

EFFECT OF IRON ADDITIVES ON THE PROPERTIES OF Zr1%Nb ALLOY

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The effect of iron additives on the microstructure and properties of Zr1%Nb alloy were investigated. The Zr1%Nb alloy with microadditives of iron was obtained by vacuum-arc melting method. Microhardness of experimental samples obtained during testing was measured. It was shown that microhardness of samples of the Zr1%Nb alloy varies with increasing iron concentration. It was found that the properties of the Zr1%Nb alloy can be enhanced significantly by addition of iron into the material.

INTRODUCTION

Modern atomic energy is based on reactors in which shells of fuel elements and other details are made of zirconium alloys. Shells of fuel elements work in difficult conditions (high temperatures, powerful radiation fields, the presence of loads from static and dynamic stresses, corrosion interaction with coolant and nuclear fuel) and therefore they must have high mechanical properties, heat resistance and good corrosion resistance.

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 shell tubes with the required resistance to creep and strengthening under irradiation. In addition, the alloying of Zr1%Nb alloy with iron increases its corrosion and radiation resistance in the conditions of the operation of a nuclear reactor.

The analysis of literature data showed that there is a correlation between the structural-phase transformations and the properties of zirconium alloys (corrosion, mechanical properties, radiation growth and radiation creep). It has been experimentally found that Nb and Fe, in addition to their presence in small amounts in the α -solid solution, are found in the structure of tubes made of zirconium alloys in the form of triple Zr-Nb-Fe intermetallics (L and T-phases). These phases determine the technological and operational properties of the alloy. The main phase in the structure of alloys is the Laves phase (L) of the composition $Zr(Nb,Fe)_2$, a significantly smaller number of T-phase – $(Zr,Nb)_2Fe$. The amount of Laves phase precipitates is determined by the content of iron in the alloy. With increasing iron content in the Zr1%Nb alloy the amount of Laves phase precipitates in the structure of the shell tubes increases which positively affects their corrosion resistance in water with lithium additions, especially for shells made of

alloys based on zirconium sponge. Iron under the action of irradiation comes out from the Laves phase into the matrix with the formation of secondary finely dispersed precipitates and thus delays the formation of dislocation loops <c>-type which are responsible for accelerating the radiation growth of the alloy. At the same time it was established that as a result of additional alloying with iron the technological efficiency of the Zr1%Nb alloy decreases requiring the development of a new deformation and thermal scheme of tube manufacturing.

So, determination of the optimal iron content in the Zr1%Nb alloy is a prerequisite for providing manufacturability of the alloy and improving its operational properties.

A goal of the present study was obtaining zirconium alloys Zr1%Nb alloyed with iron and investigation of their structure and mechanical properties depending on the iron concentration.

EXPERIMENTAL TECHNIQUE AND MATERIALS

As initial materials for obtaining experimental samples a Zr1%Nb alloy based on magnesium-thermal zirconium was used. Optimization processes of melting of Zr1%Nb alloy based on magnesium-thermal zirconium by methods of electron beam and vacuum arc melting in laboratory conditions are described in detail in [4].

A vacuum-arc melting method was applied to obtain a homogeneous zirconium alloy with microadditives of iron. The Zr1%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 hours.

For alloying a pure iron refined by electron beam melting was used. Spongy carbonyl iron was used as the source material. Electron beam melting of iron was carried out in two stages. At the first stage pieces of carbonyl iron were filled up in a crystallizer with a diameter of 150 mm. There iron was sintered and melted. The gases were removed from the metal in the process of sintering and melting. Due to the high content of gas impurities a “bubble” stage of gas

emissions was observed. Then the ingot was hanging over the crystallizer and the subsequent melting was carried out by the classic drip method with the extraction of the ingot. On samples of iron after the electron beam melting chemical analysis was carried out.

Metallographic studies of the structure of Zr1%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.

RESULTS AND DISCUSSION

Iron is the main component for the creation of alloys used in nuclear energy. It is known that the content of impurities penetration strongly affects the strength, corrosion and radiation properties of metals and alloys. Therefore refining of iron from impurities is important in the creation of new alloys [5].

For the refining of iron both from metal impurities and from impurities penetration the electron-beam melting was carried out. The content of impurities in the initial samples of iron and in samples after the electron beam melting is given in Table. It is seen that after the EBM the iron contains significantly less impurities and can be used to create new alloys.

The content of impurities in iron after the EBM, wt.%

Impurity	Initial	After EBM
N	$6.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$
Al	$2.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-3}$
O	$3.0 \cdot 10^{-2}$	$2.0 \cdot 10^{-2}$
Co	$1.7 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$
Si	$2.0 \cdot 10^{-1}$	$5.0 \cdot 10^{-2}$
Ni	$1.2 \cdot 10^{-1}$	$2.0 \cdot 10^{-3}$
Mn	$1.5 \cdot 10^{-1}$	$1.0 \cdot 10^{-2}$
Cu	$1.5 \cdot 10^{-1}$	$1.0 \cdot 10^{-1}$
Ni	$5.0 \cdot 10^{-2}$	$1.0 \cdot 10^{-2}$
C	$6.0 \cdot 10^{-3}$	$3.0 \cdot 10^{-3}$

The mechanical and corrosion properties of zirconium are largely influenced by impurities, so obtaining high-purity zirconium with a low content of impurities is one of the conditions for its use in the nuclear industry. Experimental samples of Zr1%Nb alloy with low content of impurities were obtained by the method of electron-beam melting.

Then a series of ingots of Zr1%Nb alloy with an iron content of up to 0.192 wt.% was obtained by the vacuum arc melting method.

The photographs of the microstructure of Zr1%Nb alloy samples depending on the composition are presented in Fig. 1. It can be seen that the additional introduction of iron into Zr1%Nb alloy leads to the appearance of precipitates the density of which increases with increasing iron content.

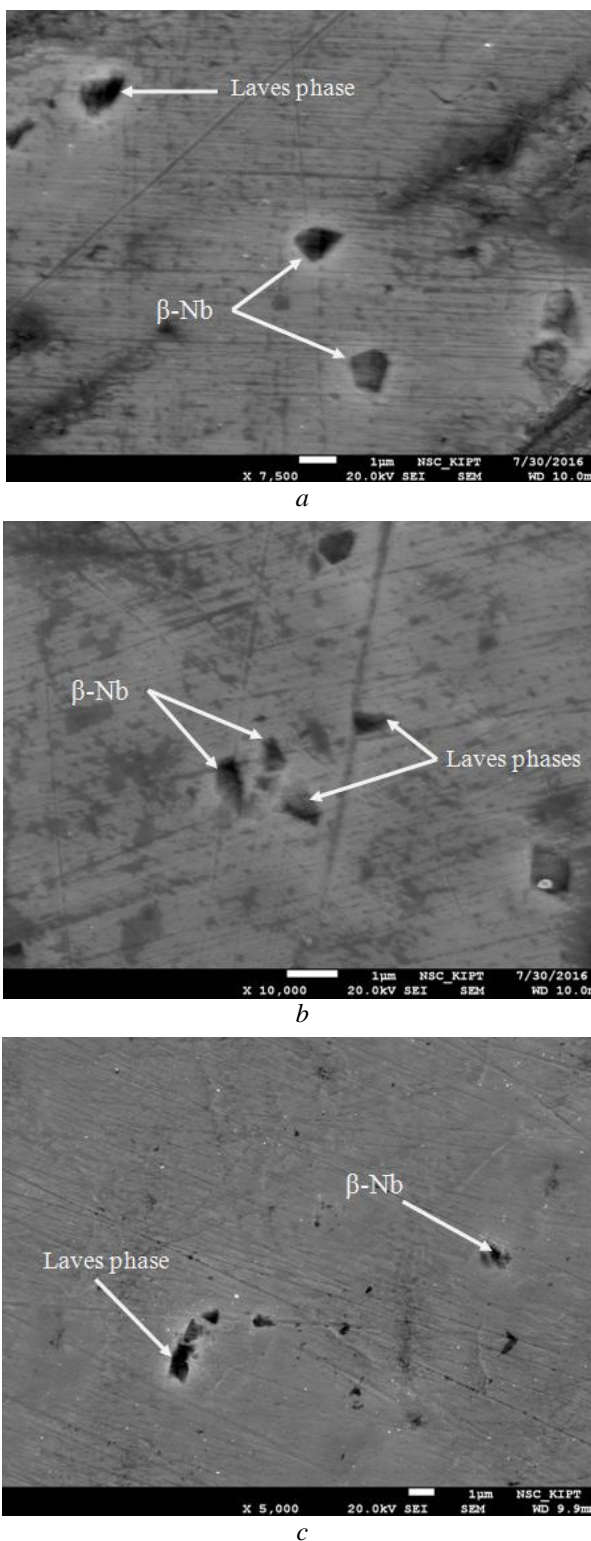


Fig. 1. Microstructure of Zr1%Nb alloy samples depending on the iron content: a – 0.042 wt.% Fe; b – 0.072 wt.% Fe; c – 0.162 wt.% Fe

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, 6, 7]. 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 [8, 9].

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.% (see Fig. 1,a). The concentration of Laves phases is much lower than the concentration of β -Nb particles and is less than 3% of it. 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 at the level of 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 alloying to 0.162 wt.% (see Fig. 1,b,c). Precipitates of β -Nb and Laves phase were detected in the structure of samples with a content of iron 0.072...0.162 wt.%. The average size of the β -Nb precipitates is 40...50 nm. The precipitates of Laves phase is slightly larger, their average size is 80...100 nm.

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.

It is difficult to distinguish precipitates of two types, since their size and morphology are close. Due to the very low solubility of iron in α -Zr, practically all of it is concentrated in the Laves phase.

The change of the microhardness of the samples with an increase in the iron content is shown in Fig. 2.

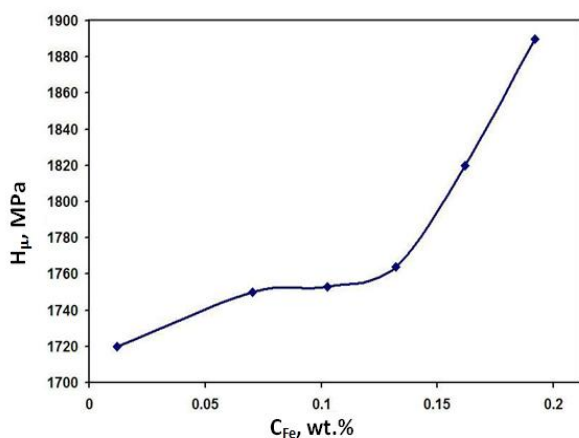


Fig. 2. Dependence microhardness of the alloy Zr1%Nb samples on the iron concentration

It is seen that the value of microhardness obtained for the alloy with an iron concentration of 0.192 wt.% is evidently higher relative to the alloy containing 0.012 wt.% of iron. The microhardness of the initial sample was 1720 MPa, the addition of iron to 0.192 wt.% increased the microhardness value to 1880 MPa.

CONCLUSIONS

Research on obtaining Zr1%Nb alloy with iron additives by vacuum arc melting has been carried out. The results of the studies have shown that the properties of the Zr1%Nb alloy widely used in nuclear power industry can be enhanced by addition into the material iron. Small additions of iron in Zr1%Nb alloy lead to a change in its structure due to the appearance of Laves phase precipitates, concentration of which increases with increasing iron content. It has been found that the number of Laves phase precipitates is determined by the iron content in the alloy. It is shown that with increasing iron content in the Zr1%Nb alloy the microhardness increases.

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ВЛИЯНИЕ ДОБАВОК ЖЕЛЕЗА НА СВОЙСТВА СПЛАВА Zr1%Nb

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Исследовано влияние добавок железа на микроструктуру и свойства сплава Zr1%Nb. Методом вакуумно-дуговой плавки получен сплав Zr1%Nb с микродобавками железа. Проведено измерение микротвердости образцов сплава Zr1%Nb, полученных в ходе испытаний. Показано, что микротвердость образцов сплава Zr1%Nb изменяется с увеличением концентрации железа. Установлено, что свойства сплава Zr1%Nb могут быть значительно улучшены в результате введения в материал железа.

ВПЛИВ ДОБАВОК ЗАЛІЗА НА ВЛАСТИВОСТІ СПЛАВУ Zr1%Nb

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Досліджено вплив добавок заліза на микроструктуру та властивості сплаву Zr1%Nb. Методом вакуумно-дугової плавки отримано сплав Zr1%Nb з мікрододатками заліза. Проведено вимірювання микротвердості зразків сплаву Zr1%Nb, отриманих під час випробувань. Показано, що микротвердість зразків сплаву Zr1%Nb змінюється зі збільшенням концентрації заліза. Встановлено, що властивості сплаву Zr1%Nb можуть бути значно покращені шляхом введення в матеріал заліза.