Influence of Simultaneous and Consecutive Implantation of Al, Fe, Mo, Y Atoms on the Corrosion Resistance of Zirconium Alloys

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Abstract – The data on distribution of the implanted Al, Fe, Mo, and Y atoms in the near surface layer of Zr-alloys' (E110, E635) samples and oxide films are presented in this work.

It has been shown that simultaneous implantation of the external surface of fuel claddings by Al, Fe, Mo, or Y atoms significantly improves the structure of oxide films and increases the corrosion resistance of alloys. A significant redistribution of the implanted atoms in simultaneously alloyed samples has been found, i.e. the typical «cupola-shaped» form of the C(x)-dependence transforms into a more complicated one. At that, a layer enriched by implanted atoms is formed in the «metal-oxide» border of an oxide film, which blocks the penetration of oxygen atoms to the «oxide-metal» border from a steam-water environment.

1. Introduction

In connection with increasing the service life of nuclear reactors and the burn-out of fuel, the requirements to reliability and operational safety of devices of a reactor nuclear core, including fuel elements, will be increased. One of the factors influencing the reliability of fuel element's activity of the WWR type reactor is the corrosion of fuel claddings in a steam-water atmosphere, which is firstly determined by the structure of alloys, and secondly by operation conditions [1, 2]. One of the possible ways to increase the corrosion resistance of fuel claddings is to modify their surface layers by methods of ion technology. Previously it was shown [3] that the corrosion resistance of El10 and E635 alloys was increased as a result of ion implantation by Fe, Mo, Sn atoms. To investigate the features of the oxide films' formation at the initial oxidation stage of E110 and E635 samples, the surface of these alloys was modified by ion mixing and the structure of oxide films obtained after oxidation in a steam-water atmosphere was studied.

2. Experimental Procedure

Tubes of fuel elements $\varnothing 9$ and $\varnothing 13.5$ mm in diameter (with a wall thickness of 0.65 and 0.9 mm) were chosen for the investigation. The tubes were cut into samples 10 mm in length. A film (30–50 nm in thickness, Fig. 1) of alloying atoms was applied onto the external surface of samples by thermal vaporization in vacuum at $P < 10^{-4}$ Pa (Fig. 1). Then the samples were irradiated by a polyenergetic Ar^+ ion beam with a mean energy of 10 keV at a fluence of $(7–10) \cdot 10^{17}$ ion/cm^2 on the installation «VOKAL» [4]. While irradiated, a part of the film atoms was implanted into the surface layer at a depth of 150–200 nm. The use of a polyenergetic ion beam provides a more uniform penetration of the film atoms along the depth of samples under a less extent of radiation damages in the implanted layer, which has more benefits as compared to other traditional methods of action (irradiation by monoenergetic ion beams or in a glow-discharge plasma) [5, 6].

The oxidation was carried out in stainless steel ampoules in a steam-water atmosphere ($t = 10$, 100 and 300 h, $T = 350$ °C, $P = 20$ MPa). The structure of alloys and oxide films was studied by transmission electronic microscopy (TEM) on devices of EMV-100 and JEM-200XC types. To investigate the samples of alloys by the TEM-method, they were exposed to one-sided thinning in an electrolyte of acetic and chloric acids. Oxide films were formed by extraction in a weak hydrofluoric acid solution.

The chemical composition of films and the surface layers of samples were investigated by the Reserford back scattering method (RBS) and the secondary ion spectrometry method (SIMS).
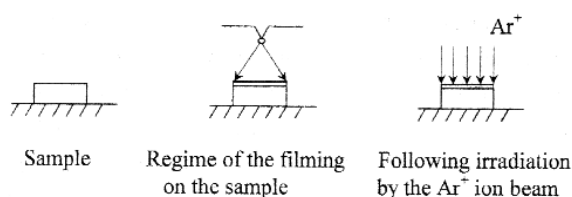

Fig. l. Application of films on the surface of a substrate and following implantation of the film atoms by ion mixing

3. Experimental Results

A comparative analyses of the surface layer's ($x = 100$ nm) chemical composition of samples exposed to modification, annealing in vacuum (for 10 h), and irradiation by a $H^+ – He^+$ ion beam (under various combinations) showed that the anneal in vacuum for 10 h did not result in a significant change of the material composition, i.e. thermally activated processes are absent or their velocity is small.

The processed data of spectra for initial samples of E110 and E635 alloys after their alloying by Al and Mo atoms are presented in Fig. 2. They have a small change in the distribution of implanted atoms in the surface layer because of radiation-stimulated diffusion of the alloying atoms along the depth of samples [5].
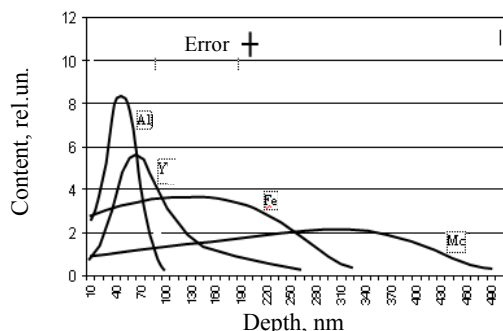

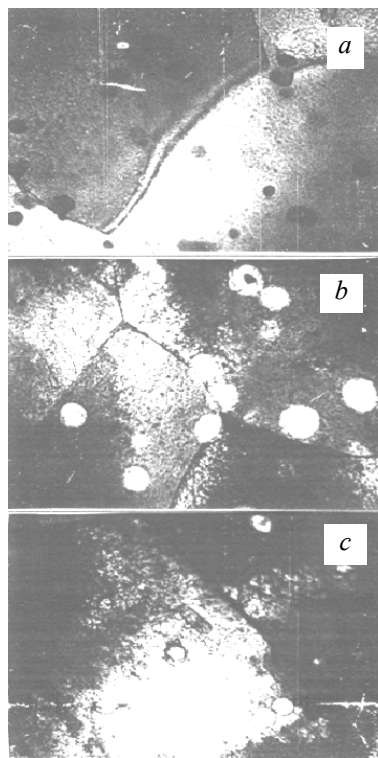Fig. 2. Distribution of simultaneously implanted Al, Fe, Mo, and Y atoms in polycrystalline zirconium of the 100 type

Fig. 3. Microphotos of the foils of E635 alloy samples: *a*, initial state, *b*, irradiated by Ar$^+$ ions up to 5×10^{17} ion/cm^2, *c*, implanted by Mo atoms; x25000

Investigations on the structure of thin metal foils of the E635 alloy samples (Fig. 3, *a*) show that there are individual precipitates with a size of 0.1–0.3 μm and a density of $(3–4) \cdot 10^8$ cm^2 both in the boundary and the grain body.

In case of the structure of the E110 alloy in its initial state, line precipitates with a size less than 0.2 μm are observed in the grain body. Their density is $(1–2) \cdot 10^9$ cm^2. The irradiation and implantation result in an increase of their mean sizes up to 0.3 μm and an

appreciable decrease of their density $(2–5) \cdot 10^8$ cm^2. At the same time the mean grain size remains constant, $<d> \approx 10$ μm [7].

Typical photographs of the oxide films on zirconium alloys (Fig. 4, *a*, a sample in initial state; Fig. 4, *b*, implanted by Al atoms; Fig. 4, *c*, implanted by Mo atoms and Fig. 4, *d* simultaneously implanted by Al+Mo atoms) after corrosion tests are shown in Fig. 4. It can be seen that simultaneous implantation of Mo and Ai atoms significantly increases the homogeneity of the film structure (the density of zones connected to a break-up of the precipitates and their mean size decrease).

The presented photographs show that the film structure mainly repeats the feature of the substrate formation, i.e.: films basically grow on the grain surface in an epitaxial way (Fig. 4, *a*). There is a slight difference in the velocity of growing the films on individual grains after irradiation and alloying (Fig. 4, *b*, *c*). Zones with an increased content of elements, that the precipitates have, form in the oxide film, i.e. in the area of precipitates. A detail study of the zone formation shows that that these zones have a complex (ring) structure and their formation seems to be determined by compressive stresses resulting from the formation of a zirconium dioxide ZrO$_2$ [8, 9, 10]. At that, the most zone density is observed on the external boundary of a ring that is also characterized by a developed system of the dislocation grid. The made estimations in the dimensional distribution of zones with an increased content of elements from precipitates showed that the irradiation by Ar$^+$ atoms and alloying by Al, Fe, Mo, and Sn atoms decreases the mean sizes of zones in the oxide film of E110. At that their density slightly changes (samples in standard state – $N = (8 \pm 0.5) \cdot 10^7$ cm^2, alloyed samples – $N = (7–10) \cdot 10^7$ cm^2). An analogous decrease in the mean sizes of zones is observed in oxide films obtained on E365, but their density is less as compared to samples in standard state (standard state – $N = (8 \pm 0.5) \cdot 10^7$ cm^2, alloying – $N = (7–10) \cdot 10^7$ cm^2).

An analysis of the elementary composition of zirconium alloys and the data obtained by X-ray small-angle dispersion make it possible to conclude the following. Line precipitates are present in E110 in standard state. They are connected to formation of β-Nb (their mean size and density are $<d> = 0.07$ μm and $N = 1.2 \cdot 10^9$ cm^2, respectively). The alloying of E110 by Al, Fe, Mo, and Y atoms results in precipitates which differ from β-Nb and contain such zirconium compounds as Zr-Al, Zr-Fe, Zr-Mo, Zr-Sn, as well as pure metals – Zr, Nb, Al, Fe, Sn, Mo.

The intermetallic compounds containing Zr, Nb, Sn, and Te ($<d> \approx 0.15$ μm, the density $N = 4.4 \cdot 10^8$ cm^2), for example Zr(FeNb)$_2$, are present in E635 in its initial state [2, 8, 10]. Precipitates of a new type are formed after irradiation; a part of them can be identified.
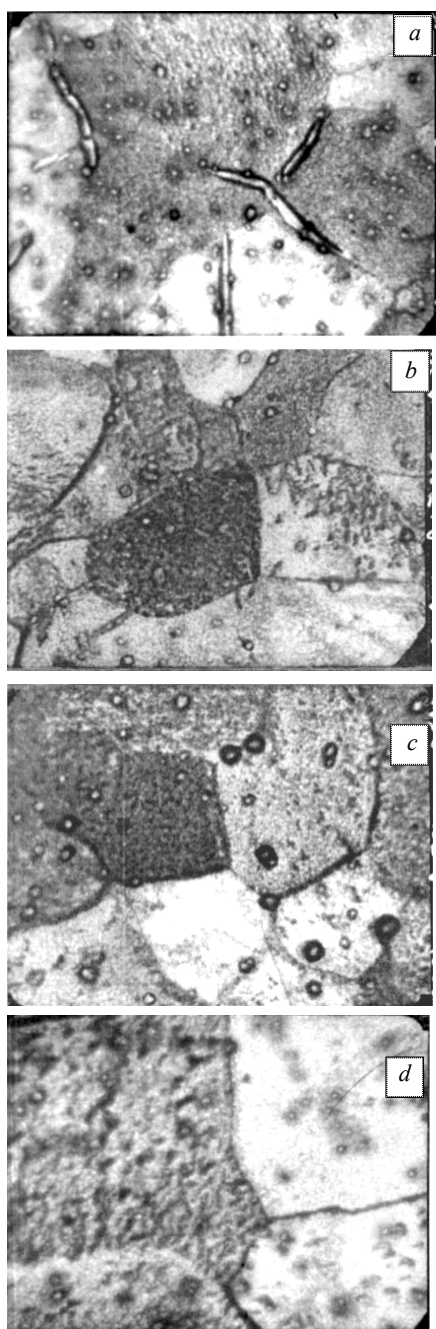
Fig. 4. The structure of oxide films on a E635 alloy tested for 10 h: *a* – initial state; *b* – implanted by Al atoms; *c* – implanted by Mo atoms, *d* – implanted by (Al + Mo) atoms; x10000

The results on changing the overweights (Δp) of samples made of E110 and E635 are presented in table 1, in initial state, irradiated by Ar^+ ions, and alloyed by different elements (Al, Fe, Mo, Sn) after tests for 100 h. They show that the alloying results in a decrease of the overweight for these alloys and the most effect is observed for E110 alloyed by Al and Fe, as well as for E635 alloyed by Al and Mo. In a number of cases the surface alloying of E635-tubes by Mo atoms decreases overweights up to 2.5 times in comparison with the initial state.

Table 1. Overweights of Zr-alloy samples (Δp, mg/cm^2) after corrosion tests in a water-steam environment for testing time 100 h, 350 °C, 20 MPa

Impl. atoms	Init. state	Ar^+	Al	Fe	Mo	Sn
E110	0.061	0.066	0.054	0.055	0.058	0.057
E635	0.074	0.075	0.065	0.066	0.029	0.069

The experimental error of measurements is ± 0.001 mg/cm^2.

The overweights of samples after corrosion tests for 300 h are shown in Table 2. It is seen from the table that E110 has a sufficient corrosion resistance in comparison with E635. The complex alloying by Al+Mo+Y, Al-Fe-Mo, Al+Fe+Mo+Y and others slightly increases the overweight of E110 and decreases the overweight of E635.

Table 2. Sizes of increase in weight of samples (Δp, mg/cm^2) Zr-alloys after corrosion tests in steam-water environment, testing time 300 h, 350 °C, 20 MPa

Alloys	Init. state	Al-Mo	Al-Y	Mo-Al-Y
E110	0.069	0.171	0.135	0.113
E635	0.207	0.190	0.189	0.152

The experimental error of measurements is ± 0.001 mg/cm^2.

An analysis carried out by SIMS, Auger-spectroscopy and RBS methods of the distribution of implanted atoms in samples after corrosion tests gives grounds to point out the following general tendency. A redistribution of the implanted atoms is observed with increasing the time of corrosion tests, i.e. a typical cupola-shaped form (Fig. 1) transforms into a more complicated dependence.
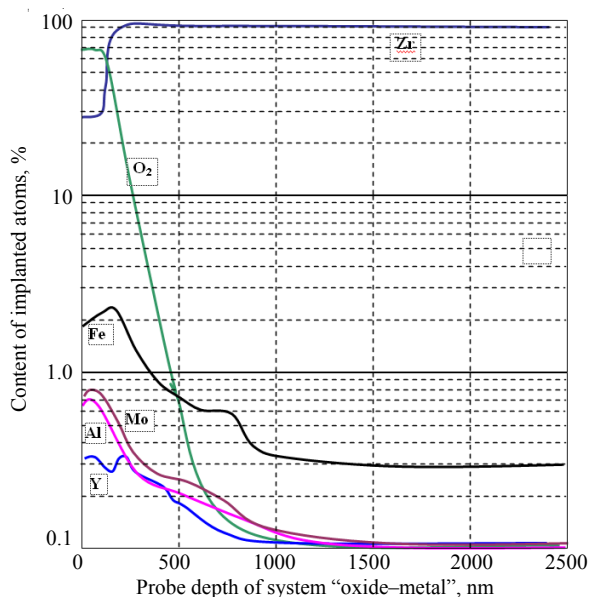

Fig. 5. The distribution of simultaneously implanted Al, Fe, Mo, and Y atoms in the "oxide-metal" system of E635 after corrosion tests ($T = 350$ ^{o}C, $P = 20$ MPa, $t = 300$ h)

For example, Fig. 5 shows the distribution of implanted Mo, Fe, Y, and Al atoms in the "oxide-metal" system after corrosion tests of E635 for 300 h, which was obtained by the SIMS method. It is seen from the figure that an increased content of implanted atoms (at the concentration of Al − 0.07 ± 0.03 at%; Fe − 0.5 ± 0.1 at%; Mo − 0.1 ± 0.03 at.%; Y $< 0.05 \pm 0.03$ at%) is observed at a depth more than 500 nm.

Also it is necessary to point out the presence of the second concentration maxima of Fe and Mo atoms at depths $X = 700–800$ nm, $Y − X \approx 300–350$ nm. The occurrence of the second maximum C(X) for Y is probably connected to a change of the oxygen concentration on the «metal–oxide» border, and the second maximum for Fe and Mo is possibly caused by diffusion processes and requires additional researches.

4. Conclusion

Features of the structure-phase state of surface layers for E110 and E635 alloys depending on irradiation conditions and the concentration of implanted atoms (mono-atoms, Al, Fe, Mo, Sn; multi-atoms, Al-Mo, Al-Y, Mo-Al-Y, and Al-Fe-Mo-Y) have been found:

Monatomic alloying

A transfer of the precipitates' atoms into the solid solution is observed at the concentration of implanted atoms of 1–2 at% and the penetration depth of 10–150 nm; the secondary phases partially decompose.

An increase in the concentration of implanted atoms up to 2–4 at% promotes an increase of the precipitates' size (particles of the second phase), hypothetically, owing to transfer of a part of atoms from the matrix into the precipitates.

Polyatomic alloying

A simultaneous implantation of Al, Fe, Mo, and Y atoms up to a concentration of 2–5 at% (the distribution depth of the implanted atoms increase up to 500 nm and more) improves the structure of oxide films, equalizes the oxidation front, decreases the size of precipitates and their density, which positively influences the corrosion resistance of alloys.

A redistribution in the content of simultaneously implanted Al, Fe, Mo, and Y atoms in the oxide film of alloys during the corrosion tests ($T = 350\ °C$, $P = 20$ MPa, $T = 300$ and 600 h) has been revealed, i.e. their concentration increases along the depth to the "oxide-metal" boundary in the oxide. Secondary distribution maxima at the depth of 700–800 nm have been found.

Thus, the experimental data obtained give grounds to suppose that the increased corrosion resistance of the modified alloys is due to two processes. On the one hand, a uniform multiphase oxide film is formed. On the other hand, a layer which blocks the penetration of oxygen from a water-steam environment to the "oxide-metal" boundary is formed.

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