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THE INVESTIGATION OF ZIRCONIUM ALLOYS CHARACTERISTICS DURING THE OXIDATION IN THE GASEOUS MEDIUM

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The processes of high temperature oxidation of zirconium-based alloys in air atmosphere were investigated and the analysis of correlation of these processes with the results of the testing of the alloys in water with high parameters was conducted.

INTRODUCTION

Nuclear and technological properties of zirconium and alloys based on its resulted widespread and almost choiceless use of them as one of the best materials fuel claddings, chilled by water, steam and steam-water mixture up to 300 - 350 °C. Still widely used alloys Zr - 1%Nb and Zircaloy-2, which successfully work in pressurized water reactors at a temperature of about 300 °C. Requirements to capacity for work of zirconium alloys in water with high parameters are constantly increasing.

The creation of new zirconium alloys is impossible without investigating of mechanism and kinetics of processes occurring in corrosive medium under irradiation and voltage, and without investigating various factors that are determine behavior of alloys in water and steam. In the experiments of initial stage of corrosion of zirconium alloys analysis found that on the inner side of the oxide film formed ZrO_2 in the monoclinic modification. It was also found that even in the binary alloy of Zr-1,07% Sn under the influence of corrosion formed fine-dyspersated oxides SnO_2 in a matrix of ZrO_2. The previous obtained data are mainly explained in the temperature range in the beta area of zirconium alloys. It is caused by the fact that the self-diffusion rate in the α-phase is less than the self-diffusion rate in the β-phase in about 100 times. Diffusion of impurities in α-Zr for tin, iron and nickel gives low values of the activation energy Q and the diffusion coefficient D_0, moreover, that the temperature dependence of the diffusion coefficient in zirconium does not obey the Arrhenius equation. This is related to the α-, β-transformations. Impurity diffusion investigation of α-Zr showed the existence of both vacancy (for Sb and Sn) and interstitial (for Cr, Mn, Fe, Co, Ni, Cu) mechanism. This difference is caused by the low solubility of alloying elements of the second group in α-Zr and the allocation of intermetallic inclusions, migration of which in deformed alloys during thermal annealing in the range 300-800 °C occurs with a sufficiently high speed. The relationship between diffusion and corrosion characteristics of metals and alloys is obvious. The more important experimental parameters and evaluations obtained as a result of corrosion testing of zirconium and its alloys in different active media. Such active media are include water with high parameters, high-temperature steam, oxygen, air. At the same time it is important to consider the diffusion activity of the matrix atoms of zirconium alloys and dopants.

Investigation and analysis of the relationship diffusion characteristics of zirconium and its alloys with corrosion processes occurring on the surface alloys with their oxidation in gas air atmosphere at a temperature of about 1000 °C represent the scientific and practical interest. In the analysis of these processes it is advisable to use the method of differential thermal analysis in conjunction with the methods of analysis the structure and phase composition of alloys.

The aim of this work was to investigate and analyze the relationship of diffusion characteristics of zirconium and its alloys with corrosion processes, occurring on the surface of alloys at their oxidation in air gas atmosphere at a temperature of about 1000 °C.

1. TECHNIQUE OF EXPERIMENTAL INVESTIGATIONS

Alloys based on iodide and calcium thermal zirconium were prepared by the method of electron beam melting in a vacuum. The composition of the alloys is shown in the table.

Ingots were rolled with triple process annealing at 700 °C for 3 hours in vacuo $1{,}3\cdot10^{-4}$ Pa. Thereafter the samples were undergo rolled to a thickness ranging from 1 mm to 50 microns at room temperature with a reduction ratio of about 90 %. X-ray diffraction studies of alloys were conducted by ionization methods on installing DRONE 3.0 in Cu k_α -radiation.

Table 1

Composition of zirconium alloys

#	Composition of alloy -mass %
1	Zr-1% Sn
2	Zr-1% Sn-0,31%Fe
3	Zr-0,63%Fe
4	Zr-0,31%Fe
5	Zr-0,31%Fe-0,3% V
6	Zr-0,31%Fe-0,3% Cr
7	Zr-0,31%Fe-0,5% Nb
8	Zr-0,31%Fe-1% Nb
9	Zr-0,31%Fe2,5% Nb
10	Zr-0,31%Fe-0,3% Mo
11	Zr-0,31%Fe-0,5% Mo
12	Zr-0,31%Fe-1% Ta
13	Zr-0,31%Fe-0,3% Cu
14	Zr-0,31%Fe-0,3% V-0,3% Cu
15	Zr-0,31%Fe-1% Nb-1% Cu
16*	Zr-0,5%Fe-1% Nb-0,5% Sn
17*	Zr-0,5% Nb
18*	Zr-0,5% Sn-0,5% Nb

X-ray structure analysis showed, that at all stages of TMT of zirconium-based alloys phase composition is represented only by α-phase Zr. Corrosion tests of zirconium alloys in water with high parameters and oxygen were conducted on alloys foils preliminary annealed at 973 K for 0.5 hours.

Also was produced the oxidation of zirconium alloys at the atmosphere of pure oxygen at a temperature of 773…823 K and the air atmosphere with registration of DTA curves.

On the obtained DTA curves were recorded peaks corresponding to the allocation, or the absorption of heat. Also according to obtained DTA curves were determined weight gains for zirconium alloys.

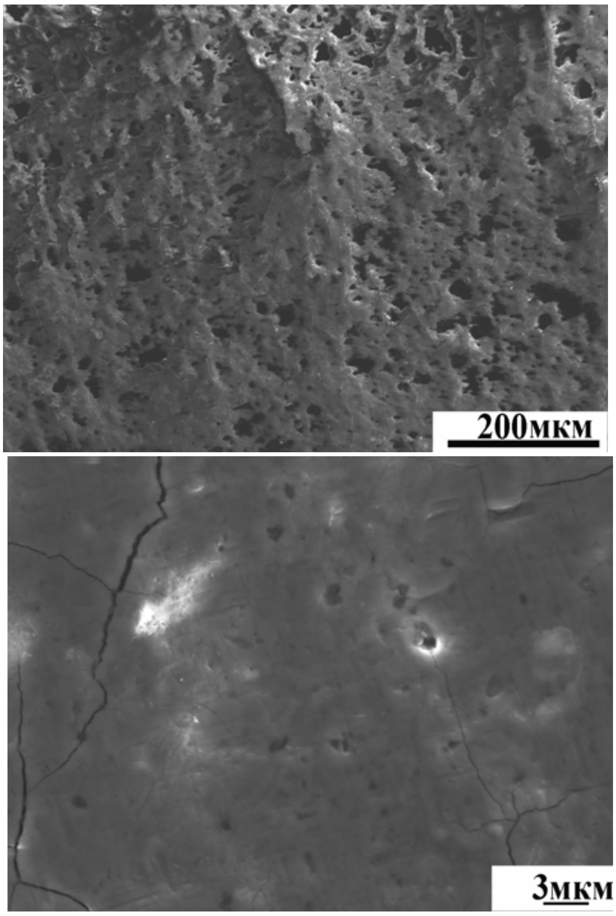
On the specimens with high corrosion resistance formed dense black film with high degree of adhesion to the surface of the sample. Mossbauer spectra were recorded in the backscattering geometry using the upgraded spectrometer YAGRS-4M. Electron microscopic investigations were performed on a scanning electron microscope JSM-7001F.

2. RESULTS AND DISCUSSION

Analysis of the results of scanning microscopy of the zirconium alloys surface after oxidation in pure oxygen at a temperature of 550 °C with different scaling confirmed that the oxide film grows on the surface of zirconium alloys in the form of a heterogeneous porous structure. It was found that the formula zirconium oxide is shifted from the stoichiometric composition upward to the oxygen concentration.

Depending on the composition of the alloy as a result of corrosion in pure oxygen were formed porous and scaly structure (of a type «dry-type playa»). Pore size distribution, depending on the zoom level of the microscopic analysis, became more heterogeneous in zoom level out to 0.2…1 microns.

Corrosion of the system Zr-Sn alloys in pure oxygen at 550 °C led to the formation of complex oxide films (Fig. 1).



Element	Percent by weight	Atomic percent
O K	29.06	70.00
Fe K	0.44	0.31
Zr L	69.52	29.37
Sn L	0.98	0.32

Fig. 1. The microstructure of the surface of the Zr-Sn alloy, oxidized in pure oxygen at a temperature of 550 °C and and the elemental composition of the surface layer

Intermetallics and grain boundaries are the places of localized corrosion, so the corrosion resistance of alloys in general depends not only on the phase composition, dispersivity and uniformity of distribution on the surface of particles intermetallic, but also on the microstructure of the metal matrix. For pure zirconium the temperature of beginning recrystallization may fall depending on the purity of the metal and the mode of thermomechanical processing to 170 °C.

The zirconium oxide formula was shifted from the stoichiometric composition in the direction of elevated concentration of oxygen (described as $ZrO_{2,3}$). The content of tin in the film, compared to the surface of the original alloy decreased from 1.03 at. % to 0.3 at. %. Previously, in the process of oxidation of this alloy was found, that tin oxide is released in the form of microparticles. This was confirmed by the results of scanning electron microscopy at 150x and 3000x magnifications (Fig. 2).

With increasing 150x became visible large pores (size 20…30 microns), with increasing 3000x - small pores (size 0.5…1 micron).

The results of EDS microanalysis of alloy Zr-Fe-V (Fig. 2) showed that the content of iron on the surface of the oxide film is the same as on the original surface of the alloy – 0.28 at. % and 0.3 at. %, respectively.

Formula of zirconium oxide has been shifted from the stoichiometric composition in the direction of elevated concentration of oxygen (described as $ZrO_{2.55}$). Increasing of the oxygen content may be the result of ions presence which have a higher chemical activity and bound one atomic percent of the oxygen, what is lead to greater displacement of oxygen in formula unit.

In the microstructure of the surface oxidized Zr-Fe-V alloy in pure oxygen at 550 °C except for the presence of large pores (size of 20…30 microns at 150x magnification) manifested presence grid cracks, limiting land type «dry-type playa» (Fig. 2, top).

Small pores, 2…5 microns in size, observed at 3000x magnification as partially repeated «dry-type playa» structure of the oxide film, and had the character of healing pores.

At the early stage of corrosion was formed oxide layer based on ZrO_2 in monoclinic modification. Large particles of intermetallic caused to the formation of voids in the film, so their size must be < 1 micron. With film thickness 100…200 microns surface was covered by the epitaxial islands of ZrO_2, oxide became solid when a thickness became about 1000…2000 microns.

In the thin oxide film and on the boundary of metal-oxide appeared compressive stresses. The outer layer was subjected to tensile stresses. Cracks formed under the influence of these stresses were the underlying cause of the break point of the kinetic curves. The alloying is effect on the process, changing the ductility of the oxide layer, which, in our case, led to a significant difference of the microstrains in the oxide film and zirconium alloy matrix. Annealing also led to a redistribution of the phases in the intermetallic inclusions (decomposition of phase 1 and the growth of phase 2), migration of intermetallic phases with the subsequent output on the surface of the alloy sample in the form of plates.

Shown in Figs. 3, 4 distribution diagrams of number of pore by size for the oxide film on the surface of zirconium-tin alloy characterized by different types of distribution depending on the zoom level

In the range of the pore size of 5…30 microns constitute of the bulk the pore size of about 5…10 microns, with decreasing the level of scaling by an order to 0.5 micron pore size distribution became more uniform. This may be due to a different mechanism of pore formation, the restriction of their growth, reached a certain size (about 20 microns).

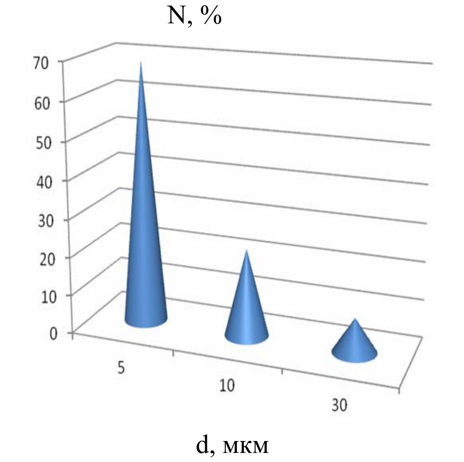


Fig. 3. The distribution diagrams of number of pore by size for the oxide film on the surface of zirconium-tin alloy at 100x magnification

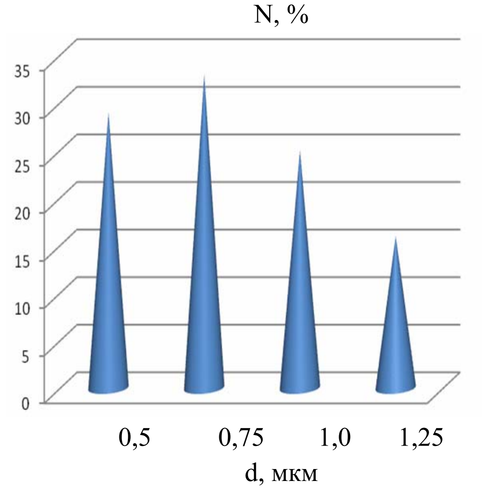


Fig. 4. The distribution diagrams of number of pore by size for the oxide film on the surface of zirconium-tin alloy at 3000x magnification

Shown in Figs. 5, 6 distribution diagrams of «dry-type playa» structure and number of pore by size for the oxide film on the zirconium-iron-vanadium alloy show minimal difference of form distributions, depending on the zoom level. In the range of «dry-type playa» structures 20…100 microns constitute the bulk of «dry-type playa» patches with a size about 20…60 microns, with decreasing the level of scaling by an order to 0.5 micron pore size distribution has also become more uniform. This may be due to a different mechanism of oxidation of alloys with additions of iron and vanadium and limitation of their growth when a certain size is reached (about 100 microns) because of cracking on the boundary of "dry-type playa" patches. Apparently "dry-type playa" structure is a manifestation of the column structure of the oxide

The results of the investigations of zirconium alloys oxidation in air atmosphere using differential thermal analysis (DTA) allowed as to define the nature of corrosion in iron-containing alloys when a complex composition oxide film forming, and get mixed correlation weight gains values during corrosion process in water with high parameters and air atmosphere.

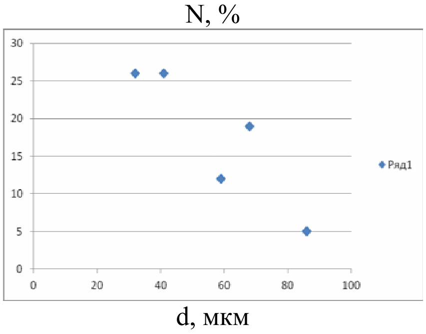


Fig. 5. The distribution diagrams of «dry-type playa» structure by size for the oxide film on the zirconium-iron-vanadium alloy at 100x magnification

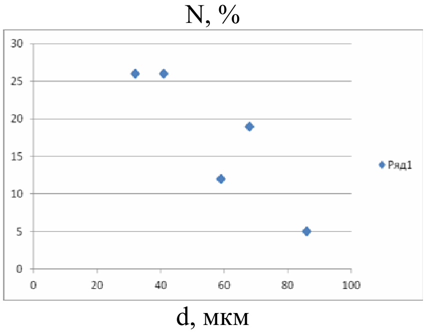


Fig. 6. The distribution diagrams of number of pore by size for the oxide film on the zirconium-iron-vanadium alloy at 3000x magnification

Received DTA-charts were used to calculate dependencies weight gain from the test temperature. The highest values of weight gain characteristic for such iron-containing alloys as zirconium - iron - vanadium.

It is caused by an increased content of the second phases and by more complex mechanism of corrosion, including the diffusion mechanism of the decomposition of iron-containing intermetallics.

In DTA-analysis, due to the presence of iron oxide in the form of hematite on the surface oxide films, at the zirconium alloys, along with increased corrosion resistance, high concentration of iron ions on the oxide film ZrO_2 can lead to zirconium matrix alloys depletion by dopants. This is possible at the initial stage of an oxide film formation and can lead to decreasing of mechanical properties of zirconium alloys matrix in the exploitation process, particularly, to the increasing of creep alloys of zirconium alloys.

Corrosion of zirconium alloys in air atmosphere was conducting at the differential thermal analysis. On Fig. 7 are shown typical DTA charts for samples of pure iodide zirconium with different weights. The reproducibility of the results is high enough.

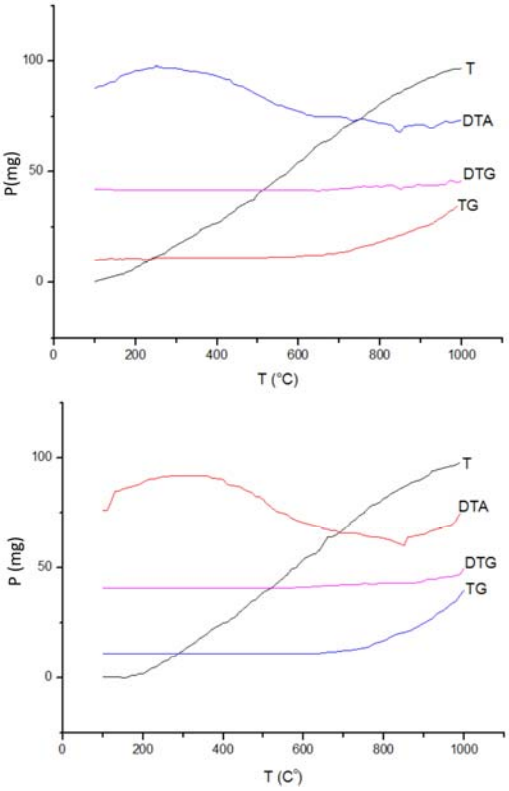


Fig. 7. Typical DTA charts for samples of pure iodide zirconium with different weights

In the Fig. 8 showed the similar chart for the Zr-Fe alloy.

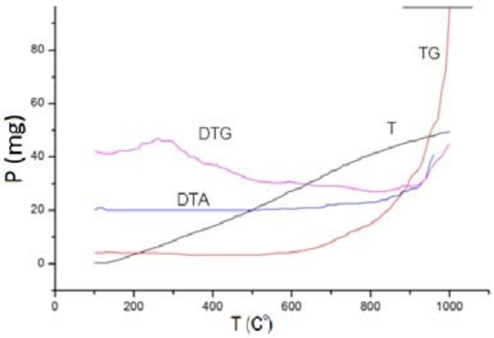


Fig. 8. DTA charts for the sample of Zr-Fe alloy

In the original Zr-Fe alloy iron is found in the form of intermetallic. Perhaps, such a complex structure of the alloy was the reason of splitting it into two equal parts by the end of corrosion during DTA. Mossbauer spectra of oxidized through the entire thickness of the alloy are given in Figs. 10 and 11. It is seen that on the external layer of the oxide film preserved the fraction of unfused intermetallic. This is evidenced by an extended doublet spectrum of the central part of the spectrum. Complex six linear spectrum is among the highest iron oxide – hematite.

Comparing with the spectrum given below, which characterizes the inner layer of the splitting sample as a result of oxidation, it is seen that in this layer is present only hematite, what qualitatively indicates the presence of concentration gradient of the oxygen in the depth of the oxidized sample.

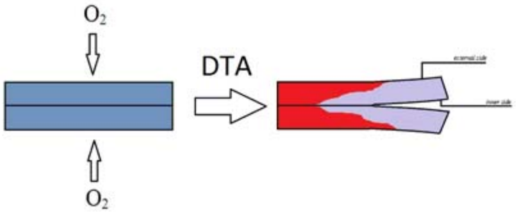


Fig. 9. The scheme of splitting into two equal parts plate with the thickness of 1 mm of Zr-Fe alloy after DTA analysis

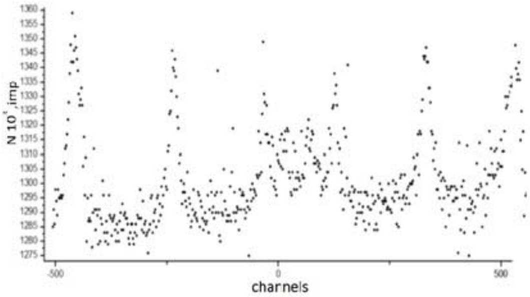


Fig. 10. The spectrum of back scattering of the sample P2 (700 ^{0}C , 15 hours) after DTA - external side

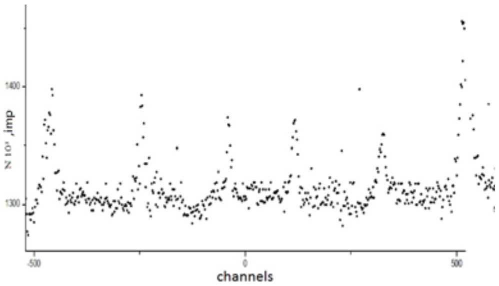


Fig. 11. The spectrum of back scattering of the sample P2 (700 ^{0}C , 15 hours) after DTA – inner side

Obtained DTA-charts were used to calculate the dependencies of weight gain from the test temperature (Fig. 12).

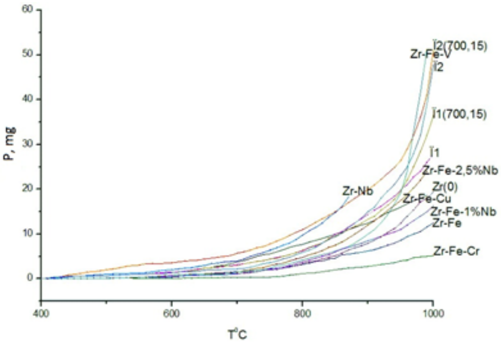


Fig. 12. The curves of dependence of the weight gain from the temperature for zirconium alloys

The highest values of weight gain was demonstrated by zirconium-niobium (0.5%), zirconium-iron - molybdenum and zirconium - iron - vanadium alloys. In the case of iron-containing alloys it is due to the high concentration of the second phases and a more complex mechanism of corrosion, which including the diffusion mechanism of the decomposition of the iron-containing intermetallics.

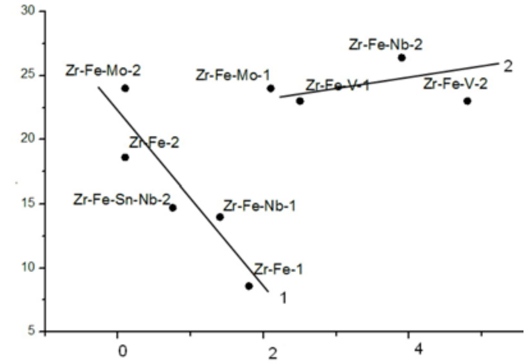


Fig. 13. Dependence of weight gain for zirconium alloys after corrosion in the air medium from the weight gain in the water with high parameter

The weight gain obtained data for the alloys after corrosion in air atmosphere were compared with the published data [6] for weight gain of the same zirconium alloys in water with high parameters (Fig. 13).

The graph can be divided into two parts to the values of the gain in water with high parameters 2 mg/mm^2 and a second area, for values of weight gain above 2 mg/mm^2. The character of correlations in these areas is different

CONCLUSION

The analysis of the results of scanning microscopy at 150x and 3000x magnification confirmed that the oxide film grows on the surface of zirconium alloys in the form of a heterogeneous porous structure. It was also found that the zirconium oxide formula was shifted from the stoichiometric composition in the direction of increasing the oxygen concentration.

Corrosion in the pure oxygen characterized by the formation of, characterized by a porous structure and the structure of a type "dry-type playa" depending on the alloy composition. Pore size distribution depends on the zoom level of the microscopic analysis and becomes more uniform when downscaling to 0.2…1 microns.

Data of DTA investigations allowed as to determine the corrosion pattern of iron-containing alloys during the formation of an oxide film with complex composition, and to get mixed correlation between weights gain during the corrosion in water with high parameters and air atmosphere.

During DTA analysis due to the presence of iron oxide in the form of hematite on the surface of oxide films on the surface of zirconium alloys, along with increased corrosion resistance, the observed high concentration of iron ions in the oxide film ZrO_2 can lead to depletion of dopants of the zirconium alloy matrix during the formation of the oxide film, and to decreasing of the mechanical properties of zirconium alloy matrix in the process of exploitation, in particular, to increase the creep of zirconium alloys.

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ИССЛЕДОВАНИЕ ХАРАКТЕРИСТИК СПЛАВОВ ЦИРКОНИЯ ПРИ ОКИСЛЕНИИ В ГАЗОВОЙ СРЕДЕ

Н.А. Азаренков, Р.Л. Василенко, В.Г. Кириченко, Т.С. Потина

Исследованы процессы высокотемпературного окисления сплавов на основе циркония в воздушной атмосфере и проведен анализ корреляции этих процессов с результатами испытания сплавов в воде высоких параметров.

ДОСЛІДЖЕННЯ ХАРАКТЕРИСТИК СПЛАВІВ ЦИРКОНІЮ ПРИ ОКИСЛЕННІ В ГАЗОВОМУ СЕРЕДОВИЩІ

М.О. Азарєнков, Р.Л. Василенко, В.Г. Кіріченко, Т.С. Потіна

Досліджено процеси високотемпературного окислення сплавів на основі цирконію в повітряній атмосфері та проведено аналіз кореляції цих процесів з результатами випробування сплавів у воді високих параметрів.