

## AIR-THERMAL OXIDATION OF ZIRCONIUM MATERIALS

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The results of the temperature effect on the process of oxide films formation on the surface of the zirconium materials are given. The changes of the morphology, structure and properties of the oxide films on the zirconium and Zr1%Nb alloy due to exposure of heat treatment in air at 500...800 °C for a time up to 10 h are analyzed.

### INTRODUCTION

Modern nuclear power engineering is based on reactors in which the most important elements of active zone are made from zirconium alloys. Widespread use of alloys based on zirconium is caused by its good physical and mechanical properties (low thermal neutron capture cross section, high melting temperature, plasticity, good corrosion resistance).

The corrosion resistance of zirconium alloys is caused by the formation on the surface of a dense oxide film which slows further oxidation. Oxidation of zirconium alloys has been studied for a long time and a good understanding of the processes for high temperature conditions in oxidizing environments has been achieved [1-6]. However discussion about the role of various physical processes that affect the growth rate of oxide films and corrosion regimes still continues.

Currently established that features of kinetics of corrosion zirconium materials explained by changes occurring in the oxide films during their growth and degradation. It is important to find correlation between the characteristics of the oxide films formed on the alloys during corrosion and their protective action in order to predict the corrosion behavior of zirconium materials under actual operating conditions.

Purpose of work is study the influence of air-thermal oxidation on the growth kinetics, surface structure and mechanical properties of the oxide films formed on the samples of zirconium and Zr1%Nb alloy.

### MATERIALS AND METHODS

As the samples for research the plates of zirconium and Zr1%Nb alloy size 15 × 15 × 1 mm were used.

For obtaining a protective oxide film the prepared samples were subjected to air-thermal oxidation in the laboratory electric resistance furnace at temperatures of 500...800 °C with weighting at the beginning and end of the test on the microanalytical scales VLR-200 accurate to 0.5 mg after which their mechanical and corrosion properties were investigated. Holding time of samples in the specified temperature range is from several minutes to 10. Evaluation parameters of corrosion properties of the samples were: characteristic of surface (denseness, color uniformity of oxide films) and the corrosion rate which determined by the sample weight gain per unit surface over the test period.

The surface structure of the obtained films and their elemental composition were investigated by the auto-emission scanning electron microscope JSM-7001F with energy dispersive microanalysis system INCA Energy 350. The microstructure of the samples was studied by standard metallographic method on optical microscope MMP-4. The thickness of the oxide film on the oxidized samples was determined by fractography images of the fractures using a scanning electron microscope FEI Quanta 600 FEG. Microhardness measurements were carried out on the device PMT-3 with load of 100 g, the Brinell hardness (HB) was determined with load of 1000 kg on the device TSh-2.

To measure the roughness parameters of the surface of samples the portable profilometer-profilograph TR200 production of the company Time Group Inc was used by which the magnitude of  $R_a$  (average arithmetic roughness surface according to international standard ISO 4287) was determined.

### RESULTS AND DISCUSSION

To determine the regularities of relief and structure formation of zirconium and Zr1%Nb alloy due to thermal influence the electron microscopic studies on the oxidized samples have been made.

After oxidation in air at 500 °C for samples of Zr1%Nb alloy a structure typical for a deformed material is observed. As a result of oxidation at 600 °C solid black oxide film without cracks is appeared (Fig. 1,a). Such morphological structure of the coating indicates a good quality of sample. At 700 °C thickness of the oxide film is increased, there are small cracks and whitish layer. At 800 °C inhomogeneous structure with some separation on fragments is formed (see Fig. 1,b).

Samples of pure zirconium after oxidation at 500 °C are covered with glossy film of homogeneous structure. At increasing the annealing temperature to 600 °C significant changes in the external and structural view is not noted. Any defects in the oxide films or their flaking are not observed. The films in this temperature range are firmly engaged with the sample surface. On the plates annealed at 800 °C white oxide film is formed, already cracks with clear boundaries are seen (see Fig. 1,c). It is obvious that a coating with such morphological characteristics cannot provide effective protection of the surface.

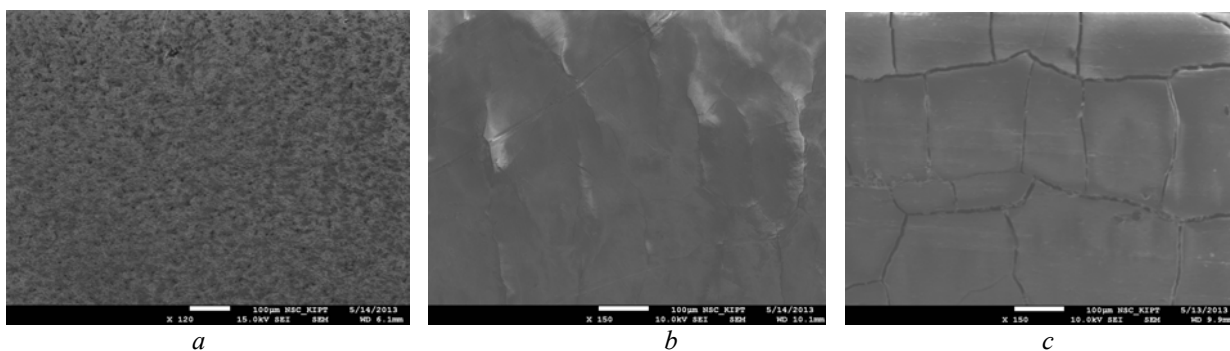


Fig. 1. Surface morphology of the Zr1%Nb alloy (a, b) and Zr (c) after oxidation for 8 h at 600 °C (a) and 800 °C (b, c)

At complex study of functional oxide coatings on zirconium materials it has been found temperature effect of air-thermal oxidation on morphology and composition of the modified surfaces. At temperature up to 600 °C durable black oxide film of uniform structure is formed on the surface of the zirconium and its alloy. Further increase of temperature to 800 °C leads to an increase in the oxygen content and the oxide film growth (Table). With increasing thickness of the oxide film the mechanical stresses at the border oxide-metal are increased and therefore a sharp change in corrosion resistance is observed [7]. Long-term oxidation times and higher oxidation temperatures violate the coating integrity. Formation of cracks and destruction of the oxide film occurs.

Except the temperature and duration of the process [8] also the chemical composition has a significant impact on the structure of the oxide layer. Composition of oxide films affects on their mechanical and protective properties since a dense solid oxide film can protect the metal from further oxidation. In the study of the oxidation process it was found that for pure zirconium and zirconium doped with niobium onset temperature of cracking of the oxide film is different. After annealing at 500...600 °C all samples were covered with continuous glossy film. At 800 °C for Zr1%Nb alloy an inhomogeneous structure with some separation into fragments is formed while for pure zirconium cracks are clearly visible due to the formation of smaller amounts of the tetragonal phase in the oxide layer (see Fig. 1,b,c). Due to the low volume fraction of tetragonal oxide a fracture toughness of the oxide layer becomes much lower therefore the oxide layer is susceptible to microcracks and loses its protective structure [9]. In the structure of Zr1%Nb alloy after oxidation the presence of a significant amount of a light tetragonal phase is observed so the formation of cracks in the oxide layer occurs not as intensively as in the case of pure zirconium.

The minimum film thickness which is necessary for the protection and stabilization of metal corrosion process depends on many factors: temperature, chemical composition and structure, the manufacturing process and preparation of the sample surface, etc. Oxidation kinetics of zirconium materials was determined by periodic weighing samples. It was found that with increasing holding time the weight gain of sample increases and significantly depends on temperature. From the results of studies follows that the oxidation rate of the

zirconium materials continuously increases with increasing thickness of the film formed. The highest intensity of the weight gain of samples occurs at a temperature of 800 °C as shown in Table.

Corrosion behavior of zirconium materials is determined by properties of the barrier oxide film. The growth of the oxide film under isothermal conditions in the temperature range studied is not subject to any one law and cannot be described by one kinetic equation. At certain temperatures the transition from one to another oxidation law is observed. In the oxidation of zirconium materials there are several stages [3-4].

Growth of the oxide film in the temperature range 500...600 °C occurs according to a parabolic or cubic law up to oxide thickness of 2...3 µm. The inner part of the film is nonstoichiometric, the outer part is close to the stoichiometric composition. Such oxide film is an effective protective barrier for oxidation. According to a parabolic law a rate of the oxidation process is inversely proportional to the thickness of the oxide film. This law applies when on the metal surface during its oxidation a film which has protective properties is formed, i.e. it is solid and nonporous.

With further growth of the oxide film thickness more than 3 µm the growth kinetics is replaced by quasilinear. At temperatures above 700 °C corrosion rate increases sharply. This oxidation stage is characterized by rapid oxidation and a large number of oxide film defects such as cracks and pores (Fig. 2). Transition from the protective oxide film to the peelable film occurs for relatively short time after which zirconium and Zr1%Nb alloy are oxidized with increased rate to complete destruction.

The research results of oxide films formed on the surface of zirconium samples showed that growth process of the oxide film thickness depends on the holding time and heating temperature. Furthermore as seen from Fig. 2 at the same temperature of 800 °C thickness of oxide film formed during corrosion on an alloy almost 2 times less than the thickness of the film on pure zirconium. This fact is explained by the presence in the alloy of niobium which stabilizes the corrosion resistance of undoped zirconium that is eliminates the adverse effect of small amounts of impurities present in pure zirconium [4]. It is known that the doping of zirconium may significantly reduce the oxidation rate after transition [7].

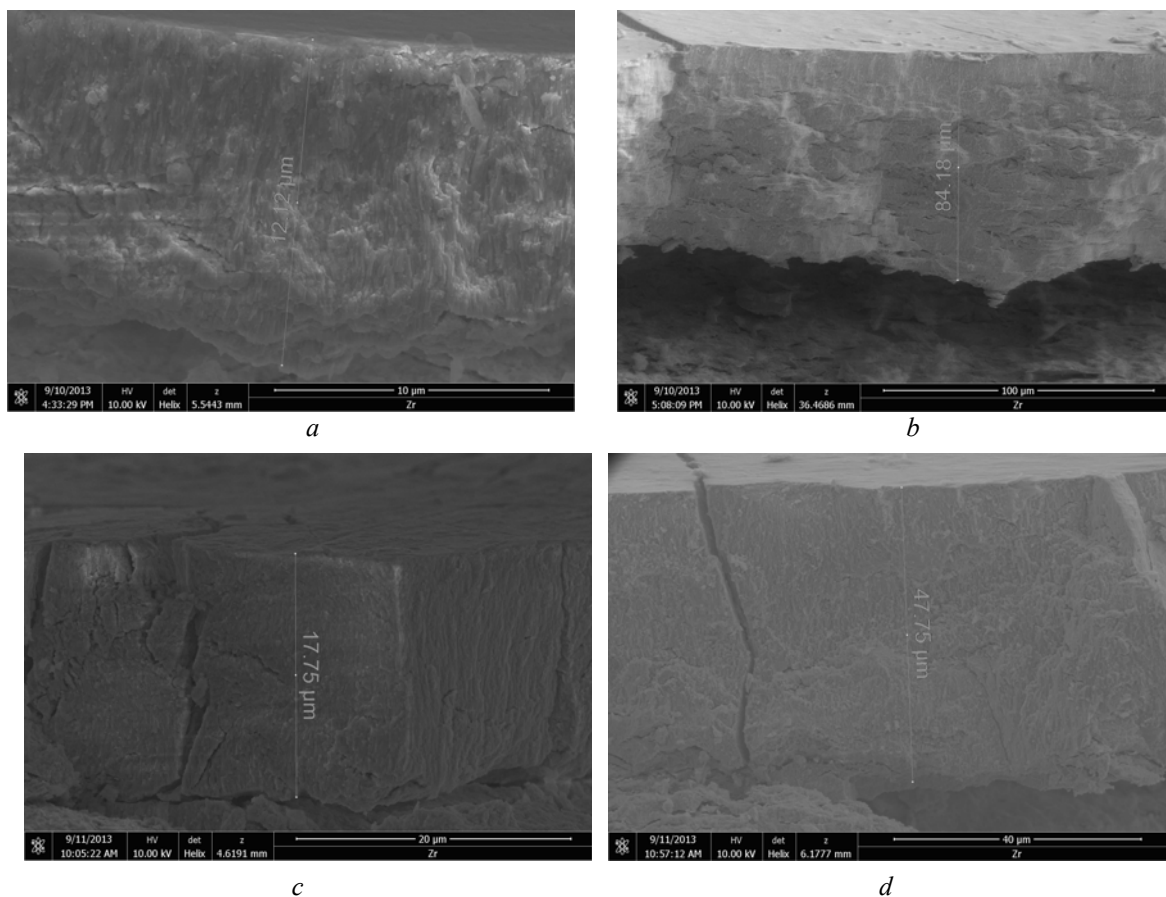


Fig. 2. Fractography images of the fractures of the samples of zirconium (a, b) and Zr1%Nb alloy (c, d) at 700 °C (a, c) and 800 °C (b, d)

Roughness parameter  $R_a$  of the oxide film formed at a temperature up to 600 °C is not more than 0.1  $\mu\text{m}$ . When tested of zirconium materials in more severe conditions (raised temperature) a thicker oxide film is formed, roughness is increased (see Table).

The value of Brinell hardness is increased from 2500 MPa for the initial samples Zr1%Nb alloy to 2770 MPa for all samples after oxidation. The microhardness values of the samples after oxidation at differ-

ent temperatures of heating and times of annealing are significantly different. The measurement results show that with rising temperature microhardness is increased. The microhardness values for zirconium plates as well as the results of determining the amount of oxygen, weight gain, roughness and thickness of the samples are shown in Table.

Oxygen content, weight gain ( $\Delta m$ ), roughness ( $R_a$ ), thickness (h) and microhardness ( $H_{\mu}$ ) of oxide films formed on zirconium samples

Values	Samples					
	Zr			Zr1%Nb		
$T, ^\circ\text{C}$	600	700	800	600	700	800
t, h	8	10	8	8	10	8
$O_2$ , wt.%	22.7	26.2	32	23.13	24.5	26.17
$\Delta m$ , mg	4.1	43.9	62.9	4.4	15.95	51.7
$R_a, \mu\text{m}$	0.072	0.270	1.981	0.100	0.632	1.848
h, $\mu\text{m}$	3.3	12.12	84.18	2.2	17.75	47.75
$H_{\mu}$ , MPa	3720	7340	7880	5190	8240	8350

It should be noted that despite the fact that the corrosion is the destructive process the formation of the dense oxide films on the surface of zirconium materials may lead to positive effects due to creation of the protective barrier on the path of further degradation of material. In order to have protective properties the oxide film must fulfill the following requirements: be solid, nonporous, chemically inert to the aggressive environ-

ment, have high hardness, wear resistance, adhesion to metal.

Thus the choice of optimal temperature and time of oxidation allows to create on the surface of zirconium materials the dense oxide films. The protective oxide film of a certain thickness and perfect structure (no cracks, pores) on the surface of zirconium and alloy Zr1%Nb prevents further penetration of the corrosive

environment in the deeper layers and therefore protects the metal from further destruction.

### CONCLUSIONS

It is shown that air-thermal oxidation of zirconium and Zr1%Nb alloy at temperatures above 500 °C results in the formation of the oxide films on surface. Process of growth thickness of the oxide film on zirconium samples depends on the holding time and oxidation temperature.

Regimes of air-thermal oxidation of zirconium and its alloy for the production of protective oxide films have been determined. It has been established that at temperature of 500...600 °C the films characterized by high strength and density are formed. Raising the oxidation temperature leads to the formation and growth of cracks and micropores in the structure of the oxide films on the zirconium materials and consequently to reduce their protective properties.

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## ВОЗДУШНО-ТЕРМИЧЕСКОЕ ОКИСЛЕНИЕ ЦИРКОНИЕВЫХ МАТЕРИАЛОВ

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Приведены результаты исследований влияния температуры на процесс образования оксидных пленок на поверхности циркониевых материалов. Проанализированы изменения морфологии, структуры и свойств оксидных пленок на цирконии и сплаве Zr1%Nb в результате воздействия термической обработки в воздушной среде при 500...800 °C в течение 10 ч.

## ПОВІТРЯНО-ТЕРМІЧНЕ ОКИСЛЕННЯ ЦИРКОНІЄВИХ МАТЕРІАЛІВ

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Приведено результати досліджень впливу температури на процес утворення оксидних плівок на поверхні цирконієвих матеріалів. Проаналізовано зміни морфології, структури і властивостей оксидних плівок на цирконії та сплаві Zr1%Nb в результаті впливу термічної обробки в повітряному середовищі при 500...800 °C протягом 10 год.