STUDY OF MODIFIED ZIRCONIUM ALLOYS CLADDINGS AFTER IRRADIATION

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ABSTRACT

Modified zirconium alloys E635M, E635opt and E635M1 based on E635 alloy have been developed at Bochvar Institute. Fuel rods with such claddings were manufactured at Bochvar Institute and were irradiated at MIR reactor to a burnup of 150 MW·d/kgU. Our objective was to study behavior (mainly corrosion including hydrogen pick-up and strengthening) of modified zirconium alloys claddings under irradiation compared to master alloy E635. The results from the PIE performed at RIAR are presented. Such features of claddings as microstructures, corrosion resistance (width and structure of oxide), hydrogen contents, distribution of hydrides, mechanical properties were examined and discussed.

1. Introduction

Russian zirconium alloys E110 and E635 are widely used as fuel rod claddings in water-cooled nuclear power reactors. E110 alloy (Zr – 1Nb) operability is limited by nodular corrosion under particular conditions such as of coolant boiling and high oxygen content [1]. Corrosion resistance of the alloy is extremely sensitive to the water chemistry of the coolant and the heat treatment during production of fuel rods. It is subject to a significant shape change under irradiation (radiation growth). Therefore, it is of interest to develop a cladding material that is not prone to nodular corrosion.

The use of zirconium alloys of the Zr-Sn-Nb-Fe system, in particular, of the E635 alloy (Zr – 1Nb – 1.2Sn – 0.35Fe) developed in SC "VNIINM" [2] is promising. Its main advantage over the E110 alloy is the absence of nodular corrosion of the claddings under any irradiation conditions, including the boiling of the coolant. The alloy is insensitive to the water-chemistry of the coolant and the oxygen content in it. The use of the E635 alloy is promising for reactors with increased characteristics. In-pile tests of experimental fuel rods with E635 claddings in nuclear icebreaker reactors have successfully completed.

However, the E635 alloy is inclined to increased uniform corrosion and hydrogen pick-up compared to the E110 alloy. At the operating cladding temperature (280-340 ℃) most of the hydrogen is in the solid solution, but after temperature decreasing to 20-150 ℃ it precipitates in the form of zirconium hydride platelets. Under irradiation along with increasing hydrogen content in claddings, radial hydride precipitation may occur under applied tensile stress that leads to anisotropic embrittlement during cooling down [3, 4]. So modified alloys of the Zr-Sn-Nb-Fe system were developed in SC "VNIINM" in order to reduce uniform corrosion and hydrogen pick up while maintaining the resistance to nodular corrosion. Niobium provides high resistance to uniform corrosion and hydrogen pick up. The presence of iron in the alloy increases the resistance to nodular corrosion and reduces the radiation growth. Tin is a α-stabilizer and increases the corrosion resistance of the alloy by the mechanism of reducing the content of anionic vacancies in the oxide layer. Therefore, the modification of the base alloy E635 was in the direction at optimizing the content of niobium, iron and tin [5, 6].

It was assumed that modified alloys should retain the positive properties of E635 (the absence of nodular corrosion, the lack of sensitivity to the water-chemistry of the coolant and the oxygen content in it) and at the same time exceed it in resistance to uniform corrosion and hydrogen pick up.

In this paper we analyze results of comparative post-radiation investigations of fuel rods with claddings of zirconium alloys: well-known E110 and E635 and modified E635M, E635opt, E635M1. The shortened fuel rods for reactor tests were manufactured in SC "VNIINM" and assembled in two units (fuel assemblies no. 4 and 7). The composition of the investigated alloys is given in Tab 1 and Fig 1.

Fuel assembly	Alloy	Sn	Nb	Fe	O
4, 7	E110	-	1.0	0.01	0.03
4, 7	E635	1.2	1.0	0.35	0.04
7	E635M	0.8	0.8	0.33	0.06
4	E635opt	0.8	0.96	0.3	0.09
4	E635M1	0.8	0.65	0.28	0.09

Tab 1: Chemical composition of zirconium alloy tubes, mass. %

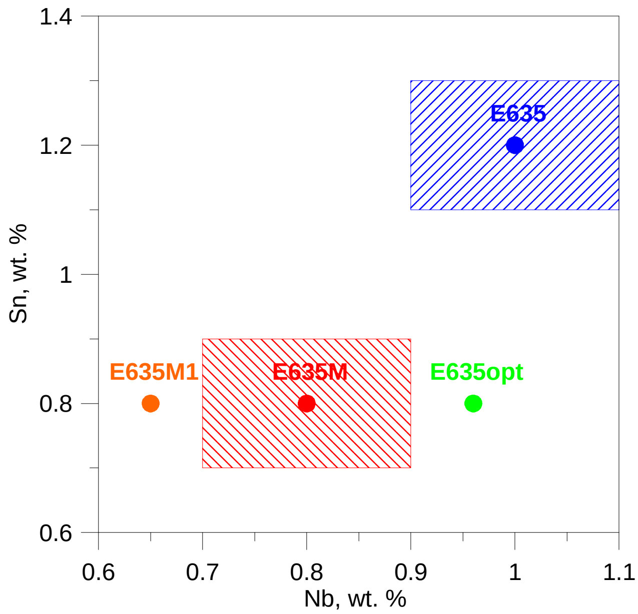


Fig 1. Niobium vs tin contents in E635, E635M, E635opt and E635M1 zirconium alloys

2. In-pile tests

The in-pile tests were carried out in two fuel assemblies of the MIR reactor (SC “RIAR”, Dimitrovgrad) in conditions of the ammonia coolant chemistry. In-pile conditions were close to those of VVER (non-boiling; contents of oxygen in coolant – 0.005-0.01 ppm).

Reactor tests were carried out in the irradiation unit "Garland" of the MIR reactor in the ammonia water chemistry (Tab 2, Fig 2).

After irradiation roods are placed into the pool. Rate of cooling down isn’t controlled.

Feature	FA # 4	FA # 7
Cladding size, mm	9.13 x 7.73	6.8 x 5.8
Operating time at power, days	960	1008
Max linear thermal flux, W/cm	305	250
Max surface thermal flux, MW/m^2	1.05	1.2
Max burn-up, MW·d/kgU	90	123
Max burn-up with edge effects. MW·d/kgU	105	150
Fast neutron flux, (E>0,1 MeV),·10^{21} cm^{-2}	6	7

Tab 2: Irradiation characteristics

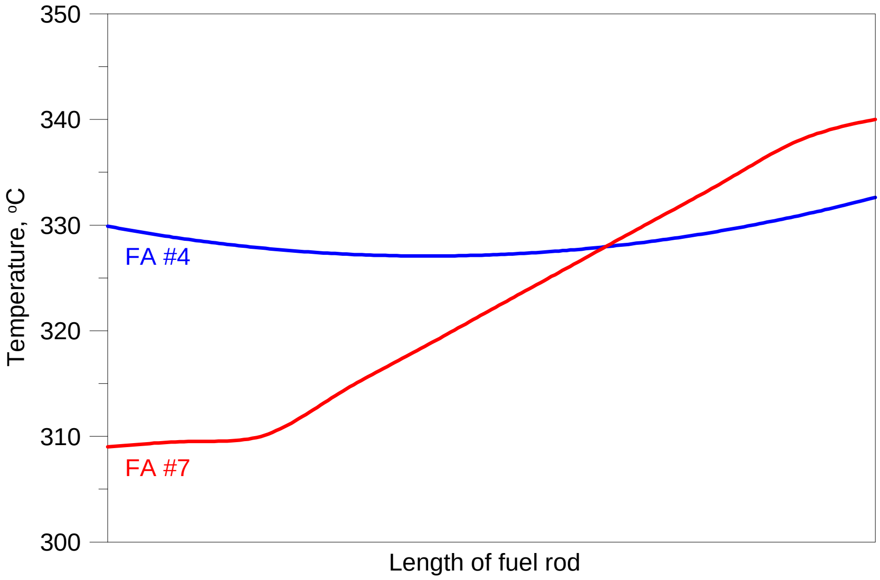


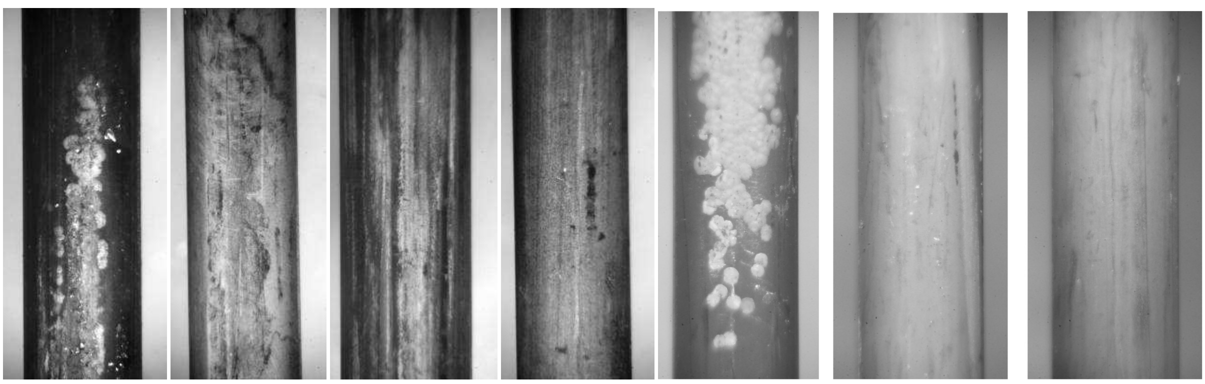
Fig 2. Distribution of typical cladding temperature along the length of fuel rod

3. Post-irradiation investigations

Post-irradiation investigations were carried out in SC “RIAR”, Dimitrovgrad.

3.1 The appearance of fuel rods

The appearances of E635 alloy and its modifications claddings were nearly the same: the oxide layers were flat, gray, and dense with no traces of nodular corrosion. The surfaces of the E110 claddings had considerable areas under nodular corrosion with the formation of a white oxide (Fig 3).



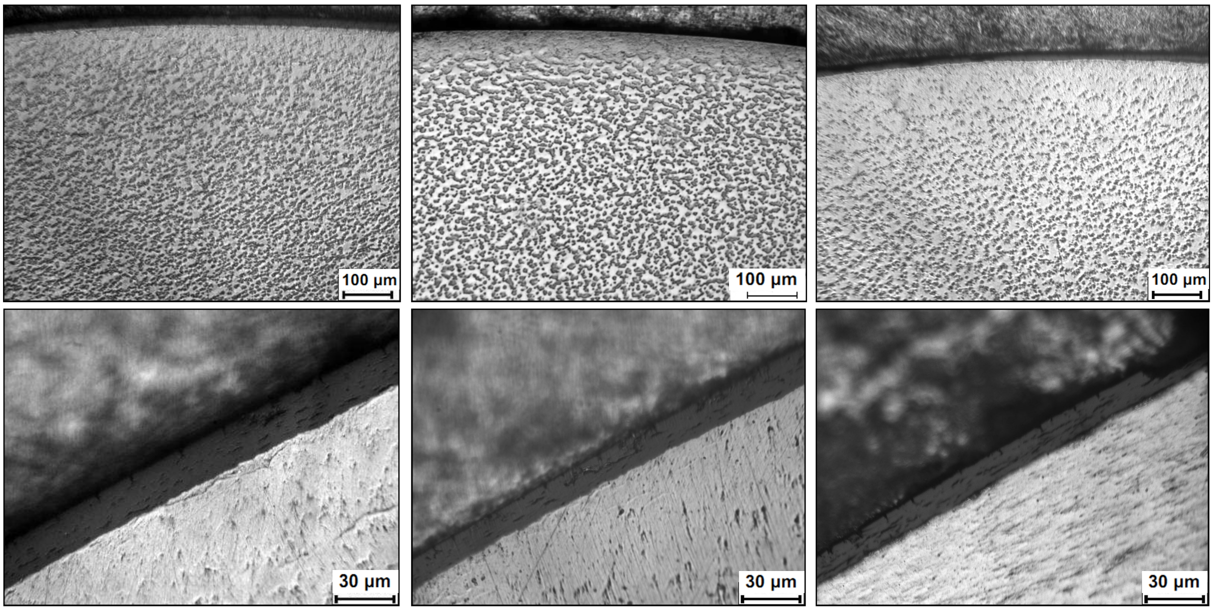
E110 FA #4	E635 FA #4	E635opt FA #4	E635M1 FA #4	E110 FA #7	E635 FA #7	E635M FA #7

Fig 3. The appearance of irradiated fuel rods

3.2 Microstructure of fuel rod claddings

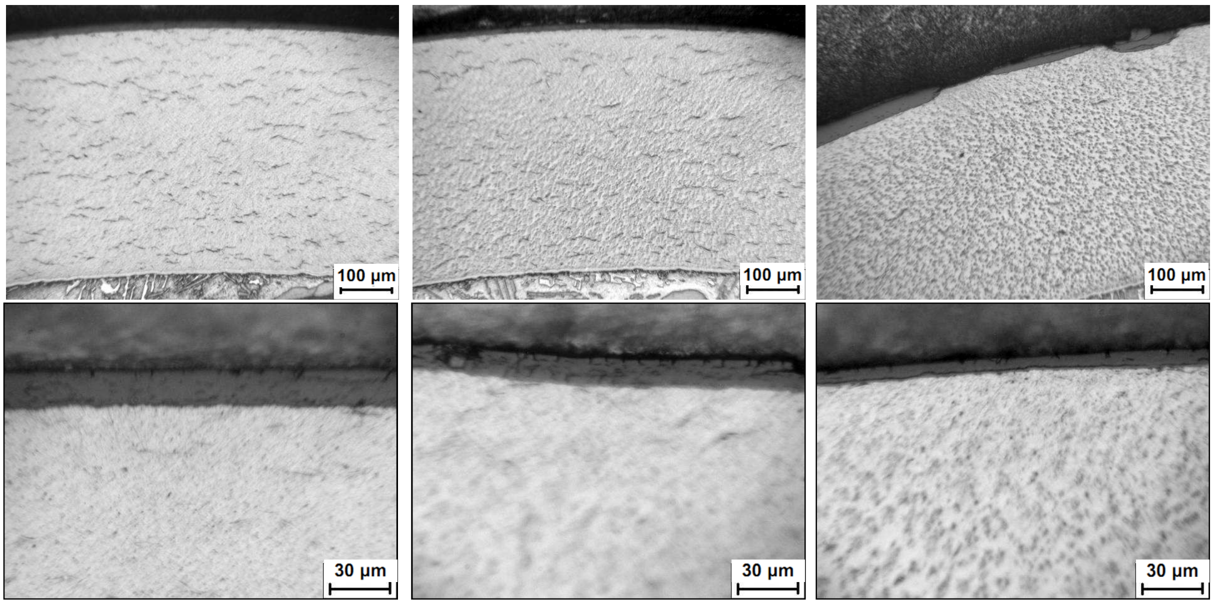
The microstructure of the fuel rods claddings is shown in Fig 4.

The thickness of the layer on the E110 cladding is small. However, on the claddings of all fuel elements of both assemblies there was nodular corrosion (see Tab 3).



Fuel assembly 4

E635 E635opt E635M1



Fuel assembly 7

E635 E635M E110

Fig 4. Microstructure of irradiated fuel rods claddings

#FA	Alloy	Max thickness of oxide layer, μm	Max deepness of nodular corrosion, μm
4	E110	10	57
	E635	25	-
	E635opt	18	-
	E635M1	22	-
7	E110	7-13	46-96
	E635	20	-
	E635M	13-17	-

Tab 3: Corrosion damages of fuel rod claddings

On the outer surface of fuel rods with E635 alloy and its modifications claddings a uniform oxide layer was observed, which had tight contact with the alloy. On the E635 claddings (FA #4) an oxide layer formed with good contact with the cladding up to a thickness of 25 μm; small radial cracks formed on the outer side of the layer adjacent to the metal; small tangential cracks up to 15 μm in thickness were observed.

The oxide layers on E635opt and E635M1 claddings (FA #4) had the same structure, somewhat smaller thickness (15-17 μm), the same small radial cracks and more extended tangential cracks.

On the surface of E635 and E635M claddings (FA #7) also uniform oxide layer formed. The layer had tight contact with the metal, however, in some areas of the surface, the layer was peeled off and partially shed. In the structure of the layer itself from the outside, small radial cracks were observed, and along the layer tangential cracks were present. The maximum thickness of the layer was observed on E635 cladding (20 μm), on the E635M cladding, the layer thickness was lower - 13-17 μm.

3.3 Hydrogen contents in fuel rod claddings

The hydrogen content in the claddings of irradiated fuel rods was determined on samples cut from the central part of the fuel rods using the ELTRA OH 900 gas analyzer. The oxide layer was not removed from claddings.

The results of the measurements are shown in Table 4.

#FA	Alloy	Hydrogen content, wt. %		
		In oxide	In alloy	Total
4	E110	-	-	0,0060
	E635	-	-	0,0153
	E635opt	-	-	0,0087
	E635M1	-	-	0,0140
7	E635	0,0057	0,0100	0,0157
	E635M	0,0054	0,0083	0,0137
	E110	0,0061	0,0058	0,0119

Tab 4: Hydrogen content in fuel rod claddings

For FA #7 the hydrogen content was determined separately in the alloy and in the oxide layer. The analysis process took place in two stages. At the first stage, hydrogen is released only from the oxide layer. The second stage consisted of extracting hydrogen from the same alloy, but only at a higher temperature with the melting of the sample.
Thus, the results of measurements of the hydrogen content in the cladding of the fuel elements of FA #7 are more representative. Table 4 shows that the maximum content of

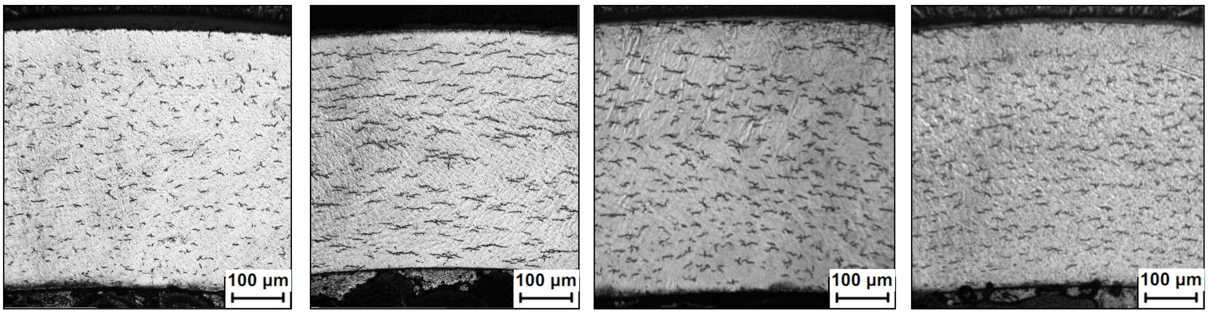
hydrogen in the metal (0.0100 wt. %) was observed in the E635 cladding, the hydrogen content in the E635M cladding was somewhat smaller and was 0.0083 wt. %. The minimum content of hydrogen is observed in E110 cladding - 0.0058% wt. %. The hydrogen content in the oxide layer of these samples is the same within the measurement error.

3.4 Hydrides in fuel rod claddings

An etching operation was performed to identify the hydride precipitates in the fuel rod claddings. The microstructure of the claddings with hydrides is shown in Fig 5.

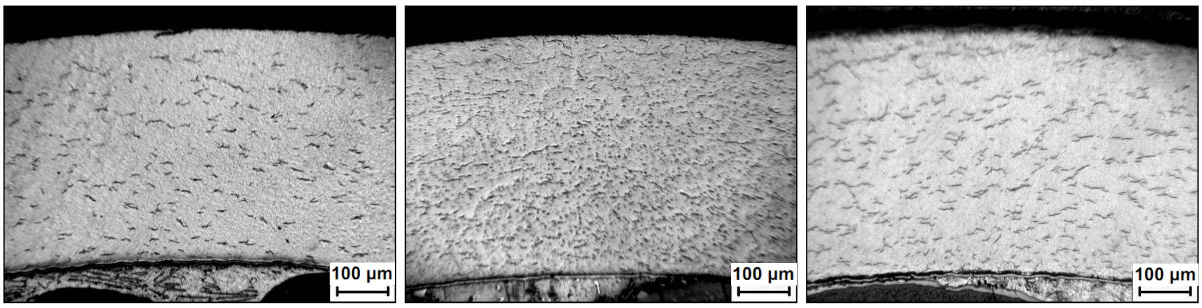
In the E110 claddings very small plate and point hydrides were observed. Plate hydrides have a predominantly tangential orientation, fairly evenly distributed along the perimeter and thickness of the claddings.
In E635 alloy and its modifications claddings, the hydrides in the form of plates, mainly of tangential orientation, are longer in comparison with the E110 alloy. The distribution of hydrides in the E635opt and E635M1 claddings is similar to each other and somewhat different from that observed in the E635 cladding - the extent of the hydrides is smaller and the "shape" is slightly different.

Hydrides in the shells of all fuel elements are oriented mainly tangentially [4].



Fuel assembly 4

E110 E635 E635opt E635M1



Fuel assembly 7

E110 E635 E635M

Fig 5. Microstructure of irradiated fuel rods claddings; etching for hydrides

4. Conclusions

For the first time, in-pile tests of fuel rods with claddings made from modifications of the E635 zirconium alloy have been performed.

The purpose of the tests was to search for more advanced compositions of the E635 type alloy for corrosion and hydrogen pick-up resistance, which can provide increased resource characteristics of fuel rods.

All fuel rods have retained their integrity, their state is satisfactory, bends, dents and other changes in shape have not occurred.

All tested zirconium alloys are well compatible with the fuel composition. There is tight metallurgical contact between the fuel meat and the claddings.

All modifications of the E635 alloy confirmed their excellent mechanical and corrosion resistance properties.

Modifications of the alloy E635opt and E635M showed higher resistance to corrosion and hydrogen pick-up compared to the E635 alloy, while maintaining high strength and ductility. These modifications have confirmed their prospects for use as cladding for fuel rods with enhanced characteristics.

5. References

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