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A. P. Mukhachev[1], O. A. Kharytonova[2,*], T. A. Evdokymova[2]

[1] *Center for Chemical Technology, Academy of Engineering Sciences of Ukraine, Kamyanske, Ukraine*
[2] *Dnipro State Technical University, Kamyanske, Ukraine*

*Corresponding author: eah@ukr.net

RADIATION TESTS OF PRODUCTS MADE OF CALCIUM-THERMAL ZIRCONIUM GRADE CTZ-110 UNDER OPERATION OF THE VVER-440 REACTOR

The paper presents the results of reactor tests of fuel assemblies with cladding made of zirconium alloy grade CTZ-110 at the material testing reactor of National Research Center (NRC) «Kurchatov Institute» at Novovoronezh and Leningrad NPP under various nuclear fuel burnups. It was shown that after all test cycles, the parts from zirconium in the fuel assemblies were in good condition, which was confirmed by metal research of the samples cut out from the fuel elements. The mechanical properties of the fuel cladding made of CTZ-110 alloy are stable and satisfactory. Maximum burn-outs were achieved in the VVER-1000 mode of 67.4 MW·day/kg of uranium and the RBMK-1000 mode – 76.0 MW·day/kg of uranium.

Keywords: zirconium, zircalloy, chlorine, extraction, extractor, quality, electron beam technology, reactor, nuclear fuel.

1. Introduction

As a structural metal for power reactors, alloys of zirconium obtained according to magnesium-thermal (USA) [1] and electrolytic technology (RF) [2] are used.

Licensed nuclear fuel (NF) from the Russian Federation is supplied to Ukrainian nuclear power plants, where zirconium alloys with 1 % and 2.5 % niobium are used. They contain more than 0.01 % (0.035 %) of hafnium. This exceeds the requirement of ASTM B-349-80. Westinghouse began supplying nuclear fuel, the USA, where an experimental alloy, zirconium alloyed with iron, tin, and niobium with Hf content of < 0.01 %, “Zirlo” grade is used.

Zirconium production technologies in the USA and the Russian Federation have existed for more than 75 yr. They do not allow reducing the hafnium content in zirconium to less than 0.005 %, increasing the purity of Zr to 99.9 %.

Both technologies produce chloride effluents that are not recycled and require their disposal. They do not use silicon oxide, which is up to 35 % by weight of zircon. It is a solid waste.

The chlorine-free new zircon processing technology, implemented in Ukraine in 1985, does not have noted drawbacks [3]. It allows you to get zirconium and hafnium of nuclear purity, and a silicon compound, white soot, which reduces the cost of zirconium.

The purity of the Zr and Hf salts (99.9 %) is achieved by extraction method in nitric acid using a tributyl phosphate extractant diluted with kerosene on a new generation of centrifugal extractors [4], which provide high kinetics of extraction and re-extraction processes and high quality of metals by impurities, a deep degree of separation of Zr and Hf salts. The zirconium salt had a hafnium content of less than 0.005 %. The technology of extraction separation of Zr and Hf in a chloride medium (USA) makes it possible to obtain zirconium with a hafnium content of at least 0.008 %.

Vacuum induction and electron beam Zr refining technologies allow you to clean the metal to a purity of 99.9 %, which corresponds to the quality of the iodide metal [5]. The reduction of ZrF_4 fluoride with calcium in the presence of niobium allows one to obtain an ingot of CTZ-110 and CTZ-125 alloy with niobium content of 1 % and 2.5 %, in ingots without pressing and sintering processes.

A comparative analysis of the zirconium quality of various production methods shows that the purest metal of 99.9 % was obtained by chlorine-free calcium-thermal technology with electron beam refining. Doping of zirconium reduces its content in the “Zirkaloy”-2 and “Zirlo” alloys, thus increasing the capture cross-section of thermal neutrons.

This paper presents the results of reactor tests of experimental fuel assemblies (FA) based on the products made of zirconium alloy with niobium CTZ-110 grade in a material testing reactor (MR) and VVER-440 and RBMK -1000 reactors.

2. The methodology of the industrial experiment

The experiment included three stages.

1. Vacuum arc melting (VAM) of the CTZ-110 alloy ingots weighing 250 kg to enlarge the ingot to a weight of 1 ÷ 2 t and obtain a fine-grained structure.

2. Reprocessing the vacuum-arc refining ingot (VAM) required for deformation according to the current technology with obtaining tubes ø 9.13·0.7 mm and fuel assemblies based on them.

3. Tests of experimental fuel assemblies under standard operating conditions at VVER-440, material test reactor (MR), in VVER-440, and RBMK-1000 modes.

Following the "Decision on the fabrication and testing of fuel assemblies with fuel elements made of calcium-thermal zirconium in existing reactors" in 1985, an experimental batch of fuel assemblies was manufactured for testing. For the manufacture of fuel elements shells, alloys CTZ-110 and E-110 were used (40 % of calcium-thermal zirconium, 35 % of electrolytic, 15 % of iodide, and 10 % of metal revolutions).

In the manufacturing process of the shell pipes, the studies on their quality and properties, ultrasonic testing, research on the microstructure and corrosion resistance were carried out. The level of product recovery was at the serial level. The first reactor tests of fuel assemblies were carried out at the NRC «Kurchatov Institute» at a material testing reactor (MR) in the VVER-440 and RBMK-1000 modes. Test conditions are presented in Table 1.

Table 1. **Conditions for reactor tests of experimental fuel assemblies**

Parameters	VVER-440 mode	RBMK-1000
Inlet coolant temperature, °C	320	280
Fuel cladding temperature, °C	350	305
Coolant pressure, kgs/cm^2	160	80

Experimental batches of fuel assemblies in the amount of 8 units out of 1008 fuel elements on VVER-440 were made under the program (13th, 14th, and 15th fuel loads). The fuel elements of the fuel assemblies were equipped with the fuel of two batches with close values of the main indicators, in one batch of 30 fuel elements, in the other 96 elements.

The layout of fuel elements with different fuel batches in fuel assemblies obtained after establishing fuel elements numbers when disassembling the beam and comparing them with the manufacturer's data is shown in Fig. 1. The weight of uranium in the fuel assembly was 120484.1 g.

The cladding of all fuel elements is made of pipes obtained from one ingot of VAM. Before the experiment, the mechanical properties of the pipes were determined; they are shown in Table 2.

A batch of experimental fuel assemblies was operated in the reactor core of the reactor of the 4th power unit as part of the 13th, 14th, and 15th fuel charges. The power test time was 24 thousand hours. The characteristics of the operation of the fuel loads are given in Table 3.

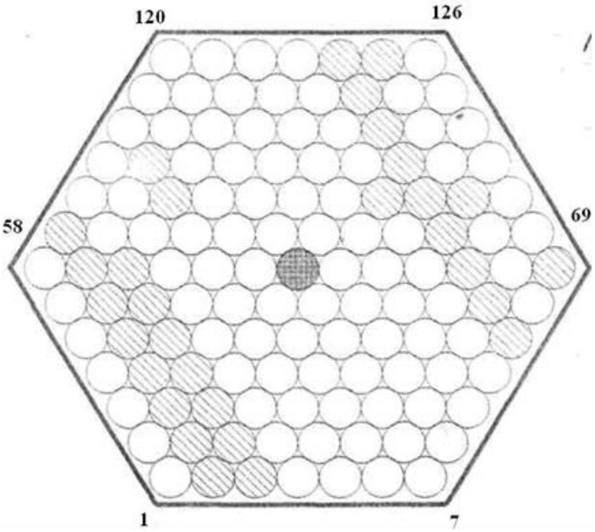

Fig. 1. Configuration scheme of fuel elements beam with the fuel of batch No. 035752400 (shaded) and batch No. 035753000.

Table 2. **The mechanical properties of pipes made of CTZ-110 alloy in the transverse direction before irradiation**

Temperature, °C	σ_B, MPa	σ_0, MPa	δ, %
20	420 - 445	345 - 380	26 - 28
350	175 - 185	160 - 170	32 - 36

Table 3. **Fuel charge operation data**

Charge number	Operation start	Operation finish	Duration	
			Calendar day	Given day eff.
13	02.09.85	06.08.86	338	333.0
14	19.09.86	22.09.87	367	360.1
15	12.10.87	16.08.88	308	296.0

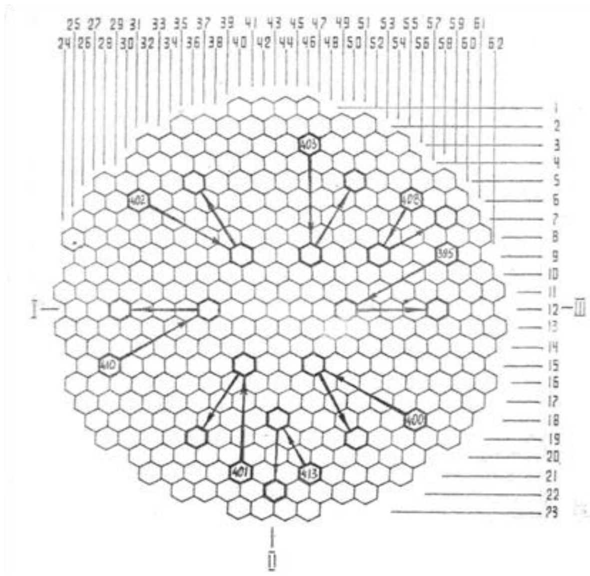

Fig. 2. The movement scheme of the fuel assemblies of the experimental batch in the reactor core during the 13th, 14th, and 15th fuel charges.

In symmetric cells of the reactor core, 6 out of 8 fuel assemblies were operated. The location of the fuel assemblies is shown in Fig. 2. The values of the operation parameters of this fuel assembly as a part of the 15th charge, when there was no thermal control, were obtained by information processing on the measurement of the corresponding parameters in symmetrical cells of the reactor core.

In the process of research, the following characteristics of the fuel elements were determined: amount of deposits; defectoscopy; elongation; measurement of the outer diameter; metallography.

Table 4. **Operating characteristics of fuel assembly No. 19403 based on CTZ-110 on VVER- 440**

Parameters	Charge			Technical Specifications
	13	14	15	
Maximum power fuel assembly, MW	4.53	4.58	3.86	≤ 5.95
Maximum coolant temperature at the outlet of the fuel assembly, °C	302	300	295	≤ 312
Maximum coolant heating in the fuel assembly, °C	37.8	35.8	30	≤ 43.5[1]
The relative energy release of fuel assemblies in the reactor core	1.13	1.13	0.98	≤ 1.35
Burn-out, MW·day/kg U	12.64	13.34	9.29	
Average[2] linear power of a fuel element, W/cm	150	146	124 ≤	

[1] According to the table of reactor operation modes.
[2] Assessment of energy production and effective time.

Reactor tests of 10 experimental fuel assemblies consisting of 360 (see Tables 4 and 7) fuel elements at the 2 RBMK-1000 unit of the Leningrad NPP were carried out from 01.02.1987 to 06.11.1987 (see Table 8). Test time is ≤ 20000 hours, burnout is ≤ 21 MW·day/kg of uranium.

Test conditions: the temperature of the coolant at the inlet is 265 °C; shell temperature is 280 °C; coolant pressure is 75 kgs/cm^2.

3. Test results

The results of reactor tests of fuel assemblies from CTZ-110 on MR are shown in Table 5.

Table 5. **The results of reactor tests of experimental fuel assemblies**

Fuel assembly type	Number of fuel elements in the fuel assembly	Power operation up to maximum burn-out, h	Maximum burn-out, MW·day/kg U	Note
VVER-1000	12 fuel elements, uranium dioxide enrichment 17 %	22949	67.4	Tests successfully completed
	16 fuel elements, uranium dioxide enrichment 4.4 %	15747	58.2	
RBMK-1000	31 fuel elements, uranium dioxide enrichment 10 %	42305	76.0	As of 01.09.1990
	18 fuel elements, uranium dioxide enrichment 6.5 %	42305	56.6	

The high purity of the CTZ-110 zirconium alloy made it possible to achieve fuel burn-out at MR of 67.4 MW·day/kg U in VVER-1000 mode and 76.0 MW·day/kg U in RBMK-1000 mode. The results of tests on MR made it possible to carry out the second stage of reactor tests at VVER-440 in unit 4 of Novovoronezh NPP, the results of which are given in Table 6. All fuel assemblies remained airtight until the end of the operation and reached an average estimated fuel burn-out of 35.3 MW day/kg U and were close to the design value of 36.0. The selection of fuel assemblies for post-reactor studies was carried out from 3 fuel assemblies equipped with fuel elements with shells from the CTZ-110 alloy. As a result, fuel assembly No. 19403 was selected, which was operated before the burn-out of 35.3 MW·day/kg U and had thermal control during the first 2 yr of operation, when the fuel assembly had the highest heat loads.

Table 6. **Resize fuel elements after irradiation**

Fuel cladding material of fuel element	Irradiation before burn-out, MW·day/kg U	Elongation after irradiation, mm	Reduction of shell diameter in central parts, mm
CTZ-110	35.3	5.41	0.04 - 0.12
E-110	32.4	5.34	0.06 - 0.08

FA remained airtight, while the average fuel burn-out was close to the design value of 36 MW·day/kg U.

Table 7. **Characteristics of reactor core cells with fuel assembly No. 19403**

Charge number	Cell coordinates of the reactor core	Thermal control
13	03 - 46	yes
14	09 - 46	yes
15	05 - 50	no

The maximum values of the parameters during the operation of the fuel assemblies did not exceed the values established by Technical Specifications 95 598-79. The arrangement of fuel assemblies in the reactor core ensured a close to the symmetric distribution of energy release in fuel assemblies. The research results of this heat-generating assembly were compared with the available experimental data on the characteristics of fuel elements of previously studied fuel assemblies that had shells made of E-110 alloy. P-3.6-184 fuel assembly was chosen for comparison, which was operated under similar conditions in unit 4 of the NNPP to an average fuel burn-out of 32.4 MW·day/kg U and was studied before in the laboratories of the NNPP and NRC «Kurchatov Institute».

Table 8. **Reactor operation of experimental fuel assemblies (at the time of the scheduled repair of unit 2 of Leningrad NPP April 30, 1989)**

Fuel cladding material	Assembly No.	Charge date	Discharge date	Energy-producing MW·day/kg	Operation time
CTZ-110	4-20-3621	14.10.87		913	457
	4-20-3644	09.07.87		1293	647
	4-20-3648	06.11.87		1128	564
	4-20-3650	14.10.87		1096	548
	4-20-3658	01.02.87		1530	765
E-110	4-20-3625	25.04.87	22.03.89*		679
	4-20-3670	20.04.87			714
	4-20-3632	29.04.87			338
	4-20-3638	18.07.87			874
	4-20-3639	01.02.87			553

* Reason for discharge – hermetization for reuse.

During the research, it was shown that the details of the fuel assemblies were in good condition. The cladding control of the fuel elements (visual inspection and eddy current testing) did not reveal defects in the thickness of the shells and on their surface (including at the points of contact between the shells and the spacing grids). This indicates satisfactory workmanship and good corrosion resistance of pipes made of CTZ-110 alloy.

The number of deposits on the surfaces of the fuel elements in both cases was small. The average thickness of the layer of deposits of corrosion products of the equipment of the 1st contour on the surface of the shells did not exceed 0.1 μm.

Measurement of the size of the fuel elements during irradiation showed that the shells of the CTZ-110 alloy lengthened by an average of 5.41 mm, and the diameter of the fuel cladding in the central sections of the fuel elements decreased, as a result of creep under the influence of the coolant pressure, by 0.04 - 0.12 mm.

In the R-3.6-184 fuel assembly selected for comparison, irradiated to 32.4 MW·day/kg U before burnout, the elongation of fuel elements with the same gas emission as in the fuel assemblies was on average 5.34 mm. The average decrease in the diameter of the fuel cladding in the central sections of 15 such fuel elements was 0.06 - 0.08 mm. The difference in the geometrical sizes of fuel elements with shells of alloys E-110 and CTZ-110 during irradiation under similar conditions is insignificant. Metallographic studies of 16 samples cut from sections of 4 fuel elements of different heights indicate a satisfactory condition of the shells of CTZ-110 alloy. The thickness of the oxide films on the outer and inner surfaces of the shells did not exceed 5 μm. Hydride inclusions in the shell structure were insignificant. They had a predominantly circular orientation. According to the structure of the fuel cladding made of CTZ-110 alloy, they differ from the fuel cladding made of E-110 alloy only in the increased and uneven content of small (about 5 microns) rounded non-metallic inclusions. The structure and behavior of the electron beam welded joints of the fuel cladding of alloy E-110 and CTZ-110 are identical.

The mechanical properties of the studied irradiated fuel cladding of CTZ-110 alloy and irradiated shells of E-110 alloy are given in Table 9.

It is seen that the fuel cladding made of the CTZ-110 alloy has greater strength and slightly less ductility at the operating temperature. The mechanical properties of the fuel cladding made of the CTZ-110 alloy comply with the standards. Thus, the results of tests in the VVER-440 energy reactor of an

Table 9. **Mechanical properties of irradiated shells made of CTZ-110 and E-110 alloy**

Parameter	Temperature tests, °C	Average value	
		CTZ-110	E-110
Ultimate strength, MPa	20	702	614
	350	425	398
Yield point, MPa	20	550	541
	350	360	363
Total elongation, %	20	13.7	13.1
	350	15.6	21.8
Uniform elongation, %	20	5.0	6.9
	350	5.1	7.2

experimental batch of 8 fuel assemblies and post-reactor studies of one of these fuel assemblies showed the normal performance of the fuel cladding made of CTZ-110 alloy. For all the parameters studied, the behavior of these fuel cladding under the conditions of the VVER-440 reactor practically does not differ from the behavior of the fuel cladding currently used in the E-110 alloy. During the operation of the reactor of block 4 with 8 fuel assemblies made of calcium-thermal zirconium, it was not possible to experimentally confirm the advantages of CTZ-110 alloy fuel cladding associated with the content of hafnium < 0.005 weight. % in them, which were theoretically substantiated in [6].

4. Conclusions

1. In 1985 - 1988 reactor tests of experimental batches of fuel assemblies with the cladding of fuel elements made of CTZ-110 alloys on MR in VVER-1000 and VVER-440 and RBMK-1000 reactors were carried out.

1.1. Operating modes were characterized by standard thermal loads.

1.2. The average fuel burn-out on the MR reached 67.76 MW·day/kg U, did not exceed the design value (36 MW·day/kg U) on the VVER-440 for the 3-year fuel cycle and amounted to 35.3 MW·day/kg U (6 fuel assemblies) and 33.7 MW·day/kg U (2 fuel assemblies) and design value for the RBMK-1000 fuel cycle.

1.3. All fuel assemblies were discharged from the reactor at the end of the operation in an airtight state.

2. Post-reactor studies of one fuel assembly with the cladding of fuel elements made of CTZ-110 alloy showed the following.

2.1. The head, jacket, and fuel assembly cover did not have mechanical or corrosion damage. The length of the jacket pipe, measured along one face, increased by ≈1 mm. Turnkey size is within tolerance.

2.2. In appearance and the number of deposits of corrosion products of the equipment of the first fuel cladding contour made of CTZ-110 alloy do not differ from the previously studied fuel cladding of the standard alloy E-110 irradiated under similar conditions.

2.3. During irradiation, the fuel elements lengthened by an average of 5.41 mm with a maximum and minimum elongation of 7.12 and 3.66 mm, respectively. The diameter of the fuel cladding in the central sections of the fuel elements decreased compared to the diameter at the ends of the fuel elements by 0.04 - 0.12 mm. The indicated dimensional changes are typical for standard VVER-440 fuel elements.

2.4. Eddy current control did not reveal internal or surface defects in the fuel cladding of all investigated fuel elements.

2.5. The thickness of the oxide film on the outer and inner surfaces of the fuel cladding did not exceed 5 μm. In the structure of the fuel cladding, there is a small number of hydride inclusions with a predominantly ring orientation. Compared with standard shells, in the fuel cladding of the studied fuel elements, increased content of unevenly distributed small nonmetallic inclusions are noted.

2.6. The structure of welded joints of fuel cladding made of CTZ-110 alloy does not differ from the structure of welded joints of standard fuel cladding. There are no defects in welded joints.

2.7. The irradiated fuel cladding made of CTZ-110 alloy has satisfactory mechanical properties, characterized by high strength and relatively large plasticity reserve (13 - 15 % at a temperature of 350 °C).

3. A comparative analysis of the results obtained with the available data on standard fuel assemblies did not reveal any fundamental differences in the characteristics of fuel elements with fuel cladding from CTZ-110 and E-110 alloys after operation under the indicated conditions.

4. Intermediate data on the comparative test results of products from CTZ-110 and E-110 at RBMK confirmed their identity in energy production and operating time.

Thus, the results of the reactor tests of 8 fuel assemblies and the post-reactor studies of one of them allow us to recommend the operational testing of fuel assemblies with the cladding of calcium-thermal zirconium in an increased volume in the VVER-1000 reactor.

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А. П. Мухачов[1], О. А. Харитонова[2,*], Т. А. Євдокимова[2]

[1] *Центр хімічних технологій Академії інженерних наук України, Кам'янське, Україна*
[2] *Дніпровський державний технічний університет, Кам'янське, Україна*

*Відповідальний автор: eah@ukr.net

РАДІАЦІЙНІ ВИПРОБУВАННЯ ВИРОБІВ ІЗ КАЛЬЦІЄТЕРМІЧНОГО ЦИРКОНІЮ МАРКИ КТЦ-110 В УМОВАХ РЕАКТОРА ВВЕР-440

Наведено результати реакторних випробувань тепловиділяючих збірок (ТВЗ) з оболонками зі сплаву цирконію марки КТЦ-110 на матеріалознавчому реакторі Національного дослідницького центру «Курчатовський інститут» на Нововоронезькій і Ленінградській АЕС при різних вигоряннях ядерного палива. Показано, що після всіх циклів випробувань деталі з цирконію в ТВЗ знаходилися в хорошому стані, це підтвердили металознавчі дослідження зразків вирізаних ділянок твелів. Механічні властивості оболонок зі сплаву КТЦ-110 стабільні й задовільні. Досягнуто максимальні вигоряння в режимі ВВЕР-1000 – 67,4 МВт·доба/кг урану і в режимі РБМК-1000 – 76,0 МВт·доба/кг урану.

Ключові слова: цирконій, ціркалой, хлор, екстракція, екстрактор, якість, електронно-променева технологія, реактор, ядерне паливо.

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