LOCA Behavior of E110 Alloy

L. Yegorova, K. Lioutov

Nuclear Safety Institute of Russian Research Center "Kurchatov Institute", Moscow, Russian Federation

V. Smirnov, A. Goryachev, V. Chesanov

State Research Center "Research Institute of Atomic Reactors", Dimitrovgrad, Russian Federation

Presented by L. Yegorova

Nuclear Safety Research Conference
Washington, D.C., USA
October 20–22, 2003

Outline of the Program First Stage

1. Status of the work

During 2001–2002 Nuclear Safety Institute of Russian Research Center "Kurchatov Institute" (NSI RRC KI) in cooperation with Russian State "Research Institute of Atomic Reactors" (RIAR) with the support of Joint Stock Company "TVEL" (Russian Federation), U.S. Nuclear Regulatory Commission (USA), and Institute for Radiological Protection and Nuclear Safety (IRSN, France) carried out the first stage of the program to reassess the post-quench ductility of Russian zirconium-niobium alloys under the LOCA conditions

2. Program purpose

- to determine the embrittlement threshold of the Russian type of Zr-1%Nb cladding (E110 alloy) as a function of the ECR
- to determine the sensitivity of the E110 embrittlement threshold to:
  - oxidation scenario (temperature, heating and cooling rates, one-sided and two-sided oxidation types);
  - alloying components (oxygen (E110K alloy), iron, tin (E635 alloy))

3. Major provisions of the program and analysis of test results

See: V.Asmolov et al., "Understanding LOCA-Related Ductility in E110 Cladding", Proceedings of the 2002 Nuclear Safety Research Conference, NUREG/CP-0180, March 2003

Background of the Work at the End of the Program First Stage

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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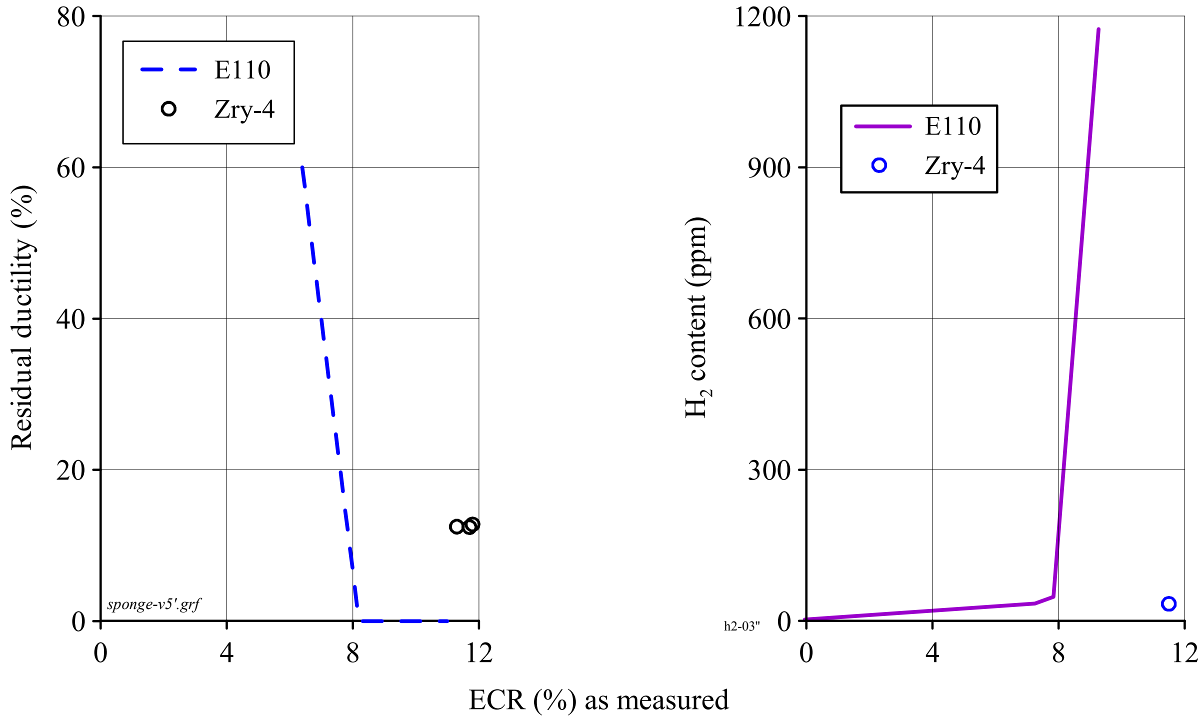
Double-sided oxidation at 1100 C



↓ ↓

8% ECR as measured corresponds to 11% ECR as calculated if Russian E110 conservative kinetics (Bochvar institute correlation) or Baker-Just Zry-4 conservative correlation is used

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Major conclusions:

- the zero ductility threshold of the E110 alloy is lower than that of Zry-4 alloy
- an earlier initiation of the breakaway effect in the nodular corrosion form and intensive absorption of hydrogen as a direct consequence are the visible reasons for the different behavior of these two alloys
- the correlation between the ductility threshold and such alloying elements as O, Fe, Sn was not observed

Discussion of the Program First Stage

1. Subject of the discussion

- M5 (France) and E110 (Russia) claddings are manufactured from the similar alloys on the basis of the Zr-1%Nb composition
- the comparison of published French data on the oxidation behavior and embrittlement threshold of the M5 cladding with the appropriate results of this study with E110 cladding allows to reveal the following general differences:
  - the embrittlement thresholds of M5 and Zry-4 alloys are similar
  - the embrittlement threshold of E110 alloy is lower than that for the M5 and Zry-4 alloys
  - unlike that of the E110 cladding, the embrittlement of the M5 cladding is not accompanied by the nodular corrosion and hydrogen uptake

2. Possible explanations of results

First version: listed differences were caused by differences in experimental procedures and approaches used to interpret test results

Second version: the similar alloying composition of zirconium-niobium alloys does not assure their identical oxidation and mechanical behavior under LOCA relevant conditions

Discussion of the Program First Stage

3. Decisions

1. To obtain the comparative test data in the same apparatus by the same technicians on the basis of ANL program with M5, Zirlo, E110, Zry-4 alloys
2. To develop coordinated ANL / RRC KI program to reveal the response of the E110 cladding to the variation of the manufacture processes

Characterization of the Factors Selected for Studies at the Program Second Stage

Type of possible factors	Specification	Approaches to demonstrate the sensitivity of test results to different factors	Involved laboratories	
			RRC KI/RIAR	ANL
1. Surface effects	Surface roughness and surface contamination	To polish, machine, etch the cladding surface	+	+
2. Bulk effects	Chemical composition of Zr ingot	To use the sponge Zr ingot and Zr ingot with low Hf instead of iodide and electrolytic Zr ingots	+	–
	Microstructure effects (grain size, phase composition, secondary precipitates (composition, size, distribution) as a function of the fabrication process	To perform comparative SEM, TEM examinations for different types of cladding specimens	+	+
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 the E110 cladding to the M5 size	–	+

Surface Effects Studies

Types of new cladding specimens:

1. E110 etched and anodized standard Russian cladding
2. E110 polished (inner and outer surface) standard Russian as-received tubing

Demonstration of the oxidation behavior of etched and anodized cladding

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1100 C, double-sided oxidation, F/F

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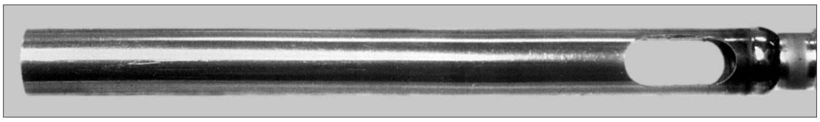
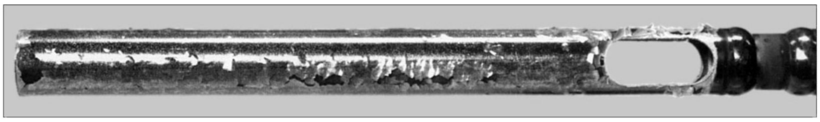
Appearance of the cladding before (a) and after (b) the oxidation test

a)



b)



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Conclusion:

The current final chemical processing of the E110 cladding does not improve the cladding oxidation behavior

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Additional comments:

- This conclusion fully agrees with results of tests with the etched E110 cladding performed by ANL
- Russian vendor of VVER fuel (JSC "TVEL") eliminates the final etching of the VVER cladding from the standard conditioning procedures

Surface Effects Studies

Demonstration of the oxidation behavior of etched and anodized cladding

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1100 C, double-sided oxidation, F/F

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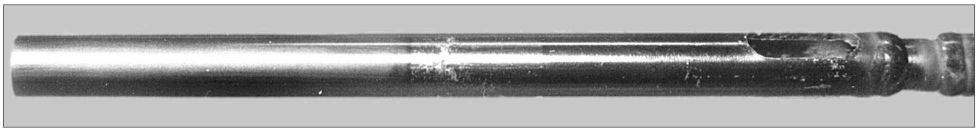
Appearance of the cladding after the oxidation test

polished ↓ as-received ↓



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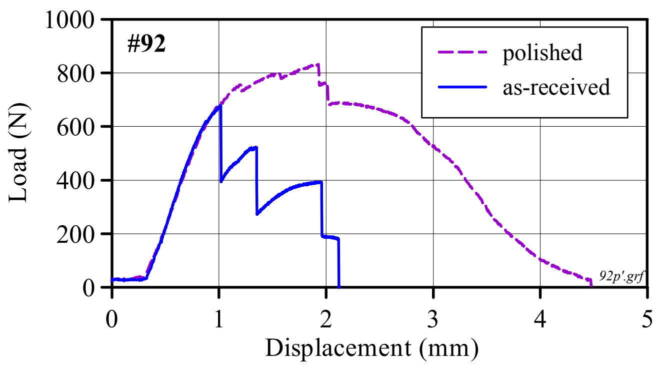
Results of ring compression tests



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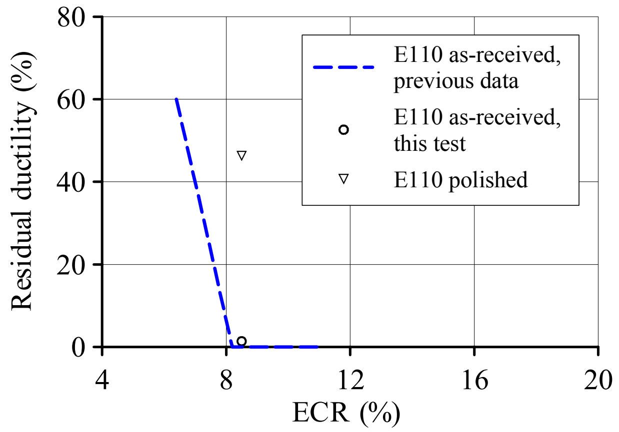

Conclusion:

Polishing of the cladding tubes leads to:

- significant delay in the start of nodular oxidation
- sufficient improvement of the ductility

Comments:

ANL independent data confirms this conclusion

Bulk Effect Studies. Introduction

1. General statement:

Let's assume that M5 (Zr-1%Nb) alloy is really better than E110 (Zr-1%Nb) alloy under LOCA relevant conditions

2. General question based on this statement

What is the reason for different oxidation behavior of these two alloys?

3. Summary of possible answers and comments

Variant of answers	Comments
1. Different oxygen concentrations in these alloys (0.04–0.06% in E110, 0.13% in M5) lead to the different oxidation behavior	Special studies of E110K alloy (oxygen concentration 0.13%) have demonstrated that the increase of oxygen concentration does not change the oxidation behavior of E110 alloy
2. Different conditioning of cladding surface (polishing for M5, etching for E110) leads to the different oxidation behavior	Surface effect studies of E110 polished specimens have shown that the appropriate manipulation with cladding surface allows to slow down the initiation of the nodular corrosion, but this procedure does not allow to avoid this type of the oxidation in the given range of ECRs (especially at 1000 C)

Bulk Effect Studies. Introduction (continued)

Variant of answers	Comments
3. Differences in the chemical composition of Zr ingot	1. All types of alloys developed for PWR reactors (including advanced zirconium-niobium alloys) are manufactured on the basis of the sponge Zr. Therefore, the differences in the chemical composition of these family of alloys are conditioned by differences in the alloying composition 2. Cladding alloys for the VVER reactor are manufactured on the basis of the mixture of iodide and electrolytic Zr 3. Thus, the chemical composition of the PWR cladding and VVER cladding with the same alloying components differ in the composition of impurities 4. To verify the sensitivity of E110 oxidation behavior to the chemical composition of impurities, it was decided to perform the oxidation and mechanical tests with advanced types of E110 claddings manufactured on the basis of the modified process of Zr ingot fabrication
4. Differences in the cladding fabrication process	1. It is known that cladding properties (mechanical and oxidation parameters) are a strong function of the fabrication process 2. Besides, it is known that a strong correlation is observed between the cladding microstructure and cladding oxidation behavior 3. Thus, if the differences in the oxidation behavior of zirconium-niobium alloys are conditioned by the cladding fabrication process, the comparison of appropriate microstructures will allow to reveal this effect

Bulk Effect Studies. Cladding Types

Types of E110 cladding material used for the bulk effect studies

Alloying composition	Components of Zr ingot	Conventional name (in the frame of this work)
1. Zr-1%Nb	iodide Zr, electrolytic Zr, recycled scrap	E110
2. Zr-1%Nb	French sponge Zr	G110-f
3. Zr-1%Nb	First step: Russian sponge Zr + iodide Zr + recycled scrap were crushed to powder Second step: This powder was used to manufacture sponge Zr ingot	G110-3ru
4. Zr-1%Nb	French sponge Zr + iodide Zr + recycled scrap	G110-3f
5. Zr-1%Nb	iodide Zr + electrolytic Zr with low Hf, recycled scrap	E110-low Hf

Bulk Effect Studies. Zr Ingot Variations

Test results with the G110-f 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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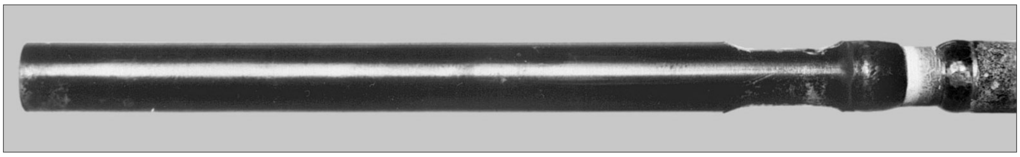
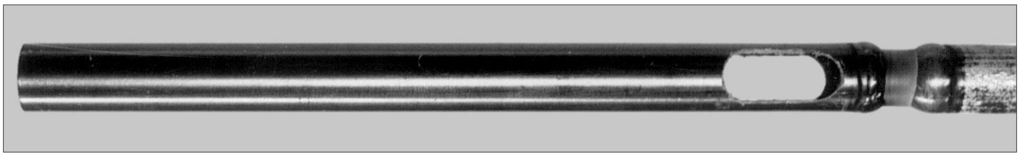
Appearance of the claddings after the oxidation test

Sample #89
10.5% ECR
(H_2→22 ppm)



Sample #90
13% ECR
(H_2→30 ppm)



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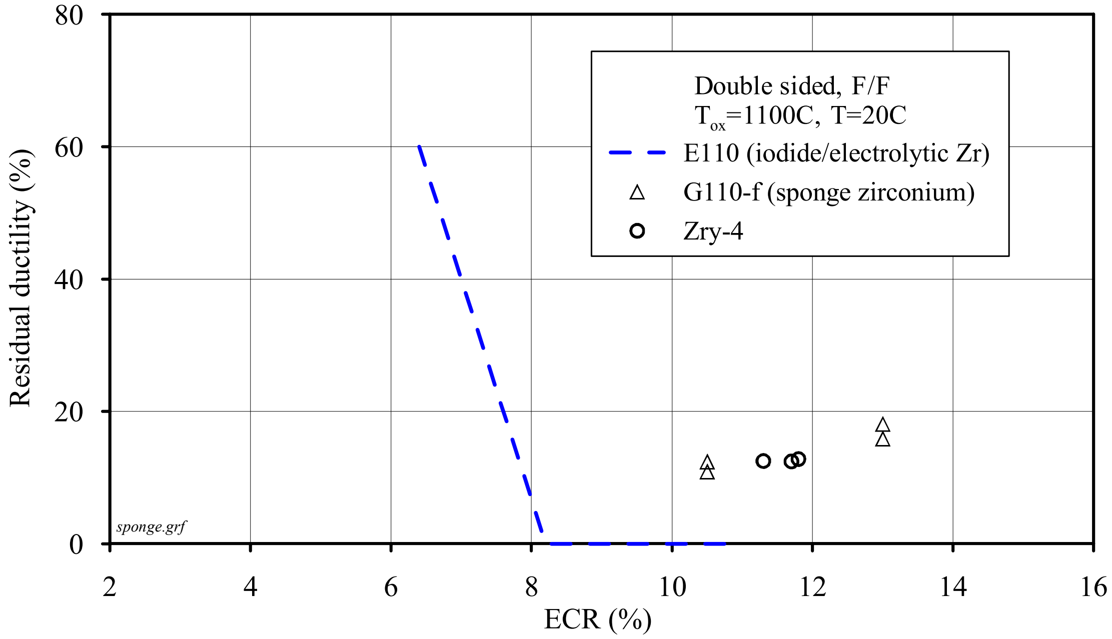
Comparison of the residual ductility vs. the ECR for E110, G110, and Zry-4 claddings



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Conclusion:

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

Bulk Effect Studies. Zr Ingot Variations

Additional information to verify the conclusions on G110-f mechanical behavior

Results of ring compression tests

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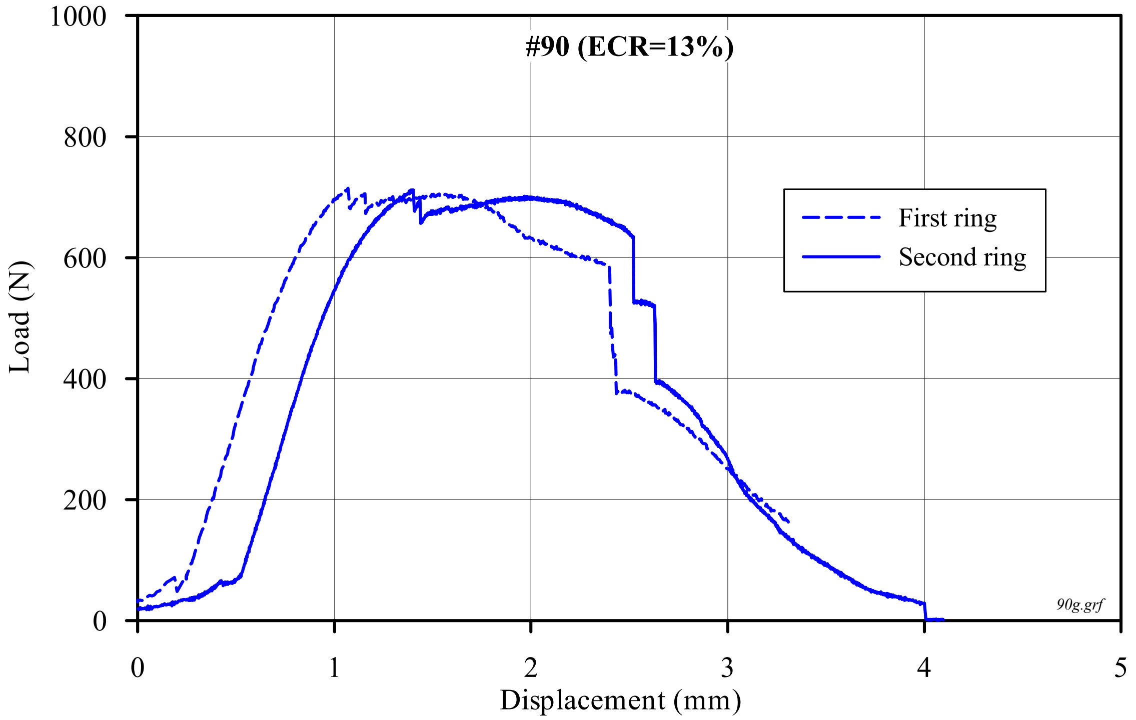
Load-displacement diagrams for two rings from the sample #90 (13% ECR)



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Appearance of ring samples after mechanical tests

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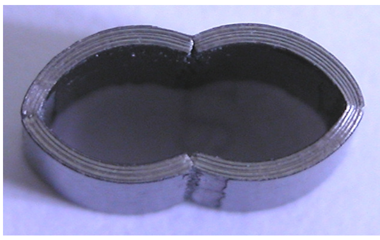
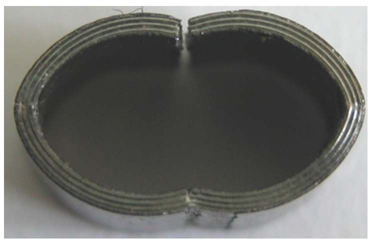
#89	#90
	

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Presented data confirm that the plastic deformation of G110-f oxidized samples was observed before the failure

Bulk Effect Studies. Zr Ingot Variations

Test results with the G110-3ru cladding (E110 alloy on the basis Russian sponge Zr)

1100 C, double-sided oxidation, 11.6–16.7% ECR

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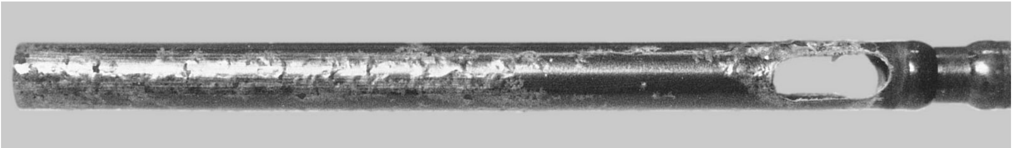
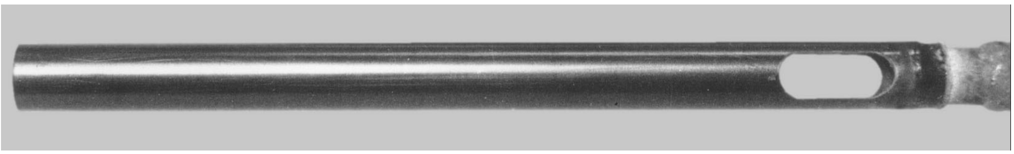
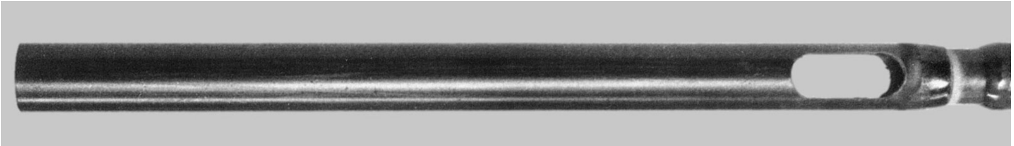
Appearance of the claddings after the oxidation tests

E110(standard), #96, 9.8% ECR $H_2 \rightarrow 4$ ppm	
G110-3ru, #95, 11.6% ECR $H_2 \rightarrow 17$ ppm	
G110-3ru, #97, 16.7% ECR	

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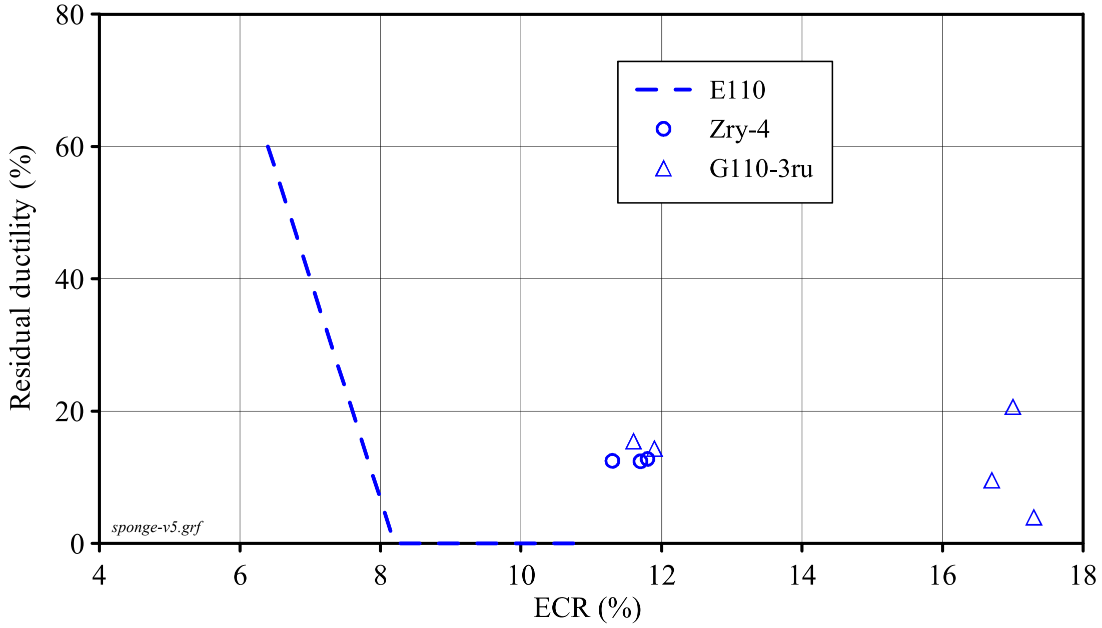

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Conclusion:

The E110 cladding fabricated on the basis of Russian sponge Zr demonstrates the same (or better) behavior as the Zry-4 cladding does at the oxidation at 1100 C

Bulk Effect Studies. Zr Ingot Variations

Comparative test results with G110-3ru and G110-3f (E110 alloy on the basis of French sponge Zr, iodide Zr, recycled scrap) claddings

1100 C, double-sided oxidation, 11.5% ECR

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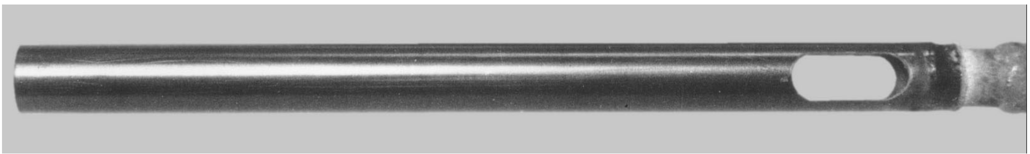
Appearance of the claddings after the oxidation tests	
G110-3f, #99, 11.5% ECR $H_2 \rightarrow$ 13 ppm	
G110-3ru, #95, 11.6% ECR $H_2 \rightarrow$ 4 ppm	

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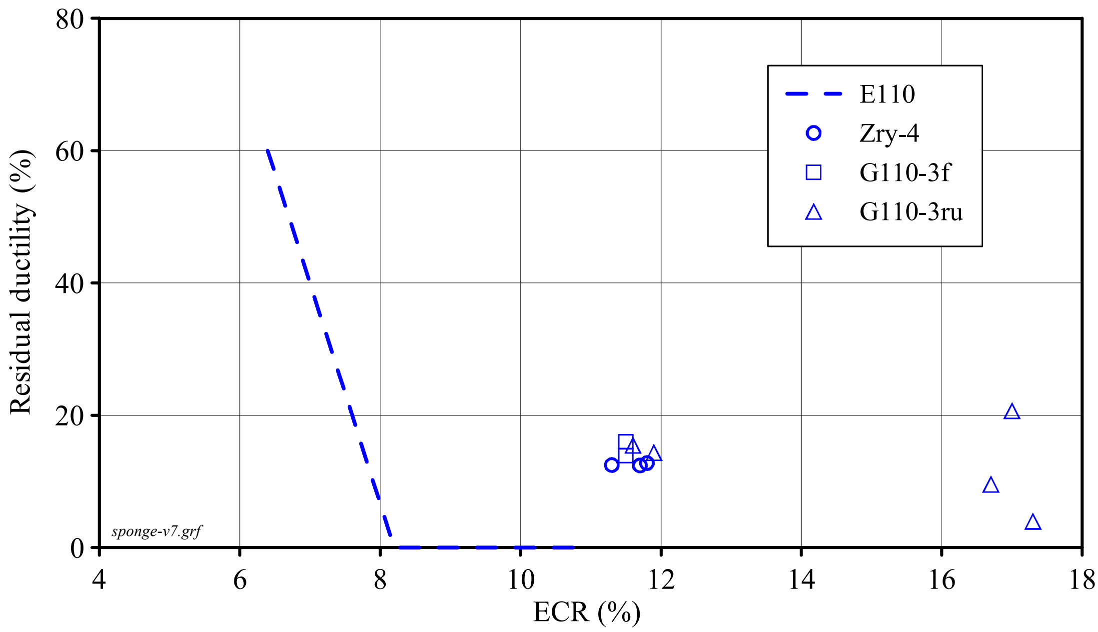

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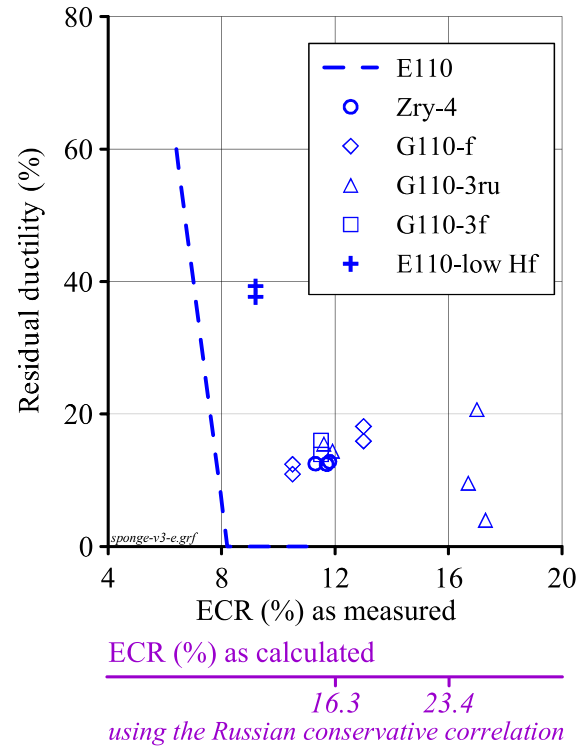
Conclusion:

The oxidation behavior and residual ductility of E110 claddings of G110-3f and G110-3ru types are approximately the same

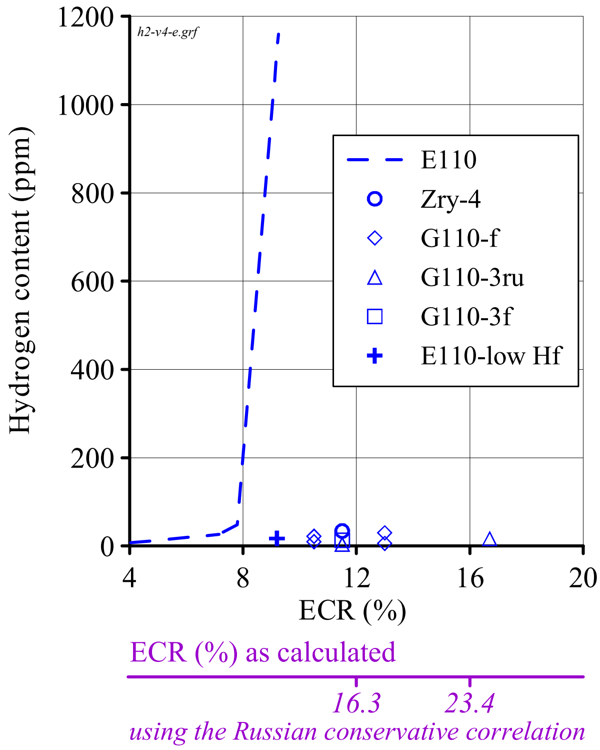
Bulk Effect Studies. Zr Ingot Variations

Summary of test results for the double-sided oxidation at 1100 C

Residual ductility vs ECR



Hydrogen content vs ECR



General assumption laid in the basis for the development of conclusions: the only parameter (Zr ingot composition) was varied in these bulk effects studies. Other fabrication procedures were the same for the whole set of tested claddings

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Conclusions:

1. All claddings manufactured without electrolytic Zr (as the component of Zr ingot) have demonstrated a high margin of residual ductility up to 17% ECR as measured (25% ECR as calculated)
2. A typical tetragonal oxide was formed on the cladding surface
3. Hydrogen concentration in the cladding was very low
4. The test with the E110-low Hf cladding has shown the encouraging result also. But an additional test should be performed at the higher ECRs for the final conclusions on this cladding type

Bulk Effect Studies. Zr Ingot Variations

The purpose and results of additional oxidation and mechanical tests performed with E110 claddings manufactured on the basis of the sponge Zr

Background of the problem

It is known that E110 claddings demonstrate the worst oxidation behavior at the temperature around of 1000 C

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Purpose of additional tests

To verify the oxidation and mechanical behavior of G110-f and G110-3ru cladding under the worst temperature conditions

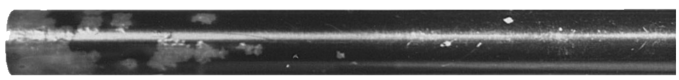
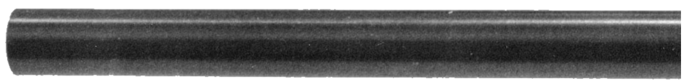
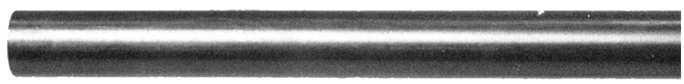
Bulk Effect Studies. Zr Ingot Variations

Comparative data on the behavior of E110, G110-f, G110-3ru claddings at the temperature 1000 C

1000 C, double-sided oxidation, 7→9% ECR

↓

Appearance of claddings after oxidation

#44	E110 ECR=7.7%	t_{ef}=865 s	
#91	G110-f ECR=6.5% (H_2→28 ppm)	t_{ef}=2016 s	
#93	G110-f ECR=8.5% (H_2→12 ppm)	t_{ef}=5013 s	
#98	G110-3ru ECR=6.9% (H_2→16 ppm)	t_{ef}=2519 s	
#101	G110-3ru ECR=8.9% (H_2→11 ppm)	t_{ef}=5028 s	

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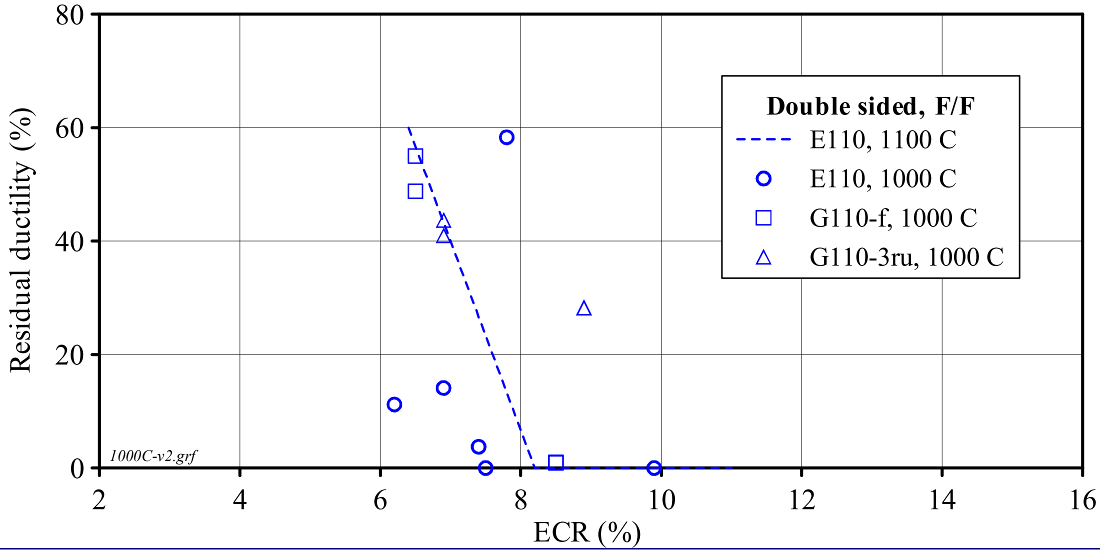
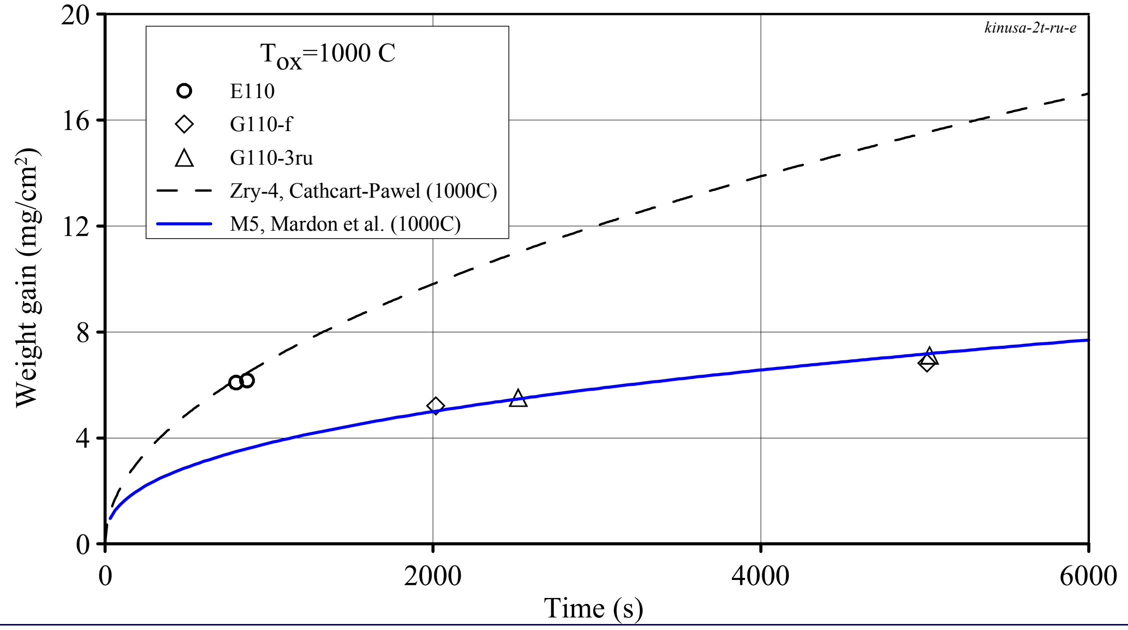
Residual ductility of E110, G110-f, G110-3ru claddings as a function of the ECR at 1000 C



Bulk Effect Studies. Zr Ingot Variations

Comparative data on the behavior of E110, G110-f, G110-3ru claddings at the temperature 1000 C



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Conclusions:

1. The following general differences in the oxidation behavior of the E110 cladding and G110-f, G110-3ru claddings were revealed:
   - ~800 s of the oxidation are needed to achieve the zero ductility threshold for the E110 standard cladding
   - ~5000 s of the oxidation are needed to achieve the zero ductility threshold for the G110-f cladding
   - ~5000 s of the oxidation do not allow to achieve the zero ductility threshold for the G110-3ru cladding
2. The G110-f, G110-3ru and M5 (in accordance with published data) claddings have the same oxidation kinetics. Moreover, the oxidation rate of these claddings is much less than that for the Zry-4 cladding
3. Such durations of the oxidation as 2000 s, 5000 s are outside of the practical interest for the large break LOCA safety analysis
4. In this context, the question about the representativity of the ECR as the universal safety criterion could be formulated

Bulk Effect Studies.
Variations of cladding fabrication process

Major provisions of the approach used for the analysis of the relationship between the cladding fabrication process and the cladding oxidation behavior

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1. The analysis of the numerous studies performed in this field during the last thirty years allows to conclude that all differences in fabrication procedures, which are important for the oxidation behavior of any of zirconium-niobium alloys are reflected in the cladding microstructure
2. In accordance with results of these investigations, the major goal for the development and improvement of the fabrication process of zirconium-niobium alloys is to develop the following parameters of the 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

3. Taking into account these findings, it was decided to estimate the dependence of the oxidation behavior of these alloys on the fabrication procedures using the comparison of the TEM data characterizing the microstructure of each of alloys. To obtain these data, special TEM examinations were performed with E110, G110-f, G110-3ru, G110-3f, E110-low Hf cladding materials

Bulk Effect Studies.
Variations of cladding fabrication process

The attempt to reveal possible differences in the cladding fabrication process using the results of TEM examinations

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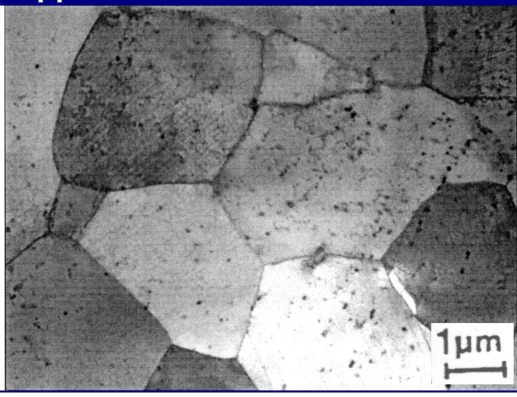
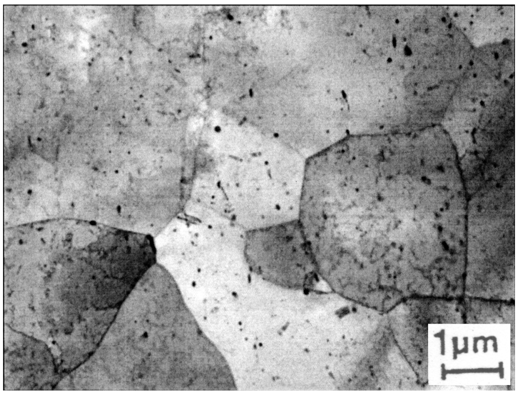
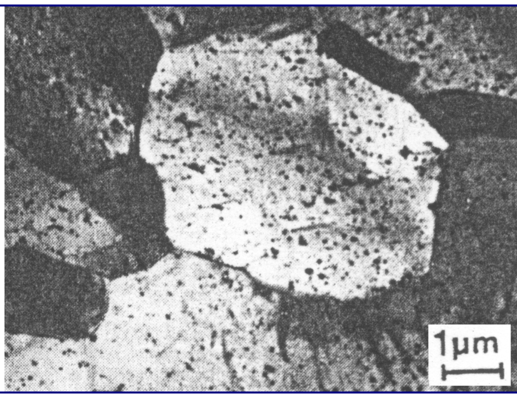
Type of cladding	Appearance of the microstructure	Characterization of the microstructure
E110 standard Russian as-received tubing		♦ fully recrystallized structure (αZr matrix with βNb globular precipitates) ♦ grain size 2.8 μm ♦ a high level of dispersion of β-Nb precipitates: D = 45, 60 nm (results of measurements in two laboratories) N = 1.84×10^{14} cm^{-3}
G110-f as-received tubing fabricated with French sponge Zr by the Russian procedure		♦ 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 = 1.8×10^{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 = 1.5×10^{14} cm^{-3}) with no alignment of particles"

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Preliminary conclusions:

1. General differences in microstructures of studied alloys (E110, G110-f, G110-3ru, G110-3f, E110-low Hf) were not revealed
2. Appearances and parameters of microstructures 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

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Conclusions

1. Experimental studies (performed during 2001–2002 with Russian Zr-1%Nb claddings manufactured from the E110 alloy) allowed to reveal that the nodular corrosion accompanied by hydrogen absorption is responsible for the earlier embrittlement of E110 cladding in comparison with Zry-4 cladding under LOCA relevant conditions
2. The scientific discussion conducted on the basis of the analysis of results from this stage of the work with the participation of specialists from JSC "TVEL", VNIINM (Bochvar Institute, Russia), ANL, NRC (USA), IRSN (France) became the basis for the development of a coordinated program of investigations performed at RRC KI/RIAR and ANL during this year
3. The following phenomena were selected for these studies:

- ♦ surface effects and effect of geometrical sizes
- ♦ bulk effects connected with the chemical composition of impurities in the cladding material
- ♦ bulk effects connected with variations of the fabrication process

4. The research performed by RRC KI/RIAR specialists allowed to conclude the following:

- ♦ different procedures for the cladding surface conditioning lead to the different oxidation behavior of the E110 cladding; surface polishing improves the oxidation behavior, but the etching leads to the negative results
- ♦ preliminary analysis of the data base obtained to determine the dependence of post-LOCA ductility as a function of current cladding fabrication processes has shown that this is not the key reason for different behavior of zirconium-niobium alloys
- ♦ in accordance with current data, the chemical composition of impurities in the cladding material is considered as a key factor responsible for different oxidation behavior of different zirconium-niobium alloys
- ♦ special tests performed with experimental types of the E110 cladding manufactured using different methods of Zr ingot preparation have shown that the oxidation behavior and embrittlement threshold of these cladding are the same as these for Zry-4 and M5 claddings