

# Formation of a Gradient Structural-Phase State in Materials under a Radiation-Beam Action

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**Abstract** – The necessity and generalization of the experimental data of the authors on studying the possibility to form corrosion-resistant structural-phase states (SPS), in principal, gradient composites in steels and claddings of fuel elements for thermal reactors (TR) and fast reactors (FR) are considered.

The action by high temperature pulsed plasma (HTPP) and liquid-phase alloying are effective to change the SPS of a surface layer of materials with complex composition, for example, steels of the fuel claddings for FRs, the corrosion resistance of which is the highest in a homogeneous state. The HTPP-action makes it possible to carry out an ultra-speed quench, including that from a liquid state. Realizing the liquid-phase alloying, results have been obtained on increasing the corrosion resistance of ferritic-martensitic steel in liquid lead and others.

As applied to zirconium alloys for the heat-generating assemblies of TRs (E110 and E635), new results are presented on the investigation and the analysis of SPS generated by the method of "ion mixing" and on the study of the corrosion resistance of these alloys. It has been shown that ion alloying results in increasing the corrosion resistance of the zirconium alloys in a water-steam environment (350–400 °C, 16MPa) owing to a change in the growth mechanism of an oxide film.

## 1. Introduction

The properties and service performance of articles are determined by the SPSs of the structural materials. As many articles working under the most severe conditions, as an example, those of atomics, are operated in sufficiently severe conditions, therefore, these materials must meet such different requirements concerning their properties, that to achieve this objective, the materials must have different SPSs in their volume and surface layer [1].

For example, the volume SPS determines long-term strength and creep resistance, radiation resistance (swelling, embrittlement), resistance to cracking and braking under constant load and fatigue, as well as fatigue resistance in conditions of creep and hydrogen embrittlement. The service performance of structural materials, including corrosion and erosion resistance, resistance to braking, friction and wear, cracking resistance in conditions of corrosion

fatigue, stress corrosion cracking, fretting corrosion and hydrogen embrittlement, and others are determined by the SPSs of *surface layers* [1, 2].

For example, initiation of braking on a surface is due, at least, to two factors. On the one hand, the presence of surface defects promotes (facilitates) the origin of cracks. On the other hand, the surface is usually the most loaded in comparison with the volume of details. It is not uncommon when stresses formed in the surface layer exceed the limiting levels. To increase the resistance to wear and fatigue braking in conditions of cycling loading, it is necessary that the surface of a detail be strong and its core be viscous, i.e. it is necessary to have a *multizone* structure [2].

The material of a detail with changeable SPSs along its section can be considered as a *gradient (multizone)* or *composite* material. Such states can be formed by various methods of the surface treatment (by modification).

In this connection, the given work is devoted to consideration of prospective methods of modifying the SFS in the surface layers of *thin-walled* articles on the example of fuel claddings made of zirconium alloys for TRs and corrosion-resistant steels for FRs.

## 2. The choice of radiation-beam technologies

Among a wide range of the technologies for the surface modification (treatment) of materials, the radiation-beam technologies (RBT) are playing an increasing role. As opposed to the traditional technologies of the surface treatment of materials in engineering, such as thermomechanical, chemicothermal, chemical and electrochemical ones, the RBTs have their specific character and features. In a number of cases they replace the traditional technologies of modifying the surface layers of materials owing to their higher efficiency, ecological purity and the uniqueness of the obtained results. The RBTs are less power-consuming since only a thin surface layer is exposed to such a treatment [3].

The RBT modifying action is realized at the expense of a number of physical processes: implantation of atoms (ions) into a material, precipitation and ion mixing of atoms in a surface layer, fast heating and cooling of a surface layer, sputtering or evaporation

poration of the atoms of a surface layer, generation of plasma on a target surface, chemical interaction of the target atoms with environment or bombarding particles, precipitation of atoms or molecules on a surface with epitaxy control, thermal and radiation-stimulated diffusion of different atoms, thermal and structural stresses, shock-wave action owing to gas-dynamic dispersion of plasma and vapor from the surface of a material [3, 4].

Various structural-phase changes take place under radiation modification. They are determined by the parameters of a radiation action. The most noticeable structural and phase changes are increasing the parameter of a crystal lattice, turn of plates of atom arrangement, formation of amorphous and super dispersed (nanostructural) phases, microstructure dispersion, dissolution and formation of radiation-stimulated and radiation-induced phases, separation of solid solutions, ordering, mass transfer in a surface layer and a volume, formation of supersaturated solid solutions, a change of the magnetic state of alloys, radiation-induced segregation, formation of laminate structures, formation of dislocation-disclination substructures, formation of gradient structural-phase states and others [3]. To treat fuel claddings, technologies of ion-mixing of zirconium alloys 5, 7, 8 and treatment of steel claddings 6, 9 by HTPP-flows are chosen in this work.

### 3. Modification of zirconium fuel claddings

Fuel claddings and other articles of thermal reactor heat-generating assemblies (HGA) made from domestic E110 and E635 alloys guarantee a planned fuel burnup. However, an increase of a fuel burnup, for example up to 70MW day/kg U in water-moderated reactors, and of a fuel exploitation time up to 5–7 years and more, as well as an enhancement of the working temperature of a heat-transfer require an increase in the corrosion- and wear-resistance of zirconium articles for HGAs.

Alloying of a surface layer in conditions of ion mixing with the use of a polyenergetic argon ion beam is the most appropriate. A more uniform (stretched in depth) distribution of implanted atoms in the target with a decreased level of radiation defects in comparison with that of a monoenergetic beam at equal mean ion energies is formed in this case.

The corrosion resistance in a water-steam environment at the temperature of 350–400 °C and the pressure of 16 MPa is chosen as the main criterion of the treatment efficiency.

The base of modification is the alloying of a surface layer by the atoms of a film preliminarily applied onto the surface of alloys by thermal evaporation. The alloying, as a matter of fact, is realized in the process of irradiation of a multilayer Al+Fe+Mo+Y film 100–120 nm in thickness by argon ions with a mean energy of 10 keV on the acceleration VOKAL. The

greater part of the film atoms is sputtered during the irradiation and the other part of these atoms is implanted into a substrate by the mechanism of recoil atoms. As a result of that, the surface layer is enriched by the film atoms. The distribution of these atoms in the surface layer obtained by the Rutherford backscattering (RBS) method has a bowl-like form with a maximum at the depth of 10–30 nm (Fig. 1) [5]. The maximum penetration depth of the film atoms into the substrate  $X_m$  at a fixed irradiation dose and a fixed energy-release depends on the reduced mass, the energy transmitted by the recoil atoms, and a difference between the electronegativity of atoms of the film and the substrate.

Zirconium intermetallics with the type  $Zr_3Al$ ,  $ZrFe_2$ ,  $Zr(FeNb)$ , and  $ZrMo_2$  alloying elements were found in the E110 alloy surface layer along with the atoms of alloying elements. As to the E635 alloy, the type  $Zr_3Al$  and  $ZrFe_2$  phases were found.

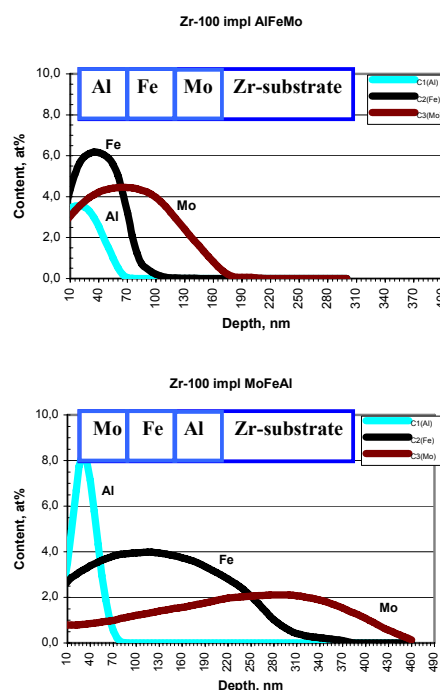


Fig. 1. Distribution of implanted atoms in zirconium

During the ion mixing, the density of initial precipitates in these alloys decreases by 1.5–2 times at the expense of dissolution of the finest precipitates. Estimation has shown that from 30 to 50 % of the atoms from these precipitates transfer to a solid solution. These precipitates located on the surface of initial zirconium alloys significantly influence the structure of oxide films by their own. A growing oxide film has a ring-shaped structure (swell) in the precipitation zone, which makes its growth nonuniform and results in the presence of defects. Therefore, a decrease in the density of precipitates during the alloying positively influences the corrosion resistance of the zirconium alloys, as the oxide film becomes more uniform.

Corrosion tests for 300–5000 h have shown that the modified alloys oxidize more intensively (Figs. 2 and 3) at the starting period of oxidation (up to 1200 h). This is due to the fact that the modified surface is activated by the irradiation, i.e. the surface atoms have an excess in free energy and a gradient of compressive stresses is formed in the surface layer that draws the oxygen atoms deep into the target. A sufficiently uniform quasi-monocrystalline film with a flat "oxide-metal" interface is formed during this stage. When the film grows, all the implanted alloying elements, especially the atoms of iron, are pushed off the oxide into the target depth.

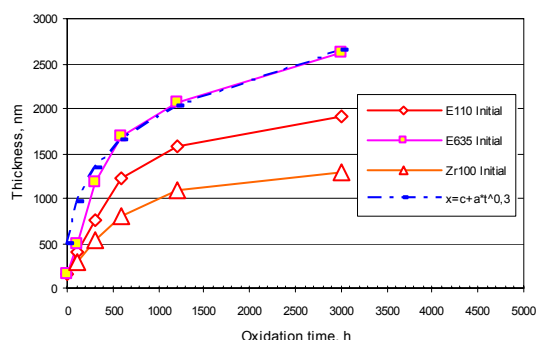


Fig. 2. Oxidation kinetics of zirconium and E110 and E635 alloys in the initial state

After exhausting the excess of free energy and relaxation of the internal stresses, the film growth velocity (as shown in fig. 3) noticeably becomes slower. As this takes place, a fine crystalline oxide is formed. The implanted atoms play a hindering role with a change in the oxide film growth mechanism in conditions of a decreased stimulus to the growth of this film.

The forming mechanism of the fine crystalline oxide consists in formation of oxide crystallites from which the implanted atoms are displaced to the periphery, where they make the diffusion of oxygen slower and hinder the growth of these crystallites. The atoms of aluminum and yttrium that have a high affinity to oxygen play a definite hindering role. Thus, a two-layer oxide film with a slowed growth velocity at the second stage is formed on modified samples of zirconium and its alloys having a gradient distribution of alloying elements in the oxidation zone.

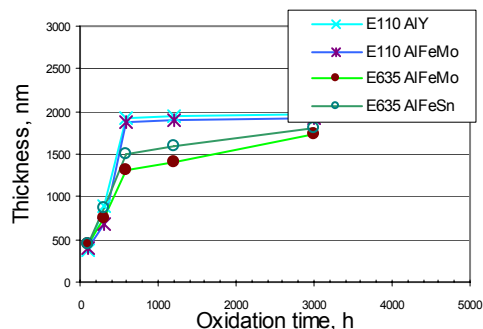


Fig. 3. Kinetics of the oxide film growth on modified zirconium

#### 4. Modification of steel fuel claddings by HTPP

Increasing the corrosion resistance of fuel claddings in a heat-transfer, for example in lead and during their storage in cooling ponds, is one of important tasks connected to guaranteeing the workability of the fuel elements for FRs [1]. The corrosion behavior of austenitic and ferritic-martensitic steels depends on the structural-phase uniformity of the steels, the presence of segregations of alloying and foreign elements in surface layers and grain boundaries. In this connection, the SPS-modification and elimination of segregations and second phase particles in the surface layers is of a definite interest.

Our previous investigations on modification of a number of low-alloyed steels (St3, St20, 25Kh1MF, 35Kh, 38Kh2MYuA and others) showed that the treatment by HTPP-flows resulted in formation of a two-phase martensitic-austenitic gradient SPS, based on the initial ferrite, in a surface layer of 10–20  $\mu\text{m}$  in thickness.

The SPS had a phase ratio depending on the type of plasma, its density, the energy density of a flow, and the number of pulses. The part of retained austenite was pointed out to increase with the number of alloying elements in the steel. In doing so, microstructure dispersion and an increase of internal stresses were observed. The treatment of corrosion-resistant austenitic and ferritic-martensitic steels by HTPP-flows with a specific power density ( $Q$ ) of a flow up to  $10^7 \text{ W/cm}^2$  has shown that the surface layers of steels up to 20–30  $\mu\text{m}$  in thickness become fine cellular with a gradient distribution of alloying elements, which is accompanied by increasing the microhardness and strengthening characteristics of the surface layers [3, 6].

As applied to modification of thin-walled fuel tubes, liquid-phase alloying can be the most effective treatment. Cuts of tubes 10.5 mm in diameter and 50 mm in length, made from the 16Kh12MVBFR (EP823) chromium ferritic-martensitic steel that is a prospective material for the fuel elements of FRs, were used as samples.

The improved technique of the liquid-phase alloying of tubes includes the following stages: preliminary purification of the tube surface by HTPP-flows under "soft" conditions, application of thin uniform layers of alloying elements onto the external surface of the tube cuts, intermediate anneal in vacuum at 500 and 600  $^\circ\text{C}$  for 3 h for diffusion adherence of the coating with the substrate and an increase of its adhesion, liquid-phase mixing of the applied alloying element with the material of the surface layers of a tube under the action by helium pulsed plasma flows.

The coatings (films) were applied onto the cuts of fuel tubes by thermal evaporating precipitation in vacuum ( $P \sim 10 \text{ Pa}$ ) of chemically pure (99.99 %) aluminum, iodide chromium, and a silumin-based alloy

(in wt. %): Al-12 %Si-0.7 %Cr-0.25 %Mo. The thickness of an applied coating changed in the 0.2–1.3  $\mu\text{m}$  range.

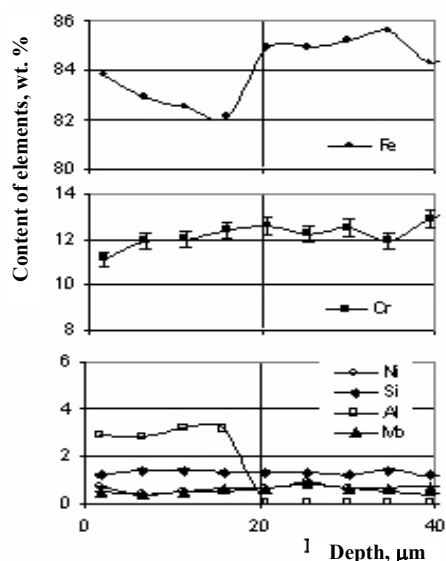


Fig. 4. Distribution of elements along the target depth

Investigations of the surface chemical composition and the element distribution along the depth of the surface-alloyed tubes were carried out by X-ray spectral microanalysis. Fig. 4 shows that the distribution of alloying elements in depth (up to 3 wt. %) is sufficiently uniform in the modified layer with a thickness that is more than by order of magnitude greater than that of the applied layer (aluminum at the coating thickness of  $\sim 0.4 \mu\text{m}$  was found at the depth up to  $\sim 15 \mu\text{m}$ ). The distribution of alloying elements sharply decreases at the modified layer interface, forming a concentration gradient along the sample thickness. The content of chromium attains 15.0–16.5 wt. % at its initial concentration in the steel of approximately 10 wt. %. At the thickness of a preliminarily applied chromium layer of  $0.3 \mu\text{m}$ , the increased content of chromium is found in the surface layers up to  $\sim 10 \mu\text{m}$  in thickness.

An X-ray structural-phase analysis has shown that the surface-alloyed steels are solid solutions without intermetallic phases [9]. The liquid-phase alloying by helium plasma flows with a power density changed in the  $1 \dots 6 \cdot 10^6 \text{ W/cm}^2$  range, at the pulse duration up to  $20 \mu\text{s}$ , results in a significant microhardness increase and a noticeable enhancement (by order of magnitude) of the corrosion resistance of a steel in a lead flow at  $650 \text{ }^\circ\text{C}$  for the time of 1680 h. If the oxide film was  $9\text{--}18 \mu\text{m}$  in thickness on the surface of a steel in its initial state, than the thickness of an oxide film obtained on the surface of the same steel alloyed by aluminum atoms didn't exceed  $1\text{--}3 \mu\text{m}$ ; for alloying by silumin and chromium it didn't exceed  $2\text{--}5$  and  $3\text{--}5 \mu\text{m}$ , respectively.

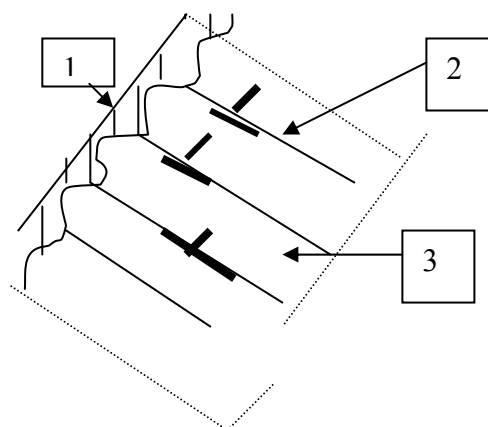


Fig. 5. Scheme of the modified sample: 1, modified layer; 2, sliding plate; 3, matrix

An important result of the HTPP-action on structural materials is an increase of the strengthening characteristics on retention of the ductility of treated samples. As shown by V.E. Panin [10], the surface layer is a special state of the substance, an important functional subsystem in a deformed solid. Under modification of a surface layer to a nonuniform and independent structural state in comparison with that of the matrix, the layer that is sufficiently strengthened and has a wavy interface with the matrix, conditions are really formed to control the plastic flow in the material (Fig. 5). Each curve of the "modified layer 1 – matrix 3" interface is a concentrator of stresses generating dislocations (2) which spread deep into the matrix under deformation. Thus, the surface layer influences the macro-characteristics of a material. Such a system doesn't admit localization of macro-stresses and deformation; it can make it possible to increase both strength and aspect ratio.

### Conclusion

Principles for the radiation-beam formation of a gradient structural-phase state in materials of thin-walled articles, if take the fuel claddings of nuclear reactors as an example, giving the claddings an increased corrosion resistance.

Under irradiation of zirconium fuel claddings of TRs by polyenergetic  $\text{Ar}^+$  ion beams, using the ion-mixing regime of Al+Fe+Mo+Y atoms with the matrix, SPSs are formed that hinder the oxidation in a water-steam environment.

The action by high temperature pulsed plasma flows (realizing the liquid-phase alloying of the EP-823 ferritic-martensitic steel by Al, Al+Si, and Cr atoms by the regime of a super-fast quench at the velocity of  $10^5 \text{ K/s}$ ) has resulted in increasing the corrosion resistance of the steel in a lead flow at the temperature of  $650 \text{ }^\circ\text{C}$  by order of magnitude.

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