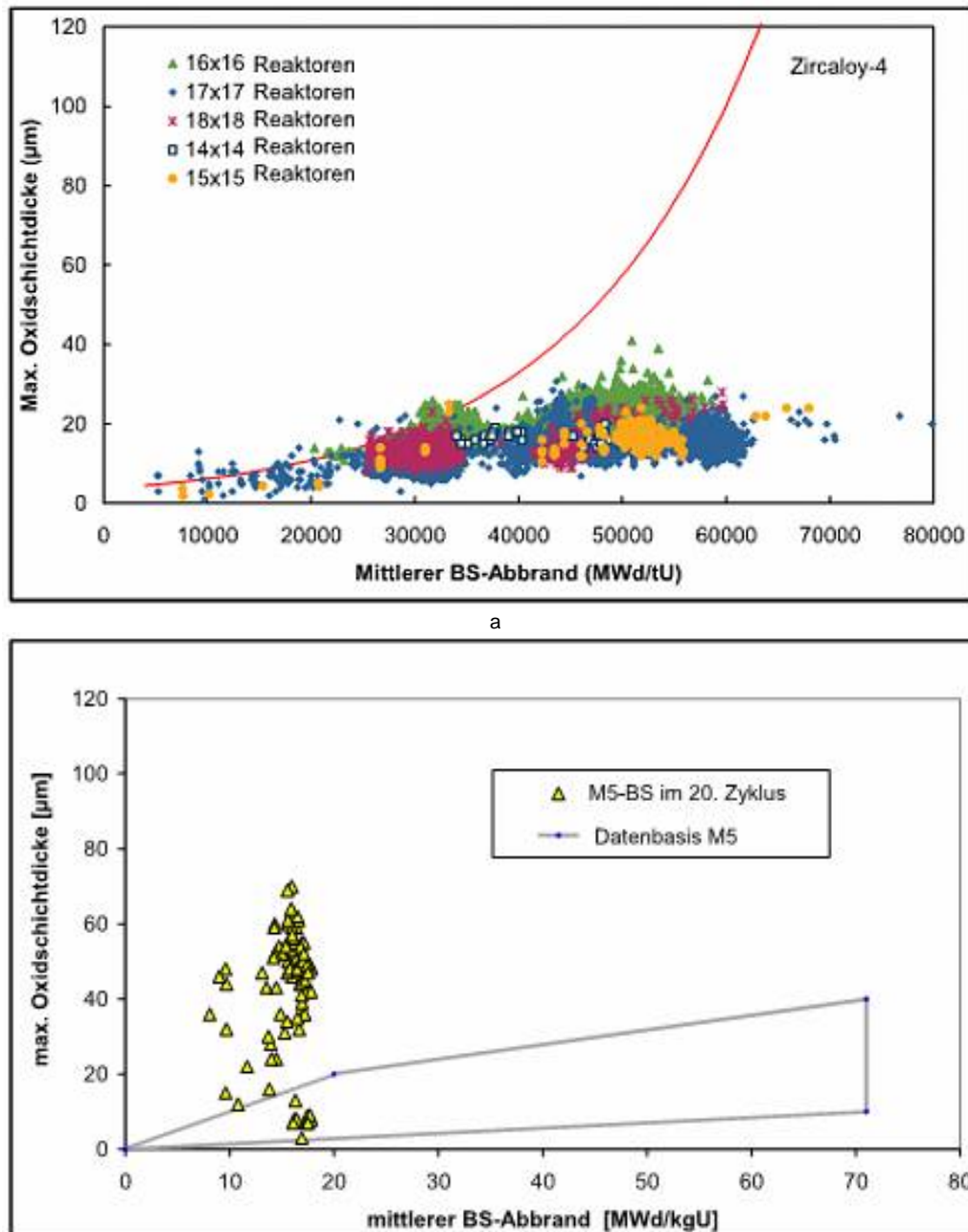


Figure 21

M5™ Corrosion Behavior in a German PWR [69]

- a Normal Behavior
- b Increased Corrosion in Spacer-Span 8

As demonstrated with Lead-Test Assemblies in the Byron plant, low-Tin-ZIRLO (LTZ) of Westinghouse [40] shows significantly improved corrosion resistance as compared with Standard ZIRLO (figure 22).

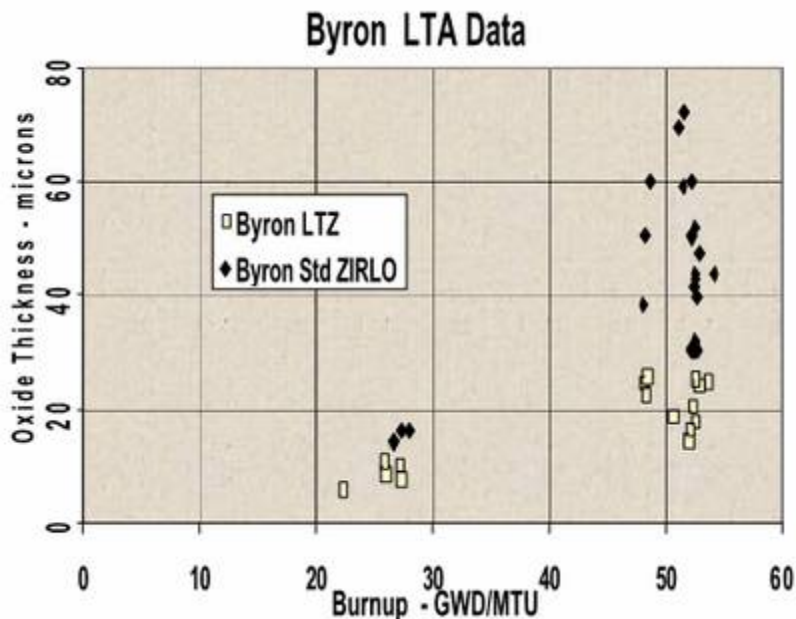


Figure 22 Optimized ZIRLO Corrosion Data [40]

At Siemens parallel to the development of the duplex-cladding, various other chemical compositions were also investigated [70]. It turned out that most promising is a Zr-2.5 material with a special heat treatment [33]. It shows the lowest in-pile corrosion at high burn-up as compared with all other new materials (figure 23). Today it is considered to be a back-up solution as liner material for advanced duplex-claddings.

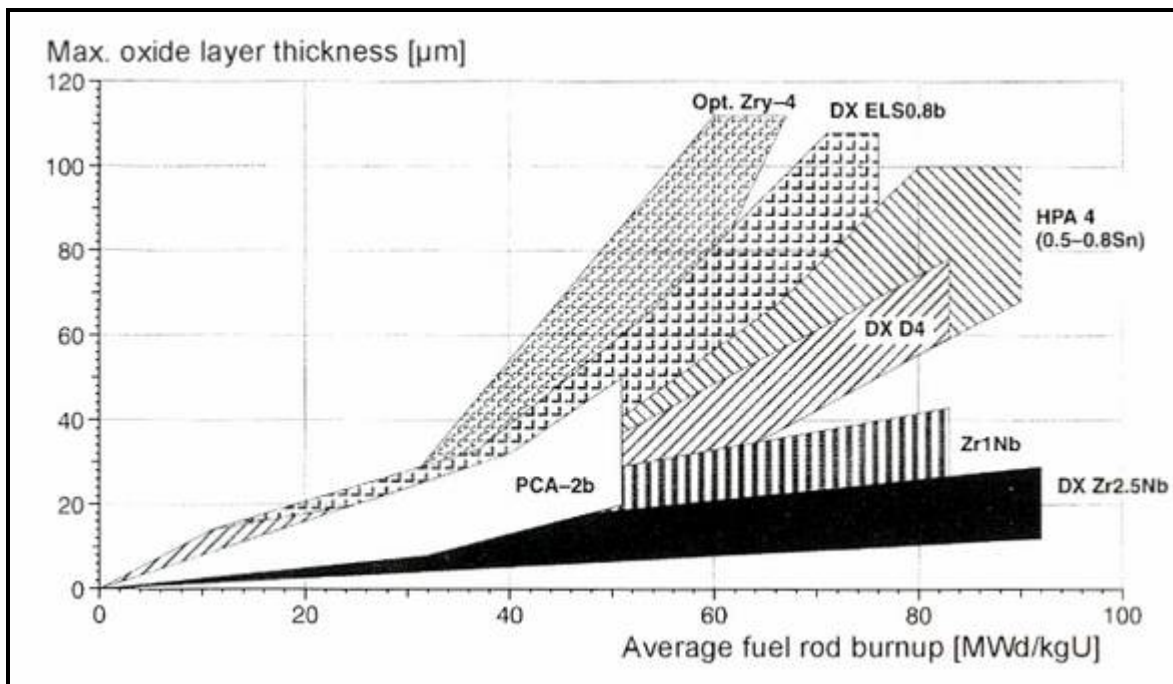


Figure 23 Corrosion Behavior of Advanced Alloys [70]

Due to the different water chemistry in Russian water cooled reactors, corrosion of fuel claddings or other fuel components was never a problem. However, for comparison, the current experience with the corrosion resistance – and the correlated hydrogen up-take - of modern Russian Zr-alloys is shortly discussed.

After 4 – 6 year cycles of operation in VVER reactors to reach fuel burn-up of 55 – 66 MW·day/kg_U the thickness of oxide coating on E-110 claddings is not higher than 15 μm. Recently publishes PIE data [56] show that the oxide film is uniform and dense and with a grey color.

However the thickness of oxide coating on claddings made of E-635 under comparable in-pile condition has been found to be much higher as compared with E-10. In figure 24 the oxide profiles along the surface of fuel rods made of E-110 and E-635 are shown after 3 cycles of operation, i.e. 35 – 40 MWd/kg_U. While the maximum oxide thickness on E-110 is around 5 -10 μm, the oxide thickness on E-635 reaches values around 40 – 50 μm.

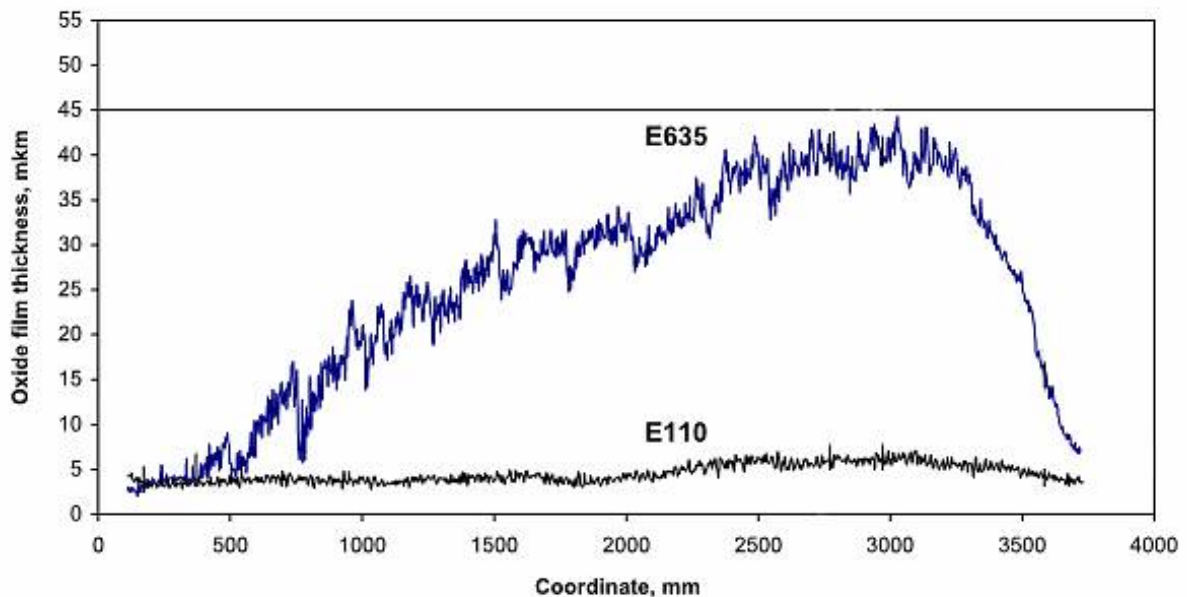


Figure 24

Oxide Film Along the FR Claddings Made of E635 and E110 Alloys after Operation within 3 Fuel Cycles [56].

Average hydrogen content in the FA components (Fig. 25) is practically the same in E 110 and E 635 with a maximum value of 140 ppm when reaching a fuel burn-up of 55 MWd/kg_U.

There are no obvious differences in hydrogen content in the FA components operated under different conditions of loading.

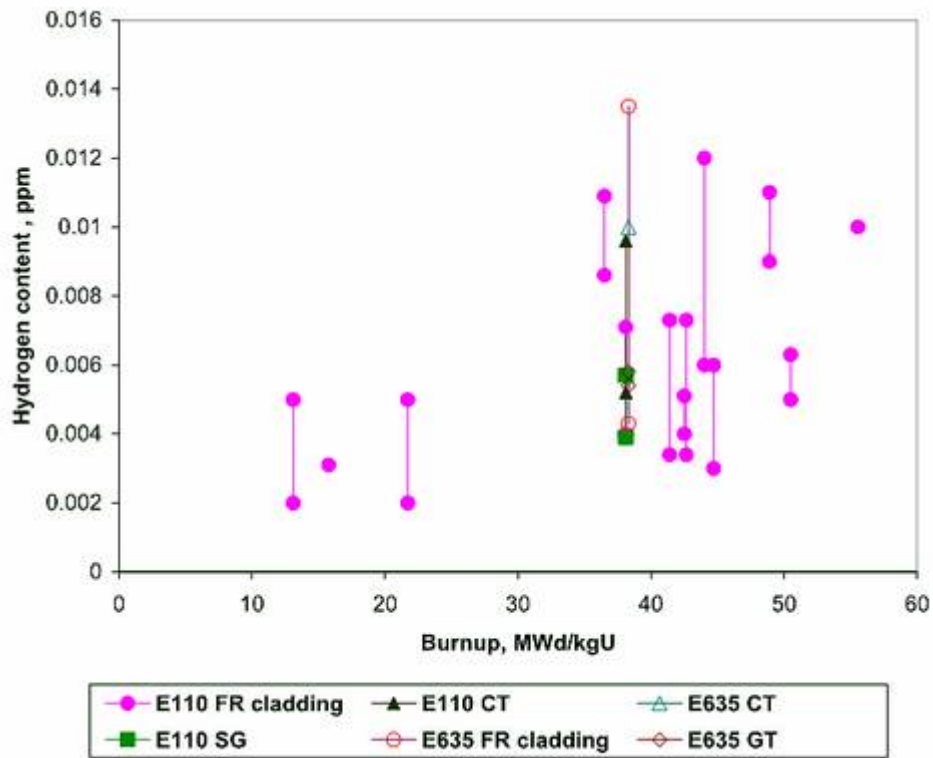


Figure 25
 Hydrogen Content in Fuel Cod Claddings and
 FA-Structure Components, Made of E-110 and E-635 [56]

These values are comparable with those from M5TM and both values show the same margin to values of Zircloy-4 (figure 26)

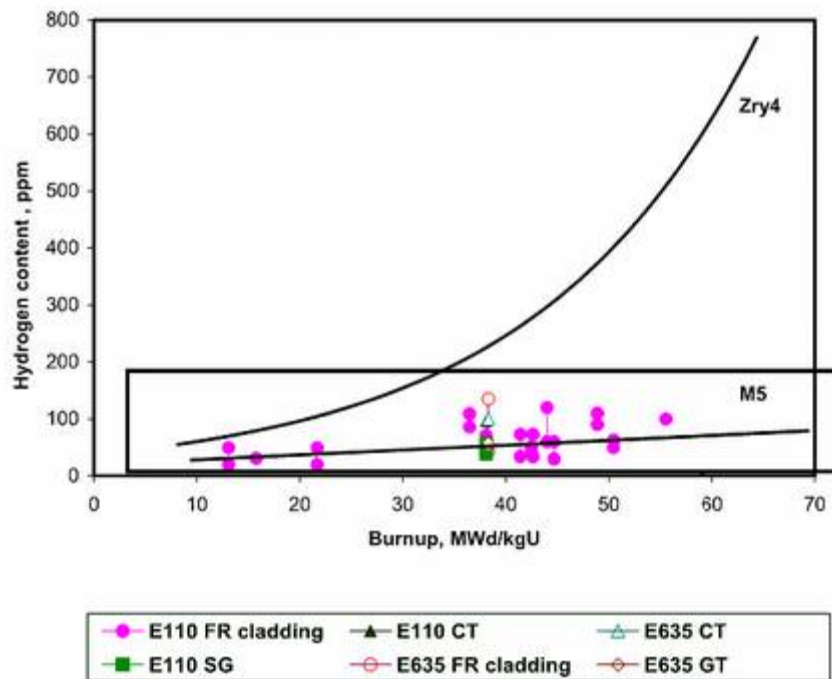


Figure 26
 Comparison of Hydrogen Uptake in E-110, E-635, M5TM and Zircaloy-4 [56]

In RBMK reactor cores fuel rod claddings made of E110 alloy operated successfully for 3 to 4 years, reaching a burn-up of ~ 24 MW·day/kg U. In some areas of the cladding surface nodular corrosion was observed [66], however, with no detrimental impact on the regular operation of the fuel.

While corrosion and hydrogen uptake in Zr-alloys never was a design limiting problem in Russian reactors, the dimensional stability of WER fuel assemblies was a point of serious concern in the past. In the meanwhile these problems have been overcome as shown in figure 27. Nevertheless advanced WER FA designs have been developed with increased FA stiffness [71]. The much better creep and growth properties of E-635 (see chapter “Regular Performance Requirements/Design Relevant Aspects”) will be helpful to further improve the WER FA designs.

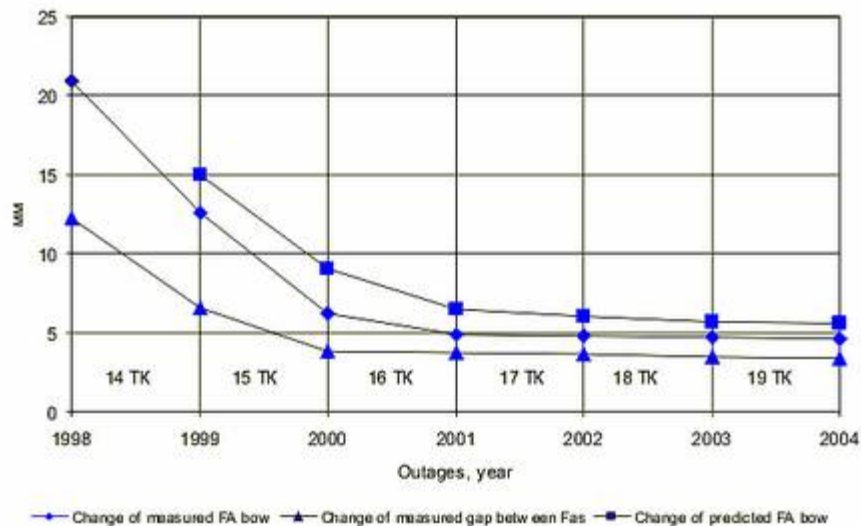


Figure 27
Change of FA bow at WWER-1000 Kalinin-1 [71]

Safety Requirements

LOCA

The subject Zr-material behavior under “Loss-of-Coolant-Accident” (LOCA)-conditions is almost as old as the whole nuclear Zr-technology. It is mainly a feature typical for all kinds of pressurized water reactors, i.e. for Western PWRs as well as for WWERs.

There are two basic concerns:

1. The ballooning of cladding tubes within a certain temperature range of the LOCA transient,
2. oxidation and oxidation embrittlement, mainly of cladding tubes and again in a certain temperature range of the LOCA transient.

Already in the late 1960'ies these concerns were a topic in an ASTM symposium on “Application Related Phenomena in Zirconium and its Alloys” [72]. Some few years later studies have been performed on potential impacts of the irradiation on the LOCA deformation and rupture of cladding tubes during a LOCA transient [73]. Up to today there is agreement that the impact of irradiation is negligible – for all kinds of Zr-cladding-materials so far in use.

From these first investigations a large international effort developed in the 1980'ies resulting in a broad and consistent knowledge on the deformation – and oxidation-behavior of Zircaloy-4 under LOCA conditions in Western PWRs [e.g. 73].

In Russia respective efforts were undertaken with Zr-1Nb cladding tubes [74, 75], also with the result of having collected a broad and consistent knowledge for the LOCA behavior of WWER fuel.

When M5TM was introduced in the Western market in the 1990'ies, new concerns came up with regard to the high temperature deformation and oxidation of this material under LOCA condition. Considerable experimental and modeling efforts [76, 77] were necessary for the French fuel designers to finally convince the licensing authorities in several Western countries that no new LOCA risks would exist with this material.

Also in the 1990'ies new questions came up with regard to the impact of very high burn-up on LOCA behavior of any cladding material. However, so far those concerns could not be confirmed by new investigations.

RIA

The “Reactivity Initiated Accident”, RIA, is a well known potential accident scenario in LWRs since a long time. E.g. a control rod ejection may cause such an accident. Originally there were no concerns with regard to Zr-materials involved. With the continuous increase of burn-up not only the acceptable amount of energy released during such an accident was reconsidered, in particular with regard of a so called “Rim-Effect” in the fuel pellets after high burn-up. Also the potential impact of the oxidized surface of the cladding tube after high burn-up exposure on the degree of destruction of the fuel rod became an issue of concern [78, 79]. Detailed metallurgical investigations have been published, discussing the potential impact of the stresses in the cladding caused by the oxide layer on the cladding and also the impact of corrosion induced hydrides in the cladding [80]. EdF proposed a “Safety Domain for Rod Injection Accidents in PWRs” [81] that includes a requirement of a maximum of 100 µm oxide layer from water-side corrosion to prevent in-reactor cladding oxide spallation and localized hydriding.

These investigations and considerations on a potential contribution of the material properties of Zr-alloys lead to the conclusion that Zr-cladding materials with substantially reduced oxide layer thicknesses on the cladding and hydrides in the cladding will contribute to the mitigation of fuel rod defects caused by RIA-accidents. First results from RIA-experiments with test rods cladded by M5TM appear to confirm this conclusion [77]. However, more experimental evidence from fully representative RIA tests should finally clarify this question.

Future Perspectives

There is no doubt that within the foreseeable future light water reactors will continue to be the backbone of nuclear production of electricity worldwide. The trend for LWR fuel clearly goes to

- further increased burn-up, i.e. at least up to 70 MWd/kg_U for fuel rods, if the enrichment barrier of 5% remains, and to even higher burn-up, possibly up to 100 MWd/kg_U, if 5% enrichment can be exceeded.
- further optimized core management and increased fuel operation flexibility.

Fuel rod cladding and fuel assembly components will continue to be made of Zr-based materials within this period. There are some speculations in the literature that for burn-up ranges above 100 MWd/kg_U, other materials will be needed that are not based on zirconium [82]. However, it is very hard to believe that any other material not based on zirconium will be available with an adequate commercial maturity at least within the next two decades.

Today the in-pile experience of advanced Zr-materials, in particular of the Zr-1Nb alloys has reached a fuel rod burn-up of up to 70 MWd/kg_U, and there is no indication recognizable why those Zr-materials should not reach successfully 80 – 100 MWd/kg_U.

Nevertheless, there is still R&D-work necessary to fully understand the physical mechanism of corrosion, as well as creep and growth of Zr-materials under reactor operation conditions, in particular under representative high burn-up irradiation conditions.

Conclusion

The history of now half a century of Zr-material in nuclear fuel technology is a success story. Many scientists and engineers were and still are involved in this success story.

Of course many lessons had to be learned and also certainly will have to be learned in the future.

For those who could contribute to this success story it always was a fascinating time and for sure it also will be a fascinating work for those who will contribute in the future.

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