RESEARCH AND DEVELOPMENT OF COATINGS FOR ZIRCONIUM FUEL CLADDINGS


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European Commission funded International Workshop
"Materials resistant to extreme conditions for future energy systems"
12-14 June 2017, Kyiv - Ukraine
Improve the performance of zirconium alloys caused by:

- Disability of serious consequences in case of accident and damage to the reactor core (Fukushima-1; \( \text{Zr} + 2\text{H}_2\text{O} = \text{ZrO}_2 + 2\text{H}_2 \)), 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 $T = 1200 \, ^\circ \text{C}$;
✓ Stability of functional properties at $T = 350...1200 \, ^\circ \text{C}$

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

<table>
<thead>
<tr>
<th>Coatings</th>
<th>Deposition method</th>
<th>Thickness, mkm</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>Vacuum arc</td>
<td>4</td>
<td>Russia, S. Korea</td>
</tr>
<tr>
<td></td>
<td>Laser ablation</td>
<td>2</td>
<td>USA</td>
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<tr>
<td>TiAlN</td>
<td>Vacuum arc</td>
<td>2-4,12</td>
<td>Russia, USA</td>
</tr>
<tr>
<td></td>
<td>Magnetron</td>
<td>2-4</td>
<td>Norway</td>
</tr>
<tr>
<td></td>
<td>Laser ablation</td>
<td>2</td>
<td>USA</td>
</tr>
<tr>
<td>TiN/TiAlN</td>
<td>Vacuum arc</td>
<td>8-11</td>
<td>USA</td>
</tr>
<tr>
<td>CrN</td>
<td>Magnetron</td>
<td>2-4</td>
<td>Norway</td>
</tr>
<tr>
<td>CrAlN</td>
<td>Magnetron</td>
<td>2-4</td>
<td>Norway</td>
</tr>
<tr>
<td>Cr</td>
<td>Thermal evaporation</td>
<td>3-10</td>
<td>France, Ukraine</td>
</tr>
<tr>
<td></td>
<td>Vacuum arc</td>
<td>10</td>
<td>Ukraine, S. Korea</td>
</tr>
<tr>
<td></td>
<td>Magnetron</td>
<td>10-20</td>
<td>France, Ukraine</td>
</tr>
<tr>
<td></td>
<td>Plasmatron</td>
<td>80</td>
<td>S. Korea</td>
</tr>
<tr>
<td></td>
<td>HVOF+ cold rolling</td>
<td>30</td>
<td>S. Korea</td>
</tr>
<tr>
<td>FeCrAl</td>
<td>Magnetron</td>
<td>1</td>
<td>USA</td>
</tr>
<tr>
<td>Mo/FeCrAl</td>
<td>HVOF+ cold rolling</td>
<td>10/30</td>
<td>S. Korea</td>
</tr>
<tr>
<td>Cr₂C₂-NiCr</td>
<td>HVOF</td>
<td>250</td>
<td>China+ GB</td>
</tr>
<tr>
<td>Ti₃AlC</td>
<td>HVOF</td>
<td>90</td>
<td>USA</td>
</tr>
<tr>
<td></td>
<td>Magnetron + laser irradiation</td>
<td>2-5</td>
<td>USA</td>
</tr>
<tr>
<td>Si</td>
<td>Plasmatron + laser irradiation</td>
<td>50</td>
<td>S. Korea</td>
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<tr>
<td>SiC</td>
<td>CVD</td>
<td>3000</td>
<td>S. Korea</td>
</tr>
<tr>
<td></td>
<td>EB-evaporation</td>
<td>10-30</td>
<td>Ukraine</td>
</tr>
<tr>
<td>Diamond</td>
<td>Plasma-CVD</td>
<td>0,3</td>
<td>Czech Republic + USA</td>
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</table>
Vacuum arc method for coatings deposition (KIPT)

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).

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.
Samples of Zr-1Nb claddings with coatings

<table>
<thead>
<tr>
<th>Initial Zr1Nb</th>
<th>TiAlN</th>
<th>TiAlYN</th>
<th>TiAlSiN</th>
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<tbody>
<tr>
<td>TiAlCrYN</td>
<td>TiAlCrY</td>
<td>Cr18Ni10T</td>
<td>Cr</td>
</tr>
</tbody>
</table>

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

The chromium coating has a dense structure without pores and cracks

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 $T=20^\circ\text{C}$.

Hardness of initial Zr1Nb alloy and vacuum arc coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Zr1Nb</th>
<th>Cr</th>
<th>Cr/CrN</th>
<th>TiN</th>
<th>ZrN</th>
<th>TiAlN</th>
<th>TiAlYN</th>
<th>TiAlSiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>H, GPa</td>
<td>2</td>
<td>5</td>
<td>25</td>
<td>30</td>
<td>28</td>
<td>32</td>
<td>34</td>
<td>36</td>
</tr>
</tbody>
</table>

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 Al₂O₃ coatings saturated with deuterium at temperatures of 350, 450 and 550 °C for 2 hours.

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 Al₂O₃ 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 $1 \cdot 10^{17} \text{cm}^{-2}$. 
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 \( T = 1100 \, ^\circ\text{C} \), \( t = 1 \, \text{h} \)

- High oxidation of the alloy E110 occurs to the depth of \( \sim 150 \, \mu\text{m} \) with formation of a monoclinic cracking \( \text{ZrO}_2 \) film;
- \( \text{Cr}_2\text{O}_3 \) oxide film is formed up to the depth of 5 \( \mu\text{m} \) and there is no phase of \( \text{ZrO}_2 \) 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.

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.

Before testing
- Initial Zr1Nb
- With Cr coating

After testing
- Ø 9,95 mm
- Zr1Nb
- Ø 9,6 mm
- With Cr coating

Graph: t, min vs weight gain, mg/dm²
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.

- 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 tests of E110 model fuel rods with coatings, $T=350\, ^\circ C$, pressurized water $P=150\, \text{atm.}$, 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.


KIPT is widely open for common research in ATFC area!

Thank for your attention!