RESEARCH AND DEVELOPMENT OF COATINGS FOR ZIRCONIUM FUEL CLADDINGS

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MOTIVATION

Improve the performance of zirconium alloys caused by:

- **Disability of serious consequences in case of accident and damage to the reactor core (Fukushima-1; $Zr + 2H_2O = ZrO_2 + 2H_2$), integrity of fuel rods under loss of coolant accident (LOCA) type;**
- **New generation LWR => Longer cycles, higher burn-up (>60 GWD/MTU)=> More hard corrosive environment;**
- **Fretting and debris damage of fuel claddings.**

ATFC – Accident Tolerant Fuel Claddings for LWR

The goal of ATF development is alternative fuel technologies for further enhance safety and economics of commercial light water reactors.

Two perspective ways to accident tolerant fuel claddings for LWR:
Long-term >10 years: new claddings (SiC/SiC composites, FeCrAl, Mo/FeCrAl etc.);
Medium term ≈10 years: current zirconium alloys with protective coatings (Cr, SiC, FeCrAl etc.)

Research and Development of Coatings for Advanced Zirconium Nuclear Fuel Claddings

E110 (Zr1Nb) alloy is the main cladding material for WWER type reactors

Requirements For Coatings On Zirconium Claddings:

- ✓High corrosion and radiation resistance at normal operation conditions;
- ✓Neutron economy (low cross section of thermal neutrons, the absence of long-lived radioactive isotopes);
- ✓High thermal conductivity;
- ✓Barrier to hydrogen penetration ;
- ✓Improving mechanical properties of claddings;
- ✓Oxidation resistance in steam and air up to T = 1200 °C;
- ✓Stability of functional properties at T = 350…1200 °C

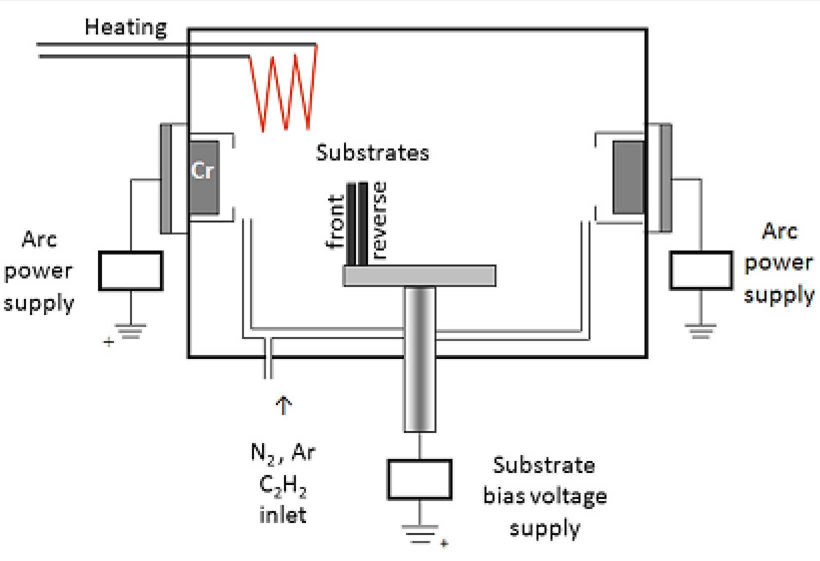
Zirconium tubes (Zr1Nb alloy) with vacuum arc coatings based on chromium

A.S. Kuprin, V.A. Belous,V.N. Voyevodin,V.V. Bryk, R.L. Vasilenko,V.D. Ovcharenko, E.N. Reshetnyak, G.N. Tolmachova, P.N. V'yugov. Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // *Journal of Nuclear Materials* 465 (2015) 400-406

Development of protective coatings for zirconium claddings in the world

	Coatings	Deposition method	Thickness, mkm	Country
Nitrides	TiN	Vacuum arc	4	Russia, S. Korea
		Laser ablation	2	USA
	TiAlN	Vacuum arc	2-4,12	Russia, USA
		Magnetron	2-4	Norway
		Laser ablation	2	USA
	TiN/TiAlN	Vacuum arc	8-11	USA
	CrN	Magnetron	2-4	Norway
		Vacuum arc	7	*Ukraine*
	CrAlN	Magnetron	2-4	Norway
Metallic	Cr	Thermal evaporation	3-10	France, *Ukraine*
		Vacuum arc	10	*Ukraine*, S. Korea
		Magnetron	10-20	France,
		Plasmatron	80	S. Korea
		HVOF+ cold rolling	30	S. Korea
	FeCrAl	Magnetron	1	USA
	Mo/FeCrAl	HVOF+ cold rolling	10/30	S. Korea
Carbides and others	Cr_3C_2-NiCr	HVOF	250	China+ GB
	Ti_2AlC	HVOF	90	USA
		Magnetron + laser irradiation	2-5	USA
	Si	Plasmatron + laser irradiation	50	S. Korea
	SiC	CVD	3000	S. Korea
			32	USA
		EB-evaporation	10-30	*Ukraine*
	Diamond	Plasma-CVD	0,3	Czech Republic + USA

Vacuum arc method for coatings deposition (KIPT)



Schematic diagram of the cathodic arc evaporation method

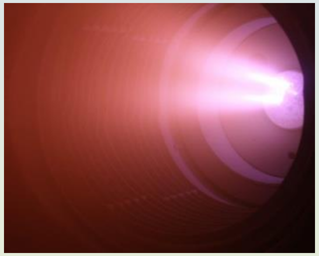


Photo of plasma stream from cathode

Methods of the investigations

✓Structure analysis - SEM, TEM, XRD;

✓Concentration of elements – EDX, XRPA, NRA;

✓Mechanical characteristics of coatings and surfaces – nanoindentation;

✓Mechanical characteristics of tubes – tensile test;

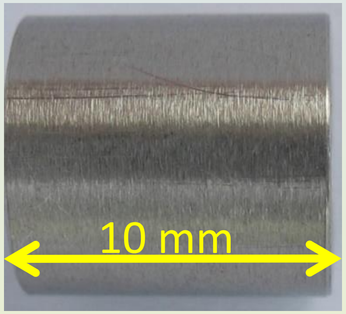
✓Saturation by hydrogen or deuterium from the gas phase;

✓Corrosion – electrochemistry; autoclave; thermocycling test in steam and air.

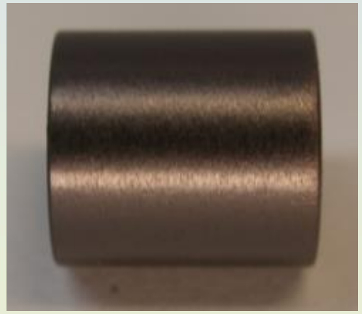
Vacuum arc deposition method has advantages :

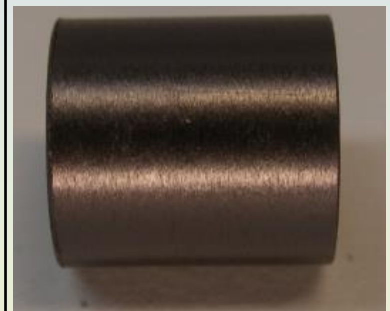
- a wide range of metallic and ceramic coatings;
- multi-layer, multi-component and nanostructured coatings;
- a high degree of ionization(30-100%);
- low deposition temperature (≤500 °C);
- high deposition rate and high quality coatings (1-30 mkm/h).

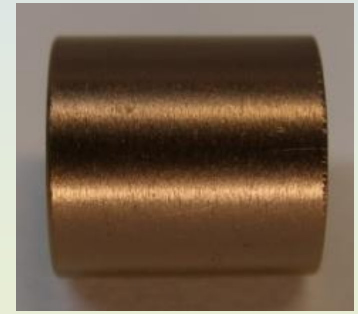
Samples of Zr-1Nb claddings with coatings

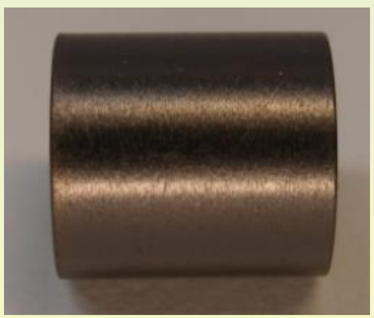


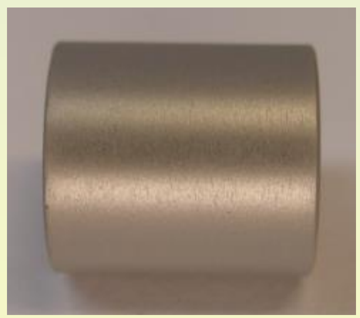
Initial Zr1Nb

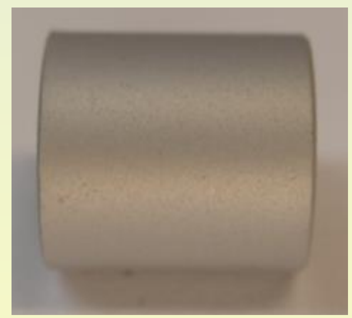

TiAlN


TiAlYN


TiAlSiN


TiAlCrYN


TiAlCrY


Cr18Ni10T

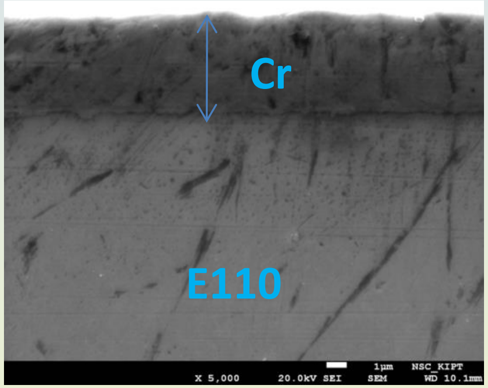

Cr

Samples of Zr-1Nb claddings : Ø -9.2 mm; wall thickness -0.7 mm; length -10 mm.

Oxidation resistant nitride and metallic vacuum arc coatings with thickness ~10 µm.

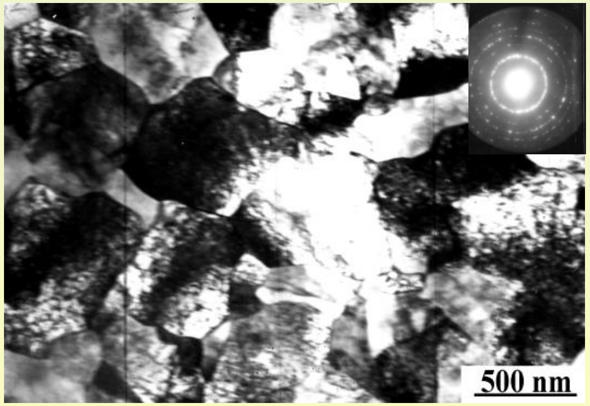
Chromium coatings on E110 alloy claddings

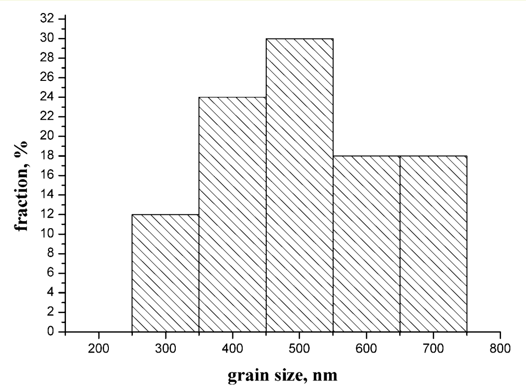
Photo of a tube fragment with Cr coating



SEM image of coating cross section on tube

The chromium coating has a dense structure without pores and cracks

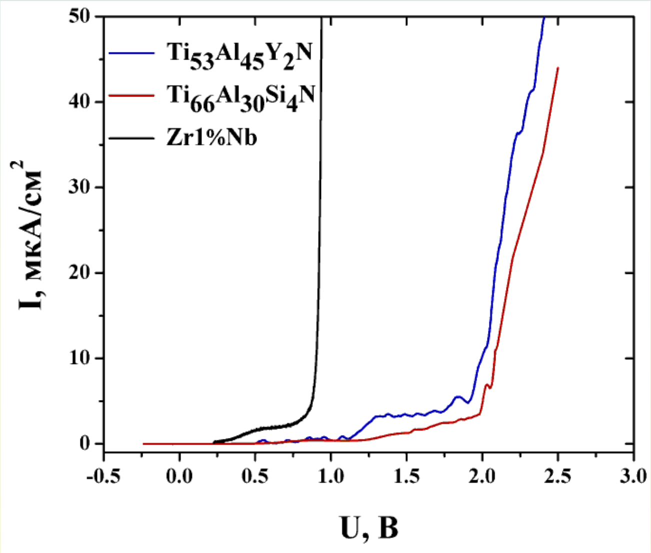




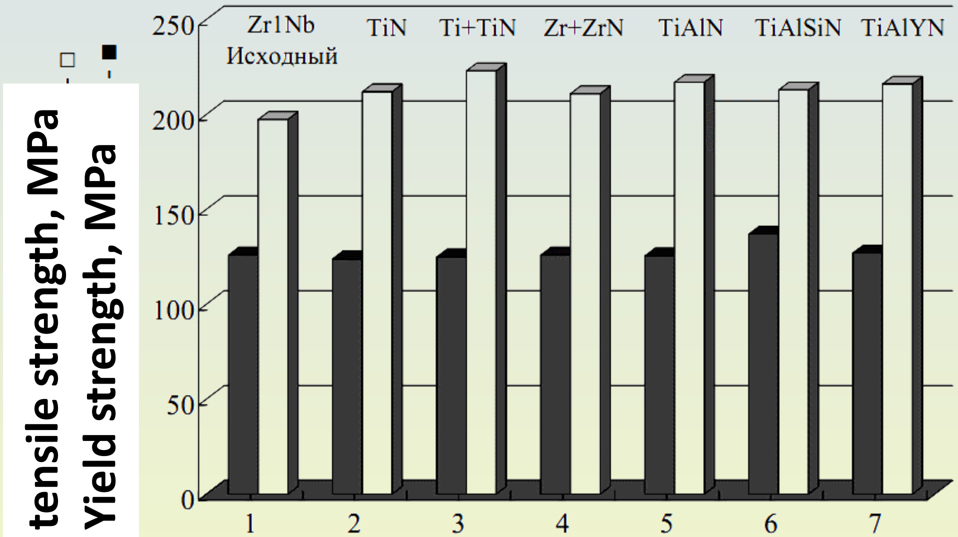
TEM image of coating structure and crystallites sizes

Crystallite size in the coating is near 500 nm

Properties of the Zr1Nb claddings with coatings



Anodic polarization curves for Zr-1Nb alloy with coatings in the reactor water T=20 ºC.



Nitride coatings increase the tensile strength σ_B from 12 to 21% at 350 ° C.

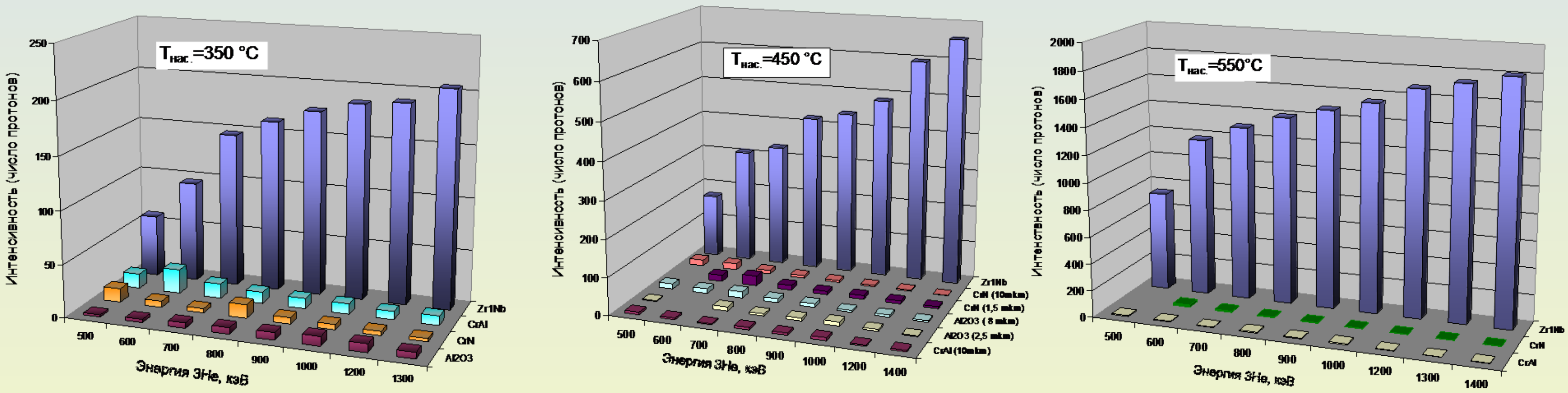
Hardness of initial Zr1Nb alloy and vacuum arc coatings

Coating	Zr1Nb	Cr	Cr/CrN	TiN	ZrN	TiAlN	TiAlYN	TiAlSiN
H, GPa	2	5	25	30	28	32	34	36

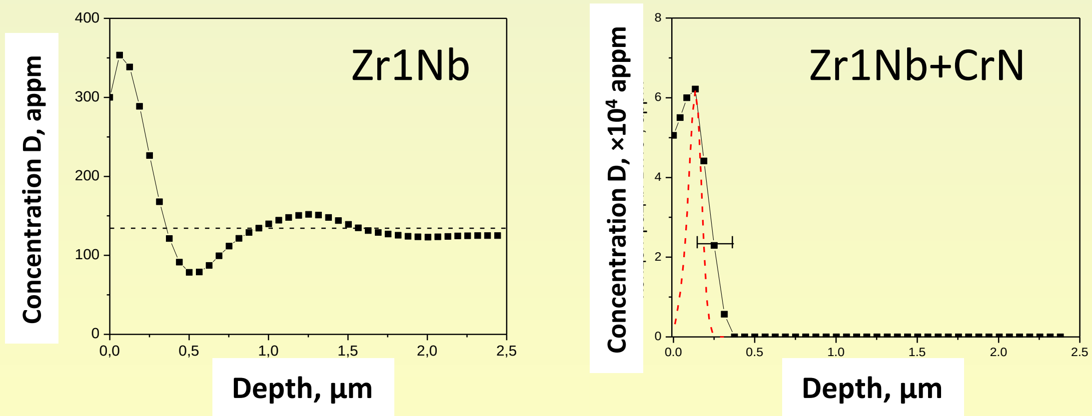
Vacuum-arc nitride coatings increase the resistance of zirconium alloy to electrochemical corrosion in reactor water;
Coatings have higher mechanical characteristics compared to uncoated zirconium alloys that should provide a higher wear resistance of fuel cladding in normal in-reactor operating conditions.

Barrier properties of coatings against deuterium penetration

Zr1Nb alloy with CrN, CrAl and Al_2O_3 coatings saturated with deuterium P = 10^{-3} Pa, t= 120 min.



Energy dependences of integral proton yields for Zr1% Nb with and without coatings saturated with deuterium at temperatures of 350, 450 and 550 °C for 2 hours.



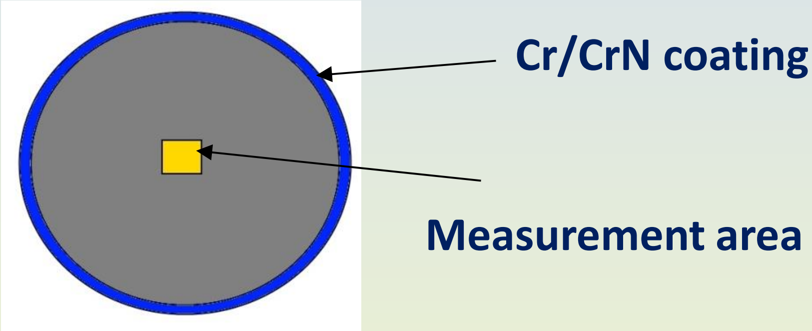
CrN, CrAl and Al_2O_3 coatings serve as a barrier against the penetration of deuterium into zirconium in the investigated temperature range from 350 to 550 °C.

Depth distribution of implanted deuterium with energy 15 keV/D at 350 °C, dose $1 \cdot 10^{17} cm^{-2}$.

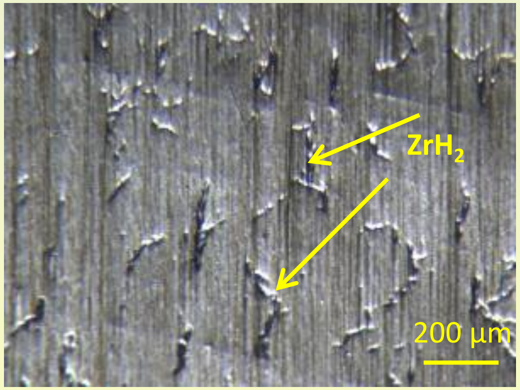
Resistance of E110 Alloy with Cr/CrN Coatings To Hydrogen Saturation

Saturation of E110 alloy with Cr/CrN coatings by hydrogen from the gas phase was carried out at a temperature of 420 °C for 50 hours.

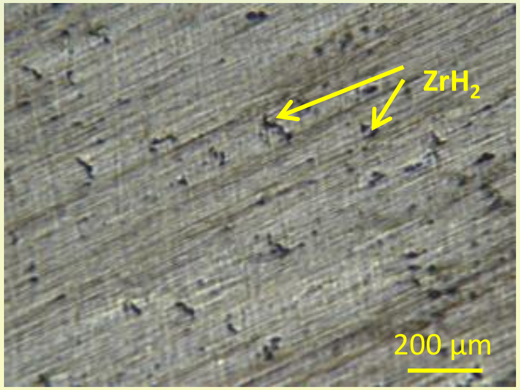
Cylindrical samples : Ø -9 mm, L – 10 mm;
Cr/CrN coatings with different thicknesses : 9 and 14 µm



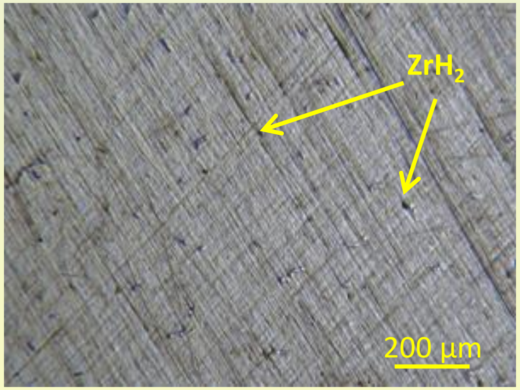
Concentration of hydrides measured on the metallographic cross-sections of the samples after tests using optical microscopy:



E110 – **240** ppm



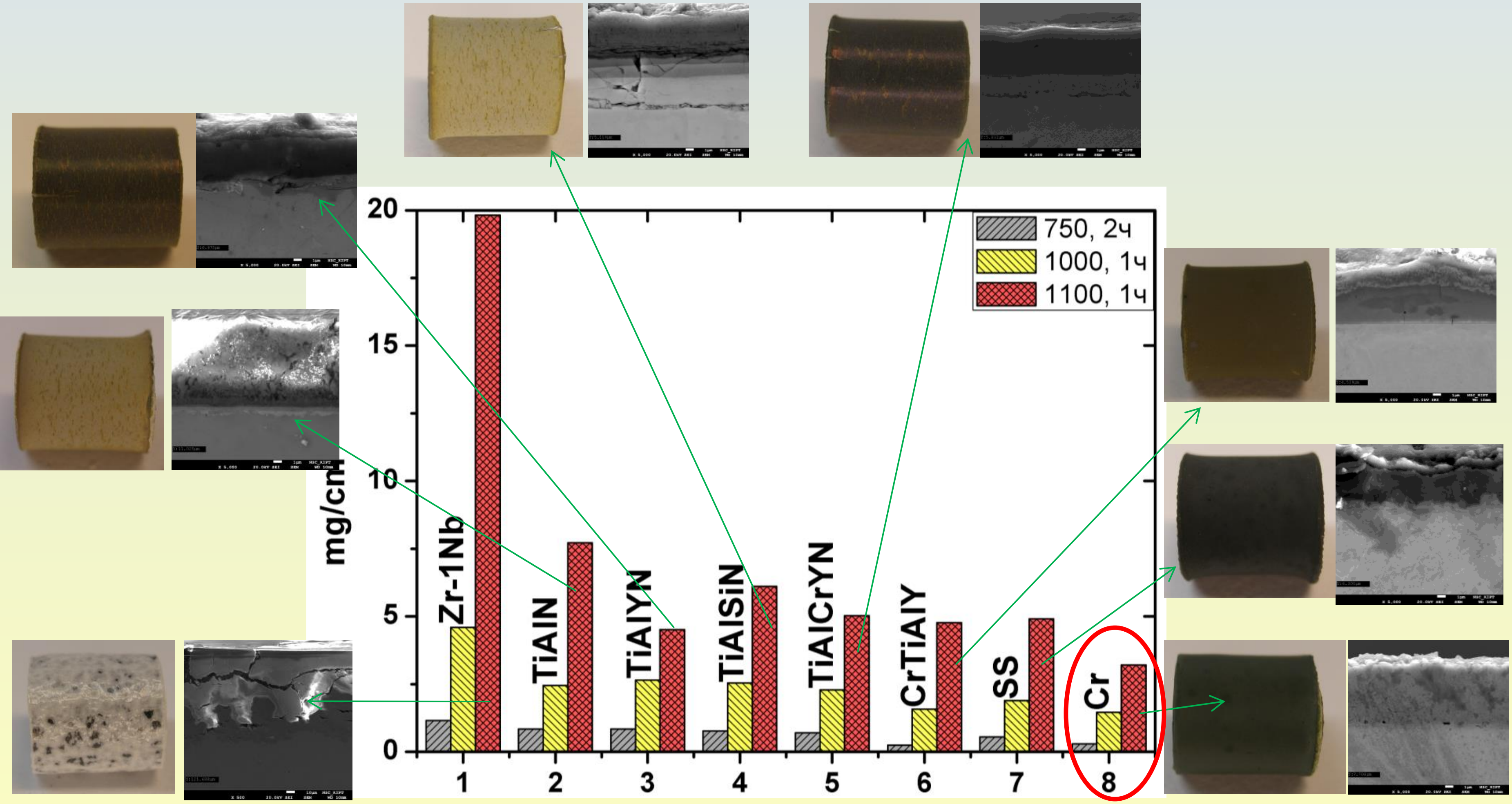
Coated (9 µm) – **100** ppm



Coated (14 µm)– **85** ppm

Cr/CrN coatings with thickness ~14 µm reduce the concentration of hydrogen in zirconium alloy E110 from 240 to 85 ppm after the test in a hydrogen atmosphere.

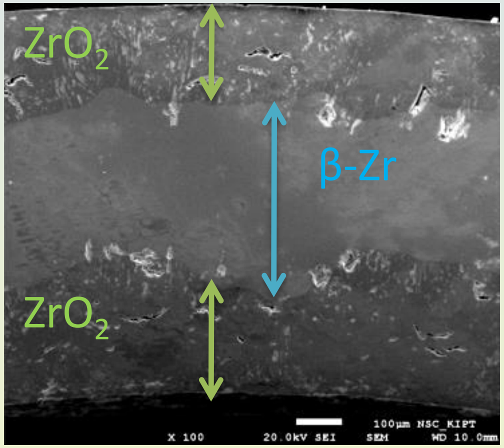
Oxidation of claddings with coatings in air at 750, 1000, 1100 °C

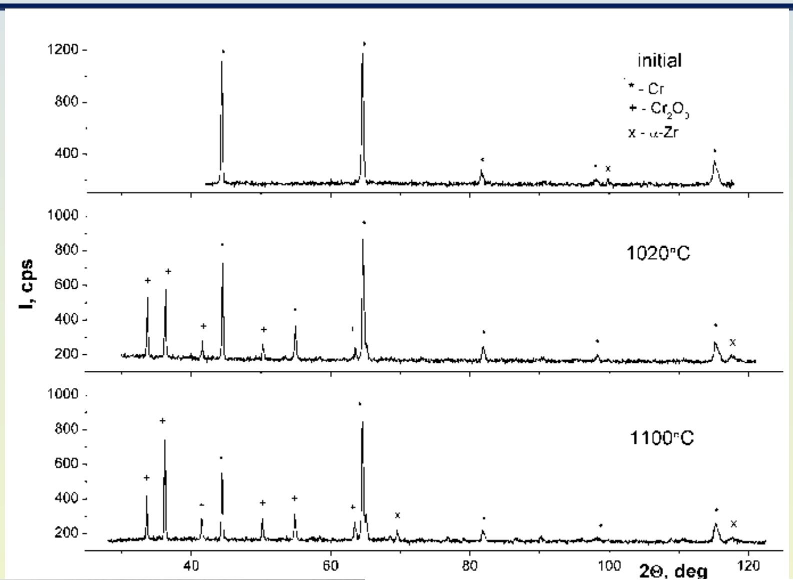


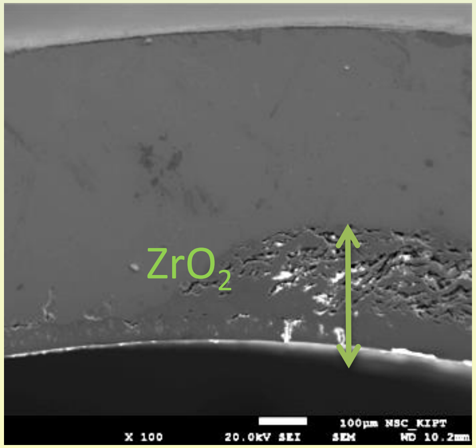
Weight gain of the samples after oxidation in air.

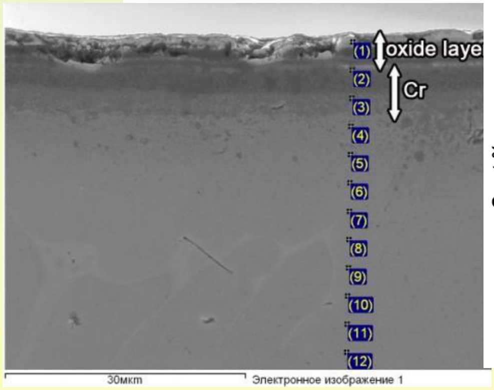
Coatings provide Zr-1Nb alloy protection from the oxidation in air for 1 h up to 1100 °C. The best result demonstrates Cr coating.

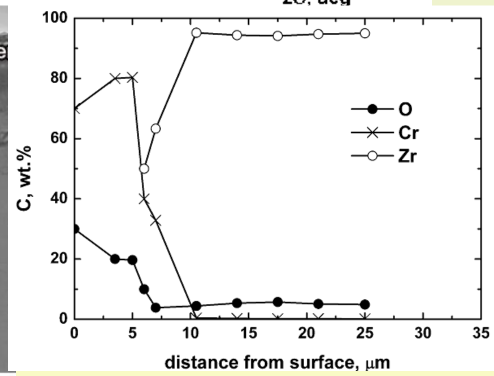
Oxidation of Zr-1Nb with Cr coating in air at T = 1100 °C, t= 1 h







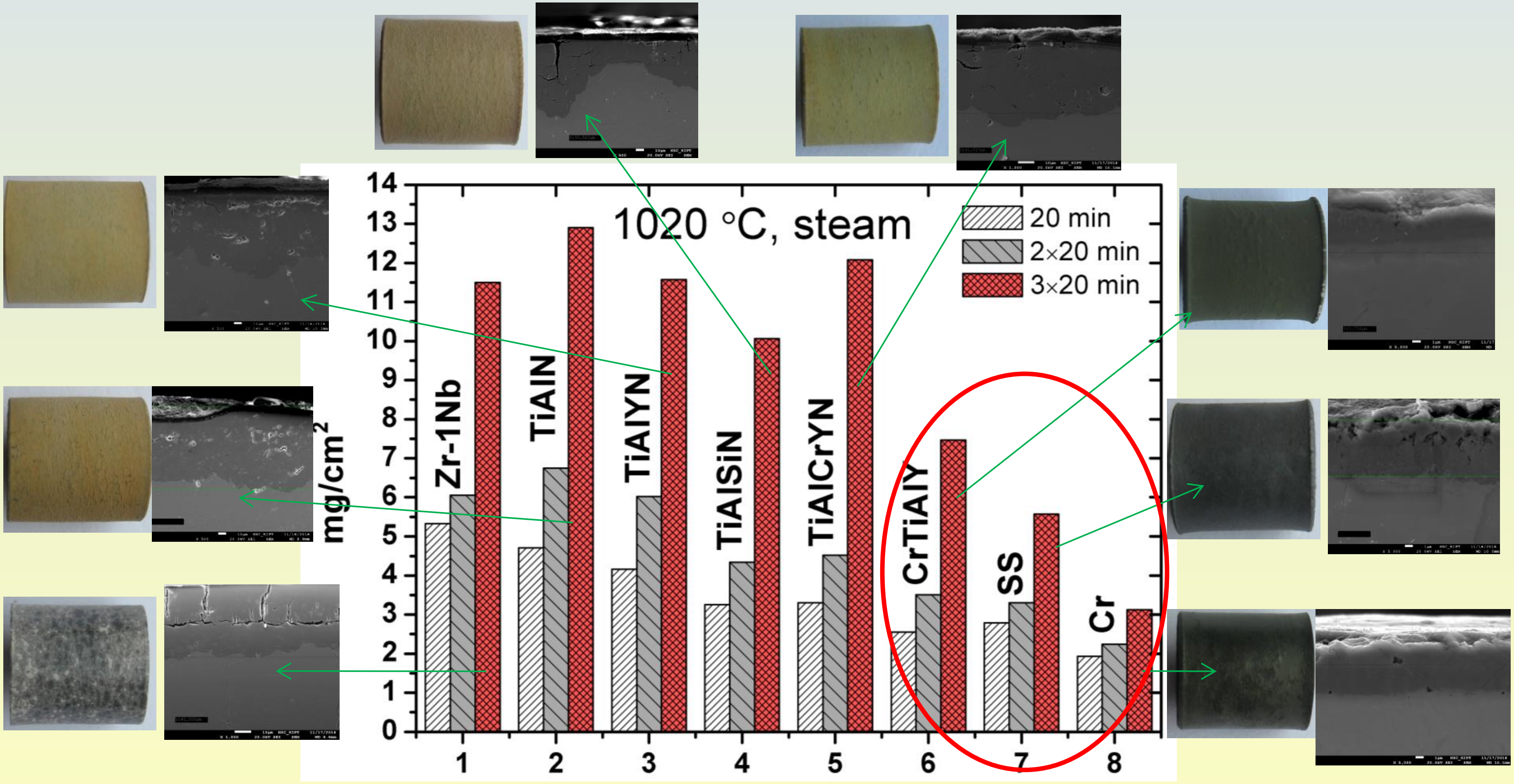




➢High oxidation of the alloy E110 occurs to the depth of ~ 150 µm with formation of a monoclinic cracking ZrO_2 film;

➢ Cr_2O_3 oxide film is formed up to the depth of 5 µm and the there is no phase of ZrO_2 in the chromium coating.

Thermocycling oxidation of coated claddings in steam at 1020 °C

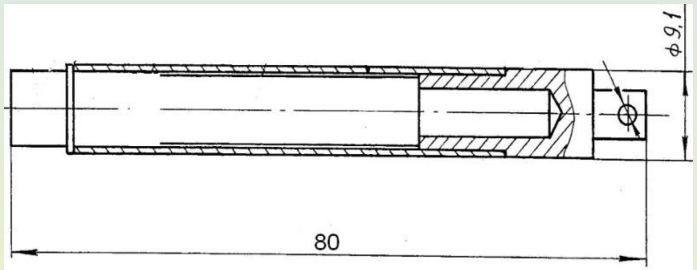


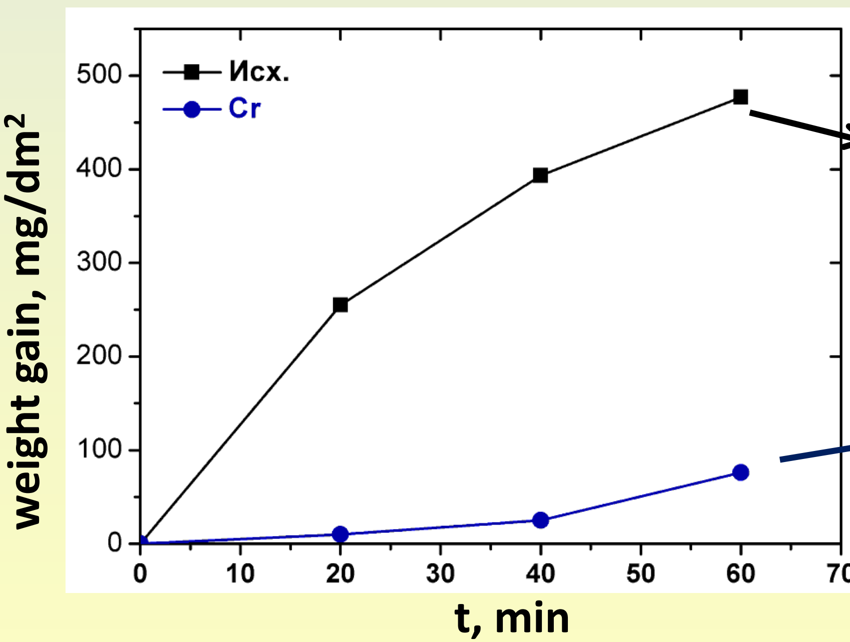
Weight gain of samples after thermocyclic (3 times for 20 min) tests in the steam flow at 1020 °C

Only metallic coatings protect Zr1Nb after thermocyclic test

Oxidation of fuel rod models with coatings at 900 °C in steam

Fuel rod models, Ø - 9.1 mm; length - 80 mm;
internal pressure 1 atm.



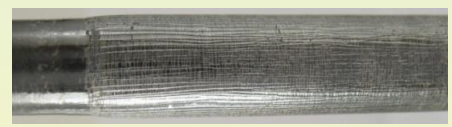


Before testing

Initial Zr1Nb

With Cr coating

After testing



Ø 9,95 mm

Zr1Nb

Ø 9,6 mm

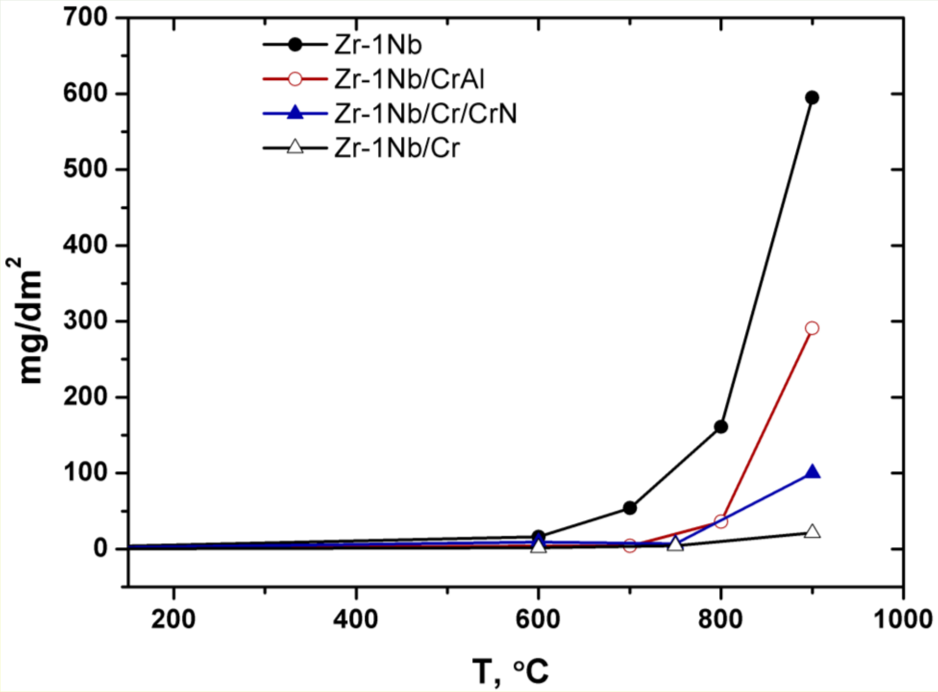
With Cr coating

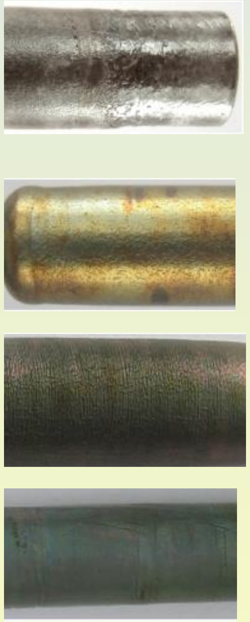
Fuel rod models with chromium coating (10 µm) demonstrate :

- corrosion resistance in steam is 10 times better than without coating ;
- lower increasing in tube diameter.

Cyclic oxidation of fuel rod models with protective coatings in steam

Thermal cycling test: model fuel rods with internal pressure of 20 atm., holding for 1 min at test temperature, cooling to 100 °C; repeat 10 cycles at each temperature.



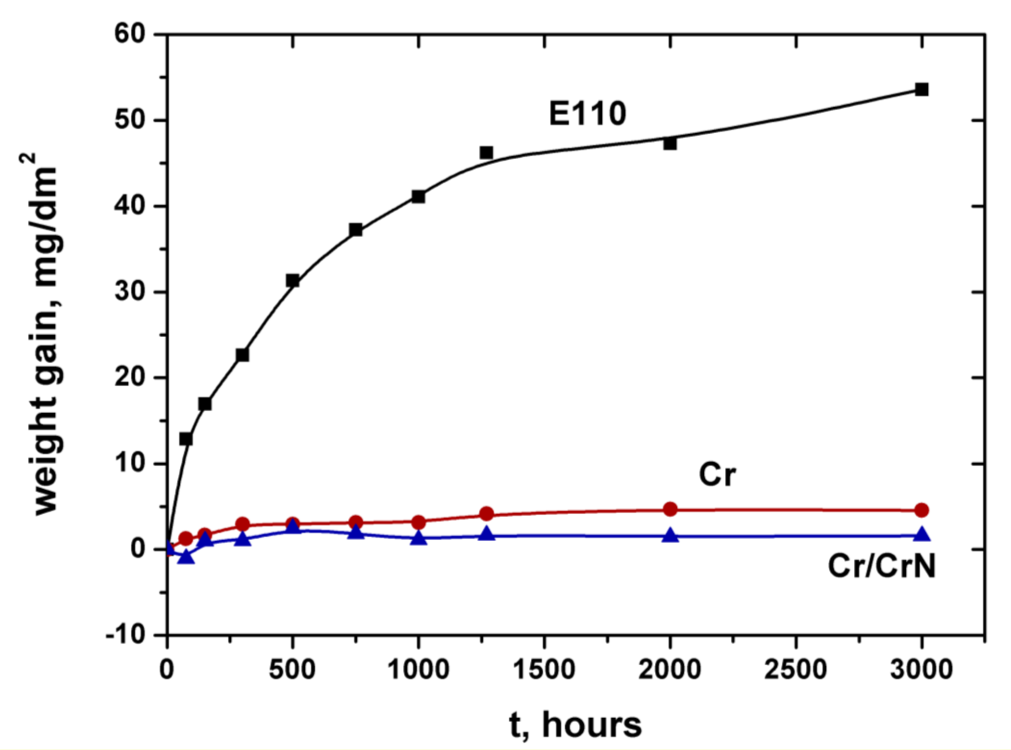


Thermal cycling tests of fuel claddings models with coatings in steam at T = 600 - 900 °C

- In the initial Zr1Nb cracking and delaminating of oxide after temperature cycling testing observed ;
- Cr and Cr/CrN coatings demonstrate the best result without cracking and delamination.

Autoclave Testing

Autoclave tests of E110 model fuel rods with coatings, T=350 °C, pressurized water P=150 atm., WWER water chemistry



Cr and Cr/CrN coatings demonstrate excellent corrosion resistance in normal operation conditions

Summary

- ✓ATFC now is the one of the main safety task in reactor materials science;
- ✓Vacuum-arc nitride and metallic coatings were designed and tested on zirconium fuel claddings in the concept of development ATFC in KIPT;
- ✓Coatings improve the mechanical properties (hardness and tensile strength) of zirconium tubes, increase the corrosion resistance and reduce the amount of absorbed hydrogen;
- ✓Vacuum arc coatings reduce the oxidation rate of zirconium alloy under high-temperature steam environment and in the air up to 1100 °C;
- ✓Zirconium claddings with chromium coatings showed the best resistance at high temperature (600-1100 °C) tests;
- ✓Zirconium tubes with Cr and Cr/CrN coatings have high corrosion resistance in nominal conditions and in the event of an accident.

Publications

1. A.S. Kuprin, V.A. Belous,V.N. Voyevodin,V.V. Bryk, R.L. Vasilenko,V.D. Ovcharenko, E.N. Reshetnyak, G.N. Tolmachova, P.N. V'yugov. Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high-temperature oxidation in air // *Journal of Nuclear Materials* 465 (2015) 400-406
2. P.I. Stoev, V.A. Belous, V.N. Voyevodin, A.S. Kuprin, S.A. Leonov, V.D. Ovcharenko, M.A. Tikhonovsky, V.M. Horoshih. Mechanical properties and acoustic parameters tubes of zirconium alloy Zr1%Nb with a protective coatings // *Problems Of Atomic Science And Technology* 2015. №5(99), p. 87 – 97
3. I.E. Kopanetz, G.D. Tolstolutskaya, A.V. Nikitin, V.A. Bilous, A.S. Kuprin, V.D. Ovcharenko, R.L. Vasilenko. The effect of Cr, Cr-N and Cr-Ox coatings on deuterium retention and penetration in zirconium alloy Zr-1Nb // *Problems Of Atomic Science And Technology* 2015. №5(99), p. 81 -86
4. G.D. Tolstolutskaya, I.E. Kopanetz, V.V. Ruzhytskiy, V.A. Bilous, A.S. Kuprin, V.D. Ovcharenko, R.L. Vasilenko, S.A. Leonov. Decrease of hydrogen saturation of zirconium alloys at modification of surface by complex ion-plasma treatment // *Problems Of Atomic Science And Technology* 2015. №2(96), p. 119-123.
5. A.S. Kuprin, V.A. Belous, V.V. Bryk, R.L. Vasilenko, V.N. Voyevodin, V.D. Ovcharenko, G.N. Tolmachova, I.V. Kolodiy, V.M. Lunyov, I.O. Klimenko. Vacuum-arc chromium coatings for Zr-1Nb alloy protection against high-temperature oxidation in air // *Problems Of Atomic Science And Technology* 2015. №2 (96), p. 111-118.
6. A.S. Kuprin, V.A .Belous, V.N. Voyevodin, V.V. Bryk, R.L. Vasilenko, V.D. Ovcharenko, G.N. Tolmachova, P.N. V’ygov. High-temperature air oxidation of E110 and Zr-1Nb alloys claddings with coatings // *Problems Of Atomic Science And Technology* 2014. №1(89), p. 126-132
7. V.A. Belous, P.N. V´ygov, A.S. Kuprin, S.A. Leonov, G.I. Nosov, V.D. Ovcharenko, L.S. Ozhigov, A.G. Rudenko, V.T. Savchenko, G.N. Tolmacheva, V.M. Khoroshikh. Mechanical characteristics of Zr1Nb alloy tube after deposition of ion-plasma coatings // *Problems Of Atomic Science And Technology* 2013. №2(84), c. 140-143.

KIPT is widely open for common research in ATFC area!

Thank for your attention!