Study of high temperature oxidation of zirconium fuel element claddings with chromiferous coatings

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Abstract. This paper presents the results of the study of resistance to corrosion of zirconium fuel element cladding fragments protected with nichrome and chrome coatings. Experiments were conducted on coatings deposition on fuel element claddings by cathodic arc deposition and electrochemical deposition methods. Argon ion beam pretreatment of the cladding surface is shown to have a beneficial effect on coating adhesion. Studies of resilience of the coatings were conducted in the atmosphere of super-heated steam at 900 °C and with an exposure of up to 10000 seconds. It has been shown that the coatings deposited impede formation of ZrO₂ oxide layer at the outer surface and reduce the depth of oxygen penetration into the metallic sublayer as compared with the samples in their original condition.

1. Introduction

Improvement of operational safety of nuclear power units (NPU) is an indispensable condition of atomic energy development. The problems of assurance of nuclear reactors safety and preset fuel burnup are to a large extent determined by operability of fuel assemblies composed of fuel elements, every one of which consisting of zirconium-based alloy cladding and uranium dioxide fuel pellets. In emergency conditions attended by temperature jump due to exothermic zirconium-steam reaction, a violent steam oxidation of the claddings occurs with hydrogen release producing explosive hydrogen-oxygen mixture. Therefore, the problem of enhancing the stability of the nuclear fuel in emergency conditions, i.e. the problem of the accident-tolerant fuel creation arises.

Currently, intensive research and technological development of various methods to enhance safety of light-water reactor fuel element claddings are carried out, ranging from modification of the existing zirconium claddings to development of new fuel element types. Different methods to protect zirconium from corrosion at elevated temperatures are proposed: formation of heat resistant metallic coatings (Al₃Ti, Cr, FeCrAl, NiCr and others) [1 – 3], deposition of protective ceramic coatings resistant to oxidation (Al₂O₃, Cr₂C₂, Si, SiC, SiO₂, Y₂O₃, ZrC, ZrN and others) [4], and modification of the structure and composition of the near-surface layer by ion implantation doping with various elements [5]. Deposition of coatings on zirconium claddings is believed to be the simplest and most optimum method to enhance safety, having virtually no effect on the enrichment of the fuel or the reactor physics, making it possible to anticipate implementation of the new fuel in a relatively short time.

There is a rather wide variety of methods to deposit protective coatings with every one of them having its particular advantages and drawbacks imposing limitations on its scope of application. This paper proposes two methods of coating deposition at the outer surface of fuel element claddings: electrochemical deposition method (galvanic deposition) and cathodic arc deposition (Arc-PVD). The
advantages of galvanic deposition are simplicity of process adjustment regarding the thickness of the metal deposited and absence of heating and therefore structural changes of the cladding material [6]. The key factors in favor of cathodic-arc deposition are the high rate of deposition of the coating and the capability to pre-clean the cladding surface with argon ion beam. The advantage of this pretreatment process is preservation of the elemental composition of the near-surface layers and the capability to achieve low surface roughness [7, 8].

2. Experimental
Fuel element claddings with an outer diameter of 9.5 mm made of E110 electrolytic zirconium-based alloy were chosen as the samples for testing.

Preparatory treatment of the samples included cutting into fragments with a length of up to 100 mm, polishing of the butt-ends, surface degreasing with ethanol and subsequent etching in acidic solution carried out to activate the sublayer in order to enhance adhesiveness of the cladding surface.

One of the factors defining quality of the coating deposited and its adhesion to the surface is ion beam pre-cleaning in the chamber immediately before deposition of the coating. To carry out ion beam pre-cleaning the etched samples were placed on a rotary table in a vacuum chamber; with the rotation frequency being (8 – 10) rpm. After the chamber was evacuated to high vacuum, a negative potential was applied to the sample and the sample underwent cleaning by argon ion bombardment for (5 – 10) minutes.

Coating deposition by cathodic-arc method was carried out with a Bulat-6 machine in argon atmosphere under a pressure of (10² – 10³) Pa, period of deposition was 120 minutes. To choose the optimum parameters of deposition, a series of experiments was conducted with variation of the shear voltage in the range of 50 V to 450 V. Adjustment of shear voltage applied to the sample made it possible to vary the sample temperature and achieve a high extent of argon ionization. The sample temperature during deposition was measured with a pyrometer.

Electrochemical deposition of a protective coating on fuel element cladding fragments was carried out by immersing the samples into chromium anhydride solution at various operational mode parameters (duration, current density, concentration and temperature of the electrolyte). The sample butt-ends were preliminarily welded with zirconium plugs to prevent ingress of the electrolyte into the interior of the cladding.

To enhance adhesiveness of the coating, diffusive annealing in a vacuum electric resistive furnace was carried out at a temperature of 700 °C for 4 hours. Heating rate of the furnace was ~ 20 °C/min, cooling - together with the furnace itself.

High-temperature corrosion testing of 10 mm long samples was conducted on GAZPAR test bench according to the procedure described in [9]. Testing in superheated steam atmosphere was conducted under stationary conditions in the isothermal zone of the furnace at a temperature of 900 °C with an exposure of up to 10000 seconds. The samples were cooled in a mixed steam-argon atmosphere at a rate of 20 °C/s at most.

Analysis of the microstructure, assessment of the deposited coating thickness and analysis of the elements distribution along the depth of the samples were conducted by electron microprobe analysis using a TESCAN VEGA3 scanning electron microscope.

3. Results and Discussion
Figure 1 presents appearances of the coatings produced at different modes of deposition (100 V, 150 V, 300 V). The appearance of the cladding at 100 V shear voltage didn't change (metallic luster remained); at 300 V shear voltage the cladding surface is oxidated due to its overheating during deposition of the coating (sample temperature reached 650 °C in the course of deposition). The optimal coating was produced at 150 V shear voltage - the cladding became dull, with no trace of spallation and discontinuity, the thickness of the coating made 3 μm (Figure 2a). To make the coating thicker the duration of the process was increased from 120 to 240 minutes making it possible to produce a coating approximately 9 μm thick.
Diffusive annealing didn’t result in change of appearance of the sample. Electron microscopy of the cladding has shown that after annealing the coating retained its original thickness with no pores, cracks and spallation detected. By the results of the electron microprobe analysis (Figure 2b) the following conclusions have been made: the annealing resulted in active mutual diffusion of elements of the cladding (Zr) and the coating (NiCr), with zirconium having diffused throughout the entire thickness of the coating, whereas in contrast diffusion of nickel into the cladding is insignificant and doesn’t exceed \((3 - 4) \mu m\); also massive redistribution of chromium towards the outer surface of the coating was observed.

Since, as a result of the annealing conducted, chromium was redistributed to the outer surface of the cladding and a massive diffusion of zirconium into the coating occurred, a conclusion can be made that the protective part of the coating has significantly thinned, because zirconium diffused into the coating is going to facilitate absorption of oxygen. In this connection a task was set to further increase thickness of the protective coating.
To that end, an additional layer of chromium was deposited on the sample by galvanic method. Rejection of Arc-PVD method is connected with the limitations thereof related to the thickness of the coating deposited and formation of droplet phase in the process of deposition [9]. The coating produced by galvanic method is dull, with no spallation and peeling detected (Figure 3a). The thickness of the deposited layer is approximately 5 μm (Figure 3b).

![Image](a) ![Image](b)

**Figure 3.** Appearance (a) and cross-section (b) of the fuel element cladding fragment after deposition of the chromium coating layer.

Figure 4 presents the results of high-temperature corrosion testing of the samples at GAZPAR test bench. The testing was carried out on cladding fragments after deposition of NiCr protective coating and subsequent annealing (Figure 4a) as well as on samples with NiCr-Cr coatings (Figure 4b).

![Image](a) ![Image](b)

**Figure 4.** Appearance of fuel element cladding fragments after corrosive testing.

The outer surface of the samples darkened; no cracking, spallation or peeling were found. The inner surface shows traces of spallation of multilayer zirconium oxide (ZrO₂). In general, the appearance of the samples shows no differences.

According to electronic microscopy studies, no formation of zirconium oxide at the outer surface of the sample is observed (Figure 5a, b). The coating retained its thickness, with no cracking and spallation detected. By the results of the electron microprobe analysis (Figure 5c, d) it can be said that a dense layer of Cr₂O₃ oxide has formed on the outer surface of the cladding, preventing penetration of oxygen deep into the coating. Presence of oxygen in the cladding is related with its surface adsorption at the sample surface in the process of sample preparation, therefore, only qualitative assessment of oxygen content in the sample can be made. Presence of internal cracks in the coating is apparently related to formation of brittle (Zr-Ni-Cr) intermetallide.
**Figure 5.** Photographs of the metallographic specimen of the cross section of fuel element cladding fragments after corrosion testing.

### 4. Conclusion

1. Chromiferous protective coatings have been formed on zirconium cladding. The coatings assure efficient protection of the fuel element claddings (E110 alloy) from corrosive oxidation in superheated steam at $T = 900 \, ^\circ\text{C}$ for 10000 seconds.

2. Samples with bi-layer coating (NiCr-Cr) have been made. In the long run, this coating is bound to assure a high degree of protection of fuel elements in emergency conditions with the coolant temperatures as high as $1500 \, ^\circ\text{C}$.

3. It has been found that diffusive annealing at a temperature of $700 \, ^\circ\text{C}$ for 4 hours results in chromium redistribution towards the outer surface of the cladding, significant diffusion of zirconium along the entire depth of the coating is observed, whereas, on the contrast, nickel diffusion into the cladding is insignificant and makes $(3-4) \, \mu\text{m}$ at most.

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