

Conference Paper

Alloying of Surface Layers of the Fuel Claddings from Sponge Based E110 Alloy to Increase High Temperature Oxidation Resistance

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Abstract

The results of experiments of parts of cladding tubes from sponge based zirconium E110 alloy near-surface layers doping by means of ion-plasma technologies are presented in this paper. Alloying of material by method of pre-deposited Fe, Y, Mo, Al, Mg, Cr films ion mixing is performed on installation ILUR-03 by means of radial Ar⁺ ion beam 3-4 keV average energy. State of modified material layer and oxides, grown on the modified samples in argon-water steam mixture at 1200 °C studied by scanning electron and ion microscopy methods, X-ray analysis and secondary ion mass spectroscopy. It is shown that treating modes defined contribute to the barrier for oxygen penetration and material oxidation formation near ion-doped surface.

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1. Introduction

Fuel rods behavior in nuclear power plants under accident conditions play great role in area of nuclear reactors operation safety. One of the most dangerous accident for pressurize water reactors – is loss of coolant accident (LOCA). In such accident conditions temperature of materials used can increase up to its melting because of reactor core overheating. At present time safety requirements set rough temperature value of 1200 °C, at which fuel claddings should remain its tightness and integrity. So-called accident tolerant fuel (ATF), operable in emergency modes, is developed in all over the world now. Among the destructive factors affecting the claddings from zirconium alloys under LOCA conditions, one of the main ones is the penetration of corrosive oxygen from the surrounding vapor-water environment. Oxygen causes a catastrophically rapid growth of oxide with various kinds of defects, as well as embrittlement of the metallic sublayer [1, 2].


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One possible way to improve the properties of the material is to create protective layers near the outer surface of the claddings, which will serve as a barrier to oxygen, slowing or completely blocking its penetration. So, for example, the possibilities of ion-plasma technologies allow to influence on the thin near-surface layer of metal, creating unique stabilized states with increased corrosion and wear resistance. At the same time, the characteristics of the bulk material do not undergo changes [3-5].

2. Materials and methods

The experiments were performed on samples from the Russian zirconium alloy E110 on a spongy basis. As shown in literature data, the E110 alloy, produced on the basis of sponge, rather than electrolytic zirconium, has a fundamentally better resistance to high-temperature corrosion, which is associated with differences in the impurity compositions of the feedstock. The samples were fragments of fuel rods made in the geometry of WWER-type reactors-an outer diameter of 9.15 mm, a wall thickness of 0.65 mm, and a length of up to 500 mm. The doping of the samples was carried out using the installation for complex ion-plasma treatment ILUR-03, the appearance of which is shown in fig. 1. Samples were fed through a gate device into a vacuum chamber with residual pressure no worse 10^{-2} - 10^{-3} Pa with an automatic manipulator. The surface was polished to a roughness $Ra < 0.3 \mu\text{m}$ by a radial beam of Ar^+ ions, which were extracted from the plasma of a glow discharge before alloying. Films of alloying elements of Fe, Y, Mo, Al, Mg, Cr with a thickness of 50-150 nm were deposited on the polished surface with one of three magnetrons, which were then driven into the near-surface layers of the material during ion mixing of the film-substrate system by the Ar^+ beam with 3-4 keV average energy. The surface temperature of the samples in the selected treatment modes did not exceed 150-200 °C. The samples were investigated on different stages of experiments by scanning electron microscopy (SEM – JEOL JSM-6610LV), scanning ion microscopy (SIM – Quatra-500, Ga^+ beam), X-ray phase analysis and microanalysis, IR-spectroscopy and secondary ion mass spectroscopy (SIMS – LECO SA-2000).

Some samples have passed corrosion tests in autoclave conditions (water, temperature 350 °C, pressure 17 MPa, time up to 500 h) and in modes of loss of coolant accident simulating (mixture argon-water steam, temperature 1200 °C, atmospheric pressure, time up to 500 s).

The degree of oxidation of the claddings was estimated from the specific weight gain - Δm , determined on analytical laboratory scales A&D (sensitivity 0.01 mg) or by equivalent cladding reacted (ECR, %). ECR parameter was determined by calculation

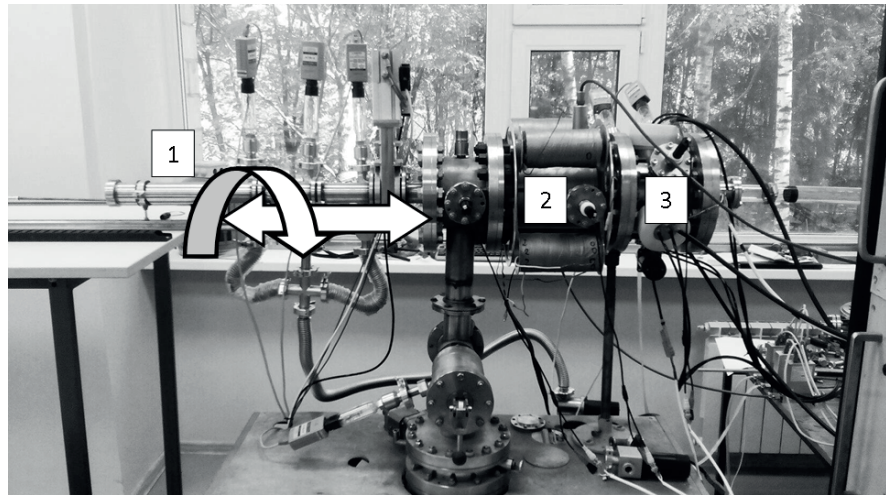


Figure 1: The appearance of the ILUR-03 installation: the gate device (1), the ion source chamber (2), the magnetron chamber (3). The arrows indicate the direction in which the sample moves.

as the ratio of the total thickness of the equivalent zirconium layer (which would react with the vapor) to the initial thickness of the cladding:

$$ECR = N \times \delta_E \times \delta_0 \times 100\%, \quad (1)$$

where ECR – equivalent cladding reacted, %; N – coefficient taking into account double-sided oxidation of the cladding, $N = 2$; δ_E – the thickness of the equivalent layer (the calculated thickness of zirconium, which would go to the formation ZrO_2); δ_0 – initial sample thickness.

3. Results and discussion

Typical concentrations of the elements in the surface layer of the samples of the material after doping in ion mixing mode, obtained by X-ray microanalysis are shown in table 1. As the data of a secondary ion mass spectroscopy, the spatial distribution of alloying elements has a gaussian shape with a characteristic decline and output signal to background values at a depth of about 1 μm .

An analysis of the surface state showed that the modification carried out increases the homogeneity of the topography and leads to a smoothing of the relief, which can be seen in fig. 2. Technological inclusions of less than 1 μm in size that present on both the treated and the original surface are found.

X-ray phase analysis shows the presence in the ion-doped samples of particles of the second phases, other than $\beta\text{-Nb}$, for example, $Zr_3\text{Al}$, $ZrFe_2$, $Zr(\text{FeNb})$, $Zr\text{Mo}_2$, and also pure metals - Zr, Nb, Al, Fe, Mo.

TABLE 1: Typical concentrations of alloying elements in the near-surface layer of material samples approximately 1 μm thick after ion mixing.

Concentration C, at. %	The alloying element / thickness of the previously applied film, nm				
	Fe / 140	Y / 90	Mo / 70	Al / 80	Cr / 65
Zr	base	base	base	base	base
Nb	0.94	0.94	1.23	0.79	0.93
Fe	3.47	0.26	0.31	0.17	0.14
Y	-	0.67	-	-	-
Mo	-	-	1.06	-	-
Al	-	-	-	1.64	-
Cr	-	-	-	-	1.16

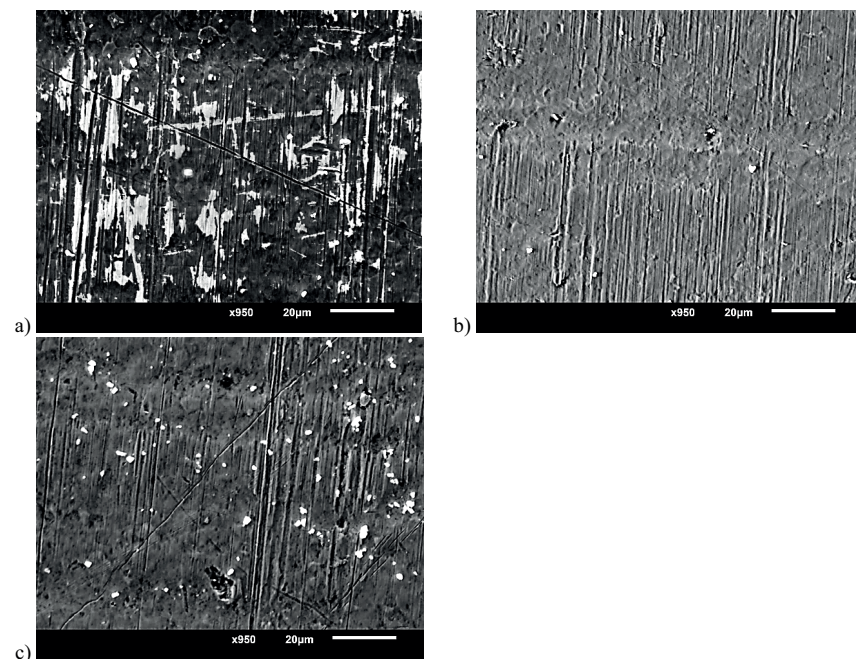


Figure 2: Typical SEM images of the surface of the samples in the initial state (a) and after doping with Fe (b) and Al (c) atoms obtained in the regime of back-scattered electrons collection.

As the analysis of the results of high-temperature corrosion tests shown in Fig. 3 shows, the kinetics of oxidation of samples in the initial state obeys the parabolic law characteristic for uniform corrosion of zirconium alloys. Doping of the near-surface layer leads to a slowing of the rates of oxidation and a shift in the kinetic dependence to the region of smaller values of the ECR parameter. A similar behavior is observed on autoclaved samples, which is probably due to the presence of a barrier for oxygen

penetration, in which a doped layer of material or an oxide film grown under less strict conditions appears.

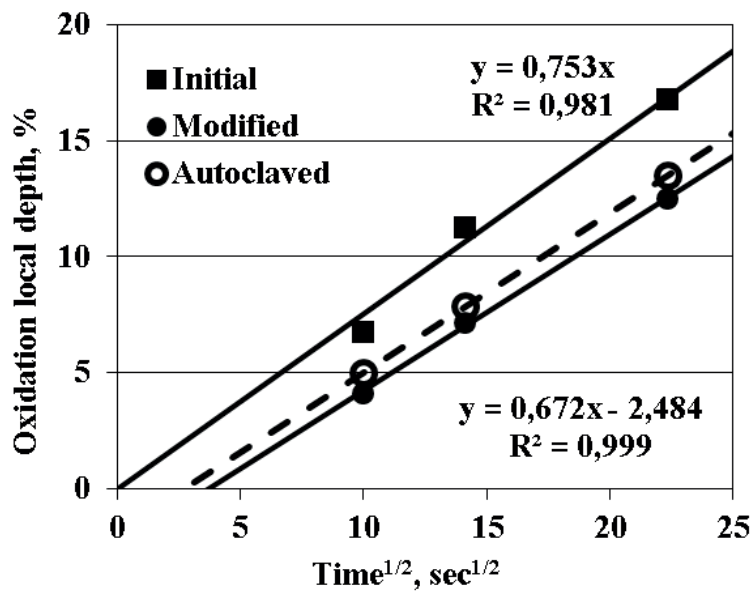


Figure 3: Kinetics of oxidation of the initial (■), ion-doped (Fe, Al, Cr - ●) and autoclaved (500 h - °) samples in a mixture of argon-water vapor at 1200 °C to 500 s.

The study of the structure of oxide films by the method of scanning ion microscopy (Fig. 4) made it possible to establish that films formed at elevated temperatures have a complex multiphase structure. Besides this, the oxide on the samples in the initial state is observed layered structure with extended cracks, located parallel to the surface of the material. Oxide film grown on ion-doped samples reveals much higher continuity and uniformity.

4. Conclusion

Doping of the outer surface of fragments of fuel claddings from the E110 alloy on a spongy basis was carried out using ion-plasma techniques. The atoms Fe, Y, Mo, Al, Mg, Cr are introduced into the near-surface layer of material with a thickness of about 1 μm, in concentrations of 0.5-5.0 atomic%. It is shown that the obtained state has an increased homogeneity and at a temperature of 1200 °C in the presence of water vapor promotes the formation of a dense oxide film, which is a barrier to the penetration of oxygen, thereby restraining the corrosion of the material.

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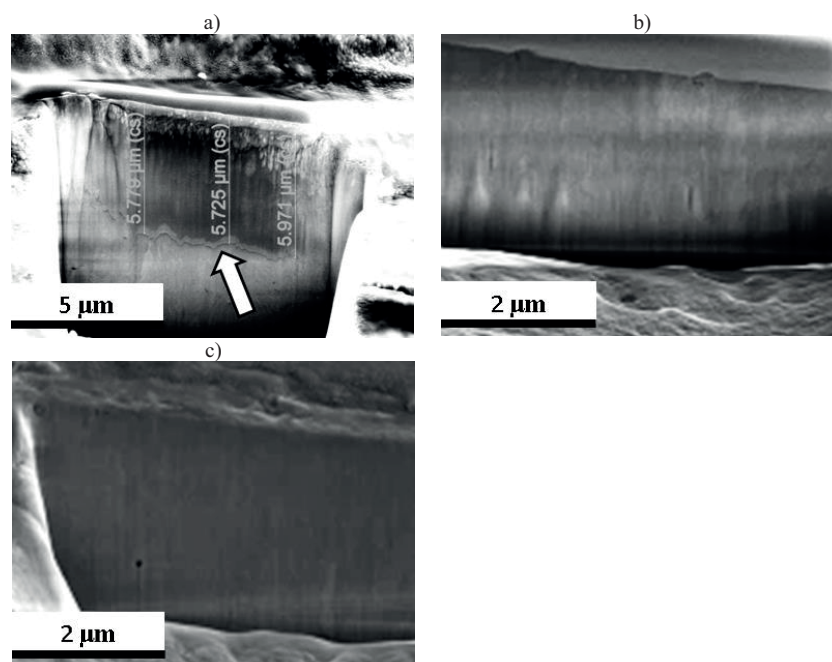


Figure 4: A typical transverse structure of oxide films grown in argon-water vapor environment at 1200 °C on the initial (a) and doped (Al, 100 s - b, 500 s - c) samples. The arrow shows a crack in the oxide.

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