UNITED STATES NUCLEAR REGULATORY COMMISSION

Office of Nuclear Regulatory Research

SUMMARY OF RUSSIAN RESULTS ON LOCA-RELATED TESTING OF NIOBIUM-CONTAINING CLADDING ALLOYS

Preliminary Results Reported by

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Office of Nuclear Regulatory Research

NRC

Argonne National Laboratory

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MID-YEAR REVIEW OF KURCHATOV's FUEL PROGRAM
at
ARGONNE NATIONAL LABORATORY
May 20-21, 2003

IRSN (France) and NRC jointly sponsor fuels research at the Russian Research Center (Kurchatov Institute), and additional support for this work is provided by Russian internal sources. Current emphasis is on understanding the cause of low post-LOCA ductility in some Russian niobium-bearing cladding alloys in contrast to better post-LOCA ductility in Zircaloy-4 and the niobium-bearing cladding alloys (M5 and ZIRLO) used in the U.S.

HIGHLIGHTS OF THE MEETING INCLUDE

! **General:** Cooperation between the ANL and Kurchatov researchers (and between French and American sponsors) provides a very effective means of discovering the cause(s) of low post-LOCA ductility in some niobium alloys so ductility can be controlled and ensured. Experimental techniques have been cross checked between laboratories, and each laboratory has multiple cladding materials that can be tested in the same apparatus by the same technicians.

Cladding materials being tested at two laboratories

ANL	RRC - Kurchatov Institute
Zircaloy-4 (Zr-1.3%Sn)	Zircaloy-4 (Zr-1.4%Sn, control sample)
Zircaloy-2 (Zr-1.4%Sn)	
E110 (Zr-1%Nb, standard Russian as-received tubing)	E110 (Zr-1%Nb, standard Russian as-received tubing)
E110 (Zr-1%Nb, etched and anodized standard E110 cladding)	E110 (Zr-1%Nb, etched and anodized standard E110 cladding)
M5 (Zr-1%Nb)	E110K (Zr-1%Nb, high oxygen like M5)
	E110x (Zr-1%Nb, low Hf, modified cold work)
	E110xx (Zr-1%Nb, 70% Russian sponge Zr , 30% electrolytic Zr and recycled scrap, fabricated by the Russian process
	G110 (Zr-1%Nb, fabricated with French sponge Zr by the Russian process)
ZIRLO (Zr-1%Nb-1%Sn-0.1Fe)	E635 (Zr-1%Nb-1.2%Sn-0.35Fe)

HIGHLIGHTS CONTINUED (2)

- ! **RRC-KI** White nodular oxide (mostly monoclinic) accumulates on E110 and becomes extensive around 7-9% ECR, accompanied by a rapid increase in hydrogen absorption and a rapid decrease in post-LOCA ductility.

- ! **RRC KI** Susceptibility of E110 to nodular oxidation is most pronounced at ~1000^{o} C.

- ! **RRC KI** Embrittlement thresholds of standard E110, etched and anodized E110, E110K, and E635 are approximately the same.

- ! **RRC-KI** G110, low-Hf E110, and polished E110 show substantially improved oxidation behavior (good black tetragonal oxide) with significant delay in onset of nodular oxidation.

- ! **RRC-KI** Weight-gain rate (i.e., oxidation rate) at 1000^{o}C is much slower for G110, low-Hf E110, and polished E110 than for standard E110 because of delay in onset of nodular oxidation (i.e., oxidation kinetics are much faster for the monoclinic form of the oxide than for the tetragonal form).

HIGHLIGHTS CONTINUED (3)

! **RRC-KI** Loss of ductility occurs at about the same ECR value (~8%) at 1000^{o}C for G110 as for standard E110, but at very much longer time (5000 s vs. 800 s) -- beyond range of interest for LOCA.

! **RRC-KI** ECR also depends on cladding thickness so that ECR may not be best means of characterizing post-LOCA ductility.

! **RRC-KI** Preliminary TEM work shows two classes of precipitates: small precipitates that are rich in Nb and large precipitates that are low in Nb and rich in Ca, Fe, Cr, Zn -- the latter type being present only in G110.

! **RRC-KI** 3-point bend tests and ring tension tests have not been completed, but preliminary results are consistent with results from ring compression test.

! **ANL** Polishing the surface of E110 substantially delays the onset of nodular oxidation (confirmed at RRC-KI).

HIGHLIGHTS CONTINUED (4)

- **ANL** Etching the relatively rough outer and inner surfaces of E110 results in extensive monoclinic oxide film formation and suggests that F from the etchant (common pickling solution used by many manufacturers) might promote early breakaway oxidation. N.B. Some fuel rods are etched after welding end plugs, and the tubing used for testing might not have been etched (e.g., the Robinson rods and their archive tubing).

- **ANL** Extensive nodular oxidation, delamination, and spallation allow rapid increase in hydrogen absorption (confirmed at RRC-KI).

- **ANL** The effect of the valence of Nb and impurity elements in the oxide was postulated. Nb with its +5 valence requires extra O atoms around the Nb to maintain charge balance, and these extra O atoms promote the growth of monoclinic oxide structure (rather than the more symmetric tetragonal oxide form). Elements with +2 (Ni, Ca, Mg) valence (e.g., Ca) or +3 valence (e.g., Fe) play the opposite role and favor tetragonal oxide formation.

- **ANL** Preliminary TEM work shows two classes of precipitates: small precipitates that are rich in Nb and have no Fe, and large precipitates that are low in Nb but have a lot of Fe. Nb-rich precipitates appear clustered in the only specimen examined to date (thus not conclusive). Clusters of Nb would promote nodular monoclinic oxide growth, consistent with that observed in E110.

SOME WORKING HYPOTHESES (STILL VERY TENTATIVE)

! All Nb-containing alloys are subject to nodular oxidation (i.e., the formation of white monoclinic oxide that is not protective) because of the +5 valence of Nb.

! Zircaloys with Sn (and without Nb) are not subject to nodular oxidation from a valence effect because Sn does not go into the ZrO_2 lattice (Sn has very low solubility in the oxide).

! More than one factor can delay nodular oxidation in Nb alloys
   " Polishing is good and etching is bad (confirmed)
   " Uniform distribution of Nb-rich precipitates may be good (rapid beta quench?)
   " Ca impurity (+2 valence) may be good (Ca contamination during Kroll process?)
   " Higher level of Fe, Cr, Al, Ni, and Cu impurities may be good (related to zircon ore?).

! Reduced critical ECR (ECR corresponding to loss of ductility) is seen even for G110 at 1000^{o}C with delayed breakaway oxidation, and this suggests that there are two mechanisms (perhaps, H embrittlement and O embrittlement) for reduced post-LOCA ductility.

WORKING HYPOTHESES CONTINUED

! Nodular oxidation is more prevalent at lower temperatures (worse at 1000^{o}C than at 1200^{o}C), so post-LOCA ductility might be more limiting for small-break LOCAs than for large-break LOCAs.

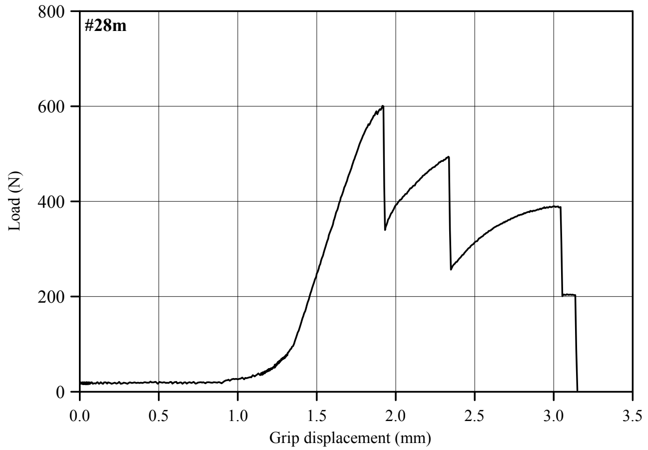
! Oxidation kinetics for niobium and tin alloys are significantly different at 1000^{o}C, whereas they are about the same at 1200^{o}C (~2200^{o}F).

! Because of variations in cladding thickness (e.g., 15x15 vs. 17x17) and large variations in oxidation kinetics at lower temperatures (e.g., Zircaloy vs. M5, and Zircaloy vs. advanced E110), ECR characterization may be misleading. Weight gain or time at temperature might be better metrics, particularly at temperatures $\leq$ 1050^{o}C.

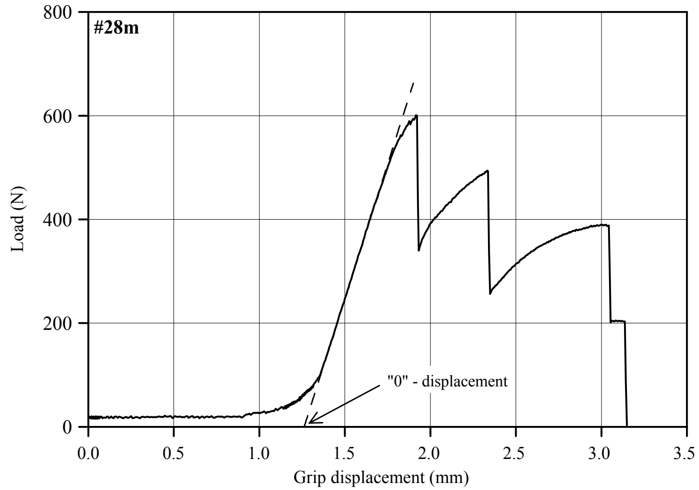
Updates of the work on E110 by the two labs will be presented at ANL in July, along with results on M5 and ZIRLO, and presentations are expected at NSRC-2003 in October. We expect to complete the work at both labs on alloy effects in unirradiated cladding by December 2003.

Processing of load-displacement curve

1) Initial "load-grip displacement" diagram



2) Determination of reference point for the specimen displacement



3) Final "load-relative displacement" diagram

$S=\Delta l/D_0*100\%$,

where:

S–relative displacement;

Δl –specimen displacement;

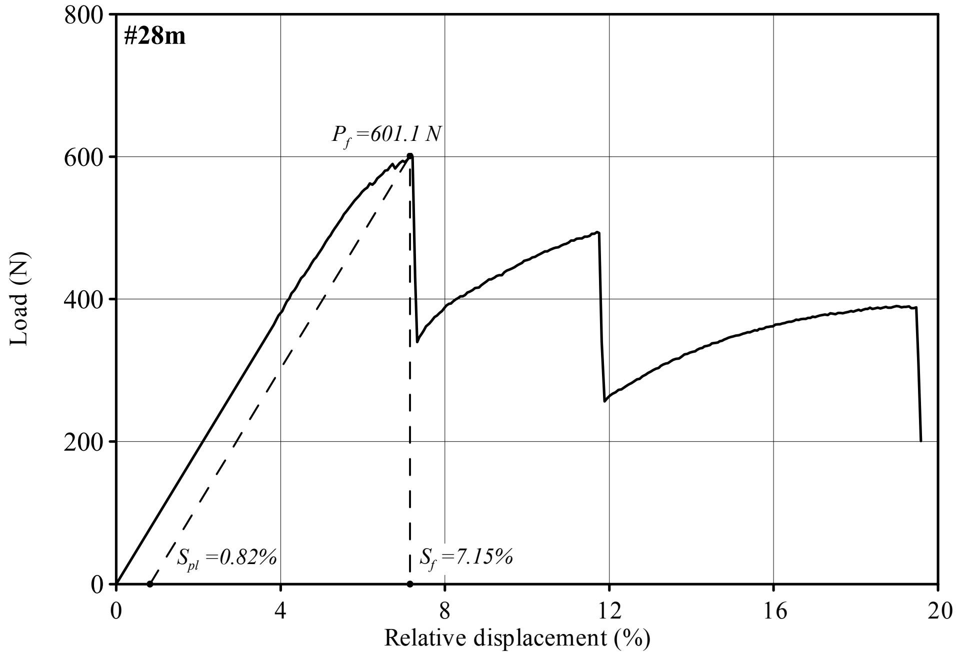
D_0 – outer diameter of undeformed ring specimen

Output parameters:

S_f – relative displacement at failure;

S_{pl} – plastic component of S_f;

P_f – load at failure.



→ 1. Plastic component of relative displacement at failure is 0.82%

2. Relative displacement is 7.15%

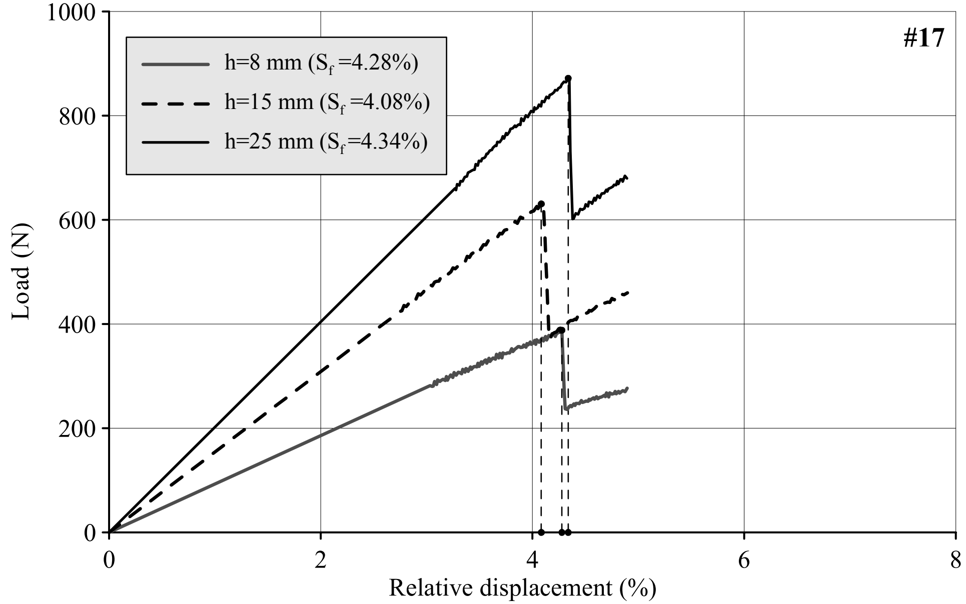
Conclusion:

This sample is nearby the zero ductility threshold

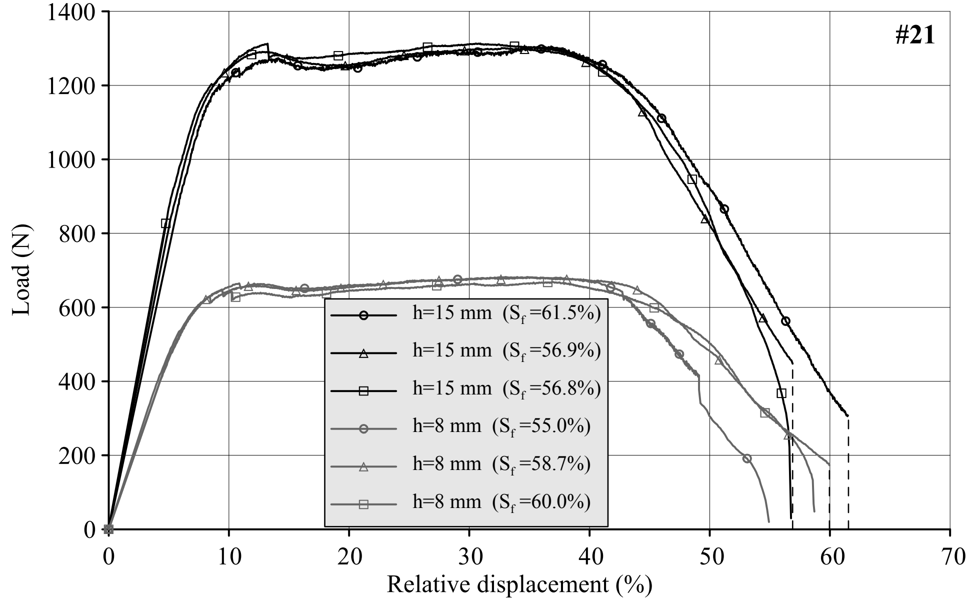
RING COMPRESSION TESTS. VALIDATION OF RING HEIGHT

Background
- No standard approach
- Various ring heights used in previous studies in U.S., Germany, Hungary, Czechia, Japan, Russia

Experimental
- Range of ring height considered: 8-25 mm
- Two types of oxidized samples: “brittle” and “ductile”



ECR=10%



ECR=6.5%

Conclusions:
- No influence of ring height on residual ductility in tested range
- 8 mm rings were selected as basic samples for the compression testing (like German and Hungarian ones, close to those in ANL'80s tests)

All procedures described above are valid only for ring sample with unoxidized ends (end effects!!!)

RING TENSILE TESTS VS. RING COMPRESSION TESTS

Analysis of representativity of ring compression tests for assessment of LOCA and post-LOCA ductility of fuel cladding

Major arguments of critics:

- Intricate stress distribution over the ring OD/ID and wall thickness;
- Loading is not prototypic for real reactor conditions

Major assumption of optimists:
Nil ductility of oxidized clad can be recognized by any testing. Critical ECR must only slightly depend on test type.

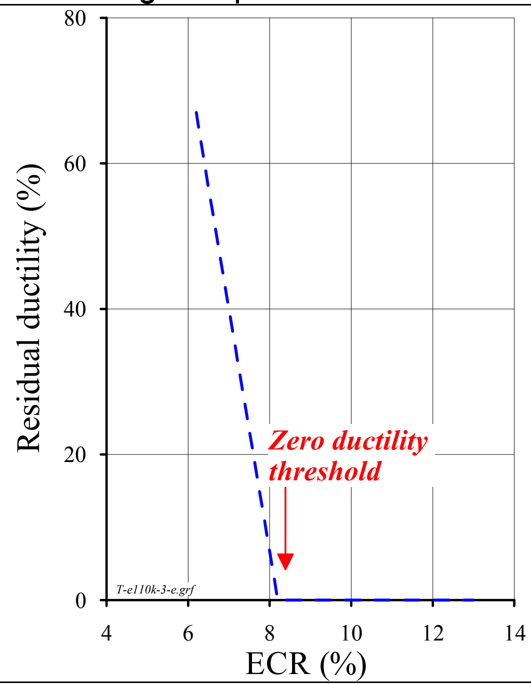
Experimental approach under discussion:
To compare ring compression results with ones of following tests:

1. ring tensile
2. axial tensile
3. impact toughness
4. three (four) point bending

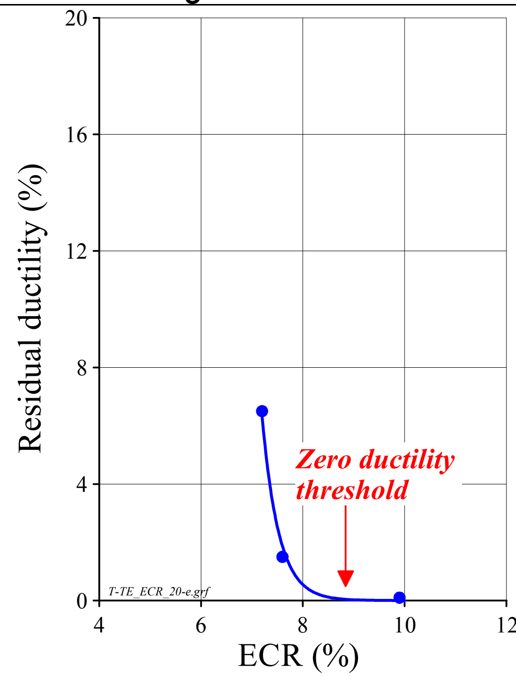
Items 1, 4 in RRC KI/RIAR: first results

E110, double sided oxidation at 1100 C

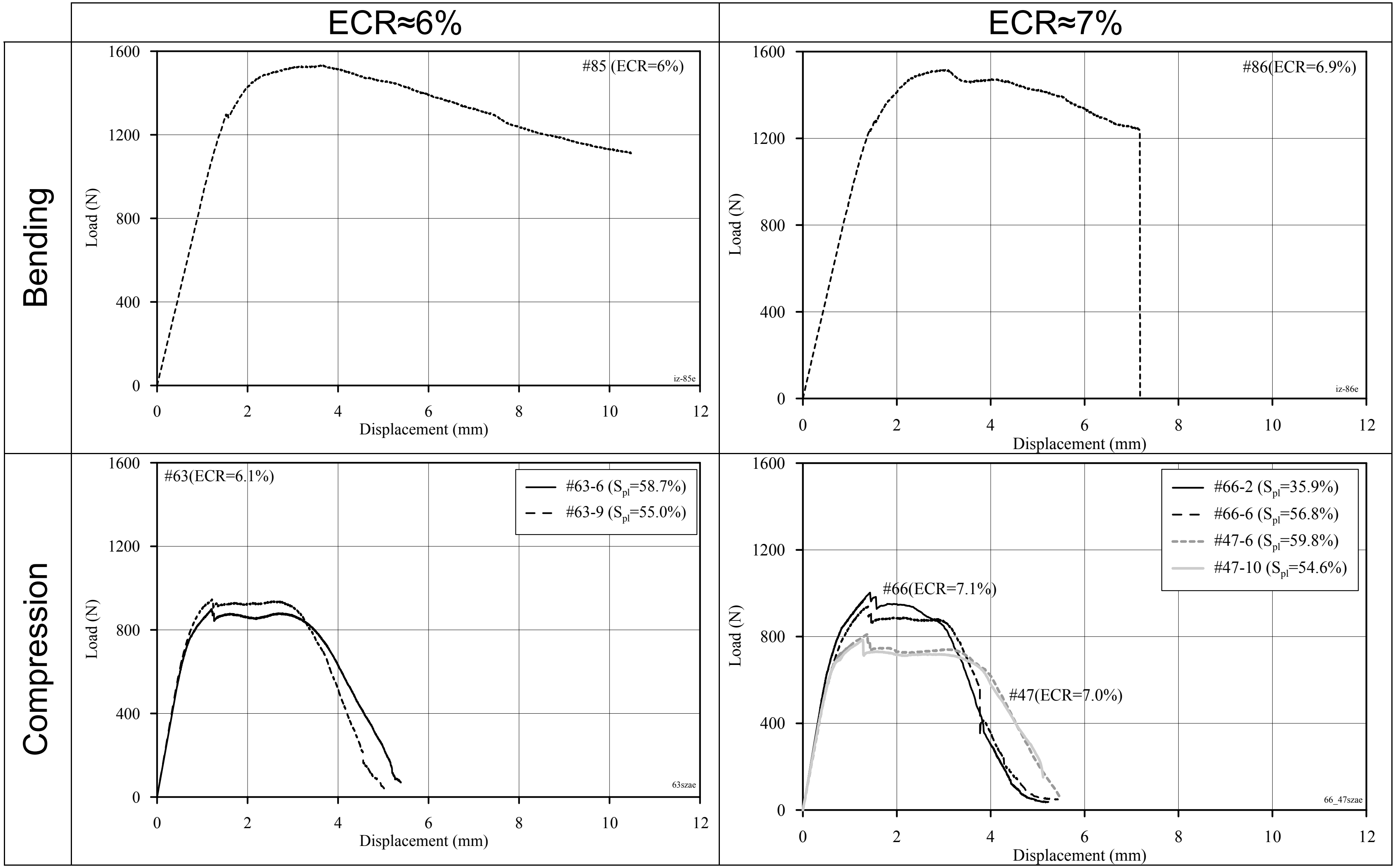
Ring compression tests



Ring tensile tests



THREE-POINT BENDING TESTS. FIRST RESULTS AT ROOM TEMPERATURE



Preliminary conclusions:

1. 3-point bend test results correlate well with ring compression data at the ECR up to 7%. At least bend testing does not shift embrittlement threshold to lower ECR.
2. Additional tests are planned for higher ECR to reach zero ductility

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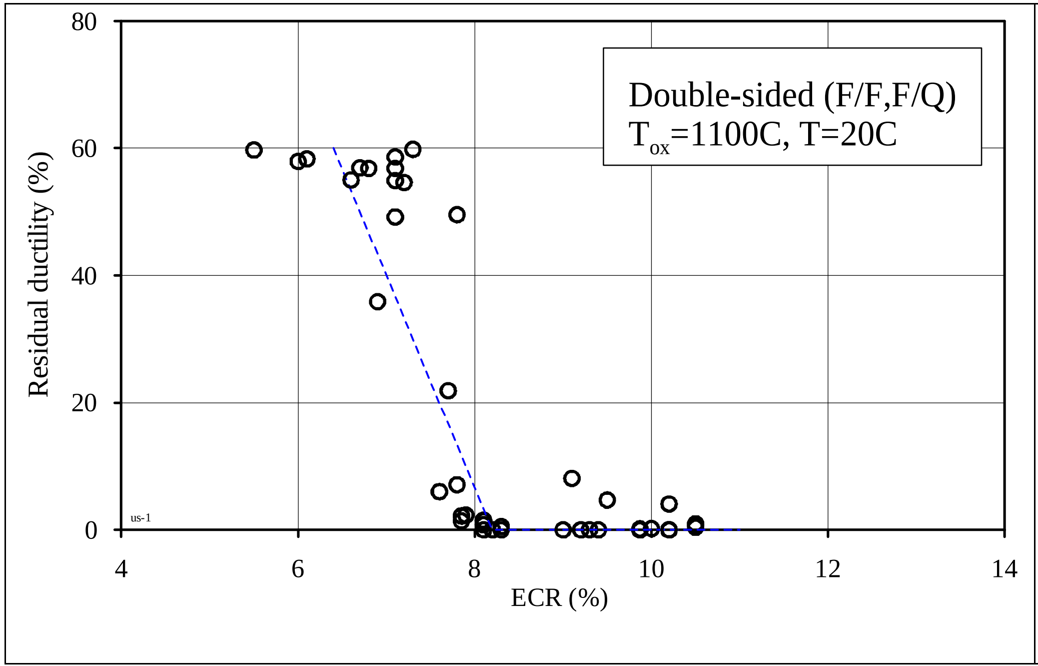
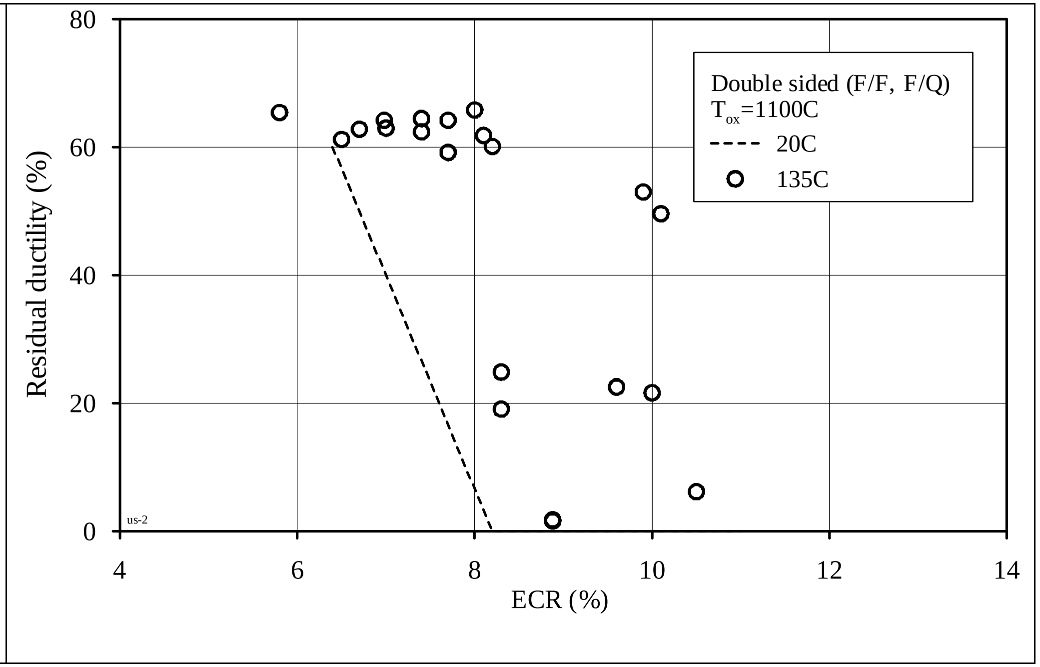
AS-RECEIVED E110. GENERALIZED RING COMPRESSION TEST RESULTS

Double-sided oxidation at 1100C





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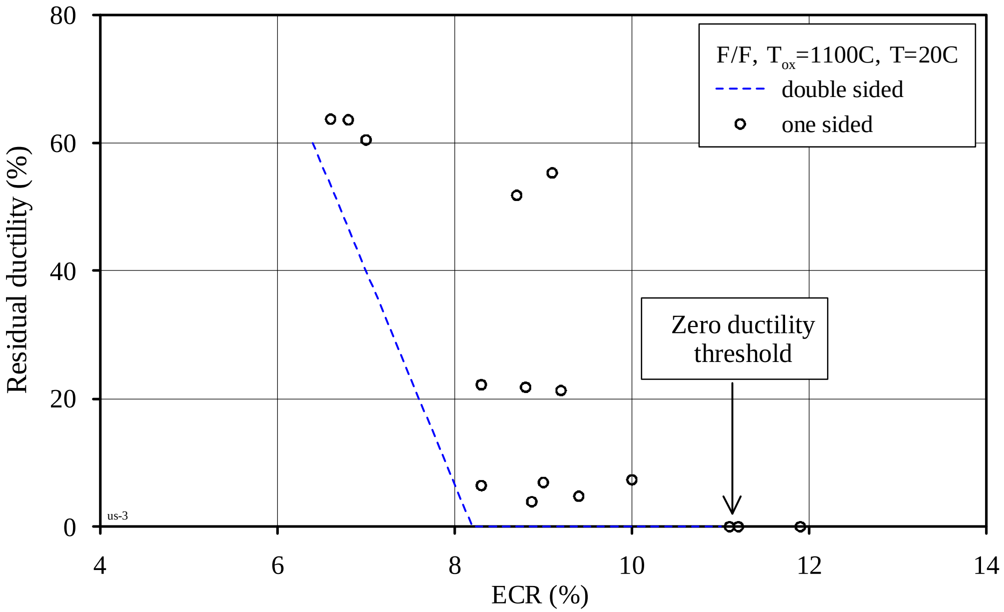
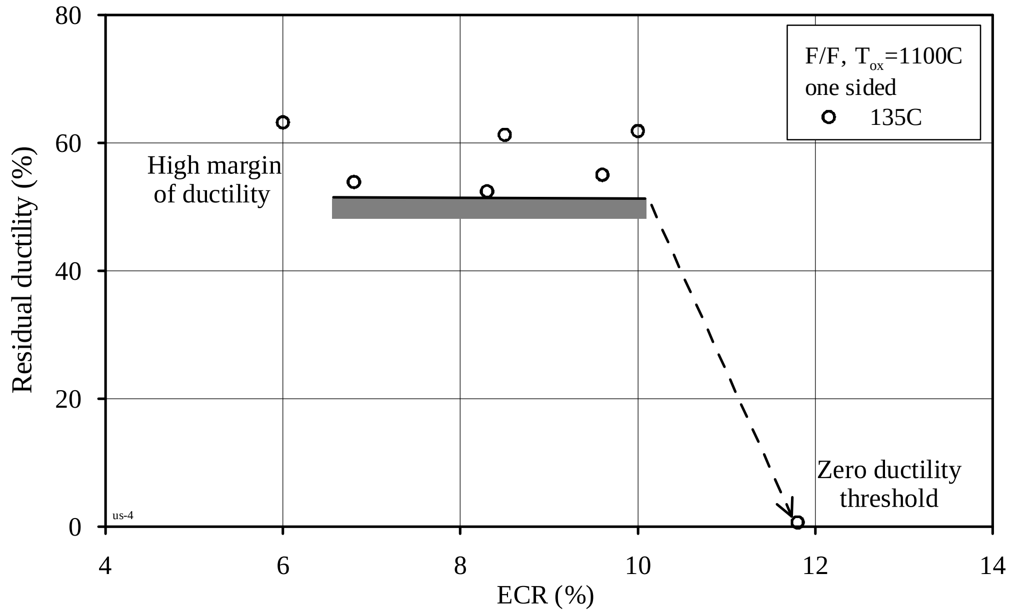
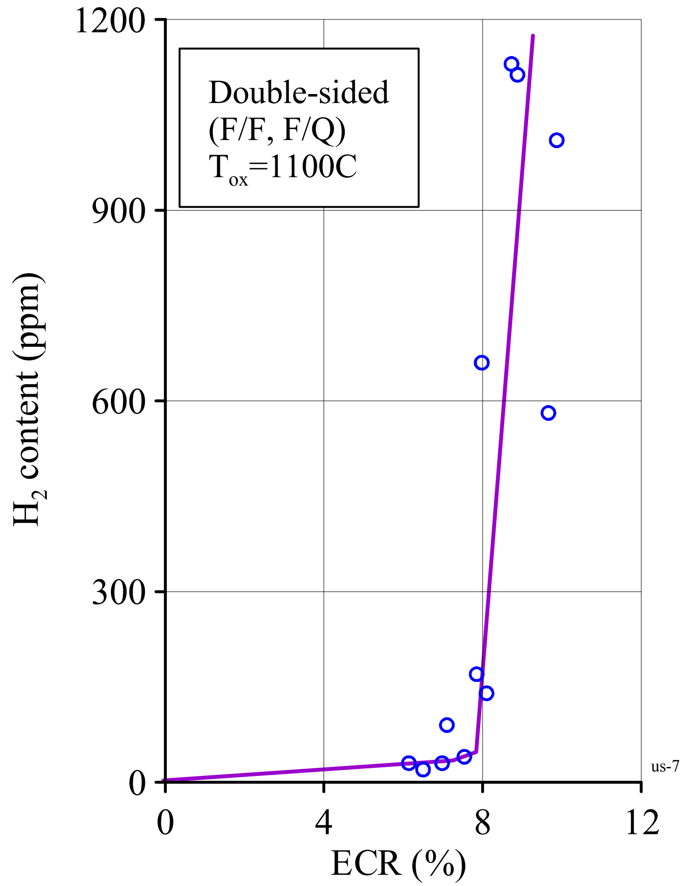
AS-RECEIVED E110. GENERALIZED RING COMPRESSION TEST RESULTS

One-sided oxidation at 1100C





AS-RECEIVED E110. GENERALIZED RESULTS OF HYDROGEN CONTENT MEASUREMENTS



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Major Provisions of the Program to Reveal the Factors Responsible for the Specific Behavior of the E110 Alloy

Type of possible factors	Detailization	Approaches to demonstrate the sensitivity of test results to different factors
1. Surface effects	Surface roughness and surface contaminations	To polish, machine, etch the cladding surface
2. Bulk effects	♦ Chemical composition of Zr ingot	To use the sponge Zr ingot instead of iodide and electrolytic Zr ingots
	♦ Microstructure effects: Nb sizes and distribution, phase composition, secondary precipitates…	To perform comparative SEM, TEM examinations
3. Geometrical sizes	Typical cladding thickness of E110 cladding is 0.69–0.71 mm. Typical cladding thickness of M5 cladding is 0.56–0.6 mm	To machine E110 cladding to the M5 size

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Test #3 (sample #92): As-received and Polished E110 Cladding

1100 C, double-sided oxidation, F/F

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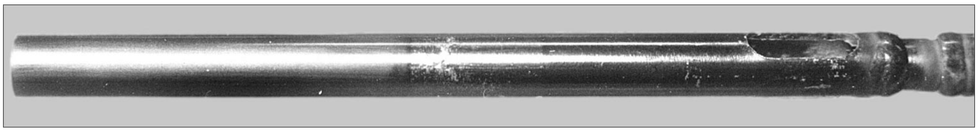
Appearance of the cladding after the oxidation test

polished ↓ as-received ↓



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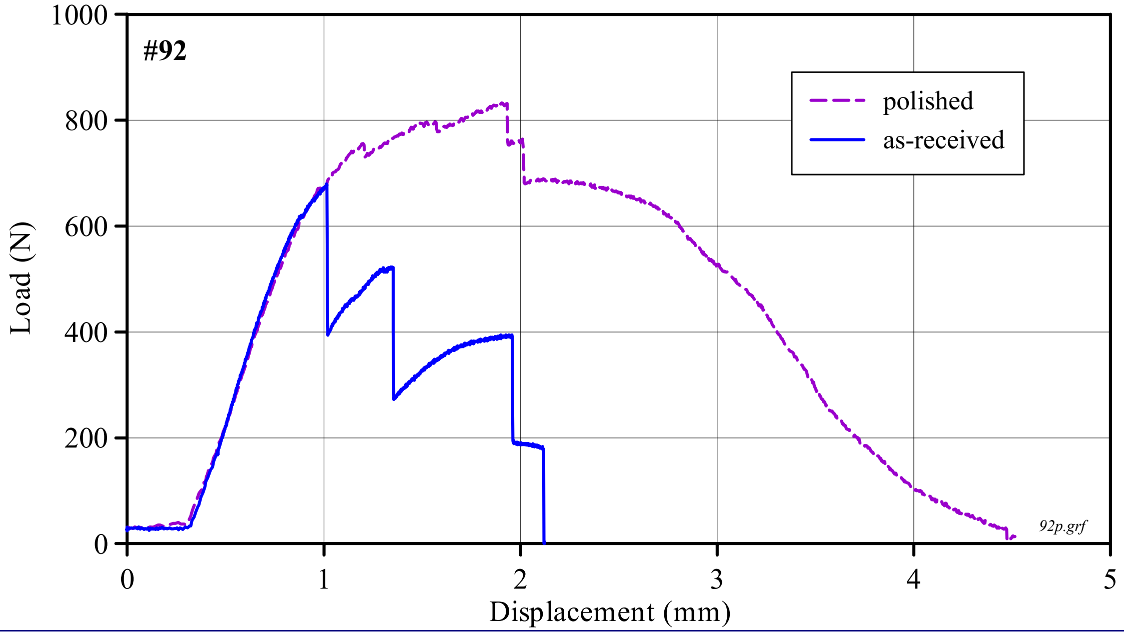
Results of ring compression tests



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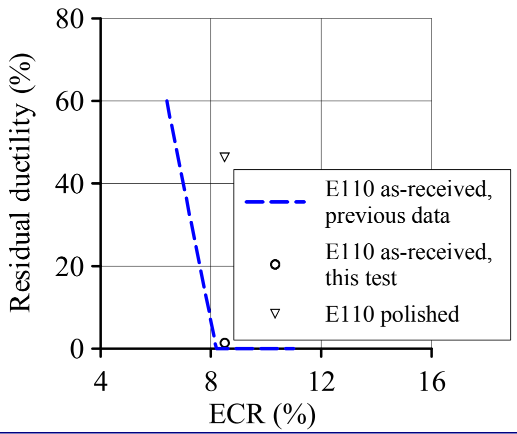

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Conclusion:

The specific behavior of the E110 cladding is a function of the surface characteristics (surface roughness, surface contamination (?))

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Tests #4, 5 (samples ##89, 90): G110 Cladding (E110 Alloy on the Basis of French Sponge Zirconium)

1100 C, double-sided oxidation, F/F, 10.5–13% ECR

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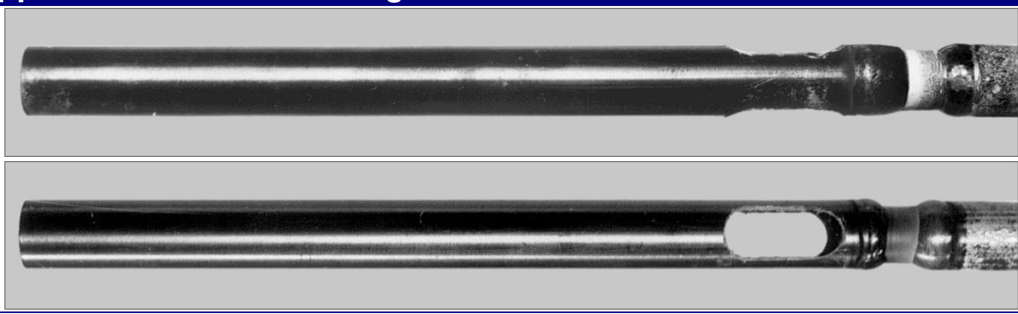
Appearance of the claddings after the oxidation test

10.5% ECR
(H_2→22 ppm)

13% ECR
(H_2→30 ppm)



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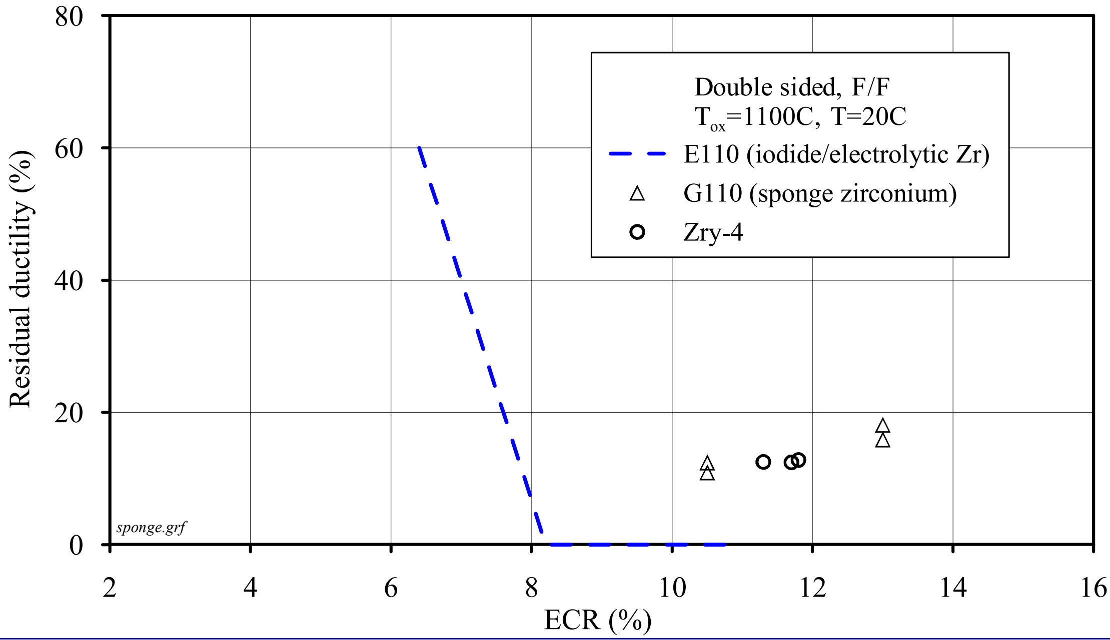
Comparison of the residual ductility vs. the ECR for E110, G110, and Zry-4 claddings



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Conclusion:

The E110 cladding fabricated on the basis of the sponge Zr (G110) and oxidized at 1100 C demonstrates the same behavior as the Zry-4 cladding (no breakaway effect, a high margin of residual ductility)

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<u>Tests ##6, 7 (samples ##91, 93):</u> G110 Cladding (E110 Alloy on the Basis of French Sponge Zirconium)

1000 C, double-sided oxidation, F/F

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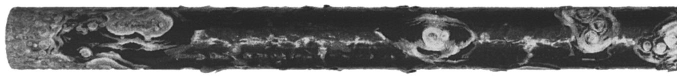
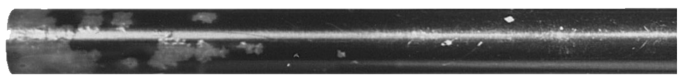
Comparison of the appearance of E110 (previous data) and G110 claddings after the oxidation tests

#44	<u>E110</u> ECR=7.7%	t_{ef}=865 s	
#45	<u>E110</u> ECR=7.6%	t_{ef}=798 s	
#91	<u>G110</u> ECR=6.5% (H_2→28 ppm)	t_{ef}=2016 s	
#93	<u>G110</u> ECR=8.5%	t_{ef}=5013 s	

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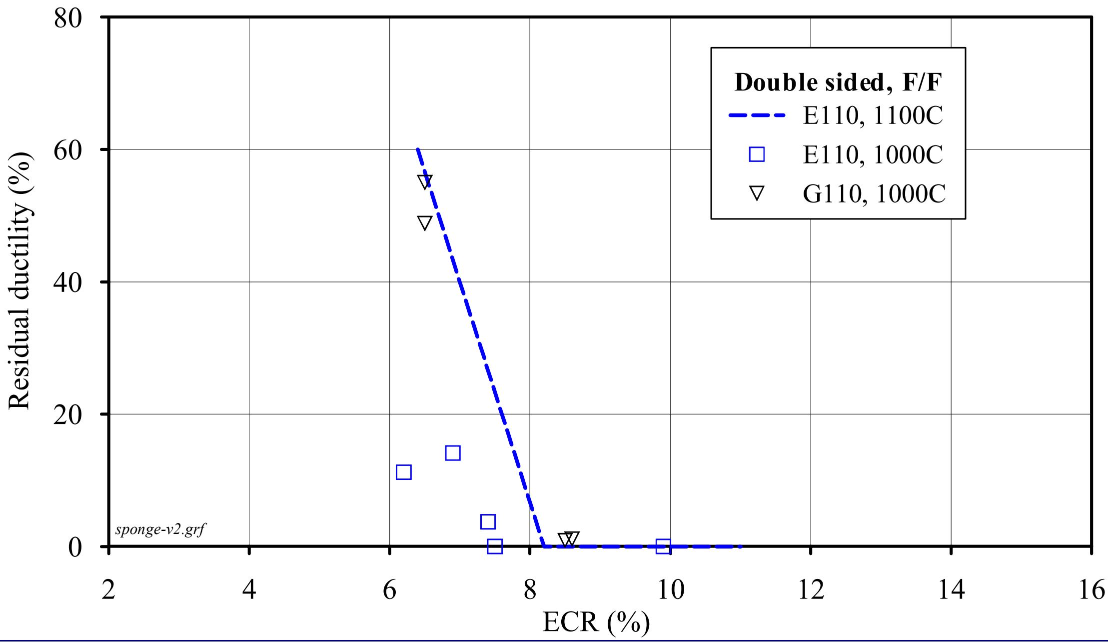
Residual ductility of E110, G110, Zry-4 claddings vs. the ECR and the oxidation temperature



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<u>Conclusions (see next slide):</u>

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Conclusion:

1. **From the formal point of view, the zero ductility threshold of the G110 cladding oxidized at 1000 C is not much higher, than this threshold for the E110 cladding (7.5% and 8.5% ECR, correspondingly)**
2. **But, general difference in the oxidation behavior of these two types of claddings was revealed:**
   - **~800 s of the oxidation is needed to achieve the zero ductility threshold of the E110 cladding;**
   - **~5000 s of the oxidation is needed to achieve the zero ductility threshold of the G110 cladding**