Major Findings of E110 Studies under LOCA Conditions

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Brief Characterization of the Data base on the E110 Cladding Behavior under Normal and Accident Conditions

1. <u>Normal operation → very low sensitivity of E110 cladding to the irradiation effects:</u>

Representative values of several parameters at 60 MW d/kg U ⇒

- **Oxide thickness 10 μm**
- **Hydrogen content 50 ppm**
- **Uniform elongation 5 %**

2. <u>Accident conditions:</u>

2.1. RIA:

- **no general differences in the behavior of unirradiated and irradiated claddings at the burnup range 0–50 MW d/kg U**
- **the insignificant decrease of cladding failure threshold at the burnup 60 MW d/kg U (without the fuel dispersal)**

2.2. LOCA:

- **no fragmentation of oxidized claddings (including claddings irradiated to 60 MW d/kg U) at the ECR less than 18 % (in accordance with thermal shock tests performed by Bochvar Institute (VNIINM))**

The Motivation to the Additional Research of the E110 Cladding Behavior under LOCA Conditions

The revealed disagreement between results of thermal shock tests and ring compression tests with E110 oxidized claddings

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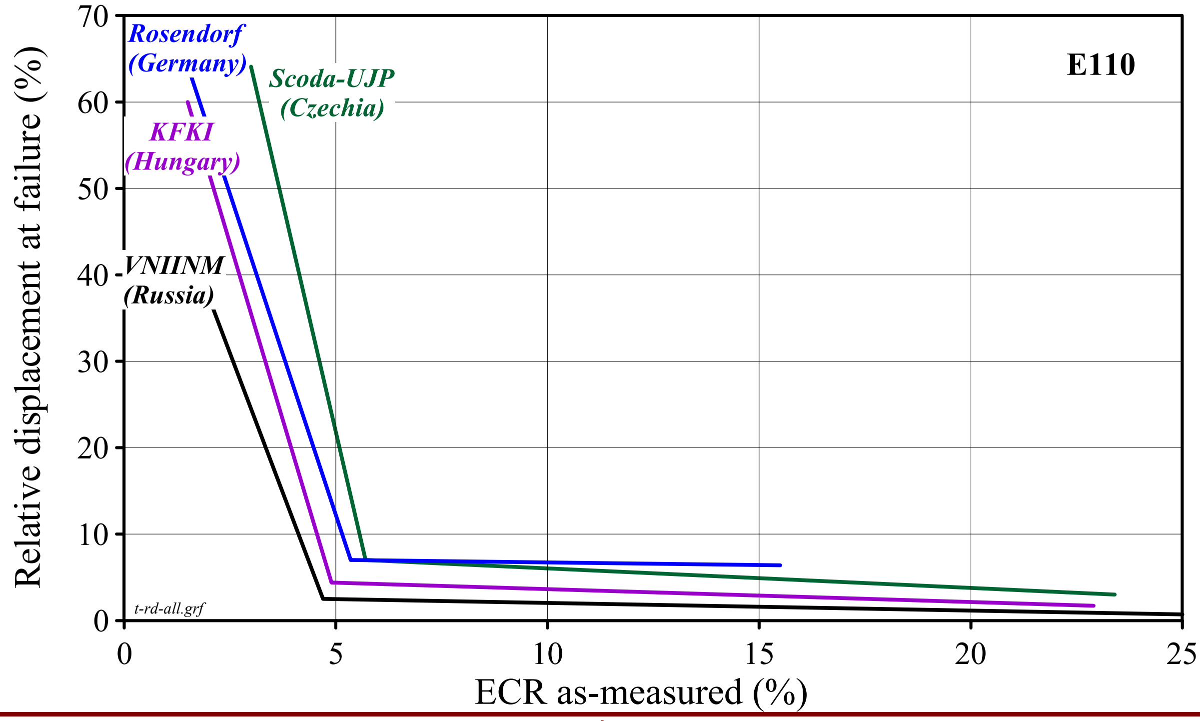
The background of a problem:
Results of mechanical tests (ring compression tests performed in different laboratories)



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Decision:
To reassess the procedure of oxidation and ring compression tests, to estimate the representativity of ring compression tests, to obtain the multiparametric data base characterizing the oxidation and mechanical behavior of E110 cladding and to develop the verified recommendations

Procedure Issues of Ring Compression Tests

The following aspects of the procedure were studied and validated on the basis of special scoping test program:

- **determination of zero-displacement point**
- **interpretation of elastic modulus characteristics**
- **identification of cladding through-wall crack (sample failure) on the load-displacement response**
- **sensitivity studies to determine the relative displacement at failure as a function of sample length (8–25 mm)**

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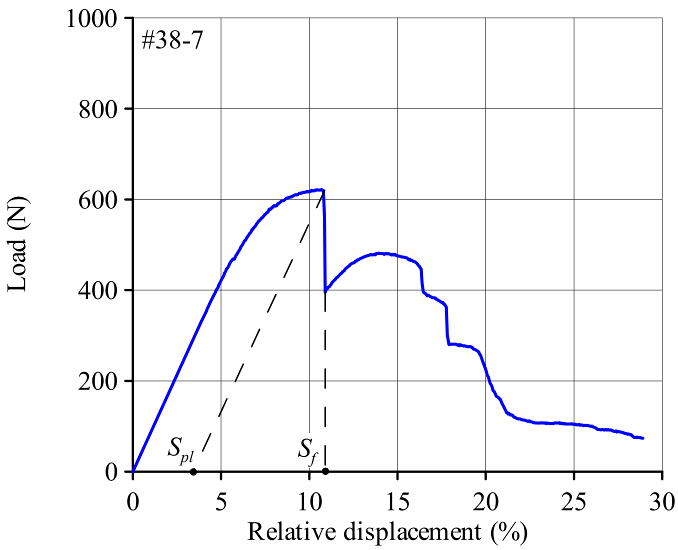
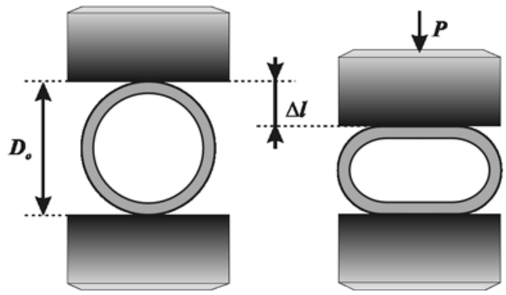
Major provisions of procedure used for the processing of load-displacement diagrams





Δl – grip displacement (mm)

S – relative displacement ($\Delta l/D_o$ 100 %)

S_f – relative displacement at failure

S_{pl} – plastic component of relative displacement

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In the context of this work the plastic component of relative displacement named “residual ductility” was used as the major result of ring compression tests

Major Results of Ring Compression Tests with Standard E110 Cladding

Comparative data to characterize residual ductility and hydrogen concentration as a function of the ECR for E110 and Zry-4 alloys

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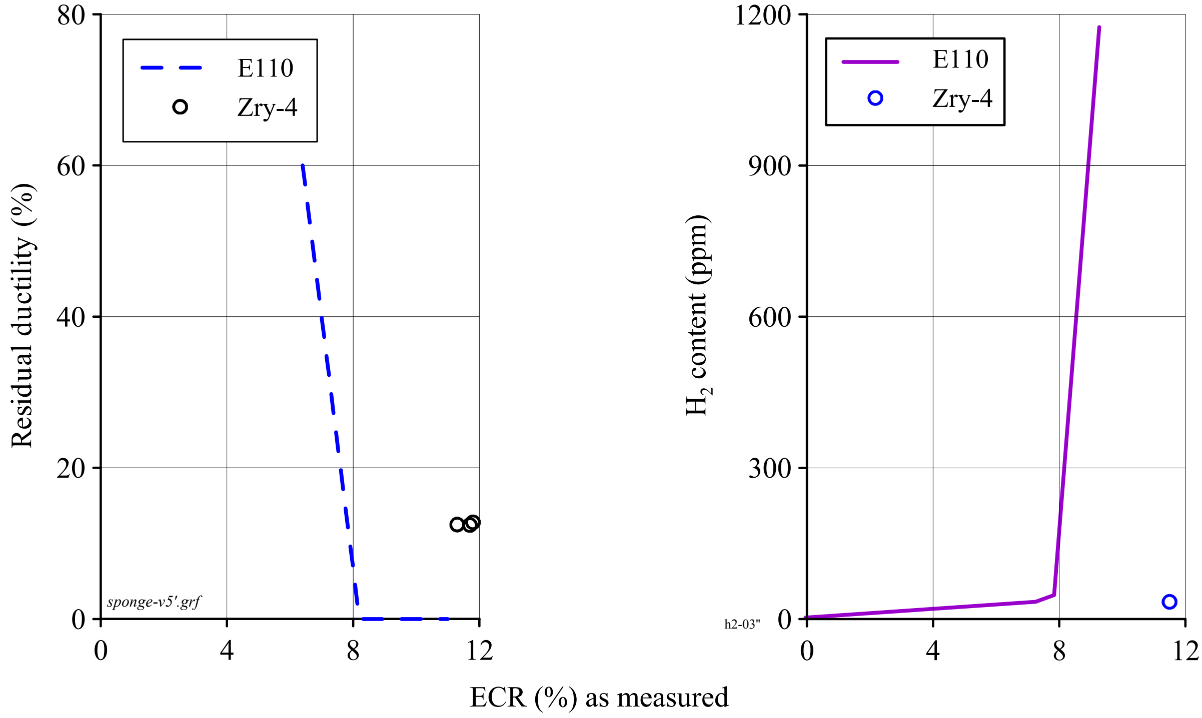
Double-sided oxidation at 1100 C



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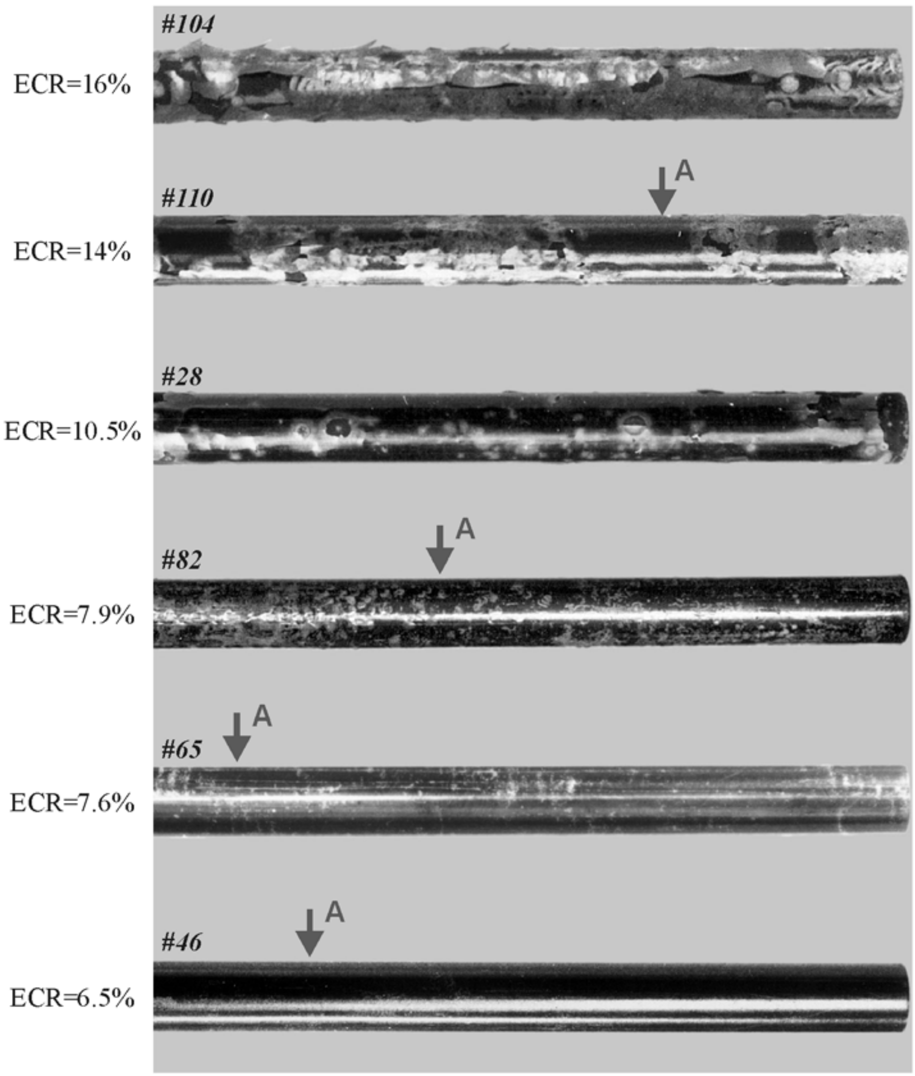
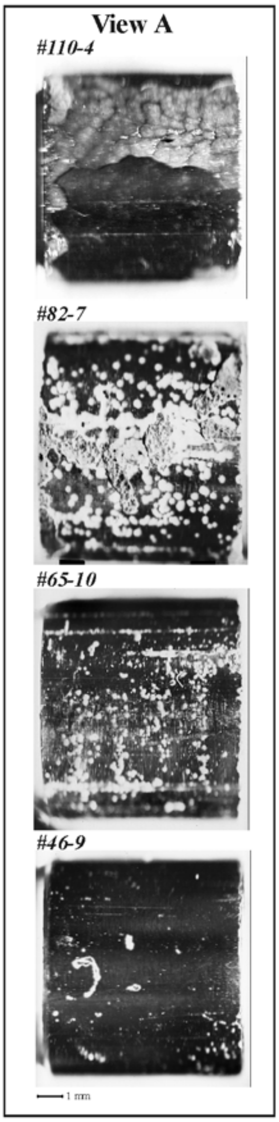
First conclusions:

- ♦ the zero ductility threshold of the E110 alloy is lower than that of Zry-4 alloy
- ♦ the E110 embrittlement threshold is corresponded with the following values of ECR:
  - ➢ 8.3 % (as-measured)
  - ➢ 11.4 % (as-calculated) if Russian E110 conservative kinetics (Bochvar Institute correlation) is used

Additional Experimental Characterization of E110 Cladding Behavior at the High Temperature Oxidation

Appearance of E110 standard as-received tubes as a function of the ECR after a double-sided oxidation at 1100 C and F/F combination of heating and cooling rates





104+110+28+82+65+46.cdr

Preliminary Interpretation of Test Results and the Development of Sensitive Studies Tasks

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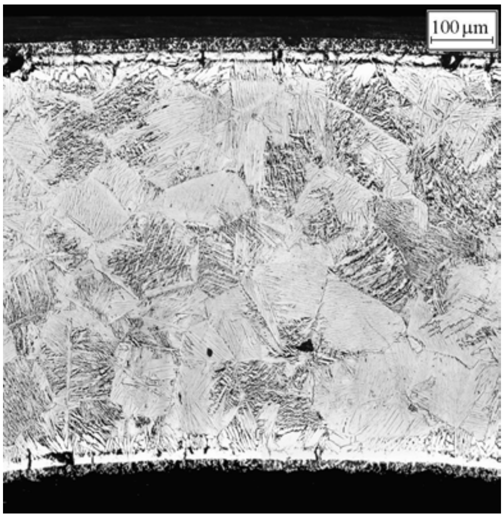
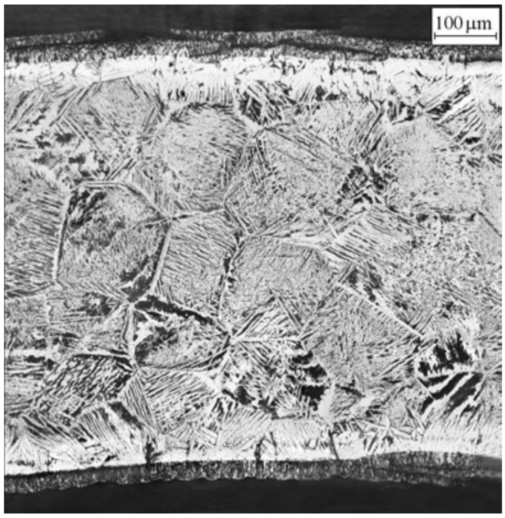
An initiation of the breakaway effect leads to: ♦ the spallation of ZrO_2 oxide; ♦ the intensive absorption of hydrogen	#46-5 ECR=6.5 % 	#30-5 ECR=8.9 % 

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General question:
What is the nature of differences in the oxidation behavior of Zry-4, M5 and E110 alloys?

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Possible answers:

1. Differences in the test condition → heating and cooling rates, oxidation type (single sided, double sided)
2. Differences in the alloying composition → tin concentration, oxygen concentration
3. Differences in the surface state

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Decision: to perform sensitive studies to listed factors

Outline of Sensitive Studies

Varied parameter	Varied range
1. Heating rates at the oxidation	⇒ 0.5 C/s, 30 C/s
2. Cooling rates at the oxidation	⇒ 0.5 C/s, 30 C/s, 200 C/s
3. Oxidation temperature	⇒ 1000–1200 C (800-900 C will be done additionally)
4. Oxidation type	⇒ single sided, double sided
5. Temperature of mechanical tests	⇒ 20, 135, 200, 300 C
6. Type of mechanical tests	⇒ ring compression, ring tensile, three point bending
7. Alloying composition	⇒ standard E110 (Zr-1%Nb), E110K with high oxygen concentration, E635 with Sn, Fe alloying components
8. Surface effects	⇒ as-received E110 tube, as-received E110 cladding (after anodizing and etching), polished as-received E110 tube

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	Major results:
1.	Any variations of above listed parameters do not allow to eliminate the breakaway effect completely
2.	Single sided oxidation, fast heating rate, polishing of cladding tube, rise of temperature of mechanical tests to 135 C lead to the increase of E110 zero ductility threshold by 2–4 % of the ECR
3.	Etching of cladding, decrease of oxidation temperature to 1000 C, slow heating and cooling rates lead to the amplification of breakaway effect
4.	It was not revealed the significant influence of the cladding alloying composition on the embrittlement behavior
5.	The comparative data base characterizing the results of different types of mechanical tests confirms the representativity of ring compression tests
6.	Oxidized and hydrided E110 claddings demonstrate the high ductility at the temperature of mechanical tests above 200 C

The Development of the Next Stage of E110 Research Program

The background of research was based on the following general question:

Why two related zirconium-niobium alloys (M5 and E110) with the similar chemical composition (Zr-1%Nb) demonstrate the different oxidation behavior under LOCA conditions?

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The general answer on the question:

These differences are the reflection of differences in the M5 and E110 fabrication processes

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The additional analysis shown that possible sources of these differences can be determined on the basis of special studies of following effects:

Microchemical effects:

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Differences in the chemical composition of impurities in the Zr ingot:

- **iodide and electrolytic Zr is used for the manufacture of E110 alloy**
- **sponge Zr is used for the manufacture of M5 alloy**

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The first direction of research

- **to perform the oxidation and mechanical tests of E110 cladding tubes manufactured on the basis of sponge Zr**

Microstructure effects:

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Possible differences in the following parameters of the microstructure

- **grain size**
- **phase composition**
- **composition, size, distribution of secondary precipitates**

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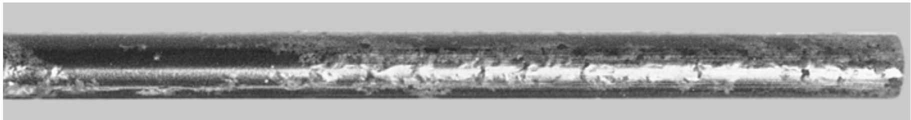
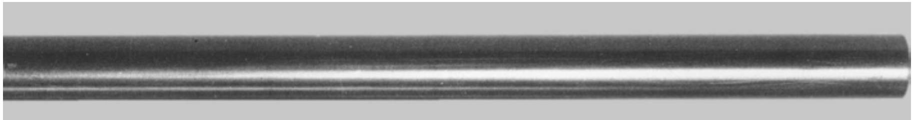
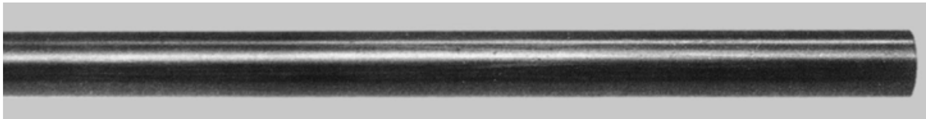
The second direction of research

- **to perform the TEM microstructure examinations of all types of E110 tubes**

The E110 Embrittlement Phenomena Revealed Due to Microchemical Effect Studies

Appearance of the claddings after the double-sided oxidation at 1100 C

E110(standard), 9.8 % ECR	
E110(sponge Zr), 11.6 % ECR	
E110(sponge Zr), 16.7 % ECR	

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Summary of test results at 1100 C

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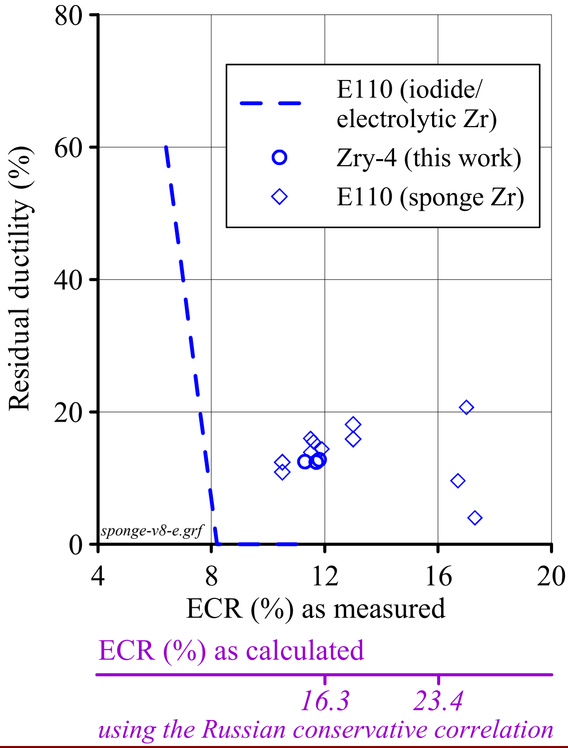
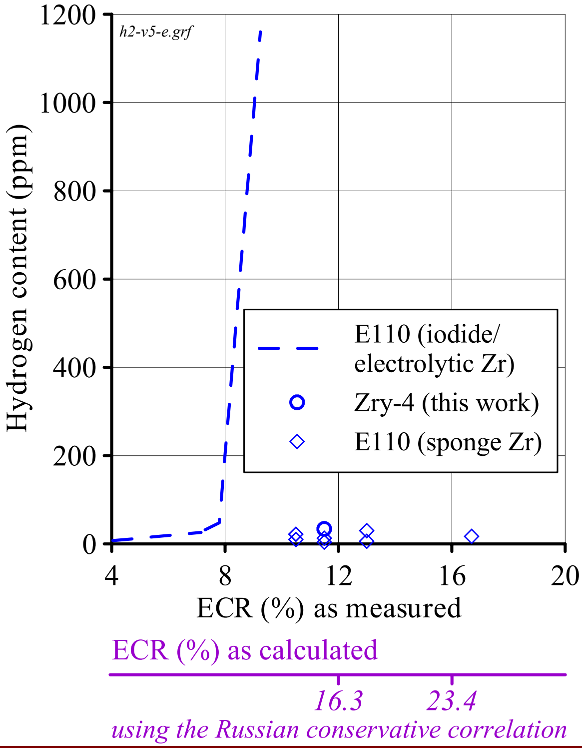
Residual ductility vs ECR



Hydrogen content vs ECR



All claddings manufactured on the basis of sponge Zr have demonstrated a high margin of residual ductility up to 17 % ECR as measured (25 % ECR as calculated)

Results of Microstructure Effect Studies

Background:

In accordance with numerous special investigations the maximal oxidation resistance is devoted at the following parameters of cladding microstructure:

- **maximum degree of the recrystallization**
- **small size of α-Zr grain**
- **uniform distribution of secondary precipitates inside the Zr matrix**
- **small size and high density of distribution of globular niobium precipitates**

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TEM data characterizing the microstructure parameters of zirconium-niobium alloys

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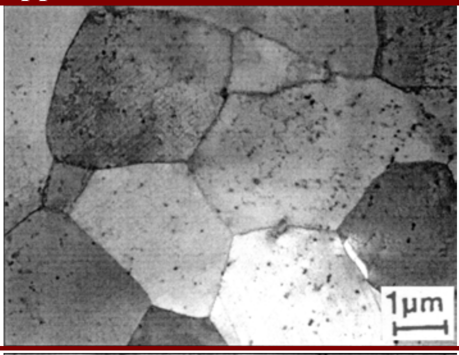
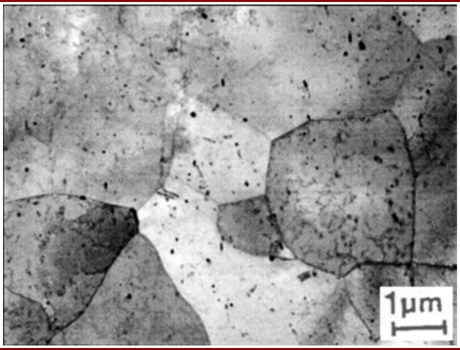
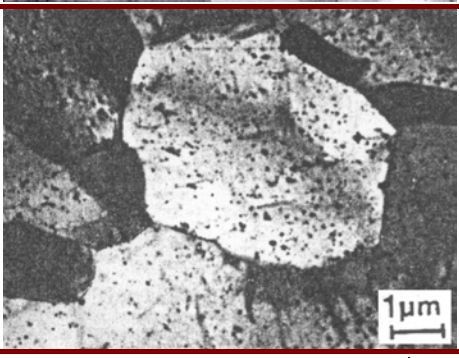
Type of cladding	Appearance of the microstructure	Characterization of the microstructure
E110 Russian as-received tubing fabricated from the mixture of iodide/electrolytic Zr		♦ fully recrystallized structure (αZr matrix with βNb globular precipitates) ♦ grain size 2.8 μm ♦ a high level of dispersion of β-Nb precipitates: D = 45, 60 nm (results of measurements in two laboratories) $N = 1.84 \times 10^{14}$ cm^{-3}
E110 as-received tubing fabricated with sponge Zr		♦ fully recrystallized structure (αZr matrix with βNb globular precipitates and $Zr(Nb, Fe)_2$ precipitates) ♦ grain size 3.2 μm ♦ a high level of dispersion of precipitates ♦ parameters of β-Nb precipitates: D = 41–43 nm (results of measurements in two laboratories) $N = 1.8 \times 10^{14}$ cm^{-3}
M5 as-received tubing (All presented data were taken from D.Gilbon et.al. "Irradiation Creep and Growth Behavior, and Microstructural Evolution of Advanced Zr-Base Alloys", ASTM-STP1354		"Thermodynamically stable microstructure is characterized by a highly refined dispersion of β-Nb precipitates (D = 45 nm, $N = 1.5 \times 10^{14}$ cm^{-3}) with no alignment of particles"

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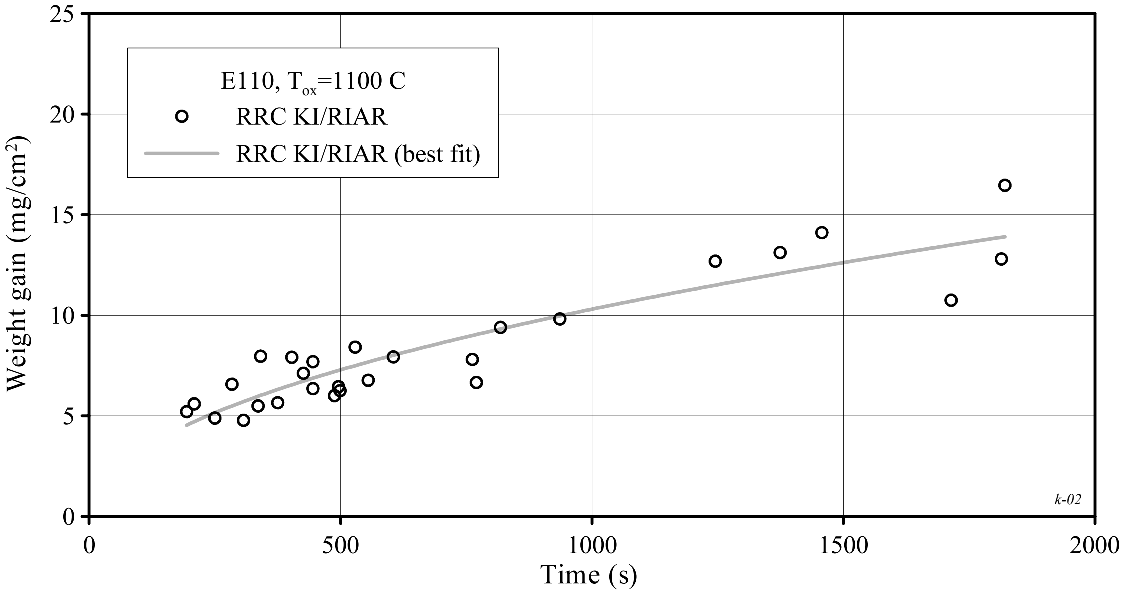
Major conclusions:

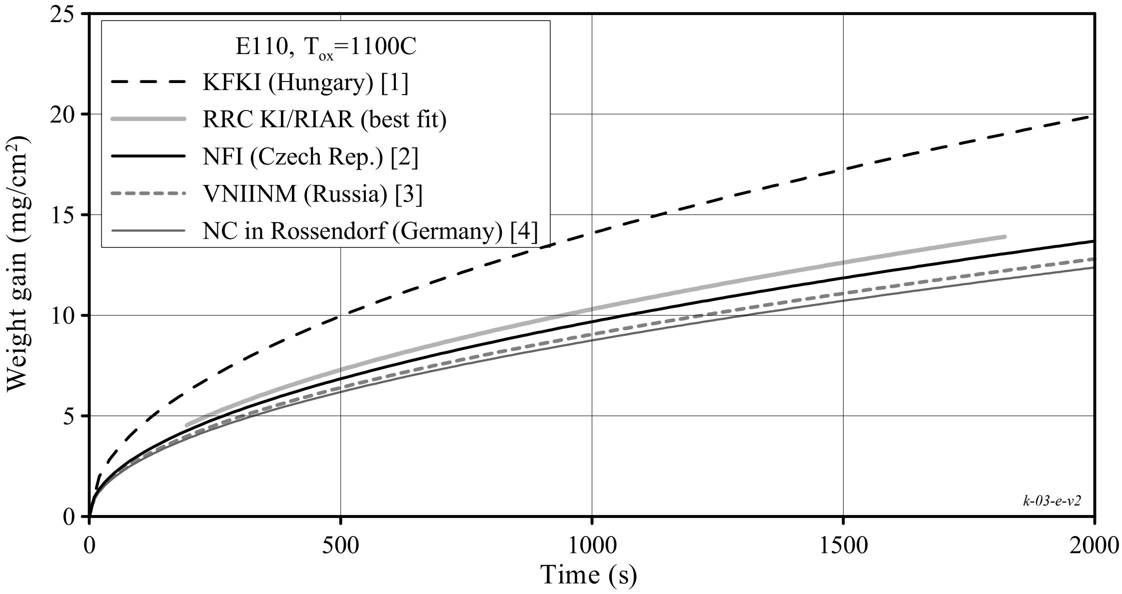
1. **There were not revealed general differences in the microstructures of E110 claddings manufactured from iodide/electrolytic and sponge Zr**
2. **Appearances and parameters of microstructure of these cladding materials are similar to these for M5 alloy**
3. **It can be assumed that differences in the oxidation behavior and embrittlement thresholds of these alloys are not a direct function of fabrication process**

The Characterization of Other Important Phenomena Revealed in the Frame of This Work

1. The E110 (iodide/electrolytic Zr) oxidation kinetics estimated on the results of this work



2. The comparative data characterizing the E110 (iodide/electrolytic Zr) oxidation kinetics



[1] Cs. Gyori et. al. "Extension of Transuranus code applicability with niobium containing cladding models (EXTRA)". *Proceedings of FISA-2003 Conference EU Research in Reactor Safety*, 10.11.2003-13.11.2003, EC Luxembourg

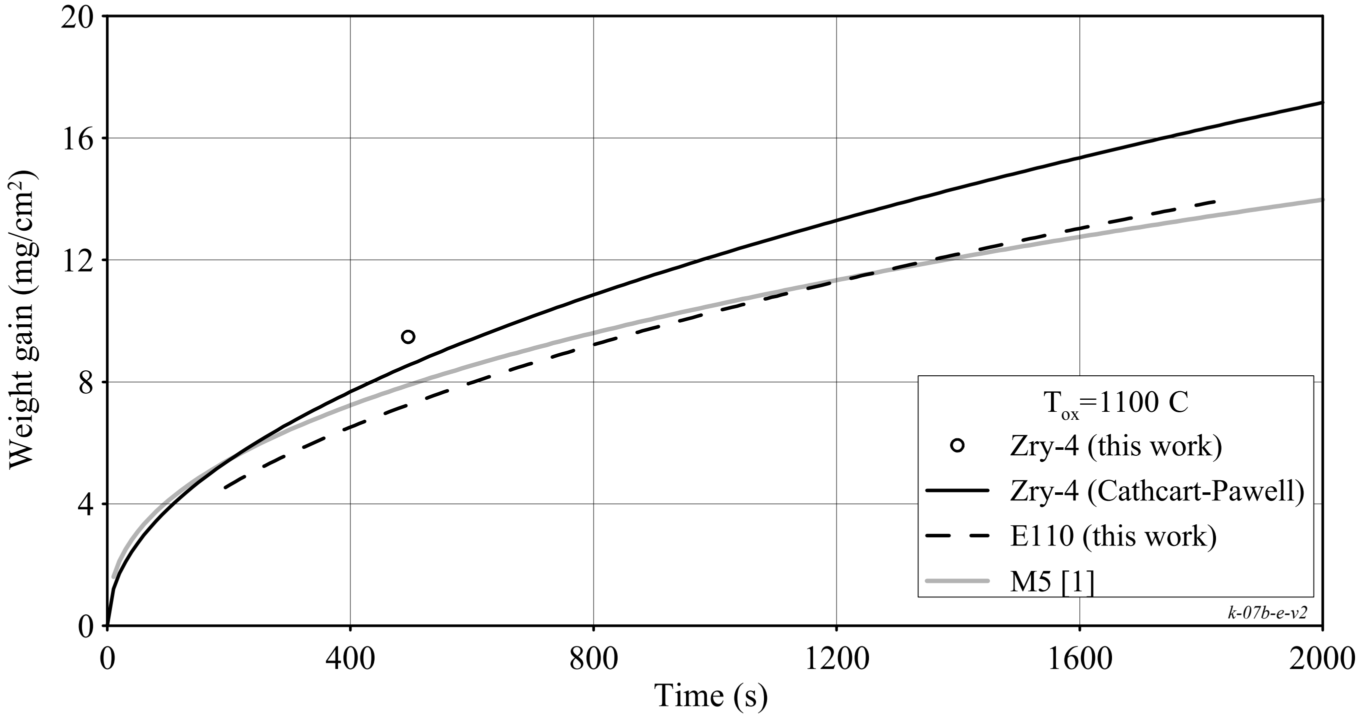
[2] Vrtilkova V., Valach M., Molin L. "Oxiding and Hydrating Properties of Zr-1%Nb Cladding Material in Comparison with Zircaloys", *Proc. of IAEA Technical Committee Meeting on "Influence of Water Chemistry on Fuel Cladding Behavior"*, Rez (Czech Republic), October 4-8, 1993.

[3] Yu.Bibilashvili, N.Sokolov, A.Salatov, L.Andreyeva-Andrievskaya, O.Nechaeva, F.Vlasov "RAPTA-5 code: modelling behaviour of VVER-type fuel rods in design basis accidents verification calculations". *Proceedings of IAEA Technical Committee on Behaviour of LWR Core Materials under Accident Conditions*, held in Dimitrovgrad, Russia, on 9-13 October 1995. IAEA-TEC-DOC-921, Vienna, 1996, pp.139-152.

[4] J.Böhmert, M.Dietrich and J.Linek "Comparative studies on high temperature corrosion of ZrNb1 and Zircaloy4", Nuclear Engineering and Design, v. 147, pp.53-62, 1993.

The Characterization of Other Important Phenomena Revealed in the Frame of This Work (continued)

3. The comparative data characterizing the E110 (iodide/electrolytic Zr), Zry-4, M5 alloys



[1] J.P.Mardon, N.Waeckel, "Behavior of M5™ alloy under LOCA conditions", *Proceedings of TopFuel-2003 "Nuclear Fuel for Today and Tomorrow Experience and Outlook" Conference*, Wurzburg, Germany, March 16-19, 2003.

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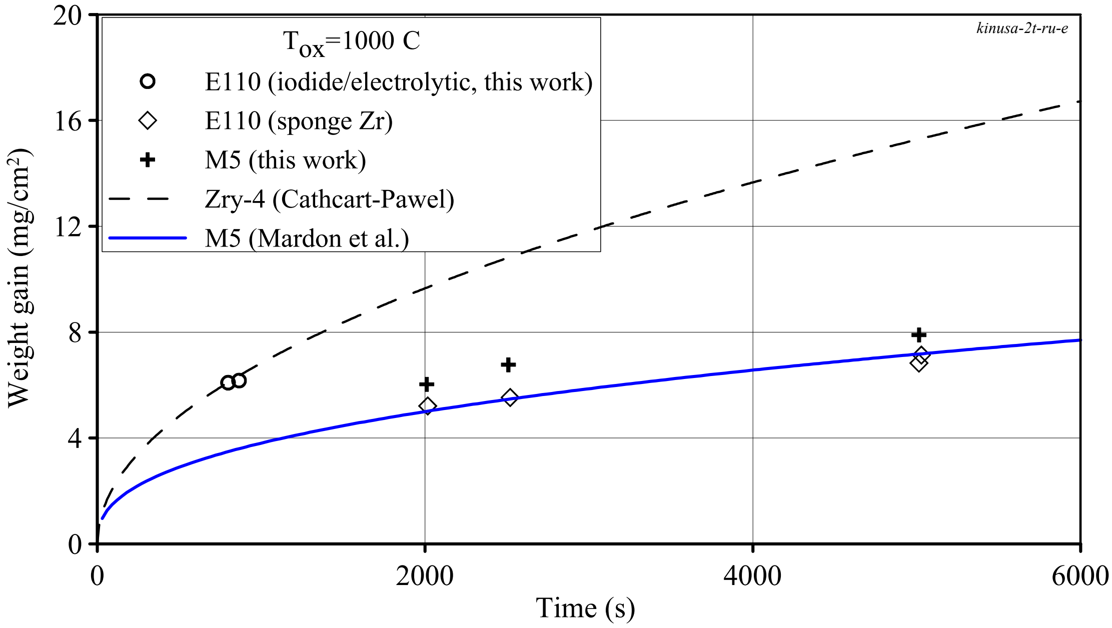
Conclusions:

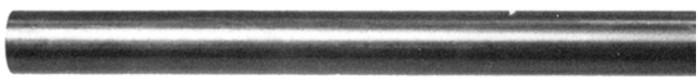
1. **The data base with results of measurements of the E110 weight gain as a function of oxidation time is characterized the high dispersion caused by the breakaway effect**
2. **The regression dependence for the E110 (iodide/electrolytic Zr) oxidation kinetics obtained on the results of this work is in a good agreement with VNIINM, NFI and NC in Rossendorf correlations. The data obtained in the KFKI overestimate the oxidation kinetics**
3. **The E110 oxidation kinetics at 1100 C is in the reasonable agreement with appropriate published data for the M5 cladding**
4. **The oxidation rate at 1100 C of zirconium-niobium alloys is some less than that for the Zry-4 alloy**

The Next Two Important Phenomena

4. The unpredicted oxidation kinetics of zirconium-niobium alloys manufactured from the sponge Zr at 1000 C



Appearance of two types of E110 claddings after the oxidation at 1000 C

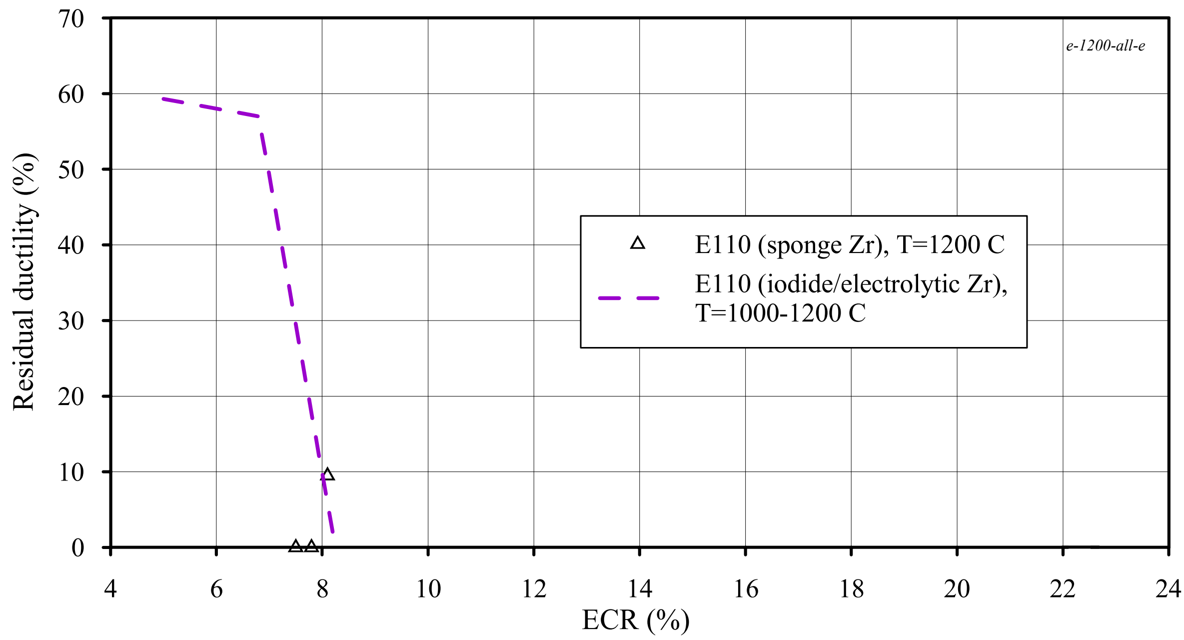
E110 (iodide/electrolytic Zr) ECR=7.7%	t_{ef}=865 s	
E110 (sponge Zr) ECR=8.9% (H_2→11 ppm)	t_{ef}=5028 s	

Conclusions:

1. The general differences in the oxidation behavior of two types of E110 claddings were revealed:
- the oxidation rate of E110 cladding manufactured from the sponge Zr is much less than that for the E110 cladding manufactured from iodide/electrolytic Zr
- ~800 s of the oxidation are needed to achieve the zero ductility threahold for the E110 cladding manufactured from the iodide/electrolytic Zr
- ~5000 s and more are needed to achieve the zero ductility threshold for the E110 cladding manufactured from the sponge Zr
2. The oxidation kinetics of E110 claddings manufactured from the sponge Zr and M5 cladding are in a good agreement at 1000 C
3. The oxidation kinetics of zirconium-niobium alloys at 1000 C are much slower than that for the Zry-4 alloy
4. Such durations of the oxidation as 5000 s are outside of the practical interest for the large break LOCA safety analysis. In this context, the question about the representativity of the ECR as the universal safety criterion could be formulated

(continued)

5. The problem of 1200 C



Conclusions:

1. **In accordance with first results the zero ductility threshold of two types of E110 claddings is not differed**
2. **The decrease of zero ductility thresholds of all types of claddings (Zry-4, Zirlo, M5) at 1200 C was confirms with results of current ANL research program (see the presentation prepared by M. Billone)**
3. **It can be assumed that the change of embrittlement mechanism occurs at this temperature**

Summary

1. **The research program was performed to study the embrittlement behavior of E110 cladding under LOCA-relevant conditions**
2. **The first stage of this program allowed to reveal the following:**

- **the oxide formed on the E110 cladding surface demonstrated the tendency to the spallation at the ECR more than 6 % (breakaway effect);**
- **this processes was accompanied with the hydrogen absorption by the cladding;**
- **the high hydrogen concentration in the cladding material is the reason of the cladding embrittlement (zero ductility threshold) at the 8.3 % as-measured ECR (11.3 % as-calculated using the conservative E110 oxidation kinetics).**

3. **Multiparametric sensitive studies performed with the variation of such factors as: heating and cooling rates, oxidation temperature, oxidation type and temperature of mechanical tests (20–135 C) have shown that any combinations of these parameters do not allow to eliminate the breakaway effect completely. Additional tests performed with the variation of alloying composition (oxygen, iron, tin) in the zirconium-niobium alloy have led to the same conclusion**
4. **The special subprogram of research was devoted to the determination of cladding response on the initial surface state. There were revealed that the etching enhances the breakaway effect and the polishing slows down the negative evidences of this effect**
5. **The second stage of the program was based on the assumption that zirconium-niobium alloys have the significant sensitivity to the initial microchemical composition of the alloy (composition of impurities) under high temperature oxidation conditions**
6. **Taking into account this assumption the comparative test data base was developed using E110 claddings manufactured in accordance with two different methods of the alloy fabrication:**

- **the iodide/electrolytic method (traditional method of the E110 fabrication);**
- **the method based on the preparation of the sponge zirconium (modified method of the E110 fabrication).**

7. Results of appropriate tests allowed to reveal the following:

- **the black protective oxide is formed on E110 claddings manufactured on the basis of sponge zirconium;**
- **the hydrogen concentration in the oxidized modified claddings was very low;**
- **the significant margin of residual ductility in the E110 cladding was fixed to the 17 % as-measured ECR at the oxidation at 1100 C;**
- **800 s of the oxidation are needed to achieve the zero ductility threshold for standard E110 cladding at 1000 C and 5000 s of the oxidation do not allow to achieve the zero ductility threshold of E110 cladding manufactured on the basis of sponge Zr;**
- **the zero ductility thresholds of two types of E110 claddings are not differed at 1200 C.**