Study of High-Temperature Oxidation of the Claddings of Tolerant Fuel Elements of VVER-type Reactor

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Abstract. The work presents the results of a study of corrosion resistance of chrome-coated fragments of zirconium cladding of VVER-1000 reactor fuel elements. The coatings had been deposited by electrochemical deposition on the standard cladding fragments with pre-treated surfaces. Gas-dynamic treatment of the surface with chrome powder proved to have a positive effect on the surface-to-cladding adhesion. Annealing at a temperature of 400 °C contributes to relieving of the residual stresses resulting from the gas-dynamic treatment. Investigation of the durability of the coatings was performed under exposure to overheated steam at a temperature of 1200 °C and exposure period of up to 1500 s. As it has been demonstrated, the produced coatings hinder formation of ZrO₂ oxide layer at the outer surface and reduce the depth of penetration of oxygen into the metallic sublayer, in comparison with the specimens in the original condition. All this contributes to retention of the residual ductility of the tested specimens at the level of no less than 2%.

1. Introduction

Ensuring safety is one of the foremost tasks in the design and operation of nuclear power plants. After a number of NPPs suffered most severe accidents (Three-Mile-Island, Chernobyl, Fukushima) the necessity of development of fuel element claddings capable to enhance the reactor safety under accident conditions became obvious. In accident situations fraught with sharp increase of the claddings temperature due to zirconium-steam reaction the claddings are aggressively oxidized by steam yielding hydrogen and forming an explosive hydrogen-oxygen mixture.

Active studies and technological developments of different methods to enhance the safety of reactor fuel elements are currently underway, varying from upgrading the existing zirconium cladding to radical methods such as replacing zirconium with another material insensitive to water at high core temperatures [1]. The researches and developers propose a variety of methods to protect zirconium from corrosive attack at high temperatures: modification of the structure and composition of the oxide layer through ion implantation of a variety of elements [2, 3], formation of heat resistant metallic coatings [4, 5], as well as deposition of protective coatings resistant to oxidation [6]. Deposition of coatings on zirconium claddings is the simplest and most optimal way to enhance the safety having virtually no effect on the fuel enrichment and reactor physics making it possible to expect introduction of the new fuel in a rather short run provided that a number of problems are solved (composition of the coating, necessary
thickness, prevention of disintegration of the coating when the fuel elements are allocated in the spacing grid, etc.).

There are various methods of protective coatings production, with every one of them having their own advantages and drawbacks imposing limitations on their applicability. Of the wide spectrum of coatings deposition techniques employed at FSUE “SRI SIA LUCH”, this paper deals with electrochemical deposition (galvanoplasty). The advantages of this method are the ease of the process control regarding the deposited metal thickness an absence of heating, and therefore – change of the cladding material structure [7].

2. Experimental

Fuel element claddings with a diameter of 9.1 mm and wall thickness of 0.585 mm made of E110 alloy based on sponge zirconium were used as the test specimens.

Pretreatment of the specimens included cutting the cladding into fragments 10 mm long, polishing of the end faces and degreasing of the surfaces with ethanol. To improve the adhesive and mechanical characteristics of the deposited chrome coatings studies were performed to determine the optimal method of modification of the near-surface layer of the fuel element cladding. Specimens were prepared using various surface processing conditions. A part of the specimens underwent gas-dynamic treatment (GDT) with chrome powder with particle size varying from 50 to 200 micron. Uniformity of the treatment was ensured by rotating the specimen with constant angular speed equal to 300 min⁻¹. Etching of surfaces of certain specimens was made using the mixture of nitric and fluoric acid commonly used for standard treatment of zirconium cladding. Annealing runs were performed in a vacuum resistive furnace at 400 and 600 °C, with heating rate being 20 °C/min and cooling of the specimens taking place simultaneously with cooling of the furnace.

High temperature corrosion testing of the specimens was conducted on the GAZPAR test bench according to the procedure described in [7]. Testing in overheated steam atmosphere was conducted under stationary conditions in an isothermal furnace under a temperature of 1200 °C and with oxidation period of up to 1500 s. These temperature-time settings are stemming from the mechanical condition of the standard cladding becoming critical due to its oxidation at a temperature of 1200 °C for 500 s.

The condition of the surfaces of the cladding specimens was analyzed visually as well as with an Olympus SZX7 stereoscopic microscope. The roughness of the coatings of the specimens was measured with a MarSurf M400 profilometer. A Zeiss Axio Observer D1m optical microscope and a TESCAN VEGA 3 scanning electron microscope were used for analyzing the structure of the original coated cladding specimen and the specimen after corrosion testing. Residual ductility of the claddings was measured by diametric compression of the ring-shaped specimens using a Zwick Z100 versatile testing machine at a temperature of 135 °C. The procedure of mechanical testing was in compliance with the instructions given in [8]. Crack resistance of the coating was evaluated by deforming the claddings until the compression rates in the interval of (3 – 20) % are achieved. Vickers microhardness testing was performed using a MICROMET-2103 microhardness tester under a load of 50 g at a pitch of (50 – 60) μm in 3 rows with an angle of 120°.

3. Discussion

The study of the effect, which the methods of pretreatment of the standard fuel element cladding surface have on the quality of the deposited protective chrome coating, has been conducted. Surface modification by GDT results in chrome particles embedding into the near-surface layer and uniform development of roughness along the entire length of the specimen (<Ra> = 0.50 ± 0.06 μm). It was determined that the optimal duration of gas-dynamic treatment of the fuel element is 30 seconds (Figure 1a): increasing the treatment duration doesn’t result in any roughness gain (Figure 1b), at the same time increasing chrome powder consumption which is extremely undesirable from economic point of view.

Chemical etching of the original cladding makes it possible to eliminate the surface oxide film, although leads to reduction of the number of the chrome particles embedded during the subsequent gas-dynamic treatment. This effect is related to the virtually nonexistent original roughness of the claddings.
which underwent the preliminary etching. Introduction of the etching operation after GDT results in smoothing of the surface (Figure 1c), having an adverse effect on the quality of coating-to-cladding adhesion.

![Figure 1. Images of the outer surface of the fuel element claddings.](image)

Presence of residual stresses in the near-surface layer of the claddings was detected for the specimens, which underwent the gas-dynamic treatment. The stresses were resulting from impacts of chrome particles. To relieve these stresses annealing was carried out at a temperature of 400 °C for 2 hours; the results of X-ray phase analysis of the annealed specimens surfaces are presented in table 1. Annealing of the specimens resulted in relief of the stresses and formation of a number of Zr and Cr based solid solutions implying occurrence of interdiffusion in the interface zone between the substrate and chrome particles embedded during GDT. Occurrence of such processes contributes to the increase of the strength of the cladding-to-coating contact. Absence of chrome at the surface of specimen 5 and presence of traces of chrome on specimen 7 corroborate the conclusions made basing on the results of the X-ray spectral microstructure analysis and are indicative of the adverse effect etching had on quality of the prepared surface.

| Preliminary treatment | Before annealing | After annealing |
|-----------------------|------------------|-----------------|
|                       | Phase composition | Lattice constant | Phase composition | Lattice constant |
| 1 Original            | Zr               | 3.23           | A number of Zr-based solid solutions | 3.25 |
| 2 GDT (30 s)          | Zr + Cr          | 3.24           | A number of Zr+Cr-based solid solutions | 3.249 |
| 5 GDT (30 s) + etching | Zr               | 3.237          | A number of Zr-based solid solutions | 3.25 |
| 7 etching + GDT (30 s) | Zr + Cr (traces) | 3.24           | A number of Zr+Cr (traces) -based solid solutions | 3.25 |

Specimens of coated claddings, with coating thickness in the range from 2 to 20 μm, were produced by electrochemical deposition. The coating was deposited as a uniform layer, no signs of spalling and flaking were observed.

High temperature annealing of the samples with preliminarily deposited chrome coatings 5 μm thick was performed in a vacuum furnace. Basing on the results of the microstructural analysis of cross sections of the specimens (Figure 2) a conclusion can be made that interdiffusion of the materials of the coatings (Cr) and claddings (Zr) occurs. It is worth noting that a longer annealing period results in a wider interdiffusion zone: 5 hours – 3 μm, 10 hours – 4 μm and 24.5 hours – 7 μm.
Thus, employment of this thermal treatment as one of the stages of coating deposition makes it possible to considerably improve adhesion of the chrome coating to the zirconium cladding and to enhance its mechanical durability.

**Figure 2.** Results of X-ray spectral microstructure analysis after high temperature annealing (600 °C).

Figure 3 presents the images of the surface of the specimens after compression for 10 and 20 % – relative strain is indicative of condition of the surface before (Figure 3a) and after (Figure 3b) occurrence of cracks. Under 103-fold magnification (Figure 3b) the fracture pattern is clearly visible and segments of sharp edged crests appear which is indicative of plastic deformation taking place in the process of disintegration of both the coating and zirconium cladding. The following values of deformation of the standard fuel element cladding are regarded as the maximum allowable: 0.2 % for inelastic deformation under the stationary conditions (at the designed burnup) and 0.3 % for inelastic deformation at elevated temperatures. An inelastic deformation of 0.7 % is allowed under accident conditions. Therefore, on the basis of the results of the tests conducted, a conclusion can be made that the coating has a considerable strength margin.

**Figure 3.** Images of the surfaces of the specimens after compression testing.

High temperature corrosion testing of the samples has been conducted at a temperature of 1200 °C in steam. Figure 4 presents the curves of the specific mass gains $\Delta m_s(\tau)$ versus time, for the specimens without coatings and the ones with coatings 12 μm thick under oxidation in steam. As it can be seen from the graph, presence of the chrome layer significantly hinders oxidation of the coated claddings as compared with the original specimens.
Figure 4. Dependence of the specific mass gain versus the oxidation period.

Metallographic analysis of the cross section samples (Figure 5) has shown that the microstructure of the specimens after corrosion testing exhibits a layered morphology and is comprised of:

- coating oxide layer and a layer of the metallic part of the coating at the outer surface;
- internal α′-Zr layer (“ex-β” – layer), occupying the central part of the cross section;
- sub-surface oxygen-stabilized sub-oxide layer of α-Zr(O) on the inner surface;
- ZrO₂ oxide layer on the inner surface.

Figure 5. Cross section of the coated specimen, oxidized over a period of 1500 s.

According to the results of the mechanical compression testing, the coated cladding specimens retain the residual ductility at a level of over 2%. It is known that the structural parameter determining the residual ductility is the “ex-β” layer thickness. Thus, the “ex-β” layer thickness for the coated cladding specimens is at about 400 μm and 380 μm for exposure periods of 1000 s and 1500 s respectively. At the same time, the “ex-β” layer thickness of the standard specimens for the same time-temperature experimental scenarios was ~ 260 μm and 120 μm.

Analysis of the microhardness of the metallic part of the cladding (Figure 6) has shown absence of oxygen-stabilized α-Zr(O) phase on the outer surface. At the same time a zone with lower microhardness is observed in the vicinity of the coating which is indicative of the lack of oxygen penetration into this zone both from the side of the coating and the unprotected side of the cladding.
Figure 6. Microhardness distribution along the cladding thickness (the coordinate $\delta = 0$ corresponds to the inner surface of the cladding).

4. Conclusion
The paper presents the results of a study of the fragments of chrome-coated claddings of the fuel elements employed in VVER-1000 reactors. Experiments on electrochemical deposition of coatings with different pretreatment variants (chemical etching, gas dynamic treatment, vacuum annealing) have been conducted. A beneficial effect on the coating adhesion is observed when the cladding surface undergoes gas dynamic treatment with chrome powder. Annealing at a temperature of 400 °C contributes to the relief of the residual stresses resulting from GDT. Corrosion resistance of the coatings was investigated in the overheated steam atmosphere at a temperature of 1200 °C and with an exposure period of 1500 s. As it has been shown, the produced coatings hinder formation of ZrO$_2$ oxide layer and $\alpha$-Zr(O) sub-oxide layer at the outer surface and reduce the depth of oxygen penetration into the metallic sub-layer, as compared with the standard specimens. All the aforesaid contribute to retention of the residual ductility of the tested specimens at a level of over 2%.

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