

SECTION 2

PHYSICS AND TECHNOLOGY OF STRUCTURAL MATERIALS

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INFLUENCE OF IRON ADDITIVES ON THE CORROSION RESISTANCE OF THE Zr-1%Nb ALLOY UNDER OPERATING CONDITIONS OF A NUCLEAR REACTOR

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This paper presents experimental data of the study of the influence of iron microadditives on the evolution of the structure of the Zr-1%Nb alloy and its corrosion properties with increasing iron content. It is shown that small additions of iron to the Zr-1%Nb alloy lead to a change in its structure due to the appearance of Laves phase precipitates. Additional micro alloying with iron makes a significant contribution to the corrosion resistance of Zr-1%Nb alloys in reactor water. The optimal amount of iron has been determined, which will lead to an increase in the corrosion resistance of the Zr-1%Nb alloy under the operating conditions of the nuclear reactor WWER-1000.

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INTRODUCTION

Current trends towards extended burnup, increased outlet temperatures and plant life extension in nuclear power facilities require the solution of a large number of problems related to the reliability of the materials used, especially in key components such as fuel cladding.

The zirconium alloys have served as one of the key structural materials for fuel claddings used in fuel assemblies of both pressurized water reactor (PWR) and boiling water reactors (BWR). Cladding tubes as a separator between fuel and coolant and a container of fuel in nuclear reactors are exposed to corrosion, creep and irradiation. Performance of the zirconium alloys in service has generally satisfactory, but there have occasional problems, including fuel cladding and pressure tube degradation and failure.

Creation of zirconium alloys for the manufacture of structural elements of the reactor core of nuclear power plants is based on alloying of zirconium with elements that provide the necessary complex of properties to zirconium alloys. Alloying elements should positively influence the corrosion resistance of products under operating conditions in the reactor and provide the necessary mechanical properties and reliability of products during operation [1–3]. Numerous works have shown that alloying of zirconium with iron is promising in developing alloys for high temperatures. The increase of the iron content in the zirconium alloy provides the material of the cladding tubes with the required resistance to creep and strengthening under irradiation. In addition, the alloying of Zr-1%Nb alloy with iron increases its corrosion and radiation resistance in the conditions of the operation of a nuclear reactor.

It is known that alloying zirconium alloys with iron increases their corrosion resistance [4]. Iron can be in zirconium oxide in the form of bivalent and trivalent ions and, replacing zirconium ions in the monoclinic lattice of the oxide, should compress it, contributing to

the coordination with a metal lattice. Crystallization of iron in the bcc lattice also stabilizes the monoclinic oxide lattice required for coordination with the metal. Therefore, alloying with iron should improve the corrosion resistance of zirconium alloys.

At the same time it was established that as a result of additional alloying with iron the technological efficiency of the Zr-1%Nb alloy decreases requiring the development of a new deformation and thermal scheme of tube manufacturing. Therefore, determination of the optimal iron content in the Zr-1%Nb alloy is a prerequisite for providing manufacturability of the alloy and improving its operational properties.

Thus the present paper reports the results of study influence of iron micro additives on structure and the corrosion resistance of the Zr-1%Nb alloy under operating conditions of a nuclear reactor.

A goal of the present study was obtaining zirconium alloys Zr-1%Nb alloyed with iron and investigation of their structure and corrosion properties depending on the iron concentration.

1. MATERIAL AND EXPERIMENTAL PROCEDURES

As initial materials for obtaining experimental samples a Zr-1%Nb alloy based on magnesium-thermal zirconium was used. Optimization processes of melting of Zr-1%Nb alloy based on magnesium-thermal zirconium by methods of electron beam and vacuum arc melting in laboratory conditions are described in detail in [5].

A vacuum-arc melting method was applied to obtain a homogeneous zirconium alloy with microadditives of iron. The Zr-1%Nb alloy samples in the form of 1 mm thick plates were prepared by rolling in a vacuum with intermediate annealing. The samples obtained were contained iron from 0.012 to 0.192 wt.% with an interval of 0.03 wt.%. After rolling all samples were annealed in a vacuum of 10^{-5} mm Hg at a temperature of

580 °C for 3 h. For alloying a pure iron refined by electron beam melting was used.

Metallographic studies of the structure of Zr-1%Nb alloy samples before and after alloying with iron were performed using a scanning electron microscope JSM-7001F with X-ray spectral analyzer INCA Energy 350. The chemical composition of the particles was studied using the X-ray spectral microanalysis. Microhardness was measured with a device PMT-3.

The study of corrosion kinetics of samples of Zr-1%Nb alloy with different iron content was carried out according to the methods developed and approved by NSC KIPT, which are based on the requirements of the ASTM standard [6]. The method of autoclaving was used for research, i.e. heating and corrosion tests of samples in an autoclave at a temperature of 350 °C, pressure of 16.5 MPa for a long time. The prepared samples were put to corrosion tests in autoclaves filled with water of a chemical composition similar to the primary coolant in water-water energetic reactor WWER-1000. The composition of the corrosive environment was as follows: Boric acid H_3BO_3 – 7...8 g/l; KOH – 0.025 g/l; NH_3 – 14 mg/l. The rest are bidistilled water. pH of the solution is 7.0-7.2.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The properties of alloys are determined by their structural-phase state and even small changes in the composition of Zr-Nb alloys lead to significant changes due to the appearance of different types of precipitates and changes in the matrix composition [1, 7, 8]. The kinetics of release of new phases in α -zirconium is determined by the composition of the alloy, the degree of supersaturation of the solid solution α -Zr, the

composition and the crystal structure of the phases. The alloying elements have a low solubility in α -zirconium (0.005...0.02% Fe, about 0.5% Nb) and are precipitated as particles of the second phase with dimensions of 50...500 nm. The composition and type of precipitates are determined by the degree of solubility of the main alloying elements of niobium and iron in α -zirconium and their total content in the alloy [9, 10].

Metallographic studies of the structure of samples of Zr-1%Nb alloy with different iron content showed that the samples have a two-phase structure: α -matrix and precipitates of the second phase. The additional iron alloying Zr-1%Nb alloy leads to the appearance of precipitates the density of which increases with increasing iron content. The microstructures of Zr-1%Nb alloy samples depending on the composition are presented in Fig. 1.

The presence of fine particles of β -Nb precipitate and a small number of larger precipitates – the Laves phases $Zr(Nb, Fe)_2$ are characteristic for samples with an iron content of up to 0.042 wt.%. The concentration of Laves phases is much lower than the concentration of β -Nb particles. The study of the chemical composition of particles using the X-ray spectral microanalysis confirmed the presence of two types of precipitates. The iron content in the matrix is 0...0.1%, niobium – 0.3...0.7%.

The change in the iron content in the alloy from 0.042 to 0.072 wt.% did not lead to a significant increase in the concentration of Laves phase precipitates. Noticeable growth occurred when iron alloying up to 0.162 wt.%. The average size of the β -Nb precipitates is 40...50 nm. The precipitates of Laves phase are slightly larger, their average size is 80...100 nm [11].

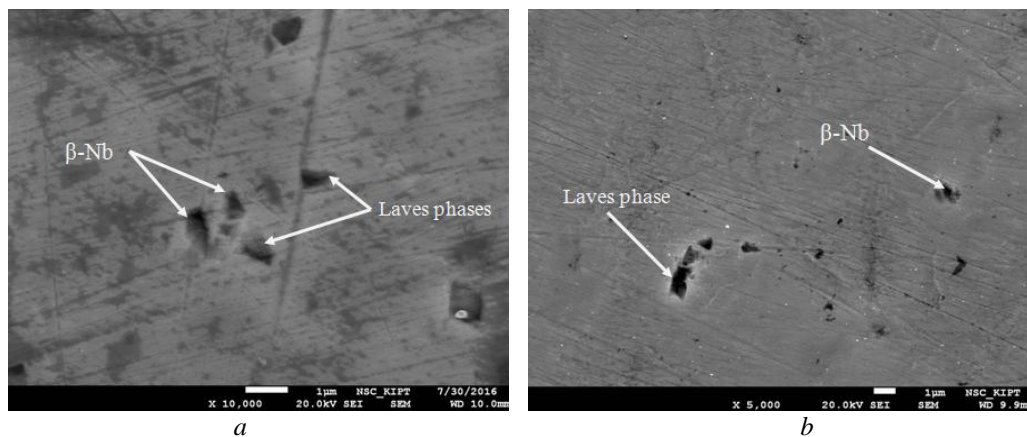


Fig. 1. The microstructure of the samples of the alloy Zr-1%Nb depending on the iron content: a – 0.072 wt.% Fe; b – 0.162 wt.% Fe

The concentration of Laves phase precipitates is much lower than the total concentration of particle. Studies show that the number of Laves phase precipitates significantly depends on the iron content in the alloy. Due to the very low solubility of iron in α -Zr, practically all of it is concentrated in the Laves phase.

With an increase in the iron content, the value of microhardness increases: the initial sample (0.012 wt.%) has 1720 MPa, the sample with 0.192 wt.% Fe – 1880 MPa. In the vicinity of a concentration of

0.1 wt.% Fe, the value of the microhardness of the alloy is 1750 MPa [12].

Long-term corrosion tests have shown that the corrosion rate of samples with different iron content is different (Fig. 2). The graphical dependence of the change in the corrosion rate of zirconium alloy samples on the iron content is shown in Fig. 3. It is seen that the lowest corrosion rate have samples of the alloy with an iron content of 0.102 wt.%. Reducing the iron content to 0.012 wt.%, increases the corrosion rate by almost two

times, and increasing the iron content to 0.162 wt.% also leads to an increase in the corrosion rate by almost 25% compared to alloy with the iron content of 0.102 wt.%. A further increase in test time showed that the difference in weight gain becomes more significant. For example, after 1000 h of testing, it is 7 mg/dm², and after 4000 h – 16.3 mg/dm². That is, after long-term corrosion tests, the alloy Zr-1%Nb, which contains 0.102 wt.% Fe, has the highest corrosion resistance compared to all other samples of the alloy.

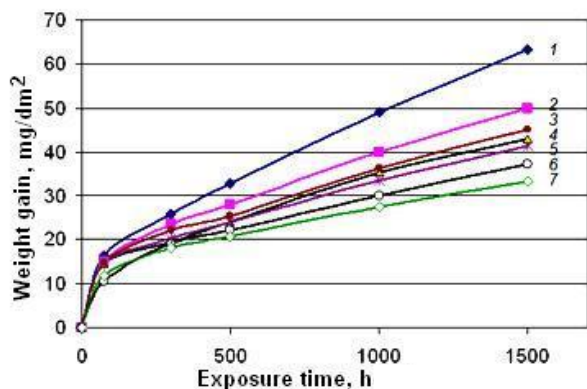


Fig. 2. Corrosion of Zr-1%Nb alloy with different iron content: 1 – 0.012; 2 – 0.042; 3 – 0.162; 4 – 0.072; 5 – 0.132 wt.%; 6 – E-110 alloy; 7 – 0.102 wt.%

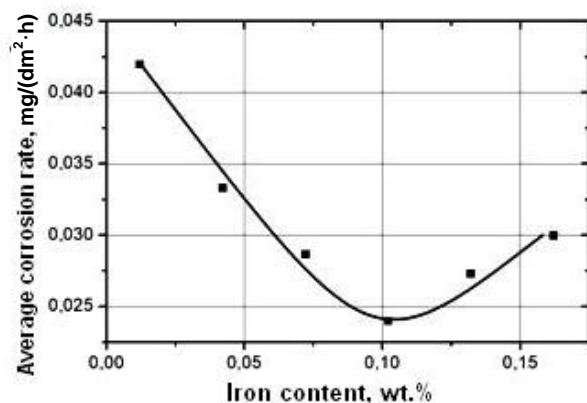


Fig. 3. Dependence of the change in the average corrosion rate of zirconium alloy samples on the iron content for 1500 h of testing

Data on the chemical composition of the alloy Zr-1%Nb indicate a fairly high purity of the alloy and the similarity of the composition of this alloy with the composition of the E110 alloy. The difference between the chemical compositions of the studied types of alloys (standard E110 alloy and experimental alloy Zr-1%Nb with an iron content of 0.102 wt.%) is essentially the difference in the amount of oxygen. The standard E-110 alloy contains 0.06...0.1 wt.% oxygen, and the all experimental alloys Zr-1%Nb contain 0.1 wt.% oxygen. In the literature there is an idea that oxygen is not a significantly harmful impurity in zirconium, which reduces its corrosion resistance. However, the data in the literature are not enough to unambiguously determine the effect of oxygen impurities on the corrosion resistance of the alloy Zr-1%Nb at different temperatures and long corrosion times. In [13] it was reported that the addition of oxygen up to 0.16% in the

alloy Zr-1%Nb (E110K) does not impair its corrosion resistance, and in [14], a slight increase in weight gain was noted during long-term corrosion tests in water of Zr-1%Nb alloys with an increase in the oxygen content in the range of 0.11...0.16 wt.%.

For comparison of corrosion resistance we used samples made of tubes for fuel cladding from a standard alloy (E110) for a WWER-1000 with a diameter of 9.1 mm and a wall thickness of 0.65 mm. According to Fig. 2, the weight gains for samples of the alloy Zr-1%Nb with an iron content of 0.102 wt.% are close to the weight gain of the samples of the standard E110 alloy or have slightly smaller values. Comparison of the surfaces of samples of both types after corrosion also showed a similar character.

3. CONCLUSIONS

The evolution of the structure of the Zr-1%Nb alloy with increasing iron content has been studied. It is shown that small additions of iron to the Zr-1%Nb alloy lead to a change in its structure due to the appearance of Laves phase precipitates. It was found that the number of Laves phase precipitates is determined by the iron content in the alloy and increases with increasing iron content. The microhardness of the alloy Zr-1%Nb increases with increasing iron content.

Long-term corrosion tests of samples of Zr-1%Nb alloy with different iron content in water of a chemical composition similar to the primary coolant in reactor WWER-1000 (temperature 350 °C, pressure 16.5 MPa) were carried out. The kinetics of weight change of samples of zirconium alloy with iron content from 0.012 to 0.162 wt.% was determined and it is shown that the additional microalloying of the alloy with iron makes a significant contribution to increasing the corrosion resistance of Zr-1%Nb alloys. The optimal amount of iron, which will increase the corrosion resistance of the alloy Zr-1%Nb under operating conditions in the core of WWER-1000, it is 0.10 wt.%. Increasing and decreasing the iron content in the alloy Zr-1%Nb from the optimal amount (0.10 wt.%) leads to an increase in the corrosion rate.

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ВЛИЯНИЕ ДОБАВОК ЖЕЛЕЗА НА КОРРОЗИОННУЮ СТОЙКОСТЬ СПЛАВА Zr-1%Nb В УСЛОВИЯХ РАБОТЫ ЯДЕРНОГО РЕАКТОРА

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Представлены экспериментальные данные исследования влияния добавок железа на эволюцию структуры сплава Zr-1%Nb и его коррозионные свойства с увеличением содержания железа. Показано, что небольшие добавки железа в сплав Zr-1%Nb приводят к изменению его структуры через появление выделений фазы Лавеса. Дополнительное микролегирование сплава железом вносит существенный вклад в сопротивление коррозии сплавов Zr-1%Nb в реакторной воде. Определено оптимальное количество железа, которое приведет к повышению коррозионной стойкости сплава Zr-1%Nb в условиях эксплуатации ядерного реактора ВВЭР-1000.

ВПЛИВ ДОБАВОК ЗАЛІЗА НА КОРОЗІЙНУ СТІЙКІСТЬ СПЛАВУ Zr-1%Nb В УМОВАХ РОБОТИ ЯДЕРНОГО РЕАКТОРА

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Представлено експериментальні дані дослідження впливу добавок заліза на еволюцію структури сплаву Zr-1%Nb та його корозійні властивості зі збільшенням вмісту заліза. Показано, що невеликі добавки заліза до сплаву Zr-1%Nb призводять до зміни його структури через появу виділень фази Лавеса. Додаткове мікролегювання сплаву залізом вносить істотний внесок в опір корозії сплавів Zr-1%Nb у реакторній воді. Визначено оптимальну кількість заліза, що призведе до підвищення корозійної стійкості сплаву Zr-1%Nb в умовах експлуатації ядерного реактора ВВЕР-1000.